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ACTIVATED SURFACES USEFUL IN THE PRODUCTION OF HYDROGEN

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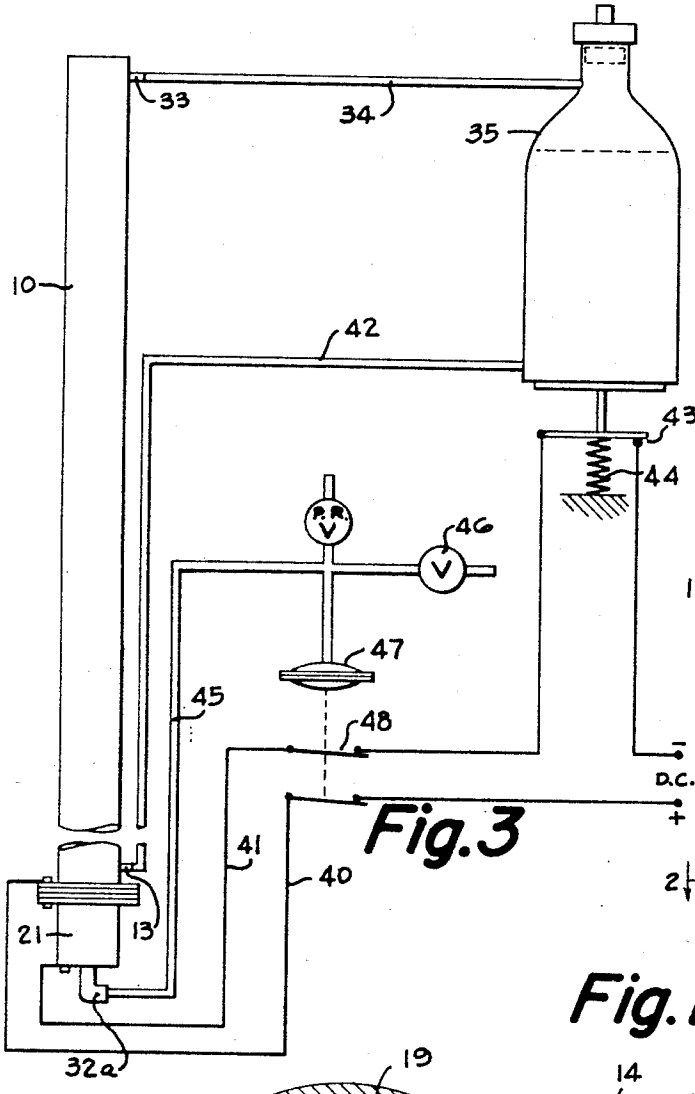


Fig. 3

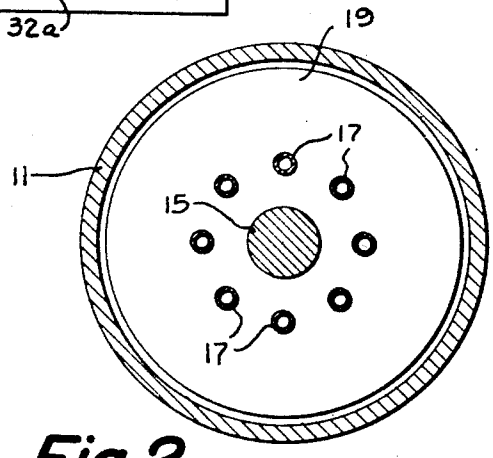


Fig. 2

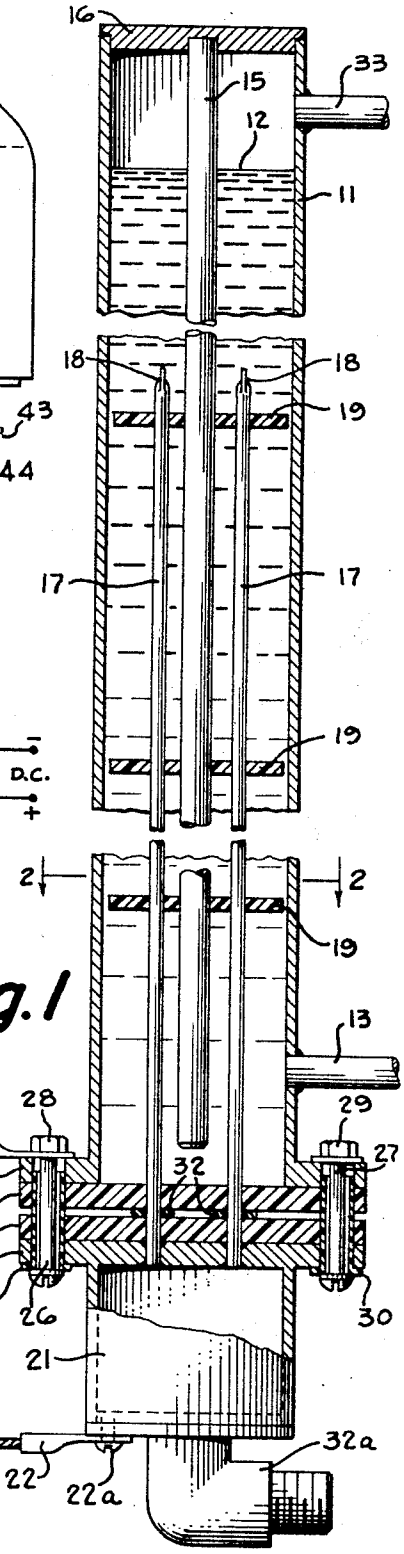


Fig. 1

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ACTIVATED SURFACES USEFUL IN THE PRODUCTION OF HYDROGEN

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U.S. Cl. 204—278 15 Claims

ABSTRACT OF THE DISCLOSURE

Method of activating palladium or palladium-alloy surfaces, and electrolytic hydrogen generating cells including such surfaces and an activated electrolyte. In prior art methods of electrolytic production of ultra-pure hydrogen involving the use of a cathode constructed of palladium alloy tubes, it has not been possible to cover substantially all of the hydrogen generated at the cathode surfaces. The invention provides a method for activating the surface of palladium or a hydrogen permeable palladium alloy involving the exposure of a clean, moisture-free surface to a molten hydroxide of an alkali or alkaline earth metal, and subsequently exposing the treated surface at a temperature of at least about 450° C. to an oxidizing atmosphere to provide an activated coating thereon. Electrolytic hydrogen producing cells including cathodes constructed of palladium or palladium alloy tubes whose surfaces include such an activated coating afford recovery in ultra-pure form of substantially all of the hydrogen generated therein.

This invention relates to the production of hydrogen and has for an object the provision of an efficient and reliable electrolytic cell including a palladium or a hydrogen permeable palladium alloy cathode characterized by activated surfaces which afford the recovery in ultra pure form of virtually all of the hydrogen electrolytically generated in the cell.

Although generally considered to be the best carrier gas for gas chromatography, hydrogen is not widely used because of the dangers involved in storing and handling cylinder hydrogen. Also, the impurities in cylinder hydrogen are often too high to be tolerated in chromatographic analyses. Accordingly, electrolytic cells for the production of ultra pure hydrogen have been suggested in which the cathode is constructed of one or more palladium alloy tubes. During electrolysis, the hydrogen generated electrolytically diffuses through the walls of the palladium alloy tubes (which are permeable only to hydrogen gas) and is thereafter recovered from the cell in a highly pure form.

The hydrogen pressure developed in such a cell may be described by the Nernst equation which relates the pressure of that gas developed on the cathode tube surface exposed to the electrolyte and the voltage applied to the cathode. Generally speaking, the pressures that may be generated are quite high, and pressures well in excess of 1000 p.s.i. have been obtained with no significant reduction in the hydrogen flow rate. The maximum value of the pressure allowable is limited only by the strength of the cathode tubes employed.

In order that a cell be practical, however, most of the hydrogen generated during electrolysis should enter the palladium alloy tubes and be recovered in a highly pure form. In this connection, it is known that the percentage of the hydrogen absorbed by the tube walls, and consequently passed into the tube for recovery as pure hydrogen, can be increased if the surface of the tubes is coated

with palladium black to increase its activity. Tubes so coated will absorb at least 60 percent of the hydrogen generated when the cell is run at 90° C. and a current density of 60 amperes per square foot. Although other methods for activating palladium cathode tubes have also been suggested, cathode tubes capable of recovering in ultra pure form substantially all of the hydrogen generated have heretofore not been available.

It is, therefore, a primary object of the invention to provide an activated palladium or palladium alloy surface.

Another object of the invention is to provide a composition of matter whose presence as a coating on a palladium or palladium alloy surface serves to activate that surface.

A further object of the invention is to provide a hydrogen transfer element including a membrane of palladium or a palladium alloy characterized by activated surfaces.

Still another object of the invention is to provide an activated hydrogen cell electrode which affords the recovery in ultra pure form of substantially all of the hydrogen electrolytically produced in the cell.

Yet another object of the invention is to provide an efficient and reliable electrolytic cell for the production of ultra pure hydrogen.

A further object of the invention is to provide an improved aqueous electrolyte for use in the electrolytic production of hydrogen.

Briefly stated, these and other objects may be attained in accordance with my invention by a process for activating a surface of palladium or a hydrogen permeable palladium alloy which has been in contact with a molten hydroxide of an alkali or an alkaline earth metal which comprises exposing said surface, whose temperature is at least about 450° C., to an oxidizing atmosphere to provide an activated coating thereon. The composition of the invention comprises the coating formed by the aforesaid process.

The present invention includes a hydrogen permeable element as, for instance, a membrane of palladium or a palladium alloy whose surfaces are characterized by an activated coating formed by the aforesaid process. To cite an example, the surfaces of a hydrogen electrode formed of palladium or a hydrogen permeable palladium alloy may be activated in accordance with my invention by immersing the clean, moisture free electrode into a molten hydroxide of an alkali or an alkaline earth metal, and subsequently exposing the treated electrode surfaces, whose temperature should be of the order of at least about 450° C., to an oxidizing atmosphere to provide the activated coating thereon. The resulting electrode, when utilized in an electrolytic cell for the production of hydrogen, affords the recovery in ultra pure form of substantially all of the hydrogen generated in the electrolytic cell, and is characterized by an operative life (i.e., a continued ability to afford the recovery in ultra pure form of substantially all of the hydrogen electrolytically generated) which far exceeds the operative lives of the palladium alloy hydrogen cell electrodes of the prior art.

An additional feature of the invention includes an electrolytic cell comprising, in combination, an electrolysis chamber including an anode and adapted to contain an electrolyte, cathode structure disposed within said chamber comprising a membrane of palladium or a hydrogen permeable palladium alloy activated by the aforementioned process, and adapted to have only one surface thereof exposed to said electrolyte when the electrolyte fills said chamber, and hydrogen recovery means for recovering in ultra pure form substantially all of the hydrogen electrolytically produced in the cell.

Further in accordance with the invention, there is provided a process for preparing a hydrogen cell electrolyte

which comprises subjecting said solution to an electrolyzing current of at least 10 amperes per liter of solution for at least 1 hour to provide a hydrogen cell electrolyte substantially free of impurities and characterized by an improved electrolytic efficiency when utilized in an electrolytic cell for the production of hydrogen.

By virtue of the present invention, there is provided an electrolytic cell for the production of ultra pure hydrogen, which cell is reliable, and which is characterized by an efficiency for recovering in ultra pure form electrolytically produced hydrogen which is unparallel by any hydrogen producing cells heretofore available in the art.

Prior to exposure to an alkali or an alkaline earth metal hydroxide, the palladium or hydrogen permeable palladium alloy surface, such as the surface of a hydrogen cell electrode, should be thoroughly cleaned with a suitable cleanser to remove all dirt and grease that may be present. This may be accomplished by washing the surfaces of the electrodes with any commercial solvent, such as carbon tetrachloride or acetone. Thereafter, the surfaces should be dried thoroughly before continuing to the activation step. Such drying may be accomplished by any suitable method as, for example, by placing the electrode in an oven maintained at an elevated temperature of the order of 200° C. for a period of time sufficient to remove all traces of moisture and cleansing solvent. It is to be noted that the cleaning and drying of the electrode surfaces prior to their activation is critical to the recovery in ultra pure form of substantially all of the hydrogen generated in the electrolytic cell.

After the electrode surfaces have been cleaned and dried, they are exposed to a molten hydroxide of an alkali or an alkaline earth metal, as for example dipping or immersing the electrodes into a bath of the molten hydroxide. Other methods for contacting the surfaces of the electrode with the molten hydroxide will readily occur to those skilled in the art as, for instance, by spraying or coating the surfaces of the electrode with the molten caustic. In this connection, it is essential that all of the surfaces of the electrode be contacted with the molten hydroxide in order to achieve maximum recovery of ultra pure hydrogen generated in the electrolytic cell. Should palladium or hydrogen permeable palladium alloy tubes be employed as the hydrogen electrode, it is preferred that the exposure to the molten hydroxide be accomplished prior to the sealing or closing of the tube ends, so that the interior surfaces of the tubes are thoroughly wetted by the molten hydroxide during exposure of the electrode thereto.

As noted above, the hydroxides useful in the practice of the invention are the alkali and alkaline earth metal hydroxides, and include potassium hydroxide, sodium hydroxide, lithium hydroxide, rubidium hydroxide, cesium hydroxide, strontium hydroxide, and barium hydroxide. It will be appreciated that a mixture of two or more of such hydroxides may be employed to activate the palladium or hydrogen permeable palladium alloy electrode in accordance with the invention. While calcium hydroxide and magnesium hydroxide individually cannot be used because their decomposition occurs before they fuse, they may be employed in the preparation of molten mixtures with one or more of the foregoing hydroxides.

The temperature of the molten hydroxide used to precondition the palladium or palladium alloy surface in accordance with the invention prior to exposure to the oxidizing atmosphere should be at least about 450° C., and preferably between 450° C. and about 550° C. It has been found in this connection that such pre-conditioning or activation proceeds more rapidly at elevated temperatures and that the speed of activation varies with the temperature of the molten bath. For example, when a sodium hydroxide melt maintained at 450° C. was employed as the activating bath, it was found that an exposure of the palladium or palladium alloy electrode surfaces to that bath for a period of five minutes was required in order to achieve maximum activation of the electrode upon subsequent contact with an oxidizing atmosphere. On the other hand, at 700° C., only a few seconds exposure of the electrode surfaces to the bath were found to be necessary. Prolonged exposure to the bath at high temperatures will result in excessive etching and loss of the palladium or the palladium alloy material. The time necessary for achieving full activation at any particular temperature of the molten bath may, therefore, be easily determined by simple testing. This time may be defined as ranging from just a few seconds at temperatures of the order of about 700° C. to an excess of several minutes at temperatures of at least about 450° C.

After the palladium or palladium alloy surfaces have been exposed to the alkali or alkaline earth metal bath in accordance with the invention, it is essential that they be exposed to an oxidizing atmosphere, such as oxygen, or an oxygen containing atmosphere such as air, in order to complete the activation procedure. It is also essential that the temperature of the surface to be so exposed be at least about 450° C. in order to achieve proper activation. Surface temperatures may range as high as 750° C. and higher. Extreme temperatures causing the surface to be treated to lose its physical integrity should, of course, be avoided.

In the event the molten hydroxide bath is vented to the atmosphere, the contact of the electrode surface with oxygen will occur as soon as the electrodes are removed from the molten bath and exposed to the surrounding air. Such exposure will result in the immediate formation of the activated composition of the invention which forms as a coating on the surfaces which have been treated as noted above.

Subsequent to the exposure of the palladium or palladium alloy surfaces, such as hydrogen electrode surfaces, to the molten hydroxide bath, and subsequent to their exposure at a temperature of at least 450° C. to an oxidizing atmosphere, they may be rinsed, as with demineralized water, to remove any trace of the molten hydroxide thereon. At this point, extreme care should be exercised not to contaminate the surfaces of the electrode once they have been so activated, and not to disturb the activated coating formed upon the treated surfaces.

For a more detailed discussion of preferred specific embodiments of the invention, reference is made to the following description taken in conjunction with the accompanying drawing, in which:

FIG. 1 is a truncated, sectional view of one form of an electrolytic cell of the invention;

FIG. 2 is a sectional view along the line **2—2** of the electrolytic cell of FIG. 1; and

FIG. 3 schematically illustrates the use of an electrolytic cell of the invention in a system for producing ultra pure hydrogen.

As shown in FIG. 1, the electrolytic hydrogen cell **10** comprises an electrolysis chamber **11** constructed of nickel or other suitable electrolyte resistant metal. An electrolyte comprising an aqueous solution of 16 percent (by weight) sodium hydroxide fills the chamber **11** to the level **12**. The liquid level of the electrolyte in the cell is maintained constant by means of the inlet port **13** connected to a suitable water reservoir, best shown in FIG. 3. It has been found that where the electrolyte volume of the cell **10** comprises one-fourth of the total volume of the electrolysis chamber plus reservoir, an initial charge of a 4 percent solution of sodium hydroxide will, after a brief period of cell operation, provide the desired 16 percent concentration of sodium hydroxide in the electrolyte contained in the cell.

Prior to its introduction into the cell, the aqueous sodium hydroxide solution is preferably electrolyzed overnight in a separate electrolytic cell at a current of 15 amperes per liter of solution to remove any impurities

in the solution, thereby improving its electrolytic efficiency in subsequent use in the hydrogen cell **10**.

In the cell **10**, the electrolysis chamber **11** forms the anode and accordingly is provided with a suitable electrical connection to a direct current source (not shown) through the terminal **14**. In order to equalize the current density between the anode and the cathode, the solid nickel rod **15** is secured, as by welding, to the upper wall **16** of the chamber **11**. The rod **15** passes downwardly into the electrolysis chamber **11** and by virtue of its contact with the chamber wall forms part of the anode assembly of the cell.

The cathode portion of the cell comprises a plurality of hollow palladium tubes **17**, whose surfaces have been activated by the process of the invention, arranged substantially parallel one to the other and circumferentially around the anode rod **15**, as best shown in FIG. 2. The tubes **17** are sealed at their upper ends **18** as by welding or pinching to make them water tight, and are additionally supported in the chamber **11** by means of Teflon spacers **19** secured to the anode rod **15**.

The lower ends of the palladium tubes **17** are welded to the upper flange **20** of the cathode header assembly **21** which is composed of nickel or other suitable metal. Electrical contact between the cathode header assembly **21** and a suitable direct current source (not shown) is made through terminal **22** secured to the header **21** by means of a rivet or a screw **22***a*.

Prior to the assembly of cell **10**, the palladium tubes **17** are carefully cleaned, degreased, and subsequently dried in a 220° F. oven to remove all traces of moisture and cleansing solvent. The cleaned, dried palladium tubes are thereafter dipped into a molten bath of sodium hydroxide maintained at a temperature of 675°–700° C., and are held in the bath for about three minutes. Extreme care should be taken not to contact any part of the nickel header assembly with the molten caustic. Thereafter, the assembly is removed from the fused hydroxide bath, cooled in air, and rinsed thoroughly with deionized water. Care is exercised to protect the palladium tubes once they were so activated from contamination. Next, the palladium tubes are tipped, i.e., their ends were closed, and the tube-to-flange welds checked.

The header assembly with the activated palladium tubes was then assembled into the cell **10**.

As further shown in FIG. 1, the cell **10** is assembled by sandwiching two polypropylene insulators **23** and **24** between the flange **25** of the chamber **11** forming the anode, and flange **20** of the cathode header **21**. The entire assembly is held together by the clamping elements **26** and **27** in the form of screws in cooperative association with the hex nuts **28** and **29**. The screws **26** and **27** are insulated from electrical contact with the cathode header flange **20** by means of the insulating annular sleeves of rubber or other suitable material **30** and **31**.

In order to prevent escape of any electrolyte from the cell, O rings **32** of polypropylene or other resilient material which is resistant to electrolyte attack are disposed around each palladium tube in the vicinity between the two polypropylene flange insulators **23** and **24**. Upon tightening of the clamping elements **26** and **27**, the tight fitting O rings are compressed, thereby providing an excellent fluid seal around the palladium tubes in the vicinity of contact with the upper polypropylene insulator **23**.

The cell **10** is operated at ambient temperatures with approximately two or three volts direct current supplied across the cell. By virtue of use of the activated palladium cathode tubes **17**, substantially 100 percent of the hydrogen generated is recovered in the tubes as ultra pure hydrogen and passes down into the header assembly **21**. The ultra pure hydrogen is then recovered from the cell by means of the pipe fitting **32***a* connected to suitable conduits (not shown).

The oxygen generated at the anode surface, i.e., at the interior walls of the electrolysis chamber **11** and at the surface of the anode rod **15**, is vented through the outlet **33**. As best shown in FIG. 3, the outlet **33** is connected through a suitable conduit, preferably of flexible, electrolyte resistant material, such as polyethylene, into the electrolyte reservoir **35** in order to conserve any electrolyte which may be entrained in the exit gas.

As shown in FIG. 3, the hydrogen cell **10** containing a cathode comprising the activated palladium tubes is supplied with a direct current from a suitable D.C. source (not shown) to electrical leads **40** and **41**. The electrolyte in the cell is consistently maintained at a fairly constant level above the electrodes by means of the electrolyte reservoir **35** which supplies the electrolyte to the cell **10** through conduit **42** made of suitable electrolyte resistant flexible material such as polyethylene. As further shown in FIG. 3, a switch **43** biased to open position by spring **44** is provided in the line **41** to interrupt current flow to the cell **10** when the level of electrolyte in the reservoir falls below a predetermined minimum.

Hydrogen is electrolytically produced in the cell **10** at a rate of about 7 ml. at standard temperature and pressure for each ampere of current supplied to the cell and is recovered in ultra pure form through the pipe fitting **32***a*, conduit **45**, and valve **46**, as required. In order to terminate electrolysis when the hydrogen pressure in the cell reaches a predetermined maximum, a pressure responsive actuator switch **47** whose contact member **48** controls the current flow between the D.C. source and the cell is interposed in the conduit line **45**. Thus, when the predetermined maximum hydrogen pressure is attained in the outlet of the cell, the switch **47** will interrupt the current flow to the cell **10** thereby terminating the electrolysis, and consequently terminating the production of the hydrogen in the cell. A safety pressure release valve **49** is also interposed in the conduit line **45** to permit the release of hydrogen gas from the cell in the event the pressure sensitive valve **47** fails to operate. Generally, valve **49** will be responsive to a predetermined value of hydrogen pressure which is greater than the pressure required to actuate valve **47**.

Although the cathode illustrated in FIGS. 1–3 is in the form of tubes of palladium or a hydrogen permeable palladium alloy having activated surfaces, other cathode configurations may also be employed without departing from the spirit of the invention. For example, the cathode may be in the form of sheets, a series of sheets or of a cylinder having hollow walls so that the hydrogen generated at the cathode wall surfaces may permeate through the walls and be recovered through suitable recovery means. Broadly stated, therefore, the cathode useful in the production of hydrogen in accordance with the invention may be described as a palladium or hydrogen permeable palladium alloy membrane whose surfaces have been activated by the process of the invention, and which is disposed in the electrolysis chamber of the cell in a manner such that only one side, or one surface, of the membrane is exposed to the electrolyte.

Further, though the cathode may be composed of a hydrogen permeable palladium alloy which is impermeable to the electrolyte, such as a silver palladium alloy containing 75 percent palladium and 25 percent silver, or a ternary alloy of palladium, silver, and gold, cathodes composed of pure palladium are preferred since palladium alloy tubes have been found to require auxiliary heating to provide higher operating cell temperatures to operate efficiently. Pure palladium cathode tubes whose surfaces have been activated in accordance with the invention, on the other hand, at 15 amperes current flow have been found to produce a steady state temperature of about 150° F. in the electrolytic cell, and under these conditions afford an initial output and recovery of ultra pure hydrogen equal to that of the palladium silver alloy cathodes with the required auxiliary heating. Further, after two months of operation, the recovery of ultra pure hydrogen afforded by the palladium-silver cathode showed

a drop of about 10 percent while a cell with pure palladium cathodes showed no loss of ultra pure hydrogen recovery. Additionally, the resistance per foot of the pure palladium tube is about one-third that of the palladium-silver alloy tubes. In this connection, it has been found that the resistance of the palladium-silver alloy tubes, and indeed of the palladium tubes as well, may be significantly reduced by inserting a conducting wire inside the tube.

Although the anodes useful in the electrolytic hydrogen cell of the invention are preferably constructed of nickel, anodes constructed of other materials such as platinum and carbon may also be employed. However, platinum is highly expensive and carbon anodes have been found to disintegrate with time. Palladium-silver anodes will also work but are handicapped by virtue of the fact that they will slowly dissolve, building up thick deposits of palladium black on the cathode surface with a resultant decrease in the flow of hydrogen through the cathode tube walls.

In general, any electrolyte capable of producing hydrogen may be employed in the electrolytic hydrogen cell of the invention. It has been found, however, that basic electrolytes are preferred to acid electrolytes. In this connection, it has been discovered that best results are obtained when the electrolyte comprises an aqueous solution of an alkali or an alkaline earth hydroxide such as mentioned above. Of the basic electrolytes employed, it has been discovered that sodium hydroxide was preferred since the ohmic losses in the electrolytic hydrogen producing cell were low, no detactable amount of ozone was generated during cell operation, and there was no noticeable decrease of hydrogen flow with time in the case where sodium hydroxide was employed as the electrolyte.

The concentration of the alkali or alkaline earth metal hydroxide in the aqueous electrolyte may vary within wide limits. In the case of sodium hydroxide, it has been found that a 15 percent solution of sodium hydroxide in water provides optimum results from the standpoint of efficient hydrogen generation.

As noted above, it has been discovered that the electrolytic efficiency of an aqueous solution of an alkali or an alkaline earth metal hydroxide may be significantly increased by subjecting said solution in a separate cell to an electrolyzing current of at least 10 amperes per liter for at least one hour to provide a hydrogen cell electrolyte substantially free of impurities. This electrolyzing treatment must be accomplished in a unit other than the cell used to generate the high purity hydrogen. It is to be noted, however, that the duration of time to which the electrolyte is subjected to an electrolyzing current in the foregoing process is not in itself critical but is rather a function of current density and original purity of the electrolyte used.

The electrolyzing of the electrolyte may be conveniently achieved by adding the specific electrolyte to be used to a separate electrolytic cell and passing a current of at least 10 amperes per liter of electrolyte through the electrodes in the cell at about 3 volts D.C. for a period of at least one hour. Nickel electrodes may be used in such an electrolyzing treatment although electrodes made of other materials such as carbon or platinum are equally effective. Generally speaking, any inert electrodes may be employed.

The present invention is thus seen to provide a new and improved process for actiavting palladium or hydrogen permeable palladium alloy surfaces as, for example, the surfaces of cathodes in electrolytic hydrogen cells, to improve the ability of the surface to permeate hydrogen therethrough. Electrolytic hydrogen generators of the invention including cathodes characterized by such surfaces provide dry, pressurized hydrogen gas. Because the cathode of such a cell comprises a palladium or palladium alloy membrane which is selectively permeable to hydrogen, substantially 100 percent of the hydrogen electrolytically generated will be recovered in ultra pure form, since it is passed through the activated hydrogen transfer element, or cathode, of the cell. The impurity content of such hydrogen has been found to be less than 10 parts per billion.

Furthermore, the recovery of ultra pure hydrogen from prior art cells, or cells having untreated palladium or palladium alloy surfaces will, within a few days, drop to about 25 percent of the total hydrogen generated. On the other hand, hydrogen cells including cathodes whose surfaces have been activated in accordance with the present invention have been found to afford virtually 100 percent recovery in ultra pure form of the hydrogen generated in the cell, and continue to exhibit such efficient recovery of ultra pure hydrogen for a period of time approaching one year with no sign of reduced efficiency.

Although specific embodiments of the present invention have been described in considerable detail, it should be understood that the invention is not to be considered limited to those embodiments, but may be used in other ways without departure from the spirit of the invention and the scope of the appended claims.

I claim:

1. A process for activating a surface of palladium or a hydrogen permeable palladium alloy which comprises immersing the clean, moisture free surface into a molten hydroxide of an alkali or an alkaline earth metal and subsequently, exposing the treated surface at a temperature of at least about 450° C., to an oxidizing atmosphere to provide an activated coating thereon.

2. The process of claim **1** in which the molten hydroxide is sodium hydroxide.

3. The process of claim **1** in which the oxidizing atmosphere includes oxygen.

4. The process of claim **1** in which the surface is a palladium surface.

5. A composition formed as a coating on a surface by the process of claim **1**.

6. A hydrogen permeable element comprising a membrane of palladium or a palladium alloy whose surfaces are characterized by an activated coating formed by the the process of claim **1**.

7. A process for activating the surfaces of an electrode formed of palladium or a hydrogen permeable palladium alloy which comprises immersing the clean, moisture free electrode into a molten hydroxide of an alkali or an alkaline earth metal, and subsequently exposing the treated electrode surfaces at a temperature of at least about 450° C. to an oxidizing atmosphere to provide an activated coating thereon.

8. The process of claim **7** including the steps of immersing said electrode into the molten hydroxide maintained under an oxygen containing atmosphere, and subsequently removing the electrode from said molten hydroxide to expose said electrode to said atmosphere.

9. The process of claim **7** in which the hydroxide comprises sodium hydroxide and the oxygen containing atmosphere comprises air.

10. The process of claim **7** including the steps of dipping the clean, substantially moisture free electrode into a bath of molten sodium hydroxide, removing said electrode from said bath and cooling said electrode to room temperature in the presence of oxygen.

11. The process of claim **7** including the steps of dipping the clean, substantially moisture free electrode into a bath of molten sodium hydroxide maintained at a temperature of from about 450° C. to about 550° C., removing said electrode from said bath and cooling said electrode to room temperature in the presence of air.

12. An electrolytic cell comprising, in combination,

an electrolysis chamber including an anode and adapted to contain an electrolyte,

cathode structure disposed within said chamber comprising a membrane of palladium or a hydrogen permeable palladium alloy whose surfaces are ac-

tivated by the process of claim **1** and which is adapted to have only one surface thereof exposed to said electrolyte when the electrolyte fills said chamber, and

hydrogen recovery means for recovering in ultra pure form substantially all of the hydrogen electrolytically produced in said cell.

13. The electrolytic cell of claim **12** in which said membrane comprises

at least one tube of palladium or a hydrogen permeable alloy having an open end and a closed end and adapted to have only its exterior surface exposed to said electrolyte when the electrolyte fills said chamber, and

hydrogen recovery means in cooperative association with said open end of said tube for recovering from said cell in ultra pure form substantially all of the hydrogen electrolytically produced in said cell.

14. The electrolytic cell of claim **12** including

a vertically disposed electrolysis chamber including an anode and adapted to contain an electrolyte,

said membrane comprising a plurality of vertically disposed, parallel tubes of palladium or a hydrogen permeable palladium alloy each tube having an open end and a closed end and adapted to have only its exterior surface exposed to said electrolyte when the electrolyte fills said chamber, and

hydrogen recovery means in cooperative association with the open ends of said tubes for recovering from

said cell in ultra pure form substantially all of the hydrogen electrolytically produced in said cell.

15. The electrolytic cell of claim **12** including a vertically disposed electrolysis chamber adapted to include an electrolyte, and including an anode and electrolyte inlet means and electrolyte outlet means,

said membrane comprising a plurality of vertically disposed, parallel palladium tubes each tube having an open end and a closed end and adapted to have only its exterior surface exposed to said electrolyte, and

hydrogen recovery means in cooperative association with the open ends of said tubes for recovering in ultra pure form substantially all of the hydrogen electrolytically produced in said cell.

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