9th International Symposium on New Materials and Nano-Materials for Electrochemical Systems
XII International Congress of the Mexican Hydrogen Society
Merida, Mexico, 2012

Performance Improve of a PEM Electrolyzer, Decreasing the Ohmic Resistance because of Manufacturing and Assembly Processes

J. L. Corona-Guinto[1*], R. G. González-Huerta[2], J. M. Sandoval-Pined[1], P. A. Tamayo-Meza[1], R. Silva-Casarin[3]

[1]Instituto Politécnico Nacional – ESIME – UA – Edificio de Posgrado y Campus Virtual, México, D.F. 02250, Tel. 5729 6000, Ext. 64525
[2]Instituto Politécnico Nacional – ESIQIE – Laboratorio de Electrocatálisis.
[3] Universidad Nacional Autónoma de México – Instituto de Ingeniería – Ciudad Universitaria.
[*]Cel: 5538831965, mail : cogui_f1@hotmail.com

ABSTRACT

Proton Exchange Membrane Electrolyzer (PEME) can be coupled to Renewable Energy Sources (photovoltaic panel, wave energy conversion device, wind turbine, etc) to obtain the necessary electricity for splitting the water. The ideal thermodynamic voltage for hydrogen production by water electrolysis is 1.23V; however the difference between actual electrolyzer voltage and the reversible electrolyzer voltage for the reactions is called overvoltage. One of the sources of overvoltage in an electrolyzer is ohmic overpotential, which arising due to the resistive losses from wrong manufacturing and assembly processes. The study goal was manufacture a high efficiency and performance PEME to produce hydrogen as an energy carrier, minimizing the ohmic overpotential. More suitable processes for the manufacture of a PEME were analyzed and proposed. Prototype methodology was used to design the electrolyzer and specify assembly processes. This methodology validates the final prototype when it was built. The PEME performance was obtained by Chrono-potentiometric technique. The experiments were carried out by applying the current pulse and determining the potential as a function of time. It is connected to a galvanostat in order to obtain its response Voltage vs. time. Experiments were recorded in the current range of 1 to 300mA at 300s. The PEME constructed had a current efficiency of 74% and an energy efficiency of 61% with overpotential of 1.8V, generating 1.456$mlH2.min^{-1}$ at 200mA. The current efficiency of the previous prototype with the same features was 11% and an energy efficiency of 3% with overpotential of 4.7V generating 0.21 ml_{H2} min^{-1} at 200mA. The energy efficiency improved from 3 to 61% and production of hydrogen in ml_{H2} min^{-1} increased by 593% in performance.

Keywords: PEM electrolyzer; Performance improve; Manufacturing and assembly processes; Design methodology of prototypes.

1. Introduction

Mexico generates around 74% of its energy from fossil fuels [1], this situation involve about 2% of global emissions of greenhouse gases into the atmosphere, which puts Mexico at 15th place of the nations polluters, the main reason is because annually about 130 million tons of CO_2 are emitted to the environment [2]. One of the alternatives that have been proposed to minimize the pollutions effects is to incorporate new sources of renewable energy. There are energy sources that can be obtained from natural fuel to be used in several applications, with less environmental impact than fossil fuels, gas and coal use.

Although renewable energy sources represent a great benefit to the depletion of fossil fuels and the impact of environmental pollution, there is a downside in terms of constant use because they are intermittent, i.e. renewable energy are not available all the time when they are required, and its storage and distribution are not fully developed. That is the main reason to propose the use of hydrogen as a carrier energy, which is a fuel that does not produces pollutants to the environment [3] and can be stored and transported anywhere to be use when it is required.

Hydrogen can be used in fuel cells to transform chemical energy into electric energy by means of a continuous process by reduction and oxidation reactions in the presence of a catalyst and removes the reaction products. There are a large number of applications of fuel cells; one of the most important of these applications is in transportation vehicles such as automobiles, airplanes, and even space shuttles.

Although the hydrogen is an excellent source of clean energy, it is not in nature state and must be extracted from some minerals or water [4-5]; in order to obtain hydrogen, a device called electrolyzer could be used. The way to generate hydrogen from water is trough electrolysis.

The design of a PEM electrolyzer will be able to be integrated to a source of renewable energy, which will generate electric energy to produce pure hydrogen as an energy carrier.

2. Experimental

This section gives a brief explanation of a GAMP methodology, which is a platform for DPEV methodology development, this was used to design and manufacture an electrolyzed prototype. Each of the specifications, auxiliary methods and validations stages to establish the design strategy are explained on this experimental section.

2.1. GAMP methodology

Good Automated Manufacturing Practice methodology – GAMP, which is shown in Diagram 1, was developed for the International Society for Pharmaceutical Engineering – ISPE. The ISPE is an affiliation society for professionals who are involved in the manufacture of pharmaceutical products. The ISPE, which now has 22,000 members in 90 countries around the world, works to keep professionals informed about pharmaceutical industry on the latest technological and regulatory trends that are occurring in the market. Core members of ISPE are pharmaceutical professionals using expert knowledge to create high quality, cost effective solutions and Good Manufacture Practices – GMP [6]. The GAMP methodology is based in the GMP which is defined by the World Health Organization – WHO as “The part of quality assurance which ensures that products are consistently produced and controlled with appropriate quality standards for the intended use and as required by the marketing authorization” [1,6].

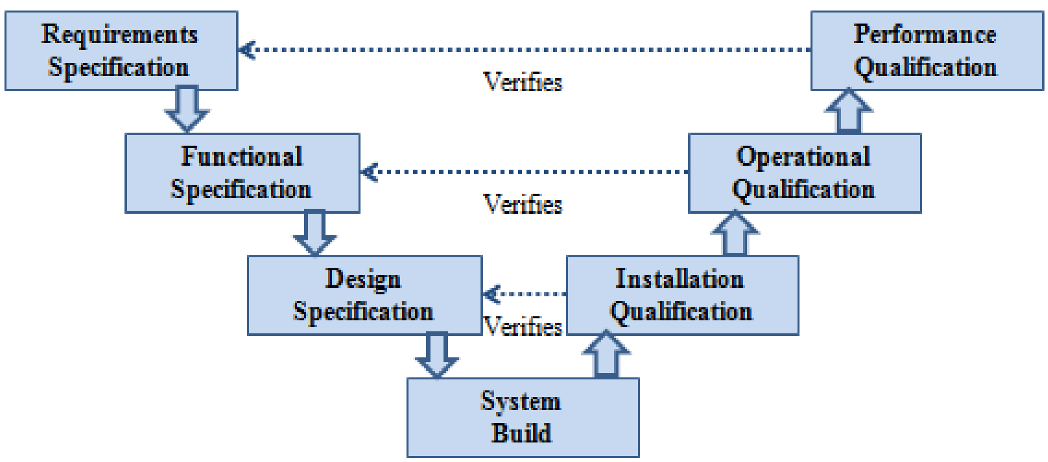


Diagram 1. GAMP-5 Methodology developed for the ISPE.

2.2. DPtSQ Methodology

Design methodology for Prototypes through specifications and qualifications – DPtSQ, sets all specifications for all different stages of prototype development, from idea conception until prototype building; in order to do it is necessary to use some support methods to determine the requirements for each stage. After the prototype building, the DPtSQ methodology provides a qualification process for each specification stage to validate and approve the design and manufacture of each parameter specified. Tests and inspection methods are designed and used to support the qualification processes to approve the prototype operation, installation in a system, and manufacture and assembly processes. Diagram 2 shows the DPtSQ methodology.

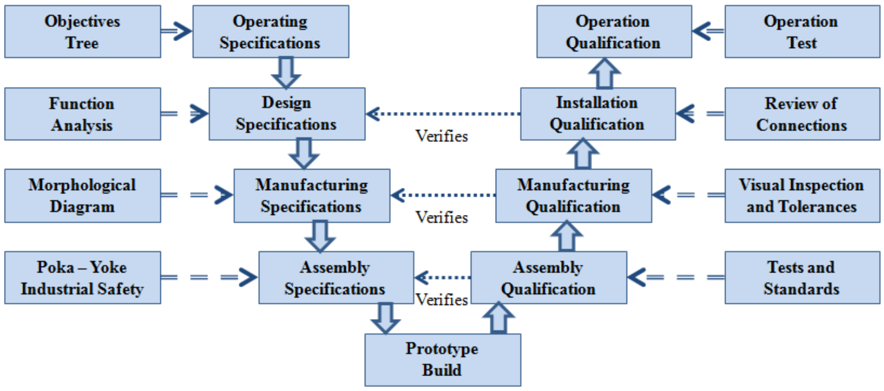


Diagram 2. DPtSQ Methodology supported on GAMP Methodology.

2.3. Operating Specifications

To determine the "Operating Specifications" is necessary to identify and clarify the prototype goals, then satisfy the main targets and link between them. Using the Objectives Tree method, it is be able to determine all the objectives of the prototype which sets 3 fundamental steps: 1) to make a list of objectives; 2) to sort the list in sets of objectives from higher to lower level; 3) to draw a diagram with data obtained. Diagram 3 shows hierarchy of each objective and interrelationships.

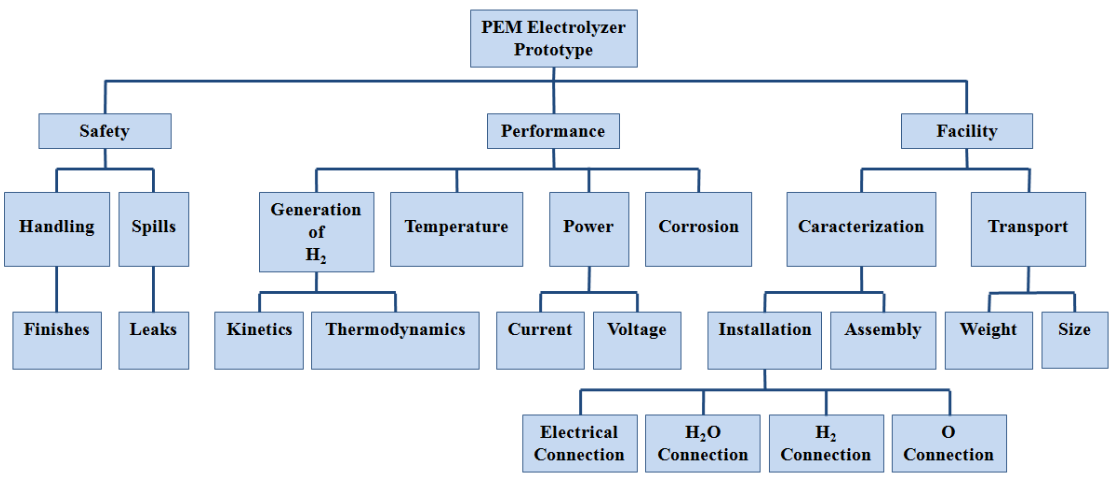


Diagram 3. Objectives Tree for a PEM Electrolyzer Prototype.

2.4. Design Specifications

Function analysis method is used to determine the "Design Specifications" which sets the required functions and system limits for a new design. There are 5 steps to complete this process [7]; 1) Expressing the overall roll of design in terms of converting inputs into outputs (black box); 2) Splitting overall function into a set of secondary functions;

3) Drawing a block diagram to show the interactions between the secondary functions, (clear box); 4) Drawing the system boundaries which define the functional limits for the prototype design; 5) Defining the appropriate components for secondary functions and their interactions. The diagram 4 shows the black box used for this prototype design; then overall function was divided into secondary functions and was drawn the line of the system boundaries as shown in Diagram 5. H_2O represent the distilled water entering the system; E_{CEL} is the electrical potential needed to carry out the oxidation reaction; H_2 is the hydrogen obtained from the system; O the oxygen; and finally L represents the heating lost.

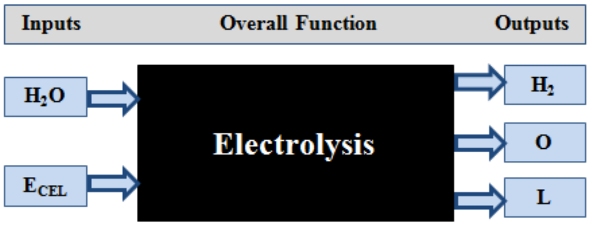


Diagram 4. Black box model for a PEM electrolyzer.

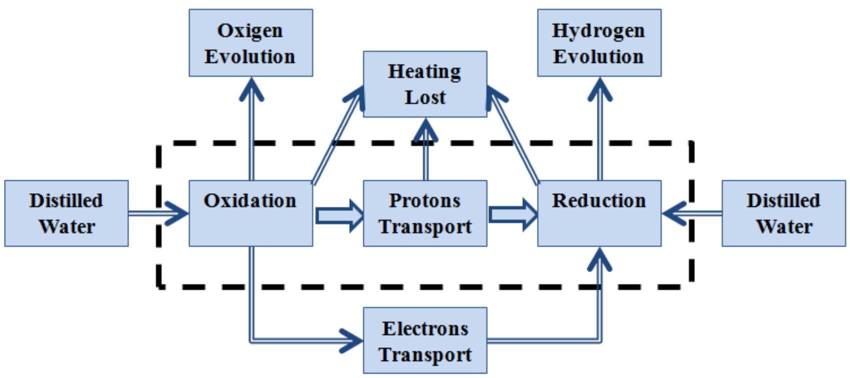


Diagram 5. Clear box model for a PEM electrolyzer.

2.5. Manufacturing Specifications

Morphological diagram is used to determine the "Manufacturing Specifications", which has the target to generate an alternatives range for product manufacture and extend the search for new potential solutions. This method involves 3 steps [7]; 1) Each one of the prototype components can be manufactured with different manufacturing processes, so it is necessary to make a list of processes; 2) Drawing a diagram that contain alternatives for each of the components; 3) Selecting the correct processes making an analysis of their characteristics, properties, benefits and costs. Table 1 shows the processes selected supported by this method.

Table 1. Morphological diagram for manufacturing processes of a PEM electrolyzer.

Products	Manufacturing Processes						
Current Distributor	(cutting) Shears	(cutting) Laser	(cutting) Flame	(cutting) Milling	(cutting) CNC	(cutting) Waterjet	(cutting) Plasma
Gas Diffuser	(cutting) Scissors	(cutting) Cutter	(cutting) Trimmer				
Catalytic Ink	(mixture) Manual	(mixture) Ultrasound	(mixture) Automatic	(mixture) Vibration			
Membrane (PEM)	(cutting) Scissors	(cutting) Cutter	(cutting) Trimmer				
Catalytic Layer	(print) Manual	(print) Airbrushing	(print) Serigraphy	(print) Spraying	(print) Tape-cast		
Housing	(cutting) Milling	(cutting) CNC	(drilling) Drill	(drilling) Drill press	(thread) Tap	(thread) Lathe	
Seals	(cutting) Scissors	(cutting) Cutter	(cutting) Trimmer	(cutting) Punching			

Alternative Manufacturing Processes   Manufacturing Processes Selected

2.6. Assembly Specifications

Devices named Poka-Yokes are used to determine the "Assembly Specifications" to avoid mistakes; safety standards are used during the assembly processes in order to prevent accidents. Poka-Yokes technique is use to eliminate human and operation mistakes, simple and effective techniques to eliminate or reduce defects; it is a tool to achieve quality "Zero Defects". These devices aim to prevent omissions, lack of understanding, identification mistakes, inexperience, volunteer mistakes, inadvertent mistakes, slowness mistakes, lack of standards, mistakes by surprise and intentional mistakes. 3 levels of hierarchy must be taken into Poka-Yokes design: 1) level 3 – Making obviously that a mistake has occurred; 2) level 2 – Making obviously that a mistake will occur; 3) level 1 – Eliminating the possibility of mistakes. Table 2 shows the Poka-Yokes devises designed for this prototype.

Table 2. Poka-Yokes designed to development of PEM electrolyzer prototype.

Level of Poka-Yoke	Type of Poka-Yoke	Purpose of Poka-Yoke	Location of Poka-Yoke
Level 2	Marks of positive and negatives poles	To identify the polarities	Housing
Level 2	Identification marks of hydrogen and oxygen	To identify the gas being generated	Housing
Level 1	Notches – Interference fit	To put the power distributors	Housing
Level 1	Guide pin assembly	To assemble the housings	Housing
Level 2	Notches – Clearance fit	To put the teflon seals	Housing
Level 2	Mark for recognition of polarity MEA	To put properly the MEA	MEA
Level 2	Membrane covering fixture	To impregnate electrocatalytic ink	External device
Level 1	Fixture for mounting of diffusers and membrane	To assemble MEA	External device

The standards used for operator safety were as follows.

- NOM-005-STPS-1998. Health and safety conditions in the workplace for the handling, transport and storage of hazardous chemicals.
- ISO-14062. Integration of environmental considerations in the design and product development.
- NOM-017-STPS-1994. Relating to personal protective equipment for workers in the workplace.
- NMX-S039-SCFI-2000. Safety products, protective gloves against chemicals, specifications and test methods.

2.7. Prototype Build

4 specifications stages were defined, it proceeds with PEM electrolyzer prototype construction using the results found in each of the stages previously evaluated.

a) Membrane activation

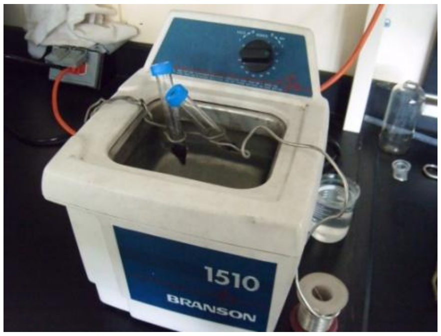
Nafion® membrane must pass through activation process for its correct functionality; the aim of this process is to release the sodium content in this polymeric material. The membrane was introduced into a container with hydrogen peroxide at temperature range of 80°C and 100°C for one hour; then the membrane was placed in other container with 2.46 ml cm^{-2} hydrogen peroxide solution and sulfuric acid at 2.19 ml cm^{-2} due to the active area at range temperature of 80°C and 100°C for one hour. After that the membrane was deposited in a container with distilled at the same temperature and time; finally it was placed in a container with distilled water at room temperature and was left for 24 hours. The reason of the temperatures is because it is the optimal range of Nafion® operating temperature and over 150°C the membrane begins crystallization process and the molecular structures of the material are broken. The Photographs 1 and 2 show part of the activation process.

Photograph 1. Activation at 80° for 1 hr.

Photograph 2. Hydrated with distilled water

b) Preparation of the electrocatalytic solutions

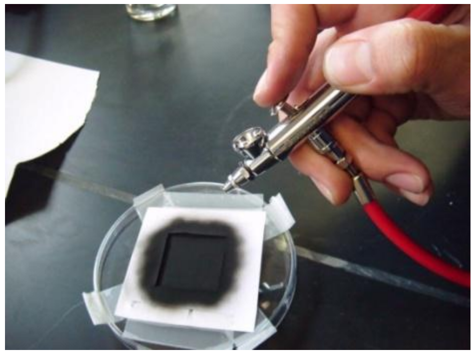
To electrodes construction was necessary to prepare an anodic solution for the oxidation process and a cathodic solution for the reduction process. The cathodic solution was a mixture of 1.2 mg cm^{-2} of 10% platinum etek, 40 µl cm^{-2} of liquid Nafion® and 700 µl cm^{-2} of chromatic grade ethanol; this last one as diluent. The anodic solution was a mixture of 1.44 mg cm^{-2} of ruthenium oxide, 1.65 mg cm^{-2} of iridium oxide, 54 µl cm^{-2} of liquid Nafion® and 667 µl cm^{-2} of ethanol; both solutions was exposed in an ultrasonic process to dilute the particles homogeneously in the solution. The Photograph 3 shows the ultrasonic process mentioned.



Photograph 3. Solution mixture using ultrasound

c) Construction of the electrodes

The next step was defined to electrodes construct, the electrocatalytic solutions prepared were impregnated in the membrane by airbrushing process; one membrane side was impregnated with anodic solution while the other was impregnated with cathodic solution; the airbrushing process was manual because there are not an automated process in the laboratory; it is necessary to identify properly the cathodic and anodic side of the membrane. The airbrushing process is completed when both solutions are entirety deposited on both faces of the membrane. The airbrushing process is shown in Photograph 4.

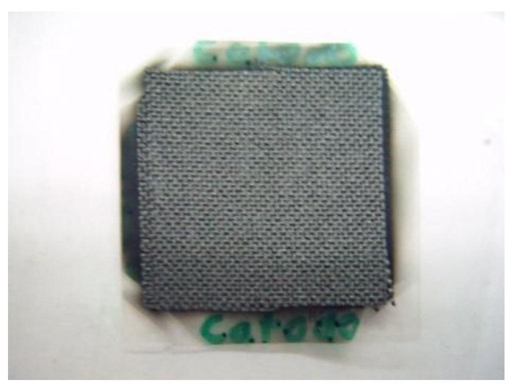


Photograph 4. Anodic solution impregnated in the membrane by airbrushing process

d) MEA Assembly

For MEA assembly, it is required to join gas carbon diffusers fiber with the membrane in order to provide a permanent contact; the process involves to introduce them into a membrane press placing between both diffusers and to protect this set with a pair of micas and a pair of aluminum plates; the hot pressing is affected at 120°C temperature with only 2 tons pressure for 5 seconds, then the pressure is released and adjusted to 0.4 tons; pressure is applied again, in this time for 2 minutes period with the plates of the press at the same temperature. 120°C is the temperature of a vitreous composition of the Nafion® membrane, above this temperature is produced a good microstructural joint between both materials, however the atomic links are broken at 150°C and a decomposition process can be initiated. Photograph 5 shows the press used in this process and MEA assembly is shown in Photograph 6.

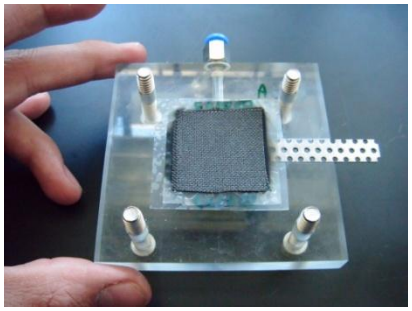
Photograph 5. Hot press process



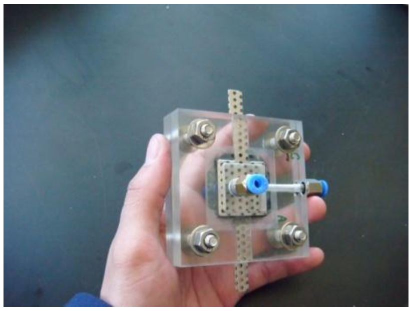
Photograph 6. MEA assembly

e) Prototype assembly

Last step was defined to assembly all the components previously manufactured of the PEM electrolyzer prototype, housings, Teflon seals, current distributors and MEA. Housings was manufactured with acrylic due to the properties of this material, such as impermeability to gases produced, resistance to the operating temperature of the PEM electrolyzer prototype, and low cost. Current distributors was manufactured with stainless steel mesh to conduct electrical current and allow flow of gasses through themselves; screws, nuts, washers, quick connectors and silicon were used to complete the final assembly. The use of the designed Poka-Yokes helped the placement and orientation of each of the components. All the components were correctly placed in housings and the silicon was applied between current distributors, Teflon seals, and housings, in order to avoid leakages. Photograph 7 a housing with its components correctly placed, and the complete assembly is shown in Photograph 8.



Photograph 7. Housing with MEA, current distributor, and seal



Photograph 8. PEM electrolyzer assembled

2.8. Assembly Qualification

To validate the assemblies made, first, it was used a visual inspection of the prototype reviewing the perfect seal of both housings, position of the washers, adjustment of the screws and the quick connectors, the correct state of the current distributors. In the MEA assembly process was verified adherence between gas diffuser and membrane. Placement of current distributors and seals was also inspected before assembling the entire prototype. To verify the absence of internal leakage was designed a test in which certain ports were blocked and water was introduced into the system using a water low pressure pump. The test is verified as successful when there are no leaks in free ports; the test was carried out according to the configuration of Table 3.

Table 3. Internal leakage test

Interconnected ports	Pressurized port	Blocked port	Free port	
Anode-Oxygen	Anode	Oxygen	Cathode	Hydrogen
Cathode-Hydrogen	Cathode	Hydrogen	Anode	Oxygen

Second test was defined to block the ports on the evolution of oxygen and hydrogen to supply water with the same pump, verifying that internal leakage are not observed at the juncture of the prototype housings; and finally one last test was performed to validate the assembly, this test consist of filling the water tanks of the prototype to a low pressure and keeping them for 24 hours to subsequently see if there is any type of leak.

2.9. Manufacturing Qualification

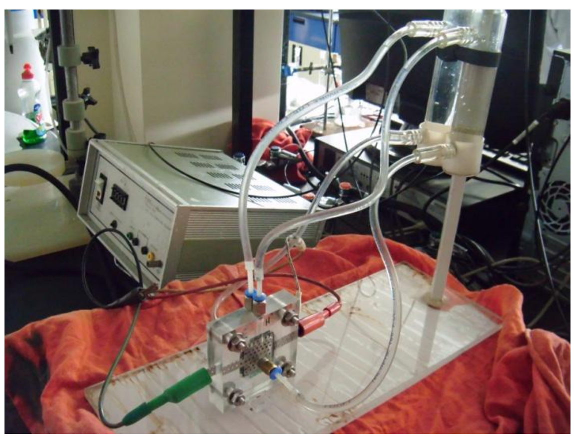
To validate that manufacture of each component, visual inspections was performed to verify gas diffusers, seals and membrane did not display defective edges; "go – no go" Poka-Yokes were designed to verify the specified dimensions of the elements of PEM electrolyzer prototype. The "go – no go" Poka-Yokes designed for this stage of qualification are shown in Table 4.

Table 4. "go – no go" Poka-Yokes designed to verify the specific dimensions of elements of PEM electrolyzer prototype.

Level of Poka-Yoke	Type of Poka-Yoke	Purpose of Poka-Yoke	Location of Poka-Yoke
Level 2	"go – no go" fixture to specific size of water tanks	To validate size of the water tanks	External device
Level 2	Calibrated screws	To validate size of the connection thread	External device
Level 1	"go – no go" fixture to specific size of current distributors	To validate size of the current distributors	External device

2.10. Installation Qualification

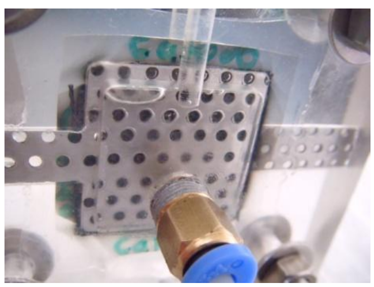
To validate the installation, the prototype was placed in a test table where it was electric and hydraulic connected to verify that there were no liquid or gas leaks and electrical connectors were right with power distributors when the prototype is integrated into a system. The photograph 9 shows the prototype mounted in the table test with its connections.



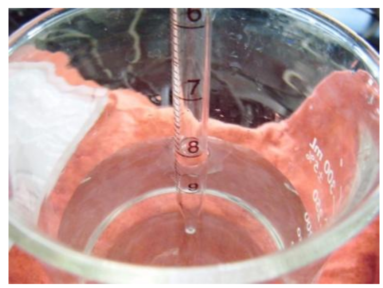
Photograph 9. PEM electrolyzer prototype connected in the table test.

2.11. Operation Qualification

In order to validate the operation of the prototype, characterization test were performed using the technique of potentiometry, for which it was necessary to have a table test consisting of a galvanostat potentiometer, a mounting base, two graduated cylinders storage gases, a container of deionized water, two water low pressure pumps and a stopwatch. The characterization test consisted of running operation of the prototype, which water was introduced into PEM electrolyzer through the anodic and cathodic ports, circulating an electric current to different levels of intensity in each test taking care to not exceed 5 volt, since this voltage is initiated a degradation process in the membrane. Galvanostat potentiometer is able to determine the voltage required to circulate the current intensity that has been setting. First phase consisted of visually checking the gases generation, then the voltage vs. current curves were obtained, the same to determine the efficiency of a PEM electrolyzer. The second phase consisted of measuring the amount of hydrogen that was extracted using a stopwatch and measuring the volume generated per unit time. The evolution of hydrogen and measuring of the hydrogen generated are shown in the photographs 10 and 11 respectively.



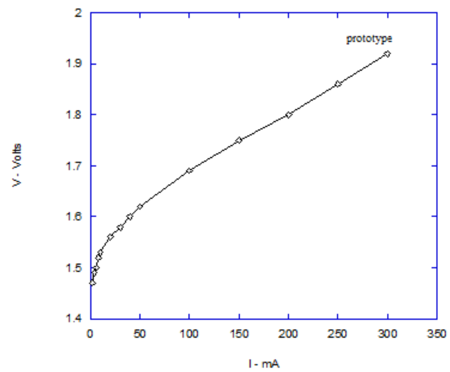
Photograph 10. Evolution of hydrogen



Photograph 11. Hydrogen measurement

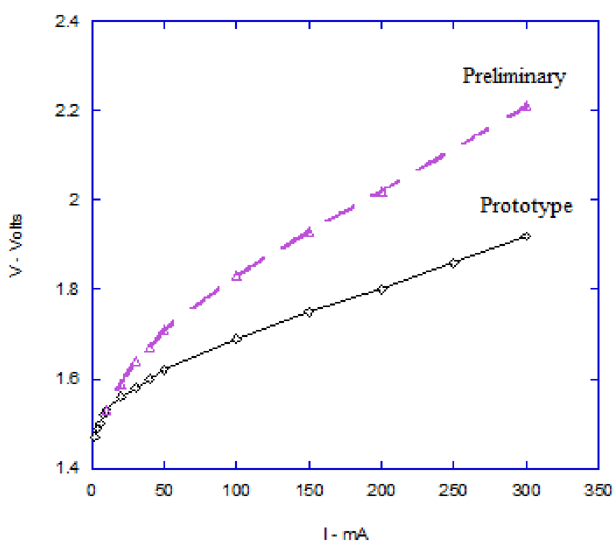
3. Results and discussion

Methodology raising specifications at each stage was established to design and fabricate this PEM electrolyzer prototype; prototype qualities were evaluated by tests that guarantee the optimal itself operation. PEM electrolyzer built with this methodology shows favorable results compared with other prototypes built without a methodology that involves aspects of manufacturing and assembly processes that finally contribute positively to the PEM electrolyzer prototype achievement. The results obtained by characterization of PEM electrolyzer prototype by potentiometry tests showed a good efficiency of it exhibit a low resistance ohmic getting a current of 300mA with only 1.92V and obtained a productivity of hydrogen in the range of 2.137$mlH_2.min^{-1}$. The amount of hydrogen produced per unit time resulted higher that other prototypes characterized by the same tests. Graphic 1 shows performance curve obtained by potentiometry in which there is a current of 300mA below 2V.



Graphic 1. Performance curve of PEM electrolyzer prototype

Graphic 2 shows a comparative of the results obtained between the PEM electrolyzer prototype and other preliminary prototype built without application of the methodology presented in this work. The results of the characterization tests show differences between both performance curves; the best performance curve is marked as “prototype”, with 300mA below 2V while the other curve shows the performance of the preliminary prototype with about half in current with the same voltage 150mA below 2V reaching the 300mA above 2V. The data presented are important because the amount of hydrogen produced per unit time is proportional to the current flowing through the active area of the PEM electrolyzer prototype; it is convenient to work with the most current but without reaching the 5V because the membrane suffers severe irreversible degradation with this voltage.



Graphic 2. Comparison of performance between PEM electrolyzer prototype and a preliminary prototype

4. Conclusions

To achieve greater current flowing through the active area of the PEM electrolyzer prototype with the same voltage results in a reduction of the ohmic resistance due to proper selection and treatment of manufacturing and assembly processes. Increase the amount of hydrogen generated per unit time using the same amount of energy result in costs reduction of hydrogen generation and becomes a major contribution to development of hydrogen economy. The results presented in this work show the effectiveness of the methodology developed for this research since it involves factors that were not previously covered in development of this kind of prototypes; other design methodologies do not involves stages with processes and tests to validate each of the stages developed during the conception of the prototype.

5. Akcnowledgements

This work has been supported by CONACyT project 130254 and IPN under multidisciplinary project SIP-1338. JLCG thanks the PIFI and CONACyT programs for the financial support (scholarship).

6. References

[1] M en I. Hilda Hernández Muñoz, Dr. Jorge Marcial Islas Samperio, Dr. Fabio Luigi Manzini Poli, M en I. Paloma Macías Guzmán, Nuevas Energías Renovables: Una Alternativa Energética Sustentable para México (Análisis y Propuesta) – Instituto de Investigaciones Legislativas del Senado de la República – 2004.

[2] CITE AS: Boden, T.A., G. Marland, and R.J. Andres. 2011. Global Regional, and National Fossil-Fuel CO2 Emissions. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tenn., U.S.A. doi 10.3334/CDIAC/00001_V2011 http://cdiac.ornl.gov/trends/emis/tre_mex.html .

[3] J. L. G. Fierro, L. Gómez y M. A. Peña, El Hidrógeno: Un Vector energético no Contaminante para Automoción – Instituto de Catálisis y Petroleoquímica. CSIC

[4] Omar Solorza-Feria, Elvira Ríos-Leal, y Héctor M. Poggi-Varaldo, Energías Renovables Biológicas-Hidrógeno-Pilas de Combustible-Primera Edición – Libros de Ciencia y Tecnología N° 1 ISBN 978-968-5441-11-7 – 2008.

[5] Rosa de Guadalupe González Huerta, Ernesto López Chávez, Blanca Velázquez Morales, Hidrógeno: Introducción a la Energía Limpia – Universidad Autónoma de la Ciudad de México – 2009.

[6] International Society for Pharmaceutical Engineering – http://www.ispe.org/about-ispe

[7] Nigel Cross, Métodos de Diseño: Estrategias para el Diseño de Productos – Limusa Wiley - 2010