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Hydrogen synthesis from seawater by means of solar energy

Síntesis de hidrógeno a partir de agua de mar mediante energía solar

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Abstract

In the electrolysis of seawater as a source of hydrogen, two options exist for the performance of the electrolysis process. The first option is the total desalination of the sea water and then add alkalis for the process of electrolysis to produce hydrogen in the cathode and oxygen in the anode. The disadvantages of this approach are the high cost of desalination and the water treatment to make it alkaline. The main advantage is the ability to use developed technology for the direct electrolysis of fresh water. The second option is to design an electrolyze system capable of utilizing sea water for direct electrolysis at a low power density and electrolyze only a small portion of the water in contact with the electrodes. The advantage of this method is the lower capital required for the system and natural elimination of the waste brine which is only slightly enriched with salts. Also using this technic is possible to produce important amounts of chlorine as a sub-product and also magnesium and sodium as hydroxides that have many uses in the chemical industry. In this research we produced hydrogen via electrolysis from simply natural resources, seawater and solar energy. In order to carry out this experiment we used water from Bahia of Kino Sonora, a place no too far from the University of Sonora, only 100 kilometers away, and a 100-W solar panel that generate DC electricity using directly sunlight that is an abundant resource in the coasts of Sonora. In this work we have been able to produce about 2 liters of hydrogen per hour and nearly 1.2 liters of chlorine per hour with a normal direct radiation of 900 W/m^2. This technique could be the solution to the fuels problematic of the ethnicities that inhabit the shores of Sonora and other states of México.

Hydrolysis, Hydrogen, seawater, Solar Energy

Resumen

En la electrólisis del agua de mar como fuente de hidrógeno, existen dos opciones para la realización del proceso de electrólisis. La primera opción es la desalinización total del agua de mar y luego añadir álcalis para el proceso de electrólisis para producir hidrógeno en el cátodo y oxígeno en el ánodo. Las desventajas de este enfoque son el alto coste de la desalinización y el tratamiento del agua para hacerla alcalina. La principal ventaja es la posibilidad de utilizar la tecnología desarrollada para la electrólisis directa del agua dulce. La segunda opción consiste en diseñar un sistema de electrólisis capaz de utilizar el agua de mar para la electrólisis directa con una baja densidad de potencia y electrolizar sólo una pequeña parte del agua en contacto con los electrodos. La ventaja de este método es el menor capital requerido para el sistema y la eliminación natural de la salmuera residual que sólo está ligeramente enriquecida con sales. Además, utilizando esta técnica es posible producir cantidades importantes de cloro como subproducto y también magnesio y sodio como hidróxidos que tienen muchos usos en la industria química. En esta investigación produjimos hidrógeno por electrólisis a partir de recursos simplemente naturales, agua de mar y energía solar. Para llevar a cabo este experimento utilizamos agua de la Bahía de Kino Sonora, un lugar no muy lejano a la Universidad de Sonora, a sólo 100 kilómetros de distancia, y un panel solar de 100 W que genera electricidad en corriente continúa utilizando directamente la luz solar que es un recurso abundante en las costas de Sonora. En este trabajo hemos sido capaces de producir unos 2 litros de hidrógeno por hora y casi 1,2 litros de cloro por hora con una radiación directa normal de 900 W/m^2. Esta técnica podría ser la solución a la problemática de los combustibles de las etnias que habitan las costas de Sonora y otros estados de México.

Hidrólisis, hidrógeno, agua de mar, energía solar

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Introduction

Global warming and fuel shortages are two dilemmas facing humanity as the world's population increases. The exploitation and consumption of fossil fuels such as coal, oil and natural gas are the main factors that aggravate air, water and soil pollution. To reduce said pollution and reduce the greenhouse effect, it is necessary to promote and increase the use of clean energies, such as wind, geothermal, maritime and solar, since these do not generate polluting substances to the environment nor do they damage the layer of ozone which protects us from ultraviolet rays from the Sun. The Earth is mostly covered by salty water from the oceans, it covers approximately three quarters of the planet's surface, it is for this reason that we seek to use this natural resource almost inexhaustible to generate fuels such as hydrogen. A water molecule contains one oxygen atom and two hydrogen atoms, which can be separated from oxygen by electrolysis using electrical energy. In this work it is proposed to use seawater from Bahía de Kino and solar energy to extract hydrogen and then use it as fuel or as reactant gas in various industrial processes. For this process, the use of solar cells to generate the electrical energy necessary to carry out electrolysis is also proposed, since solar energy is also an abundant natural resource in the region.

Problem statement and theoretical foundations

In this research, the aim is to produce hydrogen by the seawater electrolysis method, which mainly consists of the electrolysis of a solution of sodium chloride (NaCl). The electrodes, the cathode and the anode, are placed in the solution and generate the movement of electrons. Hydrogen forms at the cathode while chlorine forms at the anode. To improve the production of hydrogen, the composition of the water is usually varied by means of electrolysis, generally with the addition of salts, to increase the reaction rate; in this case, seawater is used, which naturally contains sodium chloride, so the process is more efficient. [1]

As is well known, 96.5% of the total water in the world is salt water and only 3% is fresh water. Dissolved salts in the ocean constitute almost 50 billion tons and are made up of 10 main elements to be found in greater proportions: chlorine, sodium, magnesium, sulfur, calcium, potassium, bromine, strontium, boron and fluorine. Chlorine and sodium are the main elements dissolved in seawater and are found as sodium chloride, which is known as common salt, which represents 80% of the salts in the solution. [2]

Electrolysis of sea water

The electrolysis of seawater consists mainly of the electrolysis of a solution of sodium chloride (NaCl). From a thermodynamic point of view, the species with the lowest reduction potential will be oxidized at the anode and the species with the highest potential will be reduced at the cathode. Given this particular case where the electrolysis of seawater occurs by means of graphite electrodes, it can be assumed that the polarization by mass transfer of the participating ion molecules Na^+, Cl^- and H_2O is negligible. Under these conditions it can be assumed that only charge transfer polarization influences the oxidation of the chlorine ion and the reduction of water. Suppose that the concentration of ions and cations Cl^-, OH^-, Na^+ and H^+ is enough to allow them to participate in an electrochemical reaction. [3] The sodium chloride present in seawater is dissolved, so it dissociates into Cl^- ions and Na^+ cations, Figure 1a. If a potential difference is applied to the solution, the positive ions dissolved in the electrolyte approach the negative pole and the negative ones approach the positive pole, Figure 1b. For every two Cl^- ions found at the anode, two electrons are released and a molecule of chlorine gas (Cl_2) is formed, Figure 1c. Electrons are drawn to the cathode by the voltage source and decompose a water molecule into hydrogen gas (H_2) and hydroxyl OH-, Figure 1d. Finally, the hydroxyl ion combines with the Na^+ ion to form sodium hydroxide (NaOH).

The overall reaction for the electrolysis of the brine is therefore:

$$2\mathrm{NaCl}_{(aq)} + 2\mathrm{H_2O} \rightarrow \mathrm{Cl}_{2(g)} + \mathrm{H}_{2(g)} + 2\mathrm{N_aOH}_{(aq)} \quad (1)$$

Apparently at the anode the water molecules should be oxidized, however, experience shows that the chlorine ion oxidizes instead of it. This is due to polarization phenomena that hinder the formation of oxygen. [4]

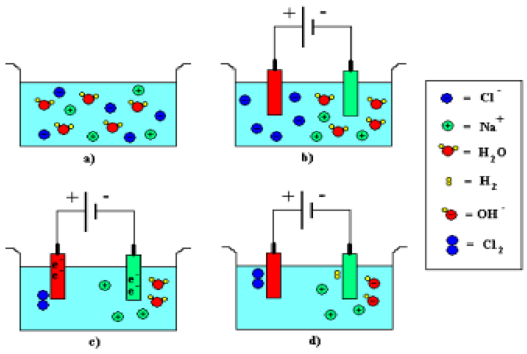

Figure 1 Schematic representation of the electrolysis of a sodium chloride solution

Table 1 shows the enthalpy, entropy and Gibbs free energy formation values for each compound present in the reaction.

Compound	ΔH° (Kcal/mol)	ΔG° (Kcal/mol)	ΔS° (Cal/mol °C)
H_2O	-68,320	-56,689	16,716
NaCl	-97,302	-93,939	27.6
Cl_2	0	0	53,286
H_2	0	0	34,602
NaOH	-112,236	-100,184	11.9

Table 1 Standard thermochemical values of the compounds involved in electrolysis

Oxidation Potential

The oxidation potential is the electrical potential required to transfer electrons from an oxidant to a reducing agent, expressed in volts. The following is the calculation of the oxidation potential of our main reaction from the half reactions presented in this, together with their standard potentials at 25 °C.

$$2\ Cl^{-}{}_{(aq)} \rightarrow Cl_{2(g)} + 2e^{-}$$

E°= -1.36V (33)

$$2H_2O_{(l)} + 2e^{-} \rightarrow H_{2(g)} + 2OH^{-}_{(aq)}$$

E°= -0.83V

$$Na^{+} + 1e^{-} \rightarrow Na_{(s)}$$

E°= -2.71V (35)

Global reaction:

$$2N_aCl_{(aq)} + 2H_2O \rightarrow Cl_{2(g)} + H_{2(g)} + 2N_aOH_{(aq)}$$

E°= -4.9V (36)

Methodology to be developed

Once the production of hydrogen at the cathode and chlorine at the anode was demonstrated in the laboratory under controlled conditions, the system was scaled up. A system to produce hydrogen was designed where two graphite electrodes of 12 cm each were used, connected to a photovoltaic panel of 100 Watts, the electrodes contained in two 100 ml test tubes each one filled with salt water with 17 cm were placed separation and inverted submerged into seawater in 87,520 cm^3 clear acrylic container. The purpose of using inverted test tubes was to quantify the gases generated. In figure 2 the experimental arrangement can be observed.

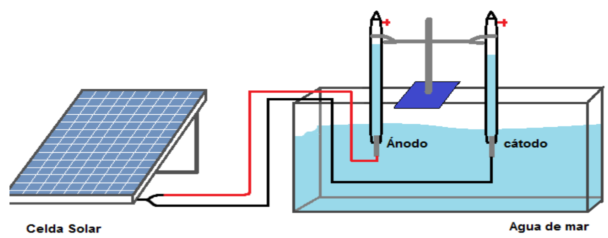

Figure 2 Schematic of the electrolysis process with seawater using a silicon solar cell

The seawater was obtained 250 meters from Av. Mar de Cortés, in Bahía de Kino, Sonora (see Figures 5a) at the discharge ramp (28.867056, -112.030846) Figure 3b, and was stored in a Rotoplas water tank of 250 L (Figure 3c). The seawater was transferred to the University of Sonora where analyzes continued. PH measurements were made in the water with the JENCO 1671 instrument, designed to measure the pH, conductivity and oxidation-reduction potential of a liquid.

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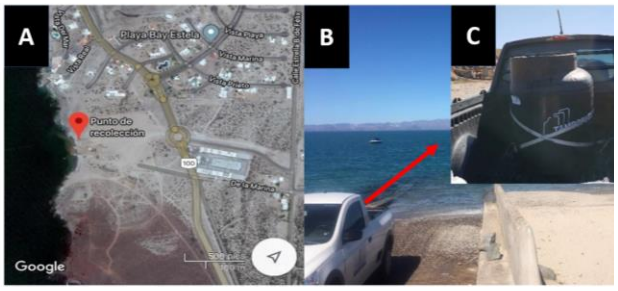

Figure 3 Seawater collection A) Satellite image of the seawater collection point in Bahía de Kino, Sonora. B) Seawater collection point, on the discharge ramp 250 meters from the extension of Av. Mar de Cortés, in Bahía de Kino, Sonora. C) Rotoplas of 250 liters capacity, where the collected seawater was stored

The transparent acrylic container was filled with 40 liters of seawater and the arrangement was assembled by connecting the electrodes to the solar cell, adding a toggle switch (see figure 3b) to be able to interrupt the passage of electrical current, this to be able to mount the pipettes and insert the electrodes into them, without the process being carried out, to obtain more specific measurements. The electrodes were fitted to an electrical eye-type copper terminal, soldered using 50-50 tin lead, to a 14 AWG copper wire (2 meters), applying a liquid insulating tape to prevent water from coming into contact with them. as seen in Figure 3c. The complete hydrogen generating experimental system is shown in Figure 3a. The PV panel was secured to a metal rod for better stability of the cell Figure 3a and was placed on a metal base (see Figure 3).

Figure 3 Experimental arrangement A) Experimental arrangement of the seawater electrolysis process in operation using a PV panel. B) On / Off toggle switch connected between the PV panel and the graphite electrodes. C) Graphite electrodes positioned inside the pipettes in the acrylic with seawater in the electrolysis process

Results and Discussions

The first measurement was performed under normal conditions on March 25, a sunny day where an irradiance of 949 W/m² was recorded at 12:50 p.m. Hermosillo time, is presented in table 1.

When using the PV panel, the amperage of the system increases to 5.1 which causes the production time of 100 ml of hydrogen to decrease, which influences the electrical efficiency, this increased by 37%, having an efficiency of the photovoltaic module of 14.78%.

The second measurement on March 26 was made using a solar controller. It is observed that when using the controller, the efficiency of the cell decreases, in the same way does the maximum power of the cell, from a value of 92.96 to 69.56 watts, the electrical efficiency as well as the electrical production time decrease by 65%. It is observed that the efficiency of the module also decreases from 14 to 11%. Which tells us that using the solar controller is not favorable for the process.

The next measurement was carried out on March 27, which was a totally cloudy day, with an average irradiance of 627 W/m² at 12:10 p.m. This caused the decrease in the measured values, this due to the amperage that the cell presents, which was 3.1 amps, it is not similar to that of the other days as it has a lower irradiance, and the temperature of the cell is also lower, the production time of 100 ml increases to 8 minutes, and the electrical efficiency decreases in a small amount (0.09%). Despite the conditions, a cell efficiency of 14% is observed.

A last measurement was made on July 4 at 1:30 pm with an irradiance of 980 W/m^2 to compare the efficiency of the process during the summer season where high values of irradiance and temperature were registered, as can be seen in the Table 1a and 1b.

In this measurement the highest values are observed compared to the previous measurements, having an amperage of 5.32 A, an average production of 1.75 lt of H_2 per hour, which shows an increase of 66% compared to the production values of the day March 7, under controlled conditions using the 13.8-volt, 4.87-amp power supply. And making the comparison of March 25, which the environmental conditions were similar to those of July 4, a difference in efficiency of 11% is observed, the maximum power of the cell also increases from the value of 92 to 95 watts, however, the efficiency value of the solar panel remains at 14%.

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I_{sc} *	V_{oc} *1	I_{max}*2	V_{max} *3	P_{max} *4	FF*5	PV PE*6	Date*7
5.1	19.9	5.08	18.3	92.964	0.915	14.782	03/25/19
5.1	14.7	5.08	13.7	69.596	0.928	11.066	03/26/19
3.1	21.2	3	19.3	57.9	0.881	13.935	03/27/19
5.32	19.97	5.32	17.9	95.228	0.896	14.662	07/04/19

*Short circuit current (I_{sc} in ampere), *1 open circuit voltage (V_{oc} in voltage), *2 maximum current (I_{max} in ampere), *3 maximum voltage (V_{max} in voltage), *4 maximum power point (P_{max} in Watts), *5 Cell Fill Factor (FF), *6 Photovoltaic panel efficiency (PV PE), *7 Date (MM/DD/YY)).

Table 1a PV panel parameters on different days

Time *	H_2 *2	Moles H_2 *3	H_2 *4	EFF *5	Date *6
4.47	1.342	0.0531	0.107	73	03/25/19
7.41	0.809	0.032	0.064	44	03/26/19
8	0.75	0.030	0.061	67	03/27/19
4.13	1.452	0.056	0.113	76	07/04/19

* Time in minutes, *2 H_2 produced in liter/hour, *3moles of H_2 produced per hour, *4 H_2 produced grams/hour, *5 EFF efficiency, *6 Date (MM/DD/YY))

Table 1b Hydrogen production on different days

pH measurements were also made in seawater after having been subjected to the electrolysis process in order to know the effect of the electrolysis process in a closed system. The pH of seawater was observed to increase. This means that seawater becomes more alkaline, and therefore the concentration of hydroxyl ions (OH-) also increases. This is due to the secondary reaction that takes place during electrolysis between hydroxyl ions and sodium ions. The increase in pH can be avoided if the production system is open and very large like the ocean, which would maintain a constant pH in the vicinity of the system.

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Conclusions

On a small scale, this experiment turned out to be an excellent alternative for the production of hydrogen, since using a 100 Watt solar panel it is possible to generate 1.75 liters of hydrogen in an hour with a voltage of 14.4 V; Taking into account that a liter of hydrogen contains the energy of 3.5 liters of diesel, this option would save us a large amount of fossil fuels and avoid polluting the atmosphere since burning hydrogen only produces water vapor. On the other hand, by increasing the number of photovoltaic panels, the amounts of hydrogen produced would be much greater without the need to pollute the environment and investing only in an initial amount for the acquisition of the equipment, since it does not need maintenance and has a time of long life, approximately 20 years. This project opens the great sustainable solution for big problems induced by hydrocarbon pollution, and Sonora State in Mexico could be a potency taking advantage of the sun like your principal natural resources, mineral graphite and seawater.

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