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- (71) **Applicant:** CHAIRMAN, DEFENCE RESEARCH & DEVELOPMENT ORGANISATION [IN/IN]; Ministry of Defence, Govt of India, Room no. 348, B-wing, DRDO Bhawan, Rajaji Marg, New Delhi 110105 (IN).
- (72) **Inventors:** ROY CHOUDHURY, Suman; Naval Materials Research Laboratory, Shil- Badlapur Road, Anand Nagar P.O, Addl. Ambernath, Thane 421 506 (IN). PIL-LAI, Janardhan, Narayanadas; Naval Materials Research Laboratory, Shil- Badlapur Road, Anand Nagar P.O, Addl. Ambernath, Thane 421 506 (IN). SOMAIAH, Boddu; Naval Materials Research Laboratory, Shil- Badlapur Road, Anand Nagar P.O, Addl. Ambernath, Thane 421 506 (IN). PARETA, Mahendra; Naval Materials Research Laboratory, Shil- Badlapur Road, Anand Nagar P.O, Addl. Ambernath, Thane 421 506 (IN). SATVILKAR, Prasad; Naval Materials Research Laboratory, Shil- Badlapur

Road, Anand Nagar P.O, Addl. Ambernath, Thane 421 506 (IN). KUMAR, Amit; Naval Materials Research Laboratory, Shil- Badlapur Road, Anand Nagar P.O, Addl. Ambernath, Thane 421 506 (IN). NEGI, Prem Kant; Naval Materials Research Laboratory, Shil- Badlapur Road, Anand Nagar P.O, Addl. Ambernath, Thane 421 506 (IN). MAHTRE, Nitin Nana; Naval Materials Research Laboratory, Shil- Badlapur Road, Anand Nagar P.O, Addl. Ambernath, Thane 421 506 (IN). ROY CHOUDHURY, Suhasini; Naval Materials Research Laboratory, Shil- Badlapur Road, Anand Nagar P.O, Addl. Ambernath, Thane 421 506 (IN). VERMA, Vaibhav; Naval Materials Research Laboratory, Shil- Badlapur Road, Anand Nagar P.O, Addl. Ambernath, Thane 421 506 (IN). DALVI, Vishal; Naval Materials Research Laboratory, Shil- Badlapur Road, Anand Nagar P.O, Addl. Ambernath, Thane 421 506 (IN). SINGH, Parvin, Kumar; Naval Materials Research Laboratory, Shil- Badlapur Road, Anand Nagar P.O, Addl. Ambernath, Thane 421 506 (IN). SURYAWANSHI, Shivaji, Eknath; Naval Materials Research Laboratory, Shil- Badlapur Road, Anand Nagar P.O, Addl. Ambernath, Thane 421 506 (IN). MANDAL, Shambhu, Kumar; Naval Materials Research Laboratory, Shil- Badlapur Road, Anand Nagar P.O, Addl. Ambernath, Thane 421 506 (IN).

(74) **Agents:** MAJUMDAR, Subhatosh et al.; S. Majumdar & Co., 5 Harish Mukherjee Road, State of West Bengal, Kolkata 700 025 (IN).

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(54) **Title:** AIR INDEPENDENT PROPULSION SYSTEM FOR SUBMARINES BASED ON PHOSPHORIC ACID FUEL CELL WITH ONBOARD HYDROGEN GENERATOR

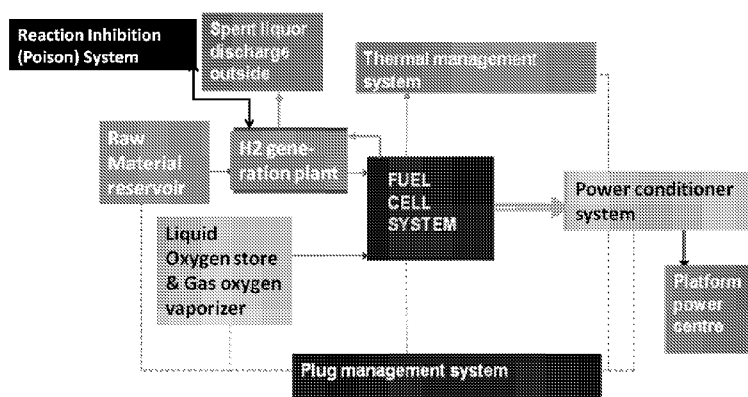


Figure 1: Block Diagram of AIP with Reaction Inhibition system

(57) **Abstract:** The present invention relates to an air independent propulsion (AIP) system. The present invention more particularly relates to Air Independent Propulsion System for Submarines based on Phosphoric Acid fuel Cell (PAFC) with onboard hydrogen generator and power conditioning system. The present invention also relates to method of increasing to increase life and performance of PAFC stacks. The major technology block of AIP system of the present invention is shown schematically in figure 1.



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**AIR INDEPENDENT PROPULSION SYSTEM FOR SUBMARINES BASED ON
PHOSPHORIC ACID FUEL CELL WITH ONBOARD HYDROGEN
GENERATOR**

5 FIELD OF INVENTION

The present invention relates to an air independent propulsion (AIP) system. The present invention more particularly relates to Air Independent Propulsion System for Submarines based on Phosphoric Acid fuel Cell with onboard hydrogen generator and power
10 conditioning system. The present invention also provides for method of increasing adhesion of phosphoric acid matrix to graphitic electrode structure. The present invention also relates to a graphite heat exchanger plate for use in a high capacity acid fuel cell stack assembly, and more particularly with graphite heat exchanger plate that are resistant to edge swelling due to acid absorption, resistant of blockage in gas port due to swelling,
15 with enhanced heat transfer properties, imperviousness to gases and higher absorption of thermal stress generated by embedded metal tubes to graphite plate.

BACKGROUND OF THE INVENTION

Submarines and underwater platforms depend on batteries and other stored form of
20 energy for propulsion power. While the land based systems have flexibility of choice of power systems and can harness the oxygen in atmosphere for burning of fuel, this is not possible for a submerged system.

Conventional submarines use hybrid power systems comprising of the lead acid batteries
25 which serve as the power supply system for propulsion needs while under water. Diesel engines provide for onboard recharging of batteries, possible only during snorkeling. The system therefore has restricted indiscretion.

Air independent propulsion (AIP) system for submarine application is primarily an
30 auxiliary power generation unit placed within a submarine. This auxiliary unit works in tandem with the existing battery bank of the vessel and operates underwater as a supplement to the submarine battery power.

Air Independent Propulsion (AIP) is a term that encompasses technologies which allow submarines and submersibles to operate without the need to surface or use a snorkel to access oxygen from atmospheric air. The term usually excludes the use of nuclear power, and describes augmenting or replacing the diesel-electric propulsion system of non-
5 nuclear vessels.

Among various types of air independent systems, hydrogen powered fuel cell based AIP is highly efficient, compact and has few moving parts. Thus the noise level is extremely low.

10 Among the various options available for AIP system, fuel cell based AIP technology has distinct advantages due to low noise levels and high power generation efficiency. However, selection of subsystems in terms of hydrogen carry mode, type of fuel cell and thermal management systems depends on the space available, specified underwater
15 endurance and power to be generated.

Fuel cells are electrochemical devices that transform chemical energy of the reactants directly into electrical energy. In principle, fuel cell operates like a battery. However, unlike battery fuel cell does not rundown nor requires recharging, it produces energy in
20 the form of electricity as long as fuel is supplied.

Any fuel cell essentially consists of an invariant electrode- electrolyte system with two porous gas diffusion electrodes and an electrolyte in between. The electrolyte is a solid or a liquid held in a suitable matrix. The fuel gas and oxygen are fed to individual electrodes
25 through gas manifolds that act as current collectors as well. Fuel-Hydrogen is oxidized at one of the electrode viz., anode where it is ionized. Oxygen gets reduced at the other electrode viz., cathode, thereby generating electricity.

US7938077 relates to hydrogen generation apparatus. The said apparatus comprising a
30 hydrolysis reaction compartment, a mass of solid lithium hydride disposed in the compartment, inlet and outlet means for passing sea water through the compartment to generate steam, lithium hydroxide and hydrogen gas, a condenser for condensing the

steam and lithium hydroxide, and a tank for collecting the hydrogen gas, the tank having outlet means for discharging the hydrogen gas to a vehicle propulsion means.

‘Fuel cell systems for submarines: from the first idea to serial production,’ published in
5 ‘Journal of Power Sources’ by Psoma et al relates to future submarines of
Howaldtswerke-Deutsche Werft AG (HDW) fuel cell power plants for air independent
propulsion.

EP1717141B1 relates to submarine with fuel cell system and a battery compartment
provided with ventilation system. This provides an improved system for collecting
10 residual gas comprising deriving the output from one of the fuel cell power plant exhaust
gases, which takes up less space and weight of the submarine.

DE202004020537 relates to underwater drive system for submarine that uses stores of
oxygen and hydrogen that are fed to fuel cell and waste heat from fuel cell to warm metal
15 hydride hydrogen store to release hydrogen. The energy supply system of this prior art
comprises one or more fuel cell an array of metal hydride hydrogen stores. In this prior
art hydrogen is stored (occluded) in metal hydride and by heating the same hydrogen is
released for fuel cell use. When back on shore the metal powder needs to be recharged
with pressurized hydrogen. Furthermore carrying hydrogen in stored form is a high-risk in
20 a closed environment setting.

US7323148 relates to hydrogen generation that is capable of operating in any orientation
and having no moving parts.

25 Conventional submarines require to surface for atmospheric oxygen to generate power
when underwater which is makes it vulnerable for detection.

Hydrogen gas is used as a fuel for fuel cells and it requires a compact, high-density,
controllable source of hydrogen gas. Hydrogen Gas cylinders are too heavy and bulky,
30 while liquid hydrogen requires cryogenic cooling. Metal hydride systems are limited to 1-
3% hydrogen by weight; are endothermic (that is, as hydrogen is evolved, the container

gets colder, which reduces the hydrogen vapor pressure); the hydrogen evolution rate is not controllable or adjustable (so that an oversized amount of hydride is necessary).

Thus there exists a need of hydrogen generation on-demand basis to quench for a longer
5 duration underwater power requirement when dived. Further AIP system needs to conform to various platform restrictions. Most important of them being low noise and vibration signatures with regards to both underwater radiated noise as well as air borne noise. Apart from low noise signatures, the unit needs to be accommodated into the constraints of space and weight specified by the platform architect in order to achieve
10 expected performance of the platform.

An AIP system that is able to generate hydrogen onboard on demand and at the same time is in conformity with various platform restrictions is the need of the hour.

15 The inventors of the present invention have devised PAFC based Air Independent Propulsion (AIP) for submarine application that houses an on-board hydrogen generation system with longer underwater endurance, low noise levels, that is operated in fully containable manner, and does not produce gaseous byproduct. PAFC is used for its very long life as proved globally and its ability to operate even with little impurity of
20 hydrogen.

The AIP of the present invention based on PAFC with onboard sodium borohydride hydrolyser provides a quieter submarine with higher endurance.

25 In the present invention the hydrogen is formed in pure state with no gaseous by product. Also there is no need to use submarine ventilation system to carry the unused gas and react the same with oxygen or expel the system.

Further the inventors of the present invention faced the problem of crystallization of
30 sodium borohydride at low temperatures when dived. The inventors have identified a

crystal inhibitor to prevent crystal formation and scaling of the concentrated NaBH_4 solution when dived.

OBJECTS OF THE INVENTION

5 It is an object of the invention to provide an air independent propulsion system that does not produce gaseous byproduct and can be operated in a fully containable manner for submarines without taking or giving out anything to the sea environment.

It is another object of the present invention to provide an air independent propulsion system that operates on demand basis.

10 It is a further object of the present invention to provide an air independent propulsion system with PAFC stacks that are robust, provide long life support baseline power, is highly reliable and tolerates parameter variation.

It is further more an object of the present invention to provide an air independent propulsion system where NaBH_4 hydrolyser and PAFC stack are operated in a decoupled mode allowing dynamic operation of the air independent propulsions (AIP).

15 It is further more an object of the present invention to prevent crystal formation or stratification of NaBH_4 solution employed in hydrolyser.

It is further an object of the present invention to improve pumpability of NaBH_4 solution.

20 It is yet another object of the present invention to provide for onboard hydrogen generation to allow longer underwater endurance as more hydrogen can be carried by chemical means.

It is yet another object of the present invention to provide an Intelligent Power conditioner that can sense submarine battery state of charge and can be programmed for specific power output.

25 It is also an object of the present invention to provide specialized safety by poisoning the hydrolysis reaction.

It is further an object of the present invention to carry stable solution of NaBH_4 for easy deployment and the same is effected by using mixed alkali (NaOH/KOH) as stabilizers – mixed form optimum reaction kinetics and smaller/lesser crystals in the spent liquor.

6

It is another object of the present invention to provide hydrolyser for onboard hydrogen generation system for underwater application with in-built heat exchangers

It is further an object of the present invention to provide a compact hydrolyser using recirculation based borohydride hydrolysis.

- 5 It is yet another object of the present invention to provide for onboard hydrogen generation to allow longer underwater endurance.

It is yet another object of the present invention to provide continuous supply of hydrogen to fuel fuel-cells in power generation unit in Air independent propulsion system.

- 10 It is an object of the invention to enhance binding strength of phosphoric acid fuel cell (PAFC)

It is an object of the present invention to provide method to determine the adhesion strength of an acid holder matrix

It is another object of the present invention to provide a method to increase the adhesion strength of the matrix with the graphitic electrode structure.

- 15 It is further an object of the present invention to provide a method to estimate acid migration to a matrix.

It is yet another object of the present invention to increase life and performance of PAFC stacks.

- 20 It is an object of the present invention to provide a conducting hydrophobic caulk material that provides thermal contact, prevents corrosion of metallic tube by preventing acid seepage and the absorbs the thermal stress owing to unequal thermal expansion of the rigid graphite material and the metallic coil

It is an object of the invention to provide variable thermal expansion of metallic coils and graphite plates without causing mechanical damage

- 25 It is another object of the present invention to provide graphite heat exchanger plates as hard plate which gives more stability in assembly of stack and enhanced heat transfer properties.

SUMMARY OF THE INVENTION

According to an aspect of the present invention there is provided an air independent propulsion (AIP) system for submarine comprising:

- 5 a. on-board hydrogen generation system, the said on-board hydrogen generation system comprising fuel solution, catalyst to generate hydrogen in a compact vessel;
- b. liquid oxygen (LOX) storage and feeding distribution system;
- c. phosphoric acid fuel cell (PAFC) system, wherein in said phosphoric acid fuel cell consumes hydrogen and oxygen to generate unregulated DC
10 power;
- d. power conditioner system wherein the said power conditioner system adapts the unregulated DC PAFC power and converts into regulated voltage controlled DC power;
- e. plug management system wherein the said plug management system
15 controls the operation and integration with the dynamic load requirement of the platform;
- f. reaction inhibition system;
- g. fuel cell balance of plant (BoP) arrangement wherein the said fuel cell balance of plant (BoP) arrangement comprises hydrogen loop, synthetic air
20 loop and pressurized water system (PWS).

According to another aspect of the present invention there is provided a method of generating power from air independent propulsion system for submarine, the said method comprising the steps of:

- 25 -generating hydrogen from raw material feed comprising fuel solution and catalyst in said on-board hydrogen system (a);
- feeding the generated hydrogen and oxygen to PAFC stacks (c) where the supplied hydrogen and oxygen is consumed to generate unregulated raw DC power;
- 30 -providing the unregulated raw DC power to power conditioning system (d) to generate regulated DC power

- interfacing the regulated DC power with platform switch board to provide power to platform
 - providing a network of heat exchangers to manage the thermal load with
 - de-mineralized water cooling circuit, the said de-mineralized water cooling circuit consisting of cooling water tank, cooling water tanks, cooling water pumps, piping network, sensor means and valve means and sea water cooling network, the said sea water cooling network consisting of hull penetrations, sea water heat exchangers, sea water circulation pumps, sea water piping network and sensor means and valve means
 - providing exhaust means to expel spent liquor and master vent means for gases substantially balancing heating and cooling requirements of the system'
 - providing control and monitoring means for automatic operation of the entire AIP system and individual components of the system and for regulating the same in accordance with the power demands on the system preferably by means of controller architecture comprising:
 - PLC type controller to operate hydrogen generator;
 - model predictive controller with an algorithm for determining fuel cell stack health and optimizing current distribution to each stack so that power from fuel cell meets the power demand of the system;
 - nodal controller to supervise overall control, efficacy, and adjust lower part controller set point to minimize instability;
 - submarine controller, with which, the said nodal controller interacts to obtain power demand and pass AIP parameters to operator.
- 25 According to another aspect of the present invention there is provided fuel solution for air independent propulsion system wherein the said fuel solution comprises:
- a) an aqueous solution concentrate of sodium borohydride in the range of 30% w/w to 40% w/w;
 - b) a stabilizer selected from potassium hydroxide or sodium hydroxide; and
 - c) a crystallization inhibitor selected from methyl paraben or propyl paraben at 0.02% to 0.15% by weight.

According to yet another aspect of the present invention there is provided a method of generating hydrogen from on-board hydrogen generation system comprising fuel tank, catalyst tank, compact vessel with in-built heat exchangers, intermediate tank, spent storage tank, pressure control means wherein, the said method comprising the steps of:

- 5 a. pumping the fuel solution and caustic solution from fuel tank and catalyst from catalyst tank to the compact vessel with in-built heat exchangers;
- b. hydrolyzing borohydride in fuel solution in presence of catalyst in the said compact vessel for generating hydrogen at higher rate than required;
- c. discharging the resultant borax solution formed as byproduct in step b,
10 intermittently to intermediate tank wherein the trace borohydride in borax solution is converted to hydrogen, the resultant residual hydrogen then joins to the main hydrogen line and remainder is discharged to spent storage tank;
- d. hydrolyzing reaction in step b, resulting in increase in pressure; which
15 activates the pressure control means to stop the fuel solution feed in step a;
- e. as hydrogen is consumed by phosphoric acid fuel cell (c), the pressure in the compact vessel falls thereby restarting the fuel solution feed;
- f. providing the said compact vessel with conformal heat exchanger for heat removal and reactant mixing;
- 20 g. providing the said compact vessel with top mounted heat exchanger for cooling product hydrogen;
- h. providing the said compact vessel with non-conventional heat exchanger coils for removal of heat and reactor temperature maintenance comprising
25 shell side circulating borate solution and tube side circulating de-mineralized water .

According to another aspect of the present invention there is provided a phosphoric acid fuel cell (PAFC) stack for air independent propulsion system for submarine wherein the
adhesion strength of phosphoric acid electrolyte to graphitic electrode structure in
30 phosphoric acid fuel cell is increased by applying wash coat on graphitic electrode structure before casting phosphoric acid electrolyte.

According to another aspect of the present invention there is provided multiple metallic tubes embedded graphite heat exchanger plates for phosphoric acid fuel cell stack assembly comprising:

- 5 a) multiple serpentine metallic tube with different path configurations embedded in a high density conducting graphite grooved plate with fuel cell cathode channel at one side surface wherein the said metallic tubes are embedded in grooved plate by using moulding mixture comprising exfoliated graphite powder and polyterafluoroethylene (PTFE) suspension between tube and graphite walls, and
- 10 b) a thin, electrically conducting sheet resistant to high temperature acid attached at the grooved side surface of high density graphite plate from where metal tubes are fitted, by applying thin glue composition.

BRIEF DESCRIPTION OF ACCOMPANYING DRAWINGS

Figure 1: Block diagram of Air Independent Propulsion system with Reaction inhibition system

- 15 Figure 2: NaBH₄ solution with and without crystallization inhibitor

Figure 3: Fuel cell power output system

Figure 4: Fuel cell Balance of Plant Arrangement

Figure 5: Schematic diagram of hydrogen system of the present invention with hydrolyser.

- 20 Figure 6: Schematic and Isometric view of Heat Exchanger

Figure 7: Top view of Heat Exchanger

- Figure 8: Blown-up view of a PAFC. The fuel cell stack is generally represented as numeral (10). Each stack 10 is comprised of number of unit cells (5) separated by gas separator bipolar plates (1). Each cell5 includes an electrolyte matrix layer (3) having an anode electrode 4 disposed on one side thereof and a cathode electrode (2) disposed on the other side. The anode electrode (4) comprises of porous gas diffusion paper coated
- 25

with catalyst layer and flow field are parallel to the plane of the paper. The cathode electrode (2) also is comprised of porous gas diffusion layer coated with catalyst layer and flow field is parallel to the plane with cross flow in direction to the fuel flow. The ribbed gas separator plates (1) form reactant gas channels on each side of the plates. The supported matrix layer (3) has phosphoric acid electrolyte disposed therein.

Figure 9: (a) depicts matrix adhesion test assembly, 26 and 27 represent height of water and diameter of the glass vessel used. 28 is the distance between the sample (25) and the stirrer (22). The sample (25) is electrode coated with SiC matrix fixed at the bottom of the vessel. In Fig 9 (b) the sample (23), electrode coated with catalyst layer and SiC matrix is held vertically at a distance (29) from the stirrer (22) and matrix side facing the stirrer. (26) and (27) are the height of water and diameter of the glass vessel.

Figure 10: Assembly fixture for acid migration test.

Figure 11: Acid migration of different matrix at 0.7 Mpa with time

Figure 12: Comparison of three matrix performance in unit cell with H₂/O₂.

Figure 13: Comparison of three matrix performance in unit cell with H₂Air.

Figure 14: Dosing Methodology of the inhibitor powder for poisoning NaBH₄ hydrolysis reaction inside the H₂ generator.

Figure 15: Effect of poison (sodium methacrylate powder) of about 0.8 kg injected to a 40 kw scale down H₂ generator of the AIP system.

Figure 16: Plate with channel for the metallic coil tube and integrated flow groove on the bottom

Figure 17: Single metallic coil tube

Figure 18: Cover plate with flow grooves on top

Figure 19: Fully assembled heat exchanger with soft hydrophobic, conducting caulk around the tube for better contact.

DETAILED DESCRIPTION OF THE INVENTION

The following description with reference to the accompanying drawings is provided to assist in a comprehensive understanding of exemplary embodiments of the invention. It includes various specific details to assist in that understanding but these are to be regarded as merely exemplary.

The present invention is described in connection with such embodiments, but the invention is not limited to any embodiment. The scope of the invention is limited only by the claims and the invention encompasses numerous alternatives, modifications and equivalents. Numerous specific details are set forth in the following description in order to provide a thorough understanding of the invention. These details are provided for the purpose of example and the invention may be practiced according to the claims without some or all of these specific details. For the purpose of clarity, technical material that is known in the technical fields related to the invention has not been described in detail so that the invention is not unnecessarily obscured

Accordingly, in an embodiment of the present invention there is provided air independent propulsion (AIP) system for submarine comprising:

- a. on-board hydrogen generation system, the said on-board hydrogen generation system comprising fuel solution, catalyst to generate hydrogen in a compact vessel;
- b. liquid oxygen (LOX) storage and feeding distribution system;
- c. phosphoric acid fuel cell (PAFC) system, wherein in said phosphoric acid fuel cell consumes hydrogen and oxygen to generate unregulated DC power;
- d. power conditioner system wherein the said power conditioner system adapts the unregulated DC PAFC power and converts into regulated voltage controlled DC power;
- e. plug management system wherein the said plug management system controls the operation and integration with the dynamic load requirement of the platform;

- f. reaction inhibition system;
- g. fuel cell balance of plant (BoP) arrangement wherein the said fuel cell balance of plant (BoP) arrangement comprises hydrogen loop, synthetic air loop and pressurized water system (PWS).

5

In the AIP system of the present invention, the hydrogen is generated onboard through sodium borohydride hydrolysis. Oxygen required is supplied from cryogenically stored liquid oxygen (LO_x). The hydrogen and oxygen is supplied to a battery of phosphoric acid fuel cell stacks (PAFC) to generate unregulated DC power and water is formed as a byproduct from the fuel cell. The unregulated DC output is conditioned and converted to submarine quality of power through power conditioners. The water generated in the fuel cell is in turn fed to the hydrogen generator (sodium borohydride hydrolyser) and the spent liquor (borax solution) generated along with hydrogen is either expelled to the sea or held inside the tanks and used for compensating purpose of the submarine. A plug management system controls the operation and integration with the dynamic load requirement of the platform. The major technology block of the proposed AIP is shown schematically in figure 1.

Figure 1 depicts the overall process of the PAFC based AIP system of the present invention. Hydrogen generation is the first subsystem in the process train. Hydrogen generation is on-demand basis and comprises the raw material feed tanks, the hydrogen generation system and the spent material storage tanks. The hydrogen flows into the fuel cell stacks where it is consumed along with oxygen to form water and unregulated raw DC power. Water produced in the fuel cell is used in hydrogen generator and the unregulated DC power is fed into the power electronics system. The output of the power electronics system resulting on regulated user specified quality DC power is interfaced with the platform switch board which in turn provides power to the platform.

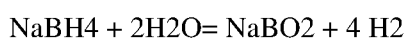
In the present invention, a network of heat exchangers manages the thermal loads of the AIP system and finally the heat is ported out and exchanged with sea water in sea-water heat exchanger.

An intelligent control system operates the entire AIP system of the present invention and the hierarchal strategy allows the plant operation in totally automated mode. A diagnostic module and valued applets such as real-time energy calculator that allow planning of
5 endurance are also interfaced with the control system.

In the present invention the hydrogen generator uses a compact one vessel system which also acts like a hydrogen buffer vessel. The hydrogen is generated on demand and to acquire the load following characteristics, the following methodology is used.

10 According to an embodiment of the present invention there is provided a hydrolyser using recirculation based borohydride hydrolysis. Capacity or scale of hydrogen generation by sodium borohydride hydrolysis process is first time developed in the present invention. In the present invention process of sodium borohydride hydrolysis, aqueous solution of
15 sodium borohydride (NaBH_4) is used for generating hydrogen by dosing it inside reactor system along with Catalyst in form of NiCl_2 or CoCl_2 solution which get converted inside the reactor in presence of NaBH_4 to Ni / NiB or Co/CoB particles which act like a catalyst. Sodium borohydride reacts with water to generate hydrogen and borate slurry in presence of this catalyst. Hydrolysis reaction is exothermic in nature and generated heat is
20 dissipated by pumping the NaBH_4 / catalyst /product liquor slurry through a heat exchanger which could be cooled by water or even air. The slurry after heat exchanger is flashed into the same vessel from which it was pumped out.

NaBH_4 solution stored in feed tanks along with the catalyst in solution form is pumped to
25 the H_2 generator at a rate which can produce hydrogen higher than the required rate. This increases pressure of the hydrogen generator and through a pressure control system stops the NaBH_4 solution feed pump to control hydrogen generation. As H_2 gets used up, the pressure in the H_2 generator falls and the pump restarts. This philosophy allows decoupling of hydrogen generation from the usage of the same in the downstream fuel
30 cell which depends upon the power requirement. The reaction that happens inside the H_2 generator is:

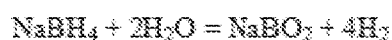


The spent liquor i.e. NaBO₂ solution along with the catalyst particles and trace NaBH₄ is discharged intermittently from the H₂ generator to an intermediated hold tank to maintain the level of liquid inside the H₂ generator vessel. The trace NaBH₄ in the spent liquor
5 reacts in presence of catalyst inside the intermediate tank and the hydrogen generated joins the main hydrogen stream which is filtered and sends out for PAFC use through a controlled dosing.

In an embodiment of the present invention, there is provided a method and materials for
10 the generation of hydrogen gas from storage materials. In particular, the present invention relates to generation of hydrogen gas by contacting water with sodium borohydride in the presence of a catalyst, such as cobalt or nickel.

In an embodiment of the present invention, the components of hydrolyser of the present
15 invention are as follows:

- The agitation to ensure uniform mixing and heat transfer to keep temperature of the slurry in control is achieved by re-circulating the NaBH₄ /catalyst and product slurry through a heat exchanger and a pumping device.
- The main vessel which holds the catalyst / NaBH₄ feed and NaBO₂ product also
20 acts like a gas-liquid separator and a buffer tank for the hydrogen.
- The system generates no gaseous by product and hence is ideal for underwater or enclosed area hydrogen generation.
- The hydrogen generated is filtered using micro filters and is transferred to fuel cell section for electricity production. Hydrolysis reaction take place inside reactor
25 system is as follows



- Product hydrogen cooling coming out of the main vessel is done by finned tube heat exchanger integrated at top of reaction vessel for process compaction and outlet temperature is maintained by Demineralize water circulation. Schematic
30 diagram for hydrogen generation from sodium borohydride hydrolysis process is

depicted in figure 1. Design was done considering the submarine environment conditions of tilting, shock, noise, vibration etc.

At this point the overall operation of the hydrogen generation system is explained with reference to the construction and functioning thereof. (Figure 5, 6 and 7)

Working of the Hydrolyser of the Present Invention:

Figure 6 is the schematic representation of onboard hydrogen generation from sodium borohydride solution with hydrolyser of the present invention. Sodium borohydride is dissolved in mixed caustic solution stored inside fuel tank and pumped to the main vessel containing suspended catalyst particles and reaction byproduct borax solution which is called borate slurry. The borate slurry along with reaction mass is recirculated through a pump to a heat exchanger and is returned to the vessel where the hydrogen is flashed and separated from the slurry. The hydrogen separated in the vessel is cooled and passed through an alkali line mist separation filter train followed by an acid scrubber. The clean gas is finally taken to fuel cell system. Product borate solution intermittently discharge through hydrolyser to an intermediate tank and finally to spent storage tank. Intermediate borate tank is kept to allow conversion of trace NaBH_4 in the borate slurry and this residual hydrogen generated joins the main hydrogen line. Two stage pressure regulators provided to supply constant amount of hydrogen to fuel cells irrespective of the pressure in the main vessel.

The hydrolyser of the present invention is compacted by placing the conformal heat exchanger system inside the main vessel for heat removal and reactant mixing. The product hydrogen cooling is done in the same single vessel through a top mounted heat exchanger so that condensate forms can roll back into the main vessel. Non-conventional heat exchanger coil is designed for removing reaction heat and maintaining reactor temperature as shown in figure 6 and 7. Water is used for cooling purpose.

Shell side is used for borate solution and tube side is used for de-mineralize water circulation. Tube bundle is made concentric to shell boundary to achieve process

requirements, easy integration and maintenance purpose. Inspection nozzles are provided to check health of tubes.

In an embodiment of the present invention the catalyst solution may be aqueous solution of salt of catalyst metals like NiCl_2 , CoCl_2 etc. This solution in contact with NaBH_4 reacts insitu and forms metal-boride particles like Ni_2B or Ni and is the active catalyst.

The NaBH_4 solution could be self hydrolysed albeit at a slower rate without catalyst inside the storage tanks. NaOH/KOH along with other stabilizer is mixed with NaBH_4 to reduce this self hydrolysis rate to a negligible rate.

The hydrogen from the generator is fed into multiple PAFC stacks and the unreacted hydrogen comes out of the stacks alongwith moisture is recycled to the stacks through a blower system after removing the moisture.

The hydrogen flow from the H_2 generator to the FC system is controlled by pressure and total current produced in the stacks.

Gaseous oxygen is generated by vaporizing LOX using water as the thermal media. The water in this process gets cooled and this chilled water is used for the air conditioning purpose of the Submarine micro-environment.

The gaseous oxygen is then dosed to the PAFC system after diluting it with N_2 (optional) along with hydrogen to generate power. The unreacted oxygen along with N_2 and generated moisture comes out of the PAFC stacks and the same is fed back using a blower after condensing and removing the moisture using sea water cooling. The oxygen injection to the PAFC stacks is based on the oxygen concentration in the oxygen recirculation loop.

The water from the fuel cell is pumped to the H_2 generator to allow dilution of the spent liquor to improve the pumpability of the liquor and reduce the crystallization of the same. However in certain design it is possible to use the generated water as fresh water source

for the Submarine use after treating the PAFC generated water for trace phosphoric acid removal.

5 The power generated in the PAFC stack of the present invention is connected to power conditioner system which adapts the unregulated DC PAFC power and convert into regulated (voltage controlled) DC power matching with the Submarine battery bank voltage, so that the PAFC generated power can either charge the submarine battery or can be used for various electrical loads of the Submarine.

10 The fuel tanks will have close loop air ventilation through pressure equalization burner of the exhaust system so as to avoid any hydrogen buildup on the headspace of the tank.

The tanks will have filling ports from the top and outlet at the bottom. The outlet pipes through isolation valve goes to a manifold through which fuel solution is fed to the
15 hydrogen generation system. The fuel feeding pump and the manifold can be also used for transferring of fuel solution from one tank section to other.

The tanks are laced with a cooling water limped and a insulated lagging to prevent them for getting heated up in case of external fire. The cooling water limped provision is only
20 made and in case of need the same can be connected to de-mineralized cooling water circuit for cooling the tank.

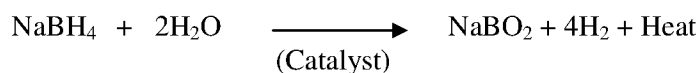
Onboard storage of NaBH₄

Solid NaBH₄ is dissolved in water and is stabilized with additives. This is essential as
25 NaBH₄ hydrolyses slowly in contact with water. Additionally the fuel solution is added with minor amount of specialized chemicals to prevent crystallization and or stratification of NaBH₄ when external sea water temperature is low. All these additives alongwith the NaBH₄ dissolved in water is thus termed as The “Fuel Solution”

30 Hydrogen gas is used as a fuel for fuel cells and it require a compact, high-density, controllable source of hydrogen gas. Metal hydrogen complexes, such as sodium borohydride (NaBH₄), zinc borohydride (ZnBH₄), potassium borohydride (KBH₄),

calcium borohydride (CaBH_4), lithium aluminum hydride (LiAlH_4), sodium boron trimethoxy hydride ($\text{NaBH}(\text{OCH}_3)_3$), and so on, are attractive solid sources of hydrogen. When reacted with water, in the presence of a suitable catalyst, these metal hydrogen complexes can provide a hydrogen gas yield from 11-14% by weight (which is 5-6 times more hydrogen released per gram than for metal hydrides).

Sodium borohydride is a particularly attractive solid source of hydrogen since its equivalent energy density is nearly equal to that of diesel fuel. Sodium borohydride reacts exothermically with water in the presence of a catalyst (or when acidified) to produce hydrogen gas and sodium metaborate (i.e., Borax) according to the following reaction:



This reaction is particularly efficient at generating hydrogen gas, since the sodium borohydride supplies two of the hydrogen gas molecules (H_2), and the water supplies the other two molecules, for a total of four molecules of H_2 . The reaction is exothermic; does not require the addition of heat or the use of high pressure to initiate; and can generate hydrogen even at low temperature.

Fuel Cell Solution of the Present Invention:

According to an embodiment of the present invention, fuel solution comprises an aqueous solution concentrate of sodium borohydride, a stabilizer and phase formation inhibitor/crystallization inhibitor.

In order to increase the hydrogen generation capacity resulting in higher power generation in fuel cells or longer duration of operation it is necessary to carry concentrated aqueous NaBH_4 solution which is stabilised with alkali. However with temperature fluctuation of the environment, crystal formation in the concentrated liquid fuel (e.g., 40 w% NaBH_4), may limit the pumpability of the solution and can choke the piping after few hours. These disadvantage become particularly severe if phase formation or scale formation in the fuel solution ultimately reflect on the production of hydrogen generation.

There is therefore a need for a material that prevents crystal formation and scaling of the concentrated NaBH_4 solution on-board. The inventors of the present invention have found that Methyl Paraben is a suitable chemical to avoid this problem. Methyl Paraben is an ester of p-hydroxybenzoic acid and is used in a wide variety of cosmetics, as well as
5 foods and drugs.

This methyl paraben dispersed sodium borohydride evenly in the alkaline solution and avoid crystal or scale formation. It also improves pumpability and forms smaller crystals in case the temperature falls to a higher extent. Further the quantity required is extremely small at about $< 0.05\%$. Methyl paraben also does not interfere with the catalyst of the
10 hydrogen generator system.

According to an embodiment of the present invention there is provided a fuel solution comprising:

- a) an aqueous solution concentrate of sodium borohydride in the range of 30% w/w to 40% w/w;
- 15 b) a stabilizer selected from potassium hydroxide or sodium hydroxide; and
- c) a crystallization inhibitor selected from methyl paraben or propyl paraben at 0.02% to 0.15% by weight.

According to another embodiment of the present invention there is provided a method of preventing crystal formation or stratification of concentrated aqueous sodium borohydride
20 solution (30% w/wt to 40% w/wt) for hydrogen generation.

According to an embodiment of the present invention there is provide a method for preparation of fuel solution that remains pumpable at low temperatures such as 15 to 25 °C.

The inventors of the present invention have found that methyl paraben prevents the phase
25 formation/scale formation in fuel solution at low temperatures.

This material prevents crystal formation and scaling of the concentrated NaBH_4 solution on-board, and at the same time is convenient to carry and store on-board. Moreover the

resultant fuel solution does not exhibit any phase formation or scale formation at low temperatures.

The present invention solves the problem of crystal/scale formation in concentrated sodium borohydride solution (40% w/v). During hydrogen production the sodium borohydride solution (40% w/v) is stored in highly alkaline medium, but after few days crystal/scale formed in that particular solution. Due to this it is impossible to pump the particulate solution and hence pose an obstacle during generation of hydrogen. To solve this problem methyl paraben is added in very small quantity (0.06% w/v) and stir the solution for 12 hours. This methyl paraben dispersed sodium borohydride evenly in the alkaline solution and avoid crystal or scale formation.

Methyl paraben and propyl paraben, more preferably methyl paraben was found to inhibit phase separation when incorporated in the metal borohydride aqueous concentrate. Sodium tartrate also showed phase separation inhibition, but performance of the same was inferior to methyl paraben.

Methyl paraben, when dispersed in sodium borohydride evenly in the alkaline solution prevents crystal or scale formation. It also improves pumpability and forms smaller crystals in case the temperature falls to a higher extent. Further the quantity required is extremely small preferably at 0.02% to 0.15%, more preferably at about 0.05 %. More importantly, methyl paraben does not interfere with the catalyst of the hydrogen generator system.

Fuel solution composition of the present invention at varying concentration of NaBH₄, stabilizer (sodium hydroxide) and methyl paraben. (Table A):

Sr. No.	Sodium Borohydride Conc. (% wt/wt)	Sodium Hydroxide Conc. (% wt/wt)	Methyl Paraben conc.
1.	20%	3.17 %	0.03 %
2.	30%	4.76 %	0.045 %
3.	40%	6.35 %	0.06 %
4.	40%	6.35%	0.1 %

A set of experiments were carried out in representative large tanks of 3-7 m³. The temperature was lowered using jacket cooling and kept for long hours to ensure steady state has reached.

5

Figure 2-1 represents fuel solution with 40%wt/wt NaBH₄ solution with 6.35%wt/wt NaOH at 25°C without any phase separation inhibitor.

Figure 2-2 represents fuel solution with 40%wt/wt NaBH₄ solution with 6.35%wt/wt NaOH and 0.06% wt/wt methyl paraben at 25°C

10 Figure-2-3 represents fuel solution with 40%wt/wt NaBH₄ solution with 6.35% wt/wt NaOH and 0.1% wt/wt methyl paraben at 25°C.

Figures 2-2 and 3-3 of the present invention illustrate that incorporation of methyl paraben in small quantity in fuel solution (concentrated NaBH₄ solution stabilized with NaOH/ KOH) results in inhibition of phase separation and crystallization.

15 With no incidence of phase separation, fuel solution is pumpable at lower temperatures in hydrogen generation system without any difficulty.

With incorporation of small quantity of methyl paraben in fuel solution, higher quantity of NaBH₄ is made available in a confined space thereby enhancing endurance.

20 ***Hydrogen generation system***

Hydrogen required for the fuel cell is generated online by hydrolysis of sodium-borohydride (NaBH₄). A fuel feed pump delivers the required amount of fuel to the hydrogen generator system from the tanks inside AIP plug based on the hydrogen demand on real time basis.

25 **Generation of hydrogen**

The fuel solution, catalyst solution and water generated (by the fuel cell system, stored in fuel cell water buffer tank) are pumped into the hydrogen generator.

The generated hydrogen after filtration to remove liquid droplets, is saturated with water vapor (as per the operating temperature of the hydrogen generator, which is around 70°C
30 and passes to the fuel cells (PAFC) section downstream. The moisture passage into the

fuel cell section is controlled by cooling the hydrogen gas at the outlet of the hydrogen generator section to the requisite level.

The reactor generates sodium borate (NaBO_2) alongwith hydrogen. Sodium borate is kept dissolved in the spent liquid stream (spent liquor) exiting from the hydrogen generator to spent buffer tanks of the spent liquor exhaust system the AIP plug. It may be noted that the fuel solution concentration is so adjusted that the sodium borate in the spent liquor remains in dissolved state. The fuel cell generated water is fed to the hydrogen generator system that after mixing with the borate solution helps to prevent crystallization of sodium borate in the spent liquor handling systems.

According to an embodiment of the present invention there is provided a method of generating hydrogen from on-board hydrogen generation system comprising fuel tank, catalyst tank, compact vessel with in-built heat exchangers, intermediate tank, spent storage tank, pressure control means wherein, the said method comprising the steps of:

- a. pumping the fuel solution and caustic solution from fuel tank and catalyst from catalyst tank to the compact vessel with in-built heat exchangers;
- b. hydrolyzing borohydride in fuel solution in presence of catalyst in the said compact vessel for generating hydrogen at higher rate than required;
- c. discharging the resultant borax solution formed as byproduct in step b, intermittently to intermediate tank wherein the trace borohydride in borax solution is converted to hydrogen, the resultant residual hydrogen then joins to the main hydrogen line and remainder is discharged to spent storage tank;
- d. hydrolyzing reaction in step b, resulting in increase in pressure; which activates the pressure control means to stop the fuel solution feed in step a;
- e. as hydrogen is consumed by phosphoric acid fuel cell (c), the pressure in the compact vessel falls thereby restarting the fuel solution feed;
- f. providing the said compact vessel with conformal heat exchanger for heat removal and reactant mixing;
- g. providing the said compact vessel with top mounted heat exchanger for cooling product hydrogen;

- h. providing the said compact vessel with non-conventional heat exchanger coils for removal of heat and reactor temperature maintenance comprising shell side circulating borate solution and tube side circulating de-mineralized water .

5 ***Oxygen storage and feeding distribution system***

Liquid oxygen (LOX) is stored in the cryogenic tank and a LOX vaporizer heat exchanger vaporizes the LOX to gaseous oxygen and the same is fed to the power production, Fuel cell plant section. The pressure of the LOX tank is maintained by a separate pressure buildup heat exchanger which vaporizes a LOX and puts it back on the LOX tank headspace to maintain necessary pressure in the tank required for feeding the oxygen. A glycol-water closed loop system is used to vaporize the LOX in the vaporizer and the pressure buildup heat exchanger and the cool water glycol solution is used for local air conditioning of the AIP section.

A tapping from the head space of the LOX tank is used for Crew breathing purpose as well. The crew breathing network is in the scope of the platform designer.

Power production, Fuel cell plant

The phosphoric acid fuel cell (PAFC) system consumes the hydrogen and oxygen to from water vapor and power. Fuel cell balance of plant (BoP) arrangement consists of the hydrogen loop, synthetic air loop along with pressurized water system (PWS), the thermal system of the fuel cell system (Figure 4). Power uptake from fuel cell is shown separately in the Electrical network, Fuel cell power output section (Figure 3).

The basic fuel cell stacks viz, N-11 units are arranged in holder frame to realize the necessary power through series and parallel combination of the stacks.

The fuel cell system works in closed loop for both hydrogen and synthetic air (oxygen). The hydrogen consumed in the fuel cell is made up by sensing drop of hydrogen pressure in the hydrogen loop while makeup oxygen is fed as per drop in oxygen concentration in the synthetic air loop. Details of these closed loops are provided in the following sections.

Table B fuel cell network and BoP as shown in Figure 4	
Equipment name	Equipment description
Pressurized water system	
T-1	Pressurized water tank (thermal medium). <u>The tank contains embedded electrical heater and hydrogen burner for pre-heating the pressurized water loop</u>
HE-5	Pressurized water cooler
P-1	Pressurized water recirculation pump
Fuel cell BoP	
VS-1	Gas liquid separator for hydrogen line
VS-2	Gas liquid separator for synthetic air line
HE-1	Inlet hydrogen pre-heater
HE-2	Outlet hydrogen cooler
HE-3	Outlet synthetic lean air cooler
HE-4	Inlet synthetic air after cooler
P-2	Hydrogen side condensed water transfer pump
P-3	Synthetic air side condensed water transfer pump
BL-1	Hydrogen recirculation blower
BL-2	Synthetic air recirculation blower

The hydrogen loop:

Humid hydrogen is fed to the PAFC stack which diffuses inside the electrode and depending upon the power uptake reacts to form water. Product water comes out through the air side loop. Un-reacted hydrogen alongwith moisture comes out from the stack and is cooled to separate any excess moisture and is fed back to the PAFC stack alongwith makeup hydrogen from the upstream hydrogen buffer tank in the hydrogen generation section. Makeup hydrogen feeding is done by sensing the pressure in the hydrogen loop. To avoid buildup of any impurities over time an instrumented purge is provided that purges in case of pressure buildup to a catalytic burner system through a managed vent. The hydrogen in the burner is converted to water by oxidizing in a loop around synthetic air stream. The water formed is condensed (P-2) and send to the fuel cell water buffer tank, from which it is eventually fed to the hydrogen generator as discussed in the hydrogen generator section.

The synthetic air loop:

The synthetic air loop uses oxygen and nitrogen mixture with oxygen concentration that of air or enriched air. Synthetic air is used in lieu of pure oxygen is to increase the

operational life of fuel cells and also to avoid any fire hazard in case of mechanical breakage and leaks.

Humidified synthetic air is fed into the fuel cell stacks through a re-circulating blower.

- 5 Un-reacted oxygen, nitrogen and water vapor comes out of the fuel cell stack where it is cooled to a pre-determined level so that a part of the moisture is condensed (P-3) and separated in the gas liquid separator (VS-2). The condensed water is sent to the fuel cell water buffer tank. Make up oxygen is added based on the oxygen sensor in the air loop and is fed back to the fuel cell.

10

The probability of increase in pressure due to impurities is eliminated by occasional purging of synthetic air into the catalytic burner as mentioned before, where the oxygen is converted into water by adding suitable amount of hydrogen from the hydrogen generator. The water formed in the generator is condensed and sent to fuel cell water buffer tank.

15

Pressurized water system (PWS) : PAFC Thermal system:

- The PAFC stacks operate upto 170°C temperature. A high purity pressurized water system (PWS) is used as the primary media to maintain the temperature of the PAFC system. The PWS re-circulates hot water, in pressurized form to avoid boiling in the loop, through the embedded heat exchangers inside the PAFC stacks. As shown in figure 4, the cooling water cools the pressurized hot water if the temperature increases during the PAFC operation. During cold startup phase, temporary shutdown or standby phase, heat from catalytic hydrogen burner or electrical heating is employed to maintain the temperature of the PWS and the same maintains the temperature of the PAFC system.
- 20
- 25 Such dual mode media based thermal system allows easy and safe control.

- In an embodiment of the present invention, pressurized water system in the fuel cell balance of plant operates on dual mode wherein the said pressurized water system maintains the temperature by re-circulating hot water, in pressurized form from pressurized water tank (T-1) to avoid boiling in the loop through embedded heat exchanger in the PAFC stacks and cooling water from pressurized water cooler (HE-5) cools the pressurized hot water when temperature increases.
- 30

Phosphoric Acid Fuel cell (PAFC) Stacks of the Present Invention:

Phosphoric acid Fuel cell (PAFC) is an electrochemical device that converts chemical energy of reactants in presence of noble catalyst supported on carbon/graphitic substrate, directly into DC power

- 5 There exists an issue with poor adhesion of acid holder matrix to the electrode substrates in a PAFC cell. There exists an unmet need to address the issue of poor adherence between acid holder matrix and graphitized supports.

The inventors of the present invention have found a method to increase adhesion strength of matrix with graphitized support, acid holder matrix, a method to determine the
10 adhesion strength of acid holder matrix and also a method to estimate acid migration in a matrix.

According to an embodiment of the present invention there is provided a method to enhance the adhesion strength of the matrix with the graphitic electrode structure though wash coat.

15 According to embodiment of the present invention the adhesion strength of phosphoric acid electrolyte to graphitic electrode structure in phosphoric acid fuel cell of the present invention is increased by applying wash coat on graphitic electrode structure before casting phosphoric acid electrolyte.

20 According to another embodiment of the present invention wash coat for increasing adhesion strength of phosphoric acid electrolyte to graphitic electrode structure in phosphoric acid fuel cell of the present invention comprises 90 to 97% Silicon carbide (SiC), 2% polyethylene oxide and 3 to 10% polytetrafluoroethylene

25 According to another embodiment of the present invention there is provided a method to estimate acid migration in a matrix

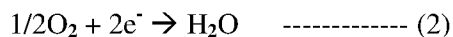
According to yet another embodiment of the present invention there is provided a method to determine the adhesion strength of acid holder matrix.

A typical PAFC assembly (Figure 8) is comprised of two electrodes and electrolyte holder porous matrix (3) is interposed in between the two electrodes (2 and 4). This assembly is then sandwiched between two graphite bipolar plates (1 and 6) for passing reactants gases to the respective electrodes. It uses phosphoric acid as an electrolyte and has to be retained in the porous inert media of the acid holder matrix for long hrs of operation. Typically hydrogen is used as fuel and air/oxygen as the oxidant. The two electrodes are coated with Pt or Pt alloys supported on carbon or graphitic substrates. The catalyst is coated on gas diffusion layer by mixing fluoro carbon binder. When the electrodes are supplied with respective reactants, reduction of oxygen or oxidization hydrogen occurs in presence of catalyst and ions move through electrolyte matrix and thus generate power. These reactions occur on an interface between the ionically conducting electrolyte held in the matrix and the electrically conductive electrodes.

At the anode:



At the cathode:



The commercial use of Phosphoric acid fuel cells demands increased life and performance of stacks. The life and performance is very much controlled by stability of the catalyst supports used. This calls for use of graphitized catalyst supports instead of carbon black to avoid corrosion of supports. However the graphitized supports are hydrophobic in nature and the binder used to form layer further increases the hydrophobicity. The low surface energy of layer prohibits the adherence of matrix slurry onto the surface and eventually matrix formed is not mechanically stable as the binding is poor. Generally paper making, screen printing, spraying, Gravure curtain coating techniques are being used for making the matrix coating on the electrodes.

The embodiments of the present invention are described in detail:-

a) A method to increase the adhesion strength of the matrix with the graphitic electrode structure though Wash coat.

A matrix is generally made by ball milling slurry of SiC and polyethylene oxide, followed by addition of Teflon and stirring the mix for few minutes and then casted on the

electrodes. To improve adhesion of the matrix with the electrode surface a wash coat method is invented. The wash coat is made from the same SiC + PTFE/ fluoroethylene polymer(FEP) casting material by diluting the same with distilled water and is applied over the electrode surface either by painting, spraying or rolling sponge in both X and Y direction. The wash coat is air dried. Subsequent to this wash coat the regular SiC slurry along with binder and slurry stabilizer is coated over the wash coat by std. practice viz, curtain coating, wire-bar coating, screen printing method etc., dried and sintered. This wash coat improves binding of the matrix on the electrode surface as well as mechanical stability of the matrix and is determined by the previously mentioned adhesion test.

Preparation of Wash coat of the present invention:

Wash coat suspension preparation: 95% of SiC powder with average particles size of 4-5 microns with 2% PEO was ball milled. To this 5% polytetrafluoroethylene is added and stirred for 5 min. From this slurry 5 parts by weight is taken, to it wetting agent (alcohols particularly, iso propyl alcohol) and water was added to make 50 parts. This diluted slurry was used as a wash coat before coating the actual matrix layer, using wire-bar coater.

b) A method to estimate acid migration in a matrix:

In a typical fuel cell environment the electrode sandwich viz, the two electrodes with the Silicon Carbide matrix in between them is held between two bipolar plates by applying sufficient contact pressure to minimize the contact resistance of the electrode, to prevent gas leakage at the periphery and to provide mechanical stability of the fuel cell stack. Depending upon this clamping pressure the electrodes and the matrix get compressed to certain level.

The spring plate assembly allows uniform pressure to the matrix and depending upon the spring constant and spring compression while tightening the pressure on the matrix can be estimated.

Acid reservoir is kept very near to the matrix and acid level at same height as of matrix to minimize any acid migration resistance coming from the wicking mechanism.

During operation the electrolyte is carried away by dry reactants gas and hence has to be replenished from the reservoir. The matrix should be able to wick by the acid under pressure and migration rate has to be determined. Acid holding capacity per unit volume of the matrix as well as acid migration properties and ion transfer resistance, changes due to compression of the matrix.

During operation of the phosphoric acid fuel cell stack, the acid is lost through the electrodes and is replenished through acid reservoirs by capillary action from the reservoir to the acid depleted part of the matrix. Thus characterizing the matrix properties like acid migration speed, ion resistance and phosphoric acid occupation (PAO) should be measured under such pressed condition of the matrix.

Phosphoric acid occupation (PAO) is defined as amount of phosphoric acid held into the SiC matrix per weight in gms of matrix.

The migration test of a matrix coated onto an electrode can be studied using an assembly fixture as shown in figure-10. The setup is explained in the figure itself.

Figure 10 shows acid migration assembly used for finding phosphoric acid migration under pressure of 0.7 MPa. 31, is the metal frame with opening for matrix view. 32 is the transparent polycarbonate or acrylic sheet. 33 is the SiC matrix supported over catalyst layer and porous gas diffusion carbon paper 34. 37 is the spring plate assembly with coiled springs evenly spread with a top metal plate for applying required pressure uniformly. 36 is the bottom pusher plate. 35 are fasteners. 38 is acid reservoir stand, 40 is acid reservoir and 39 is the wick connecting the reservoir and the matrix 33. The spring plate assembly 37 allows uniform pressure to the matrix and depending upon the spring constant and spring compression while tightening the pressure on the matrix can be estimated. Acid reservoir 40 is kept very near to the matrix 33 and acid level at same height as of matrix 33 to minimize any acid migration resistance coming from the wicking mechanism.

The dry matrix (coated on an electrode) is kept inside the assembly and fasteners are tightened so that a pressure similar to the fuel cell environment is applied through the springs to the matrix. The matrix is wet at the periphery using an acid moist fabric which is in turn connected to a small acid reservoir. The acid propagation can be seen through
5 the transparent top portion of the assembly as shown in the figure 3. The whole assembly can be kept under a hood and could be used at room temperature with acid diluted to an extent so that the viscosity of the target acid at elevated temperature is same as that of the dilute acid at room temperature. However using appropriate material the assembly could be used at elevated temperature with electrical heaters and concentrated Phosphoric acid
10 as well.

After the acid is loaded (filled) in the matrix under pressure, the assembly can be opened and the matrix could be weighed to find out the amount of phosphoric acid occupied per unit weight of the matrix.

15 Using this assembly thus one can measure the acid migration rate in a dry matrix along with the phosphoric acid occupation (PAO). Using a similar assembly with gold plated metal electrodes on either side it is possible to find out the ionic conductivity thru a DC/AC method if required.

20 An embodiment of the present invention provides a fuel cell comprising a pair of gas diffusion electrodes separated by a porous electrolyte retaining matrix of silicon carbide to produce DC power. The said matrix has minimum 90 % and maximum 97% SiC and 3 to 10 % of binder to achieve desirable properties. Most preferred binder is PTFE at about
25 5 % by wt.

In an embodiment the SiC matrix of the present invention is coated on both the electrodes or on single electrode.

30 According to an embodiment, the thickness of matrix of the present invention is more preferably in the range of 50 to 60 microns. The thickness of the coating more preferably is between 40 to 100 microns.

The average particle size of silicon carbide matrix employed in the present invention is 4 to 5 microns, and porosity of the matrix is 50%. SiC particles more preferably are not larger than 25 microns and preferably less than 10 microns.

5

The binder preferably used is fluoro carbon, particularly polyterafluoroethylene (PTFE), fluoroethylene polymer (FEP), or mixtures thereof.

10 In an embodiment, the wash coat of the present application is made from SiC and PTFE and/or FEP on graphitic as well carbon substrates to increase the adhesion.

In an embodiment, the wash coat of the present invention can be applied by brush or spray by hand or mechanized equipment.

15 In another embodiment, the composition of wash coat of the present invention for application may be varied from 2 parts to 10 parts, more preferably is 5 parts by weight.

In a preferred embodiment, the present invention provides for a method of coating using a wire bar coater with specific adapter and other coating methods like Grauver, and curtain
20 coating can also be used.

According to a preferred embodiment, the present invention provides a method of coating the matrix on hydrophobic, graphitic and carbon substrates for fuel cell electrodes particularly phosphoric acid fuel cells.

25

In another embodiment, the present invention also provides for a method of checking the stability of said matrix. The present invention also provides for a method of measuring the acid migration under pressure.

30 According to the embodiment, the present invention provides a method to produce porous, wettable, uniform and mechanical stable matrix to hold phosphoric acid for PAFC applications.

c) A method to determine the adhesion strength of acid holder matrix:-

The acid holder matrix is typically made out of SiC and polymeric binder for retaining electrolyte in phosphoric acid fuel cell. The adhesion is important for matrix, as poor adhesion will lead to increased ionic resistance, chipping of matrix during acid
5 impregnation and assembly of stack.

The general adhesion tests that is done for normal coating on soft and hard substrate, for e.g. Pull off test, cross cut test and scrap adhesion test etc. used by paint manufacturer for paint films. These tests are rendered non-applicable for evaluation in the present invention
10 as the substrate is brittle in nature, which cannot bear the force applied for coating detachment during the test.

The methodology adopted here is based on an adhesion test process that is done by dipping the electrode coated matrix (sample) in a vessel filled with water which is
15 agitated by controlled stirring. The sheer force exerted by water on the matrix layer causes abrasion of the soft matrix. A piece of the electrodes coated matrix is fixed on the base of the stirrer vessel with matrix side up with some water resistant adhesive as shown in Figure 9. Alternatively it can be held vertically, agitated in the vessel at a predetermined distance from the stirrer. The stirrer is operated at a pre-determined speed
20 and after exposing the matrix sample for a fixed time the same was taken out and visually inspected for any removal of the matrix. The piece is further dried and weighed to measure the loss and observe the surface of matrix. From the weight loss or the erosion of matrix at the surface the extent of matrix adhesion could be understood. Depending on the situation the stirrer type, vessel shape/size, stirring rpm and time of exposure could be
25 standardized to compare matrix adhesion strength for different samples.

Comparative data on result of acid migration test carried without wash coat and compaction; with wash coat and no compaction; and with wash coat and compaction are given in Table 4 below. Figure 11 is graphical representation of Acid migration of
30 different matrix at 0.7 Mpa with time. Figure 11 clearly shows that acid migration with Sic + 5% PTFE with wash coat and compaction was better. Higher acid migration value

indicates better functioning of the PAFC as migration of acid indicates better capillary action which avoids cross over of gases and lesser ionic resistance.

EXAMPLES

5 **Example 1: Matrix – example 1 without wash coat and compaction**

95 parts by weight of silicon carbide (1200 GW from Electro Abrasives USA) of 4-5 microns size and 100 parts by weight of 2% PEO suspension (PEO, 40, 0000 –Aldrich) was ball milled in a planetary ball mill for one hr. To the uniformly mixed slurry 5 parts by weight polytetrafluoroethylene (60% wt/wt from Hiflon India) was added and stirred for 10 5 mins. The matrix material contains 50 to 52 % solid in the form of SiC and Teflon. The Silicon carbide slurry was casted over the electrode with wire bar coater fixed on adapter which can accommodate thickness variation of catalyst layer. The electrodes are made by screen printing the ink of 20% Pt on graphitic substrates and 30% Teflon. The Pt loading on cathode is with 0.7 mg/cm^2 for and 0.5 mg/cm^2 for anodes used for casting and testing 15 in all examples. A smooth and uniform layer is achieved without pin holes. The layer is dried for 12 hrs at 22°C and then dried at 70°C and finally sintered at 310°C . The resultant matrix contained around 8 mg/cm^2 of silicon carbide and 50 to 60 microns thick. The electrical resistivity of dry layer was $5 \times 10^8 \text{ ohm-cm}$. The bubble pressure of single electrode was measured. The finished electrode with matrix was tested for adhesion of 20 matrix, acid migration and electrochemical performance. For stability test 3 to 4 pieces of SiC coated matrix of 40 X 40 mm size from the electrode were cut with a sharp blade and carefully the dust particles were removed from the edges. In a 1000 ml beaker 600 ml of distilled water was taken and Silverson mixer (Model – L5M, Silverson Machines Ltd., England) with $\frac{1}{4}$ " vertical slotted disintegrating head was dipped in the beaker. The test 25 piece was held at a distance of 1 cm from the head of mixer and the speed of silverson mixer was set to 6500 rpm. Electrode was held in this position for 5 min, the surface of electrode and water in beaker was checked for chipping of SiC layer or cracks and SiC particles. Setup is shown in Fig 9.

30 Figure 9: (a) depicts matrix adhesion test assembly, 26 and 27 represent height of water and diameter of the glass vessel used. 28 is the distance between the sample 25 and the stirrer 22. The sample 25 is electrode coated with SiC matrix fixed at the bottom of the

vessel. In FIG.9 (b) the sample 23, electrode coated with catalyst layer and SiC matrix is held vertically at a distance 29 from the stirrer 22 and matrix side facing the stirrer. 26 and 27 are the height of water and diameter of the glass vessel. The stirrer pot diameter (27), stirrer head, rotational speed of the stirrer, space between stirrer and pot bottom ,
 5 space between sample and the stirrer (28 & 29), water level in the pot (26) etc. to be standardized or comparison purpose.

Matrix Adhesion test assembly; a) Sample kept on the bottom; b). Sample kept vertically. The stirrer pot dia (27), stirrer head, rotational speed of the stirrer, space between stirrer
 10 and pot bottom (L), space between sample and the stirrer (S), water level in the pot (H) etc. to be standardized for comparison purpose.

The stability test showed loss of weight on drying and thin top layer got removed. This indicates long term stability problem of the said matrix. Results are given in Table 4. The
 15 phosphoric acid migration was carried out in assembly fixture as shown in fig 10. The electrode coated with matrix was assembled in acid migration fixture by placing 2 cm wide Whatmann filter paper No 1 at edge of the matrix and pressure 0.7 MPa was applied. The other end of the glass mat was dipped in acid reservoir. 25% concentrated Phosphoric acid was used at Room temperature so that viscosity of the acid remains
 20 similar to 88 % acid at 90°C. The following table gives performance using above mentioned matrix in phosphoric acid unit cell at 150°C/ 1 atm which is tightened with a clamp pressure of 0.7 MPa.

Table 1: Unit cell performance of matrix without wash coat; read with figure 12 and 13

Reactants	Potential in mV			
	OCV	100 mA/ cm ²	250 mA/ cm ²	500 mA/ cm ²
H ₂ /O ₂ (mV)	1000	750	550	480
H ₂ /air (mV)	890	700	500	375

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Example 1 represents US4017644 where in phosphoric acid electrolyte with matrix material comprising SiC and binder PTFE is casted over the electrode.

Example 2-- Matrix with wash coat and no compaction:

95 parts by weight of silicon carbide (1200 GW from Electro Abrasives USA) of 4-5 microns size and 100 parts by weight of 2% PEO suspension (PEO, 40, 0000 –Aldrich) was ball milled in a planetary mill for one hr. To the uniformly mixed slurry 5 parts by weight polytetrafluoroethylene (60% wt/wt from Hilfon India) was added and stirred for 5mins. For wash coat of the present invention, 5 parts by weight of Silicon carbide slurry was taken and was diluted 10 times with a wetting agent (e.g. Iso propyl alcohol) and water. The diluted slurry was used for wash coat application on the graphitized catalyst layer surface and air dried. The Silicon carbide slurry was casted over the electrode with wire bar coater fixed on adapter which can accommodate thickness variation of catalyst layer. A smooth and uniform layer is achieved without pin holes. The layer is dried for 12 hrs at 22°C and then dried at 70°C and finally sintered at 310°C. The resultant matrix contained around 8 mg/cm² of silicon carbide and 50 to 60 microns thick. The electrical resistivity of this layer was 5 X 10⁸ ohm-cm. The stability tests, bubble pressure acid migration of the samples were carried out as mentioned in example -1. The results are given in table 4. No peeling or weight loss was observed during stability test.

The following table gives performance using above mentioned matrix and electrodes in phosphoric acid unit cell at 150 deg C/ 1atm with oxygen and air.

Table 2- Unit cell performance of matrix with wash coat; read with figure 5 and 6

	Potential in mV			
Reactants	OCV	100 mA/ cm ²	250 mA/ cm ²	500 mA/ cm ²
H2/O2 (mV)	1000	800	675	500
H2/air (mV)	925	745	550	400

Example 3: Matrix –with wash coat and compaction:

95 parts of silicon carbide by weight and 100 parts by weight of 2% PEO solution were added and ball milled for 1 hr in a planetary mill. To this slurry 5% PTFE solution (60% wt/wt Hiflon) was added and stirred for mins. The resultant slurry was casted on pre wash coated graphitic electrodes. The matrix was dried at 22°C for 12 hrs and then at 70°C for ½ hr. The green matrix was then compacted at 6 kg/cm² and finally sintered at 310°C. The produced matrix was 50 microns thick, hydrophilic and has 50% porosity. The bubble pressure of the said matrix and acid migration under 0.7Mpa was carried out and results

are given table 4. The said was stable and showed no weight loss and peeling off. The performance of the PAFC cell with above configuration of matrix is given in Table 3 and figure 5 and figure 6 gives the comparison of the three examples in H₂/O₂ and H₂/air.

5 Table 3 Unit cell performance of matrix with wash coat and compaction:

	Potential in mV			
Reactants	OCV	100 mA/cm ²	250 mA/cm ²	500 mA/cm ²
H ₂ /O ₂ (mV)	1000	810	695	530
H ₂ /air (mV)	935	770	580	430

The unit cell performance showed improvement in performance from ex 1 to ex 3. In example 2 the adhesion improved the ionic contact between the electrode and SiC layer while compaction increased adhesion as well decreased the crossover of gases leading to voltage losses.

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Table 4.a – Matrix with 97% SiC and 3% Teflon:

Matrix	Bubble pressure cm of Hg	PAO in gms /cm ²	Adhesion stability	Acid migration in cm/hr
Matrix – example 1 without wash coat and compaction	12 to 14	20 to 22 mg/cm ²	Layer removed	2.5
Matrix – example 2 with wash coat and no compaction	12 to 14	20 to 22 mg/cm ²	Adhesion better, no SiC chipping-cracks and weight loss observed.	2.5
Matrix – example 3 with wash coat and compaction	12 to 14	20 to 22 mg/cm ²	Adhesion better, SiC particles observed in solution.	2.5

Table 4.b – matrix with 95% SiC and 5% Teflon:

Matrix	Bubble pressure cm of Hg	PAO in gms /cm²	Adhesion stability	Acid migration in cm/hr
Matrix – example 1 without wash coat and compaction	22 to 25	18 to 20 mg/cm ²	Top thin SiC layer got removed, weight loss of 0.6 mg/cm ² observed	2.0
Matrix – example 2 with wash coat and no compaction	30 to 32	20 to 22 mg/cm ²	Adhesion good, no SiC chipping-cracks and weight loss observed.	2.4
Matrix – example 3 with wash coat and compaction	45 to 48	20 to 22 mg/cm ²	Adhesion good, no weight loss observed.	2.8

5 Table 4.c – Matrix with 90% SiC and 10% Teflon:

Matrix	Bubble pressure cm of Hg	PAO in gms /cm²	Adhesion stability	Acid migration in cm/hr
Matrix – example 1 without wash coat and compaction	30 to 32	14 to 16 mg/cm ²	SiC particles observed in solution	2.0
Matrix – example 2 with wash coat and no compaction	36 to 38	14 to 16 mg/cm ²	Stable	2.0
Matrix – example 3 with wash coat and compaction	50 to 55	14 to 16 mg/cm ²	Stable	2.2

10 In phosphoric acid fuel cells, hydrogen is fed to the anode of the fuel cell and oxygen is fed as the oxidant to the cathode. PAFC fuel cells include a porous silicon carbide matrix coated anode and cathode assembly in which silicon carbide coated surface of anode and cathode face to each other. This porous silicon carbide absorbs phosphoric acid which acts as barrier for direct mixing of reactive gases. This assembly called one phosphoric acid fuel cell. This assembly sandwiched between two impervious, electrically

conducting, corrosion resistant plates having channels on both sides surface for reactive gases used in fuel cell.

5 The term "PAFC stack module" is typically used to refer to addition of number of phosphoric acid fuel cells described above in series to get higher voltage and Power output

10 The impervious corrosion resistant electrically conductive plates sandwiching the phosphoric acid fuel cells containing flow channels on both side surface for distributing the fuel cell's gaseous reactants i.e. hydrogen over the anode surface and oxygen in the form of air over the surfaces of cathode. These channels have connected with multiple headers for supply of reactant gases and multiple channels for exhaust header at opposite end of channels so multiple gas ports at the edges of plates.

15 In a phosphoric acid fuel cell stack, number of cells is stacked together in electrical series separated by impervious, corrosion resistant electrically conductive bipolar plate. In these bipolar plate there is an assembly formed by making channels for cooling fluid to take away heat generated by fuel cell or by putting metal plates having channels for cooling fluid in between the bipolar plate.

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For maintaining the required temperature of fuel cell stack, the graphite heat exchanger plate is placed. This is a planer graphite plate which takes away the heat generated by fuel cell and provides the heat for start-up operation of fuel cell through pressurized water flowing in it and it is placed in fuel cell stack after nos. of fuel cell assembly along with
25 impervious, corrosion resistant electrically conductive bipolar plates.

There exists a need to develop multiple metal tubes embedded graphite heat exchanger plates having more hardness to avoid swelling and distortion of plates, contact pressure loss due to softness of plates and contamination of pressurized water through graphite
30 surface that should be compatible with planer fuel cell geometry with thin dimension.

The problem associated with making multiple metallic tubes embedded graphite heat exchanger plates for enhanced heat transfer through moulding the metal tubes (figure 17, shows single metallic coil tube) with hard grooved graphite plate (figure 18). It is of utmost importance that the embedded graphite heat exchanger plates should not crack
5 with thermal stress generated by the tube walls to graphite plate and the same time should not swell due to the acid absorption by plate.

The graphite exchanger plates prepared according to the present invention (Figure 19) is useful for heating and cooling of PAFC stack through pressurized water system and does
10 not crack, swell, distort with thermal stress by tube walls on graphite plate. The inventors of the present invention have found a unique moulding process in which multiple serpentine metallic tubes having different path configuration is moulded inside a high density grooved graphite plate having through gas port holes, one side surface have grooved channels for metal tubes and other side surface have gas channels for any
15 reactive gases of fuel cell by filling a mixture powder developed by preparing optimized ratio of exfoliated graphite powder and polytetrafluoroethylene suspension, between wall of tubes and wall of surface of grooved graphite plate channel.

A thin, electrically conducting sheet is thin electrically conducting exfoliated graphite
20 sheet having thickness less than 0.2 mm as a protective layer, resistant to high temperature acid is attached at the grooved side surface of high density graphite plate from where metal tubes are fitted, by applying thin glue developed by mixing of fine natural graphite powder having minimal particle size, with minimal acid resistant resin then fix the sheet through proper moulding process. The developed glue composition and
25 moulding process such that plate does not resist the heat and current transfer across the plate.

This multiple metallic tubes embedded graphite heat exchanger plates are very much efficient in heat transfer of heat generated in phosphoric acid fuel cell stack by placing
30 them even after more than 6 to 12 PAFC (Phosphoric acid fuel cell) cells in repetitive manner in a PAFC stack module through pressurized water.

This type of multiple metal tubes embedded graphite heat exchanger plate will do heating and cooling of the PAFC stack to maintain the required temperature through pressurized water flow in multiple metallic tubes and there is no chance of water contamination after several hours of run due to the erosion of graphite w all surface.

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The construction of the graphite heat exchanger plates such that it will not absorb any acid by the exfoliated graphite powder and Teflon mix so there is no chance of swelling of plate with acid which will be the case if plate will be made only through exfoliated graphite powder with minimum polymeric binder. This type of metallic tubes embedded graphite heat exchanger plate is impervious to acid and gases.

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Multiple metal tubes embedded graphite heat exchanger plates construction for Phosphoric acid fuel cell stack assemblies typically include multiple (more than one) serpentine metal tubes having different path configurations embedded in a high density conducting graphite grooved plate with fuel cell cathode channel at one side surface. The multiple serpentine metallic tube of the present invention with different paths means a number of separate tubes having different path configuration embedded in the grooved graphite plate. So that cooling fluid flowing in tube dissipates heat uniformly over the surface of heat exchanger plate. The width of groove in graphite plate is in the range of 7- to 13 mm, more preferably in the range of 9 to 11 mm. The depth of groove in graphite plate of the present invention is preferably in the range of 4 to 10 mm, more preferably in the range of 6 to 8 mm.

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The tubes are embedded in grooved plates by using moulding of mixture powder, developed by preparing mixing of exfoliated graphite powder and PTFE suspensions between tubes walls and graphite walls. The mix will absorb the thermal stress generated by the walls of the tube and it will prevent shock to base graphite plate thereby avoiding the cracking of the base graphite plate. Simultaneously due to moulding of a thin electrically conducting, high temperature acid protective layer sheet at the grooved surface of the graphite plate, the acid absorption by heat exchanger plate does not take place and also there is no swelling at the edges as well as the gas port location of plate; for the reason that it is made up of high density graphite plate.

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In an embodiment of the present invention the PTFE suspension comprises 50 % to 70% PTFE and 2 to 5% surfactant and about 25 to 45% water

- 5 The graphite heat exchanger plates of the present invention are hard plate which gives more stability in assembly of stack and enhanced heat transfer properties.

This embedded graphite heat exchanger plate is qualified in higher capacity PAFC stack module for heating and cooling of stack through pressurized water.

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According to an embodiment of the present invention 'fine natural graphite mix phenolic' glue is applied on the ridges between the coil channel and the top plate allows thermal as well as electrical continuity and thus when inserted inside the fuel cell the same can support the electric current passing through the stack.

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According to an embodiment of the present invention the hydrogen and oxygen flow fields are moulded on the outer side of the graphite plate to enhance compactness of the stack.

- 20 The conducting hydrophobic caulk material of the present invention is prepared in optimized ratio that provides thermal contact, prevents metallic corrosion by preventing acid seepage and absorbs the thermal stress owing to unequal thermal expansion of the rigid graphite material and the metallic coil.

- 25 According to an embodiment of the present invention the moulding mixture comprises exfoliated graphite powder in an amount 70 to 80 % by weight and PTFE in an amount 30-20% by weight.

- 30 According to an embodiment of the present invention the particle size of exfoliated graphite powder preferably is in the range 220 micron<D₁₀>300 micron , 600 micron<D₅₀>750 micron, 1200 micron<D₉₀>1400 micron

According to an embodiment of the present invention the glue composition comprises about 80 to 95% fine natural graphite powder and 5 to 20% of phenolic resin.

Electrical network of the present invention

- 5 The electric network is divided into two subsystems as detailed below.

Fuel cell power output of the present invention

Fuel cell modules, 25 Nos. (each module : N-11 PAFC stacks) raw output DC power is fed into an array of Power conditioner system (PCS) which are essentially controlled
10 wide input DC-DC stabilizers. The system receives fuel cell generated power in the input feed and provides submarine quality controlled DC power at the output which is connected through a bus bar to the platform switch board. Figure 3 of the present invention shows the primary scheme of the electrical connection from the fuel cell output to the platform power centre through the PCS.

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The power electronics modules have high redundancies. Suitable power tapping points to match the power electronics rating from fuel cell towers are made available to each DC-DC stabilizer unit. The master controller either operates in load driven mode or user programmed load mode. Based on the health monitoring of fuel cell branches the modules
20 determine the power sharing of the DC-DC stabilizer array. Accordingly, the HFSPC controller shares the load in the DC-DC stabilizer in real time. Output of the stabilizer array is provide into a common bus bar from which a part of power is used for AIP parasite power and the balance is fed to the platform as per master controller power feed program.

De-mineralized water cooling circuit of the present invention

Various equipment of the AIP plant requires cooling. The same is done through a de-mineralized cooling water network. The heat absorbed by the cooling water is dumped into the sea water through the sea water exchanger at sea water cooling network. The de-mineralized water cooling network comprises of a cooling water tank, cooling water

pumps, piping network and relevant sensors and valves. Typically the cooling water in the tank is around 40 deg C.

Sea water cooling network of the present invention

The sea water cooling network comprises of hull penetrations (for taking sea water in and sending sea water out), sea water heat exchangers, sea water circulation pumps, sea water piping and relevant valves and sensors. Sea water flows through the primary of the heat exchanger and de-mineralized cooling water from the de-mineralized water cooling circuit flows through the secondary of the same. The sea water cooling network detailing to be done by the platform designer is based on the requirement of de-mineralized water cooling.

Exhaust system of the present invention

The exhaust system is divided into two parts as detailed below.

Spent liquor discharge system of the present invention

Spent liquor from the hydrogen generation system needs to be expelled to the sea. The spent liquor solution is transferred to one of the two spent buffer tank. While one tank is getting filled the other one isolated from the upstream is connected to the high pressure pump for expelling the liquor to the sea. The buffer tanks are strong enough to get exposed to the external sea water pressure (in case of pump failure). After a tank is filled by the liquor the expelling request is provided to the platform IPMS which operates the pump expelling liquor to the sea.

Master vent system for gases of the present invention

All the subsystems viz, the fuel feeding system, hydrogen generation system, power production fuel cell plant, oxygen storage and feeding distribution system etc. have a pressure buildup/impurity buildup prevention process through vent lines. The vent lines are connected to a catalytic burner. On sensing the excess hydrogen or oxygen in the loop, the burner control system, feeds hydrogen from hydrogen generator or oxygen from the LOX system through dedicated lines to the burner. Water formed is condensed and fed to the fuel cell water buffer tank.

In case of other impurities (gaseous) there is a master vent connected to the burner unit that expels gas from the burner block to the sea through a small compressor. All the subsystems thus in turn are connected to a single master vent port which is instrumented and actively controlled to mitigate any pressure buildup.

5 ***Specialized safety by poisoning the hydrolysis reaction of the present invention***

In an embodiment of the present invention there is provided a method to prevent hydrogen overpressure inside the hydrogen generator by injecting a chemical inhibitor to poison the hydrolysis reaction and to reduce /stop the reaction in case of such exigencies.

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The Hydrogen generator being the principal source of hazard, a chemical (poison) is identified to stop/slow down the hydrolysis reaction in the H₂ generator. The chemical is stored in powder form in a canister and in case of alarm level pressure in the hydrogen generator is dosed into the system by diverting the recirculation pump outflow through the poison holder pot. In addition a pressurized water canister is connected to the poison pot as an additional driver mechanism for injecting the poison the hydrogen generator (as shown in Figure 14).

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The chemical is sodium polyacrylate, more preferably sodium methacrylate that removes free water from the system so that the NaBH₄ hydrolysis reaction as mentioned before could be stopped or rate reduced. Other chemicals which can absorb high amount of water can be used as well the same purpose other than sodium polyacrylate powder. The powder could be deployed in different forms as depicted in the figure 14. By this method, the powder is dosed using a pressurized water system. However there may be other dosing methodologies like using a water pump to carry the dry powder and dose inside quickly.

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As an example in a 40kw system (scale down AIP) when injected with about 0.8 kg of the Sodium methacrylate the comparison of hydrogen inhibition is shown in figure 15. The case without the poison and with the poison is compared after the NaBH₄ feeding is stopped in the H₂ generator. The residual NaBH₄ reacts to generate H₂ and inhibitor

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efficacy is compared. In case of poison injected immediately after the NabH_4 feeding is stopped showed less hydrogen generated by removing water from the catalyst sites.

Control and monitoring system of the present invention

The control and monitoring system is a comprehensive distributed controller that allows
5 automatic operation of the entire AIP system.

The controller architecture is a layered structure where the primary subsystems like the hydrogen generator is operated using a PLC type controller. The Fuel cell loop is managed by a model predictive controller with an algorithm to monitor the health of the
10 fuel cell stacks through current vs voltage profiles. The algorithm is used for determining the Fuel Cell stack health and an optimizing the current distribution to each stack so that the total power from the fuel cell meets the power demand and consumes min amount of hydrogen. The same information is provided to the power conditioner systems as set point.

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The top most layer is the nodal controller which supervises the overall control efficacy and adjusts lower part controller set points to minimize instability. The nodal controller also interacts with the submarine controller to obtain the power demand and also pass on important AIP parameters for the Submarine operator use.

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According an embodiment of the present invention there is provided a method of generating power from air independent propulsion system (AIP) for submarine, the said method comprising the steps of:

- 25 -generating hydrogen from raw material feed comprising fuel solution and catalyst in said on-board hydrogen system (a);
- feeding the generated hydrogen and oxygen to PAFC stacks (c) where the supplied hydrogen and oxygen is consumed to generate unregulated raw DC power;
- providing the unregulated raw DC power to power conditioning system (d) to
30 generate regulated DC power

-interfacing the regulated DC power with platform switch board to provide power to platform

-providing a network of heat exchangers to manage the thermal load with de-mineralized water cooling circuit, the said de-mineralized water cooling circuit consisting of cooling water tank, cooling water tanks, cooling water pumps, piping network, sensor means and valve means and sea water cooling network, the said sea water cooling network consisting of hull penetrations, sea water heat exchangers, sea water circulation pumps, sea water piping network and sensor means and valve means

-providing exhaust means to expel spent liquor and master vent means for gases substantially balancing heating and cooling requirements of the system'

-providing control and monitoring means for automatic operation of the entire AIP system and individual components of the system and for regulating the same in accordance with the power demands on the system preferably by means of controller architecture comprising:

PLC type controller to operate hydrogen generator;
model predictive controller with an algorithm for determining fuel cell stack health and optimizing current distribution to each stack so that power from fuel cell meets the power demand of the system;
nodal controller to supervise overall control, efficacy, and adjust lower part controller set point to minimize instability;
submarine controller, with which, the said nodal controller interacts to obtain power demand and pass AIP parameters to operator.

Accordingly, those of ordinary skill in the art will recognize that various changes and modifications of the embodiments described herein can be made without departing from the scope of the invention. Such modifications, changes and adaptations are intended to be within the scope of the present invention. In addition, descriptions of well-known functions and constructions are omitted for clarity and conciseness.

CLAIMS

1. An air independent propulsion (AIP) system for submarine comprising:
 - a. on-board hydrogen generation system, the said on-board hydrogen
5 generation system comprising fuel solution and catalyst to generate hydrogen in a compact vessel;
 - b. liquid oxygen (LOX) storage and feeding distribution system;
 - c. phosphoric acid fuel cell (PAFC) system, wherein in said phosphoric acid
10 fuel cell consumes hydrogen and oxygen to generate unregulated DC power;
 - d. power conditioner system wherein the said power conditioner system adapts the unregulated DC PAFC power and converts into regulated voltage controlled DC power;
 - e. plug management system wherein the said plug management system
15 controls the operation and integration with the dynamic load requirement of the platform;
 - f. reaction inhibition system;
 - g. fuel cell balance of plant (BoP) arrangement wherein the said fuel cell
20 balance of plant (BoP) arrangement comprises hydrogen loop, synthetic air loop and pressurized water system (PWS).
2. The air independent propulsion system for submarine as claimed in claim 1
wherein the fuel solution in the said on-board hydrogen system (a) is selected
from zinc borohydride (ZnBH_4), potassium borohydride (KBH_4), calcium
borohydride (CaBH_4), lithium aluminum hydride (LiAlH_4), sodium boron
25 trimethoxy hydride ($\text{NaBH}(\text{OCH}_3)_3$), or sodium borohydride (NaBH_4), preferably sodium borohydride.
3. The air independent propulsion system for submarine as claimed in claim 1
wherein the fuel solution in the said on-board hydrogen system (a) further
comprising a crystallization inhibitor selected from methyl paraben or propyl
30 paraben and a stabilizer.

4. The air independent propulsion system for submarine as claimed in claim 1 wherein the catalyst in the said on-board hydrogen system (a) is selected from aqueous solution of NiCl_2 or CoCl_2 .
5. The air independent propulsion system for submarine as claimed in claim 1 wherein the said oxygen storage and feeding distribution system (b) comprises cryogenic tank and LOX vaporizer heat exchanger.
6. The air independent propulsion system for submarine as claimed in claim 5 wherein the said LOX vaporizer heat exchanger comprises glycol-water closed loop system.
7. The air independent propulsion system for submarine as claimed in claim 1 where in the said phosphoric acid fuel cell system (c) supplies hydrogen and liquid oxygen to a stack of phosphoric acid fuel cell for generating unregulated DC power.
8. The air independent propulsion system for submarine as claimed in claim 1 wherein the said reaction inhibition system (f) stops or slows hydrogen generation by injecting sodium polyacrylate, preferably sodium methacrylate in hydrogen generator.
9. The reaction inhibition system as claimed in claim 8 wherein the said sodium methacrylate is stored in poison pot which is dosed in the hydrogen generator to stop/slow down hydrolysis reaction.
10. The air independent propulsion system for submarine as claimed in claim 1 wherein the hydrogen loop in the said fuel cell balance of plant (g) comprises humid hydrogen being fed to PAFC cell stack that diffuses in to the electrode to generate hydrogen.
11. The air independent propulsion system for submarine as claimed in claim 1 where in the synthetic air loop in fuel cell balance of plant (g) comprises synthetic air fed to PAFC cell stack to generate oxygen.
12. The air independent propulsion system for submarine as claimed in claim 1 where in the pressurized water system in the said fuel cell balance of plant (g) operate on dual mode wherein the said pressurized water system maintains the temperature by re-circulating hot water, in pressurized form from pressurized water tank (T-1) to avoid boiling in the loop through embedded heat exchanger in the PAFC stacks

and cooling water from pressurized water cooler (HE-5) cools the pressurized hot water when temperature increases.

13. The method of generating power from air independent propulsion system for submarine as claimed in claim 1, the said method comprising the steps of:

5 -generating hydrogen from raw material feed comprising fuel solution and catalyst in said on-board hydrogen system (a);

 -feeding the generated hydrogen and oxygen to PAFC stacks (c) where the supplied hydrogen and oxygen is consumed to generate unregulated raw DC power;

10 -providing the unregulated raw DC power to power conditioning system (d) to generate regulated DC power

 -interfacing the regulated DC power with platform switch board to provide power to platform

 -providing a network of heat exchangers to manage the thermal load with

15 de-mineralized water cooling circuit, the said de-mineralized water cooling circuit consisting of cooling water tank, cooling water tanks, cooling water pumps, piping network, sensor means and valve means and sea water cooling network, the said sea water cooling network consisting of hull penetrations, sea water heat exchangers, sea water circulation
20 pumps, sea water piping network and sensor means and valve means

 -providing exhaust means to expel spent liquor and master vent means for gases substantially balancing heating and cooling requirements of the system'

 -providing control and monitoring means for automatic operation of the entire AIP system and individual components of the system and for regulating the same in
25 accordance with the power demands on the system preferably by means of controller architecture comprising:

 PLC type controller to operate hydrogen generator;

 model predictive controller with an algorithm for determining fuel cell stack health and optimizing current distribution to each stack so that power
30 from fuel cell meets the power demand of the system;

 nodal controller to supervise overall control, efficacy, and adjust lower part controller set point to minimize instability;

submarine controller, with which, the said nodal controller interacts to obtain power demand and pass AIP parameters to operator

14. Fuel solution for air independent propulsion system wherein the said fuel solution comprises:

- 5 a) an aqueous solution concentrate of sodium borohydride in the range of 30% w/w to 40% w/w;
- b) a stabilizer selected from potassium hydroxide or sodium hydroxide; and
- c) a crystallization inhibitor selected from methyl paraben or propyl paraben at 0.02% to 0.15% by weight.

10 15. The method of generating hydrogen from on-board hydrogen generation system comprising fuel tank, catalyst tank, compact vessel with in-built heat exchangers, intermediate tank, spent storage tank, pressure control means wherein, the said method comprising the steps of:

- 15 a. pumping the fuel solution and caustic solution from fuel tank and catalyst from catalyst tank to the compact vessel with in-built heat exchangers;
- b. hydrolyzing borohydride in fuel solution in presence of catalyst in the said compact vessel for generating hydrogen at higher rate than required;
- c. discharging the resultant borax solution formed as byproduct in step b, intermittently to intermediate tank wherein the trace borohydride in borax solution is converted to hydrogen, the resultant residual hydrogen then joins to the main hydrogen line and remainder is discharged to spent storage tank;
- 20 d. hydrolyzing reaction in step b, resulting in increase in pressure; which activates the pressure control means to stop the fuel solution feed in step a;
- 25 e. as hydrogen is consumed by phosphoric acid fuel cell (c), the pressure in the compact vessel falls thereby restarting the fuel solution feed;
- f. providing the said compact vessel with conformal heat exchanger for heat removal and reactant mixing;
- g. providing the said compact vessel with top mounted heat exchanger for cooling product hydrogen;
- 30 h. providing the said compact vessel with non-conventional heat exchanger coils for removal of heat and reactor temperature maintenance comprising

shell side circulating borate solution and tube side circulating demineralized water.

16. The method of generating hydrogen from on-board hydrogen generation system as claimed in claim 15 wherein the said fuel solution is selected from zinc borohydride (ZnBH_4), potassium borohydride (KBH_4), calcium borohydride (CaBH_4), lithium aluminum hydride (LiAlH_4), sodium boron trimethoxy hydride ($\text{NaBH}(\text{OCH}_3)_3$), or sodium borohydride (NaBH_4).
17. The method of generating hydrogen from on-board hydrogen generation system as claimed in claim 15 wherein the said catalyst is selected from aqueous solution of NiCl_2 or CoCl_2 .
18. The phosphoric acid fuel cell (PAFC) stack for air independent propulsion system for submarine wherein the adhesion strength of phosphoric acid electrolyte to graphitic electrode structure in phosphoric acid fuel cell is increased by applying wash coat on graphitic electrode structure before casting phosphoric acid electrolyte.
19. The air independent propulsion system for submarine as claimed in claim 18 wherein the said wash coat comprises 90 to 97% by weight Silicon carbide, 2% by weight polyethylene oxide and 3 to 10% by weight polytetrafluoroethylene (PTFE).
20. Multiple metallic tubes embedded graphite heat exchanger plates for phosphoric acid fuel cell stack assembly comprising:
- a) multiple serpentine metallic tube with different path configurations embedded in a high density conducting graphite grooved plate with fuel cell cathode channel at one side surface wherein the said metallic tubes are embedded in grooved plate by using moulding mixture comprising exfoliated graphite powder and polytetrafluoroethylene (PTFE) suspension between tube and graphite walls, and
 - b) a thin, electrically conducting sheet resistant to high temperature acid attached at the grooved side surface of high density graphite plate from where metal tubes are fitted, by applying thin glue composition.

21. The multiple metallic tubes embedded graphite heat exchanger plates as claimed in claim 20 wherein the said moulding mixture comprises exfoliated graphite powder in an amount 70 to 80 % by weight and PTFE in an amount 30-20% by weight.
- 5 22. The multiple metallic tubes embedded graphite heat exchanger plates as claimed in claim 20 wherein the said exfoliated graphite powder has particle size in the range of 220 microns to 1400 microns.
23. Multiple metallic tubes embedded graphite heat exchanger plates for phosphoric acid fuel cell stack assembly as claimed in claim 20 wherein the said glue
10 composition comprises 80 to 95% by weight fine natural graphite powder and 5 to 20% by weight of phenolic resin

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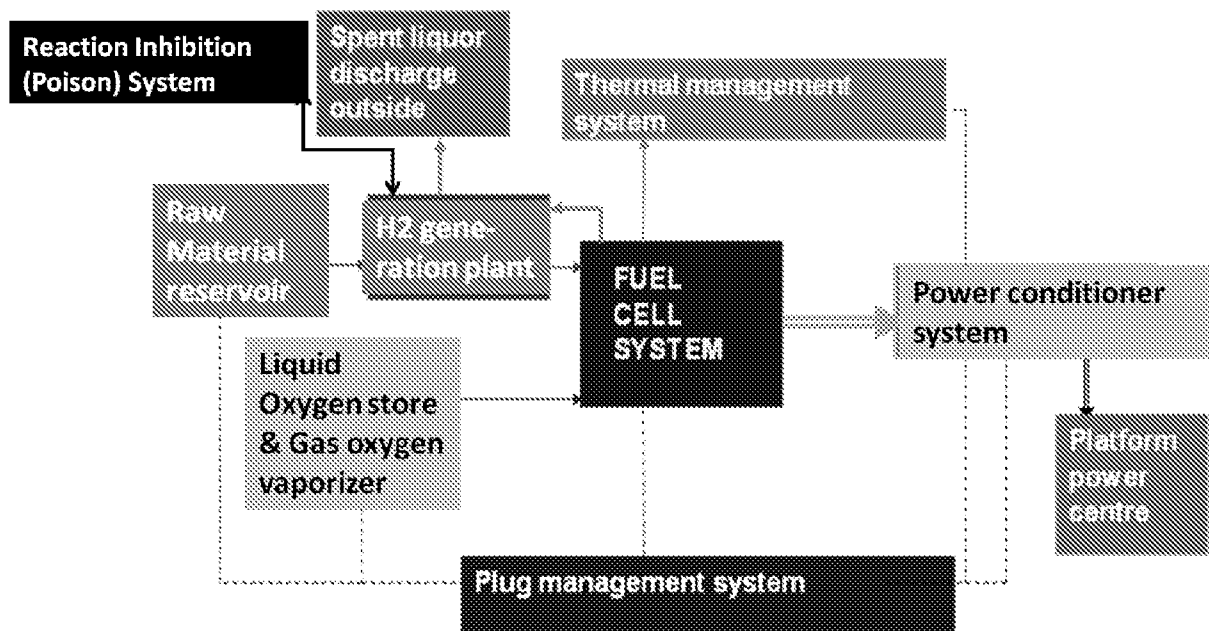


Figure 1: Block Diagram of AIP with Reaction Inhibition system

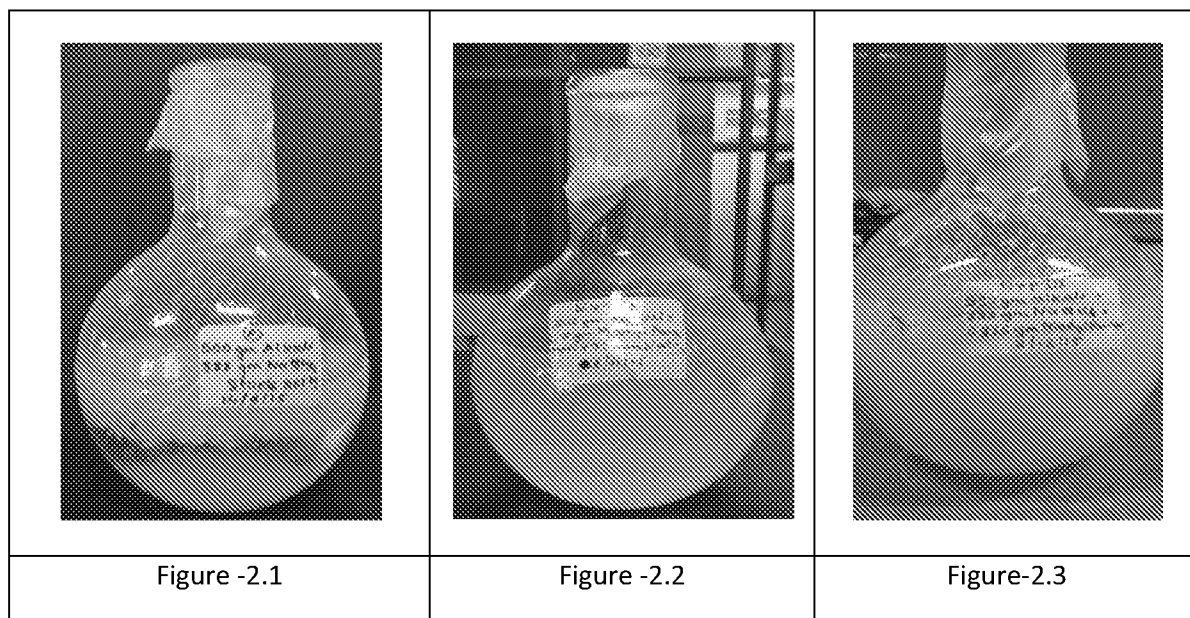


Figure 2: NaBH₄ solution with and without crystallization inhibitor

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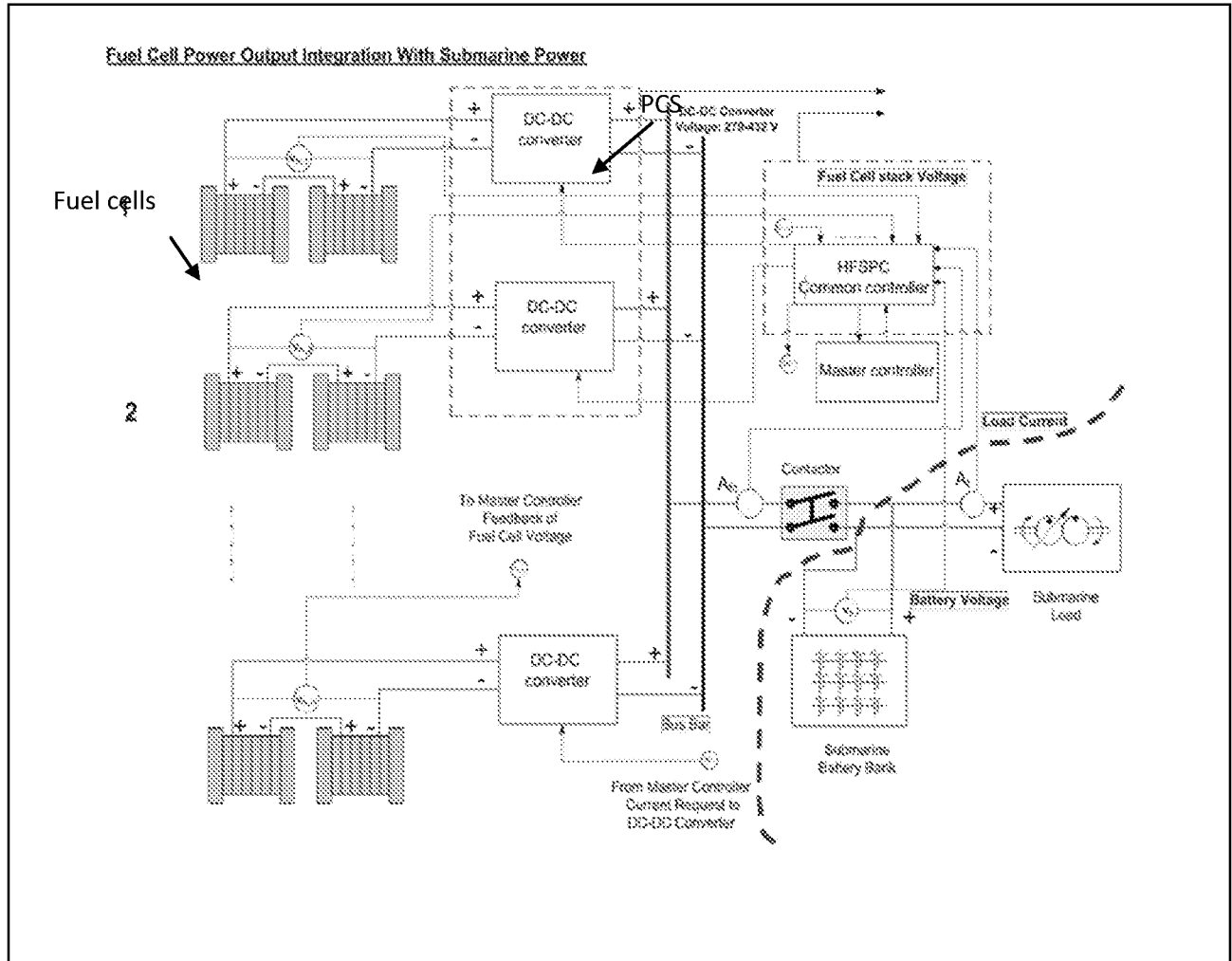


Figure 3: Fuel Cell Power Output system

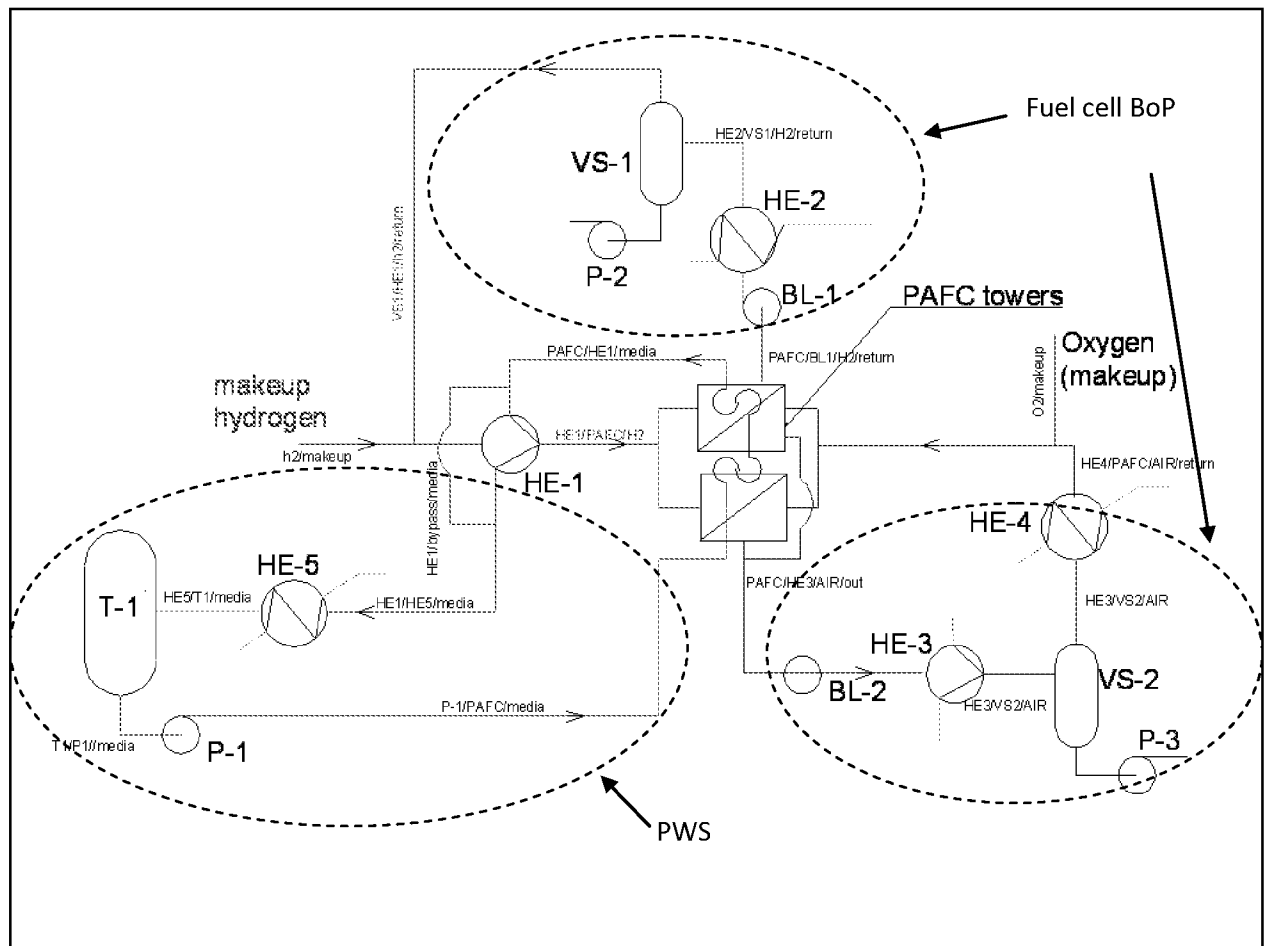


Figure 4 Power production- Fuel Cell plant

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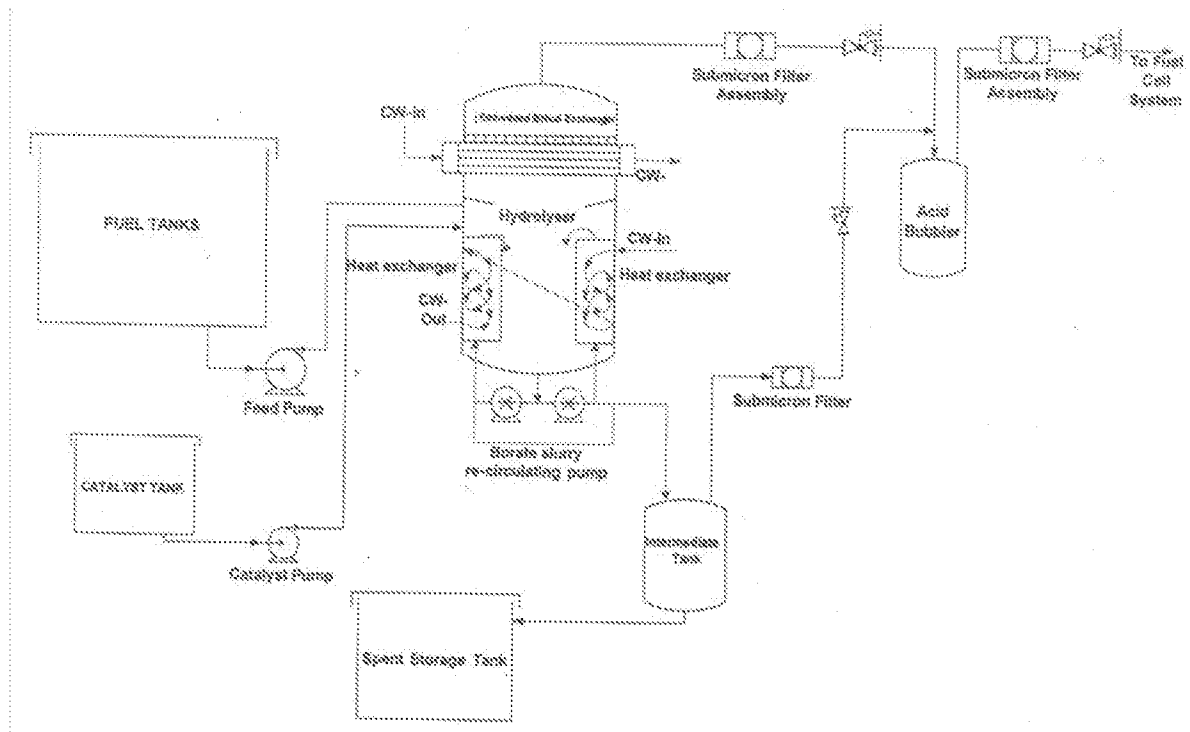


Figure 5 . Process schematic diagram for onboard hydrogen generation from sodium borohydride solution

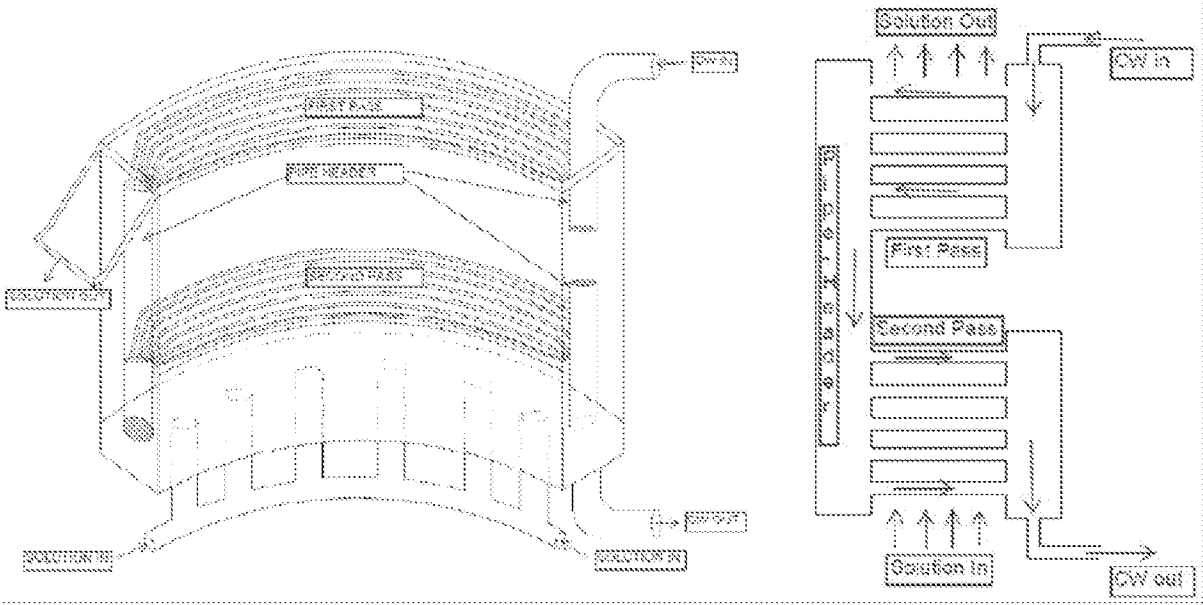


Figure 6. Schematic and Isometric view of Heat Exchanger

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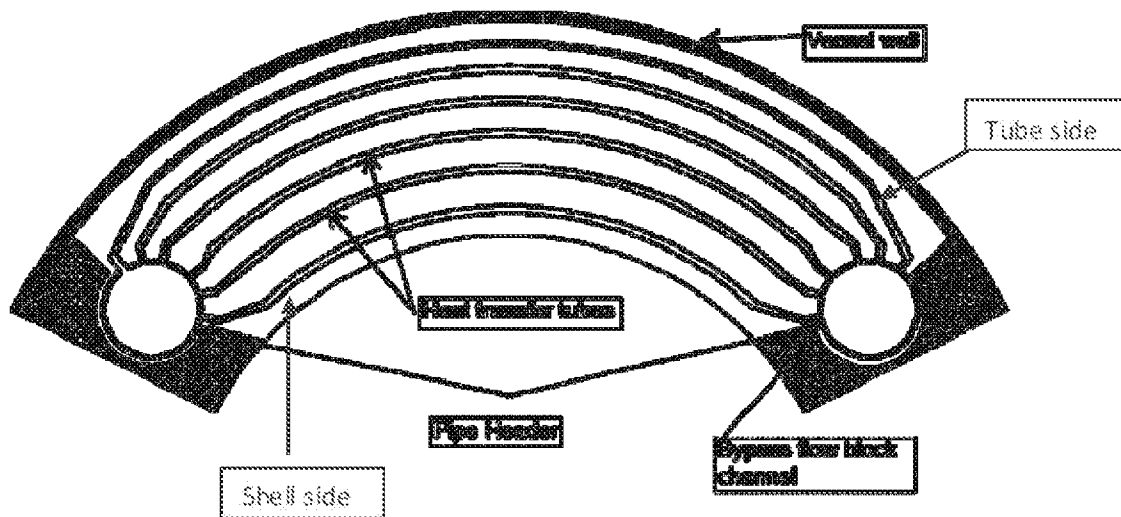


Figure 7. Top view of Heat Exchanger

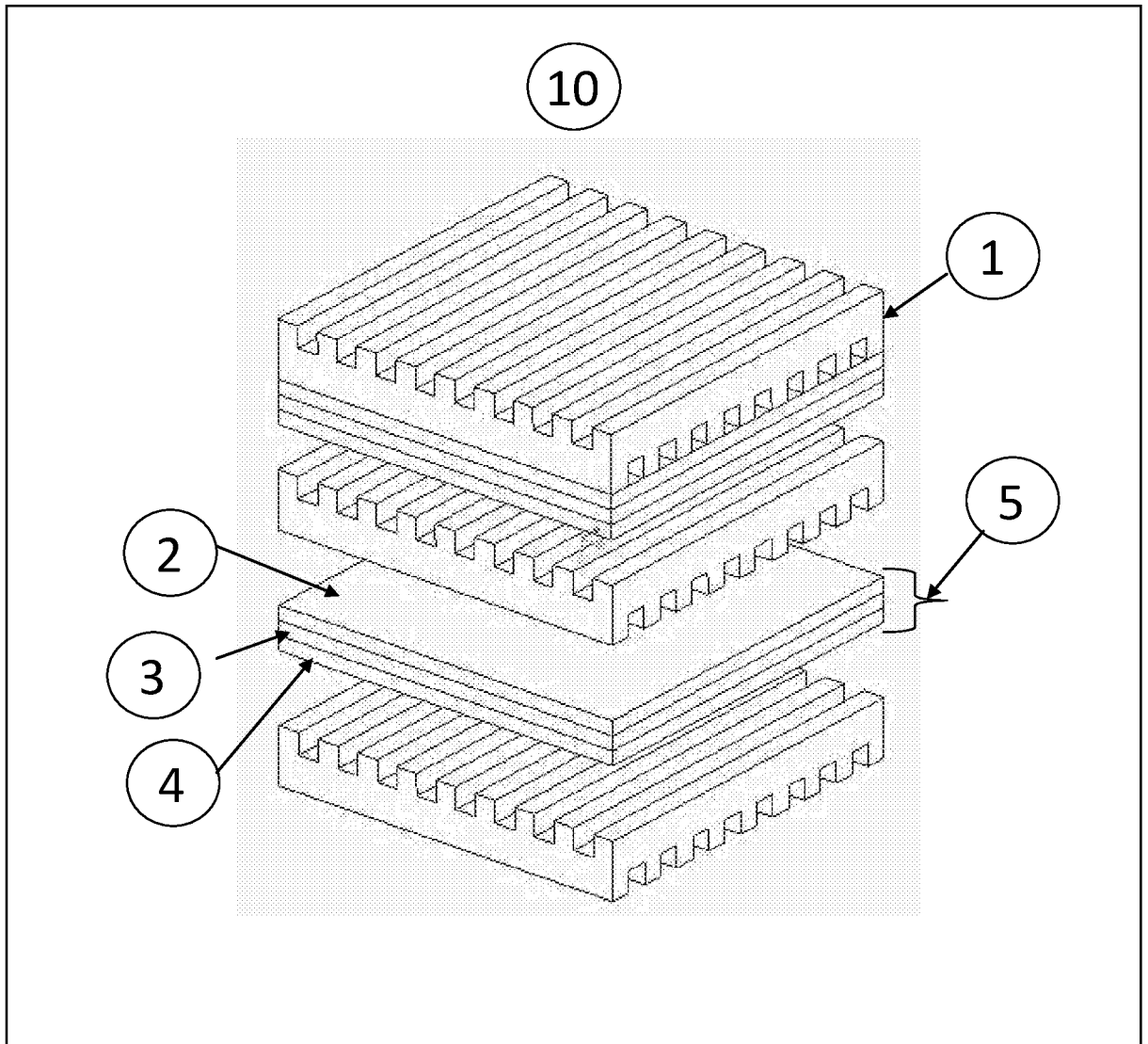


Figure 8: Blow up view of PAFC

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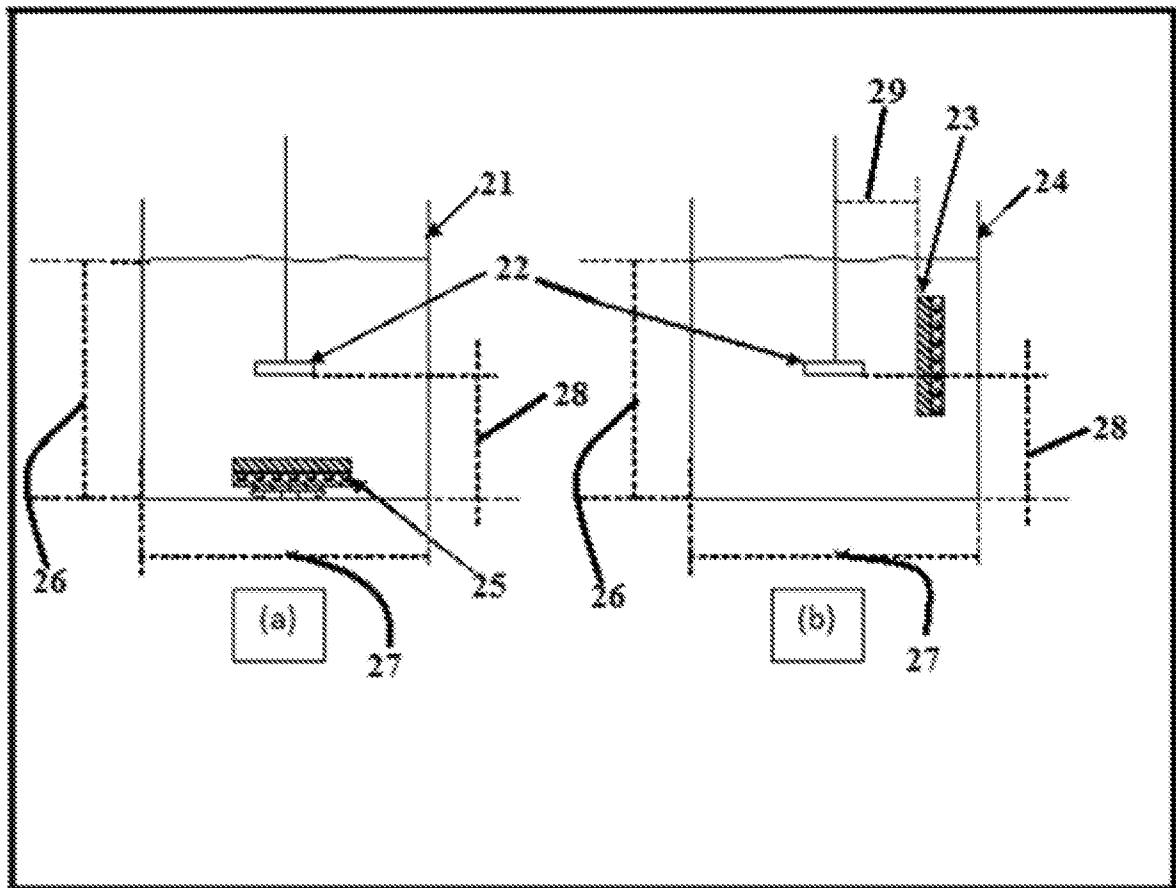


Figure 9:

Matrix Adhesion test assembly; a) Sample kept on the bottom; b). Sample kept vertically

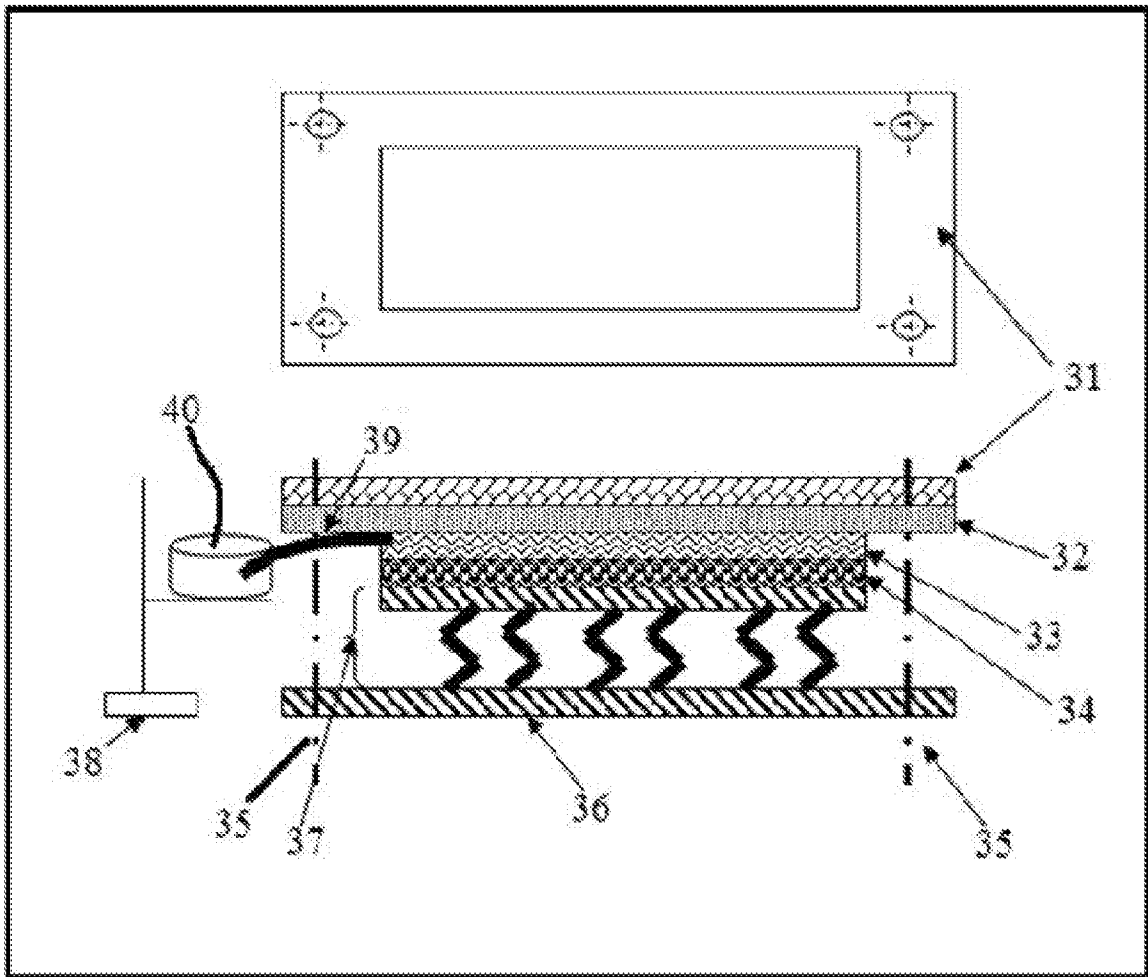


Figure 10: Assembly fixture for acid migration test

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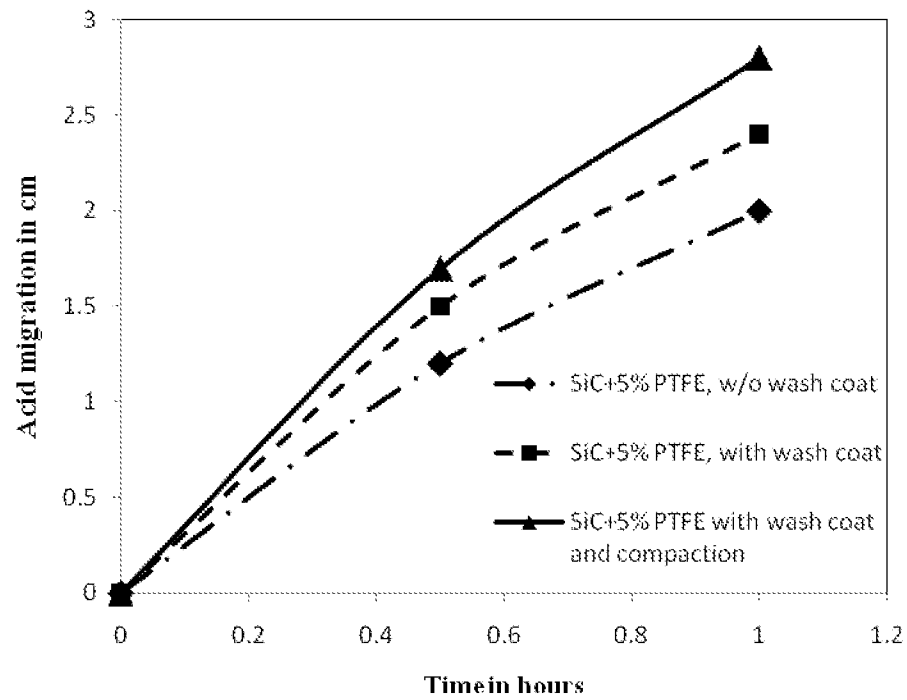


Figure 11 Acid migration of different matrix at 0.7 Mpa with time

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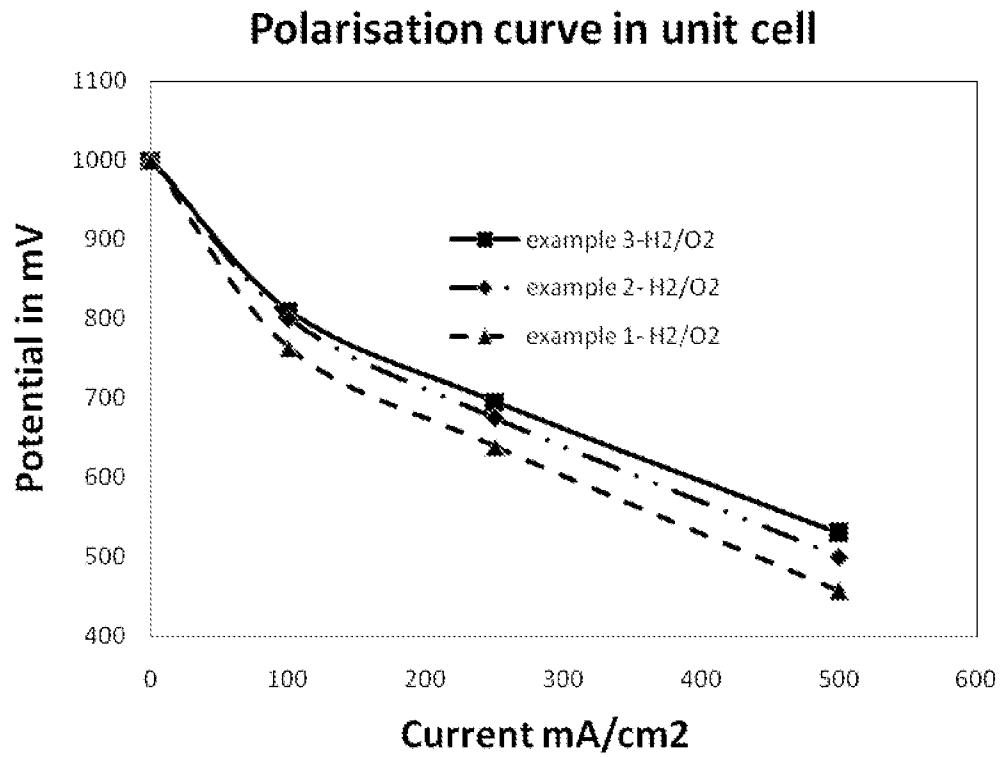


Figure 12 Comparison of three matrix performance in unit cell with H₂/O₂.

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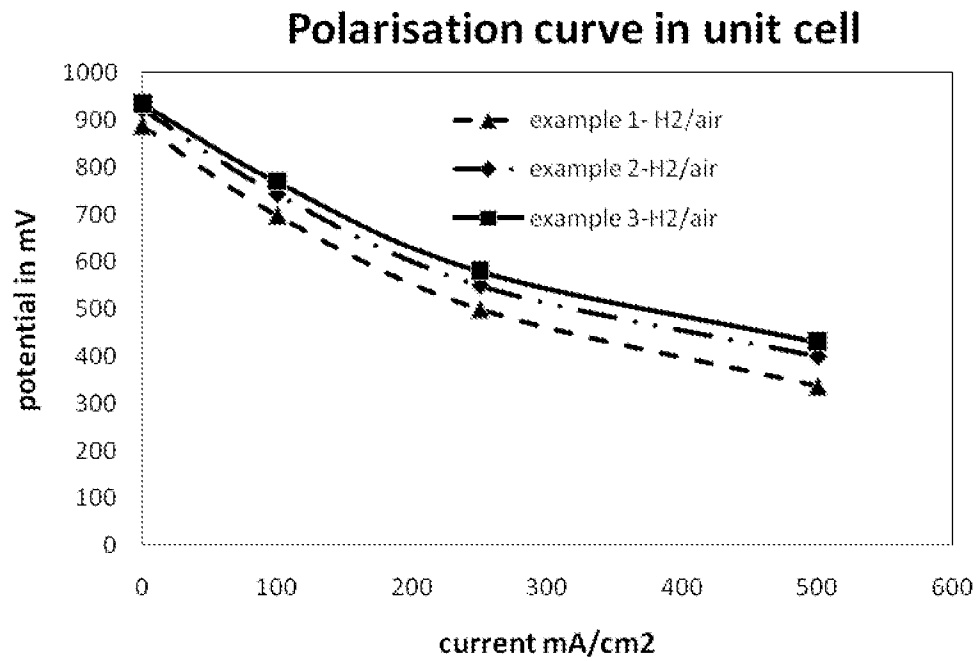


Figure 13. Comparision of three matrix performance in unit cell with H₂Air

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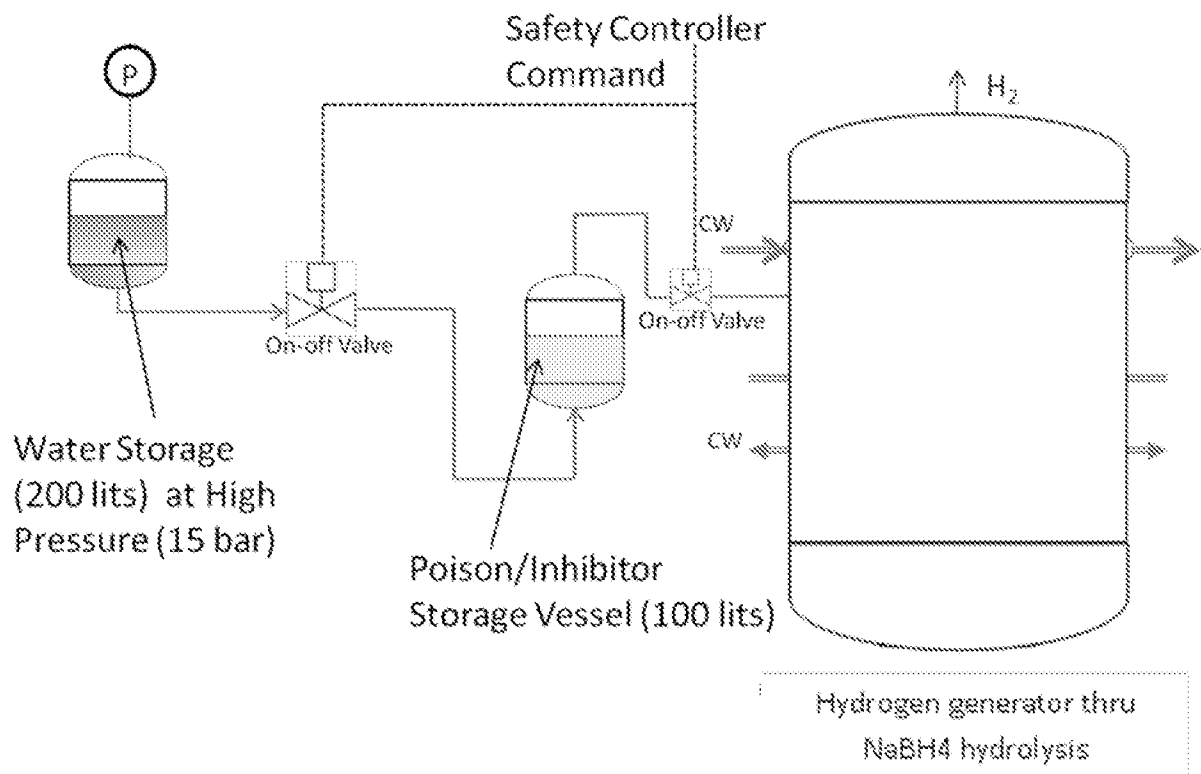


Figure -14 Dosing Methodology of the inhibitor powder for poisoning $NaBH_4$ hydrolysis reaction inside the H_2 generator

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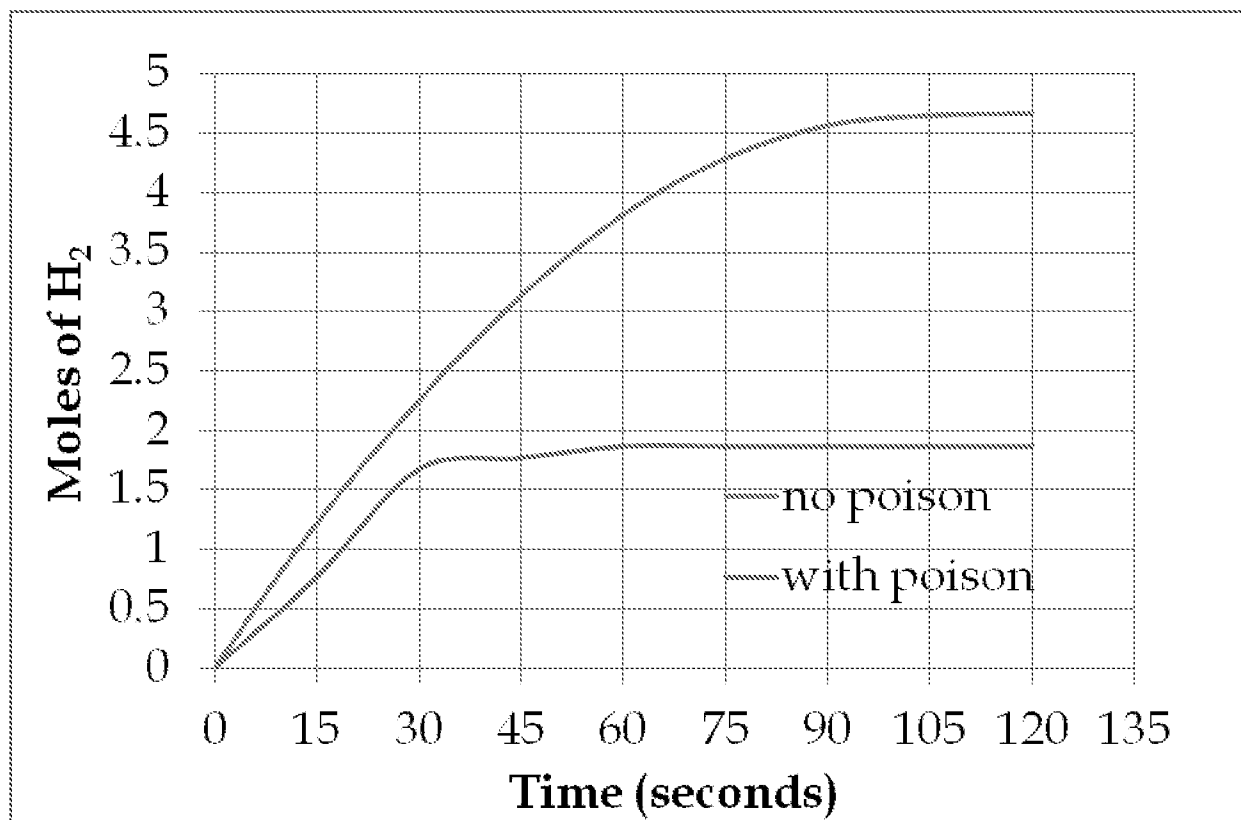


Figure 15. Effect of poison (sodium methacrylate powder) of about 0.8 kg injected to a 40 kw scale down H_2 generator of the AIP system

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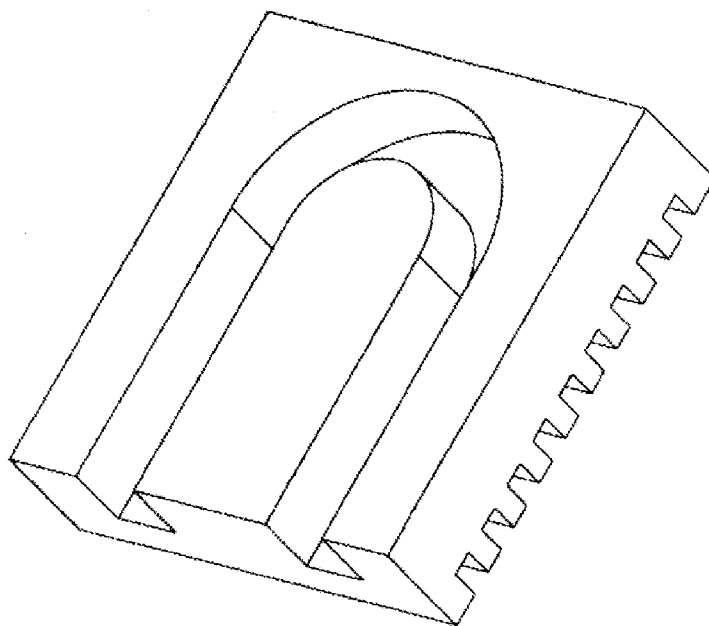


Figure 16. Plate with channel for the metallic coil tube and integrated flow groove on the bottom

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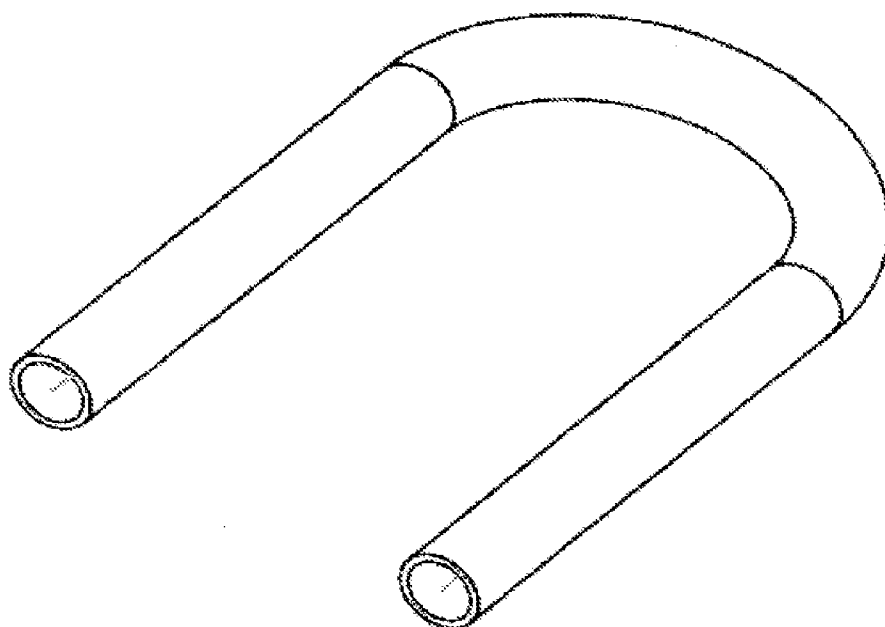


Figure 17: Single metallic coil tube

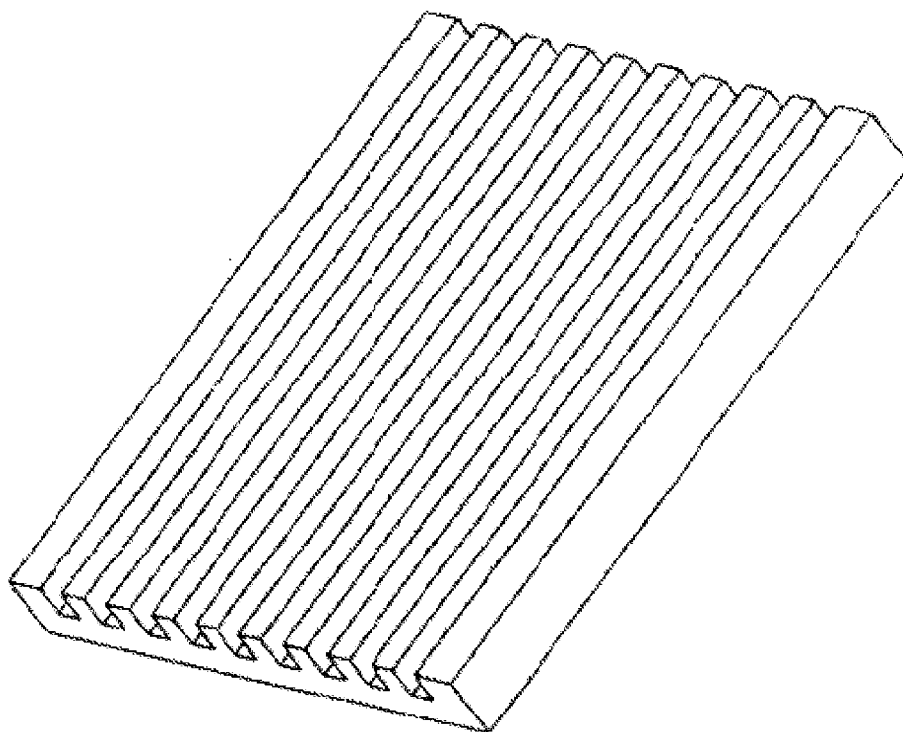


Figure 18: Cover plate with flow grooves on top

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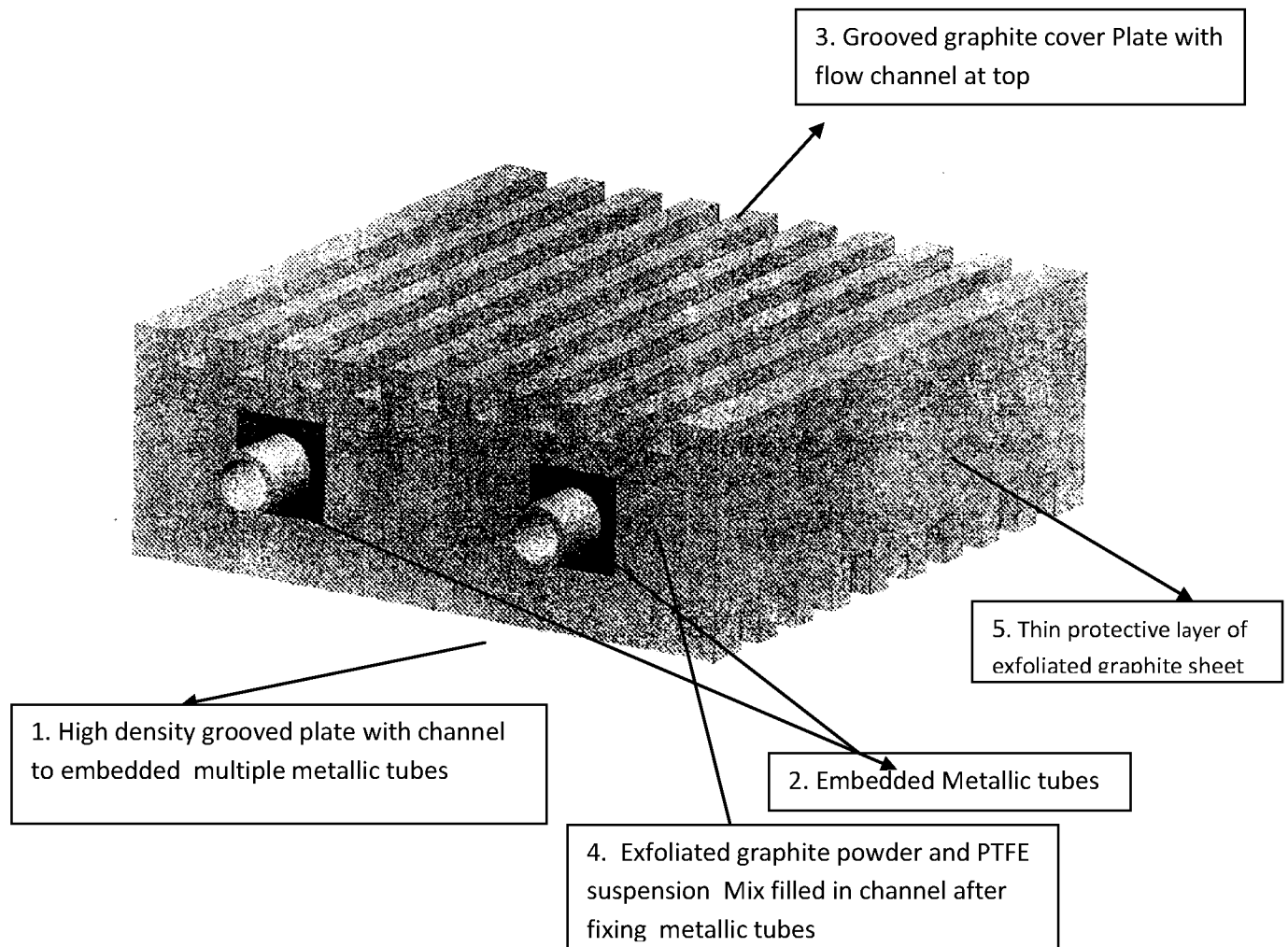


Figure 19: Fully assembled heat exchanger with soft hydrophobic, conducting caulk around the tube for better contact.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2017/051007

A. CLASSIFICATION OF SUBJECT MATTER
C01B3/06, H01M8/06 Version=2017.01

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C01B, H01M

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

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

Patseer

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	KR101259820 B1; SAMSUNG HEAVY IND CO LTD; 30-Apr-2013 (30-04-2013). Whole Document	1-23
A	KR20140044090 A; DAEWOO SHIPBUILDING & MARINE ENGG CO LTD; 14-Apr-2014 (14-04-2014). Whole Document	1-23
A	KR20150094186 A; DAEWOO SHIPBUILDING & MARINE ENGG CO LTD; 19-Aug-2015 (19-08-2015). Whole Document	1-23
A	US20110256459 A1; IDATECH, LLC; 20-Oct-2011 (20-10-2011). Whole Document	1-23

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

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

12-06-2017

Date of mailing of the international search report

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Name and mailing address of the ISA/

Indian Patent Office
Plot No.32, Sector 14, Dwarka, New Delhi-110075
Facsimile No.

Authorized officer

A. Reddy

Telephone No. +91-1125300200

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/IB2017/051007

Citation	Pub.Date	Family	Pub.Date
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		EP 1938414 A2	02-07-2008
		US 7659019 B2	09-02-2010
		WO 2007037856 A2	05-04-2007
		JP 5607302 B2	15-10-2014