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Renewable Electrolysis using Graphene electrodes for Solar water splitting

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Abstract: Producing low-cost water electrolysis processes has been considered a sustainable approach in the production of hydrogen from inputs of renewable energy, this work shows a potential for renewable to hydrogen conversion using Solar Photovoltaics (PV) and graphene electrodes, the functionality of the system is discussed, this work also reports the behavior of graphene as an independent electrolyzer unit as it eliminates the requirement of membrane for electrolysis, Graphene itself is a flat monolayer of carbon atoms compressed into a two-dimensional honeycomb lattice, and is the basic building block for graphite. Graphene has been a key contributor to environmentally benign hydrogen generation performance. The power production capacity of 5 KW panel is described initially and the literature for Electrolysis and Graphene is surveyed, and a potential solution of bringing this architecture together has been demonstrated.

Keywords: graphene; solar PV; electrolysis; renewable energy; power.

1. Introduction

Hydrogen as a fuel and its chemical means of production using solar energy can fill in as the energy-dense type of decarbonized transportation fuel and decrease the changeability of solar powered electricity generation by filling in as an energy storage system. However, to have critical effect, the innovative arrangements fit for delivering chemicals from sun based vitality should essentially be focused inside the financial substances of the commercial center¹. Advancing water electrolysis has been considered as a standout among the most proficient and solid ways to deal with delivering hydrogen from renewable sources, for example, solar energy, wind and hydropower, for network scale vitality stockpiling on the grounds that the electrolysis of water at room temperature emerges as a adaptable innovation, for which the main required sources of info are water and energy² (as power). In this way, electrochemical water splitting is drawing in broad consideration. However, the general utilization of water electrolysis as of now faces various challenges³.

Thorough financial focused investigations, connected after confirmation of-idea innovative work, can give basic direction on such venture's further asset allotment, needs and direction. Our examination recommends that accomplishing solar oriented to hydrogen framework efficiencies are more prominent than other systems at present, as in most cases it is not adequate to accomplish hydrogen generation costs focused with fossil-fuel determined hydrogen. Composite materials, work and other adjust of frameworks costs, variability of the dynamic material; add up to hydrogen generation cost values in overabundance of current hydrogen and vitality costs⁴. Drastically new materials and framework outlines that accomplish completely introduced costs like straightforward material establishments, for example, artificial grass and efficiencies close thermodynamic cutoff points are required to accomplish the similarly significant cost decreases required for

solar based hydrogen to contend with current era innovations⁵; comparative if not bigger techno-monetary difficulties hold for CO₂ lessening advancements⁶.

2. Solar Photovoltaics System

Photovoltaic power generation is a method of producing electricity using solar cells. A solar cells convert solar radiation from the sun directly into electrical energy⁷. A solar cell is essentially a semiconductor device fabricated in a manner which generates a voltage when solar radiation falls on it⁸. In semiconductors, electrons in the outer valence shell of atoms can be dislodged to move freely in the materials if extra energy is supplied like the photon energy⁹ (in solar radiation).

Table 1: Different types of PV modules with relative properties

Type of PV module	Advantages	Disadvantages	
Monocrystalline	-Highest efficiency (15-20%)	- Expensive	
Silicon	-Longest life (about 25 years)	- Very sensible to shadow	
	-Better in low light conditions		
Polycrystalline	-Cheaper	-Lower heat tolerance	
Silicon	-Simpler to produce	-Efficiency is 13 to 16%	
		-Shorter life	
Thin film	-Cheapest	-Lowest efficiency (4 times	
	-Simpler mass production	lower power than Mono)	
	-Homogenous appearance	-Shortest life	
	-Flexible	-Low space efficiency	
	-More resistant to heat and shading		

The Energy flux received from the sun before entering into the atmosphere of earth is a fixed quantity and has been determined by experimental measurements, thus the standard value of the solar constant is $I_{sc} = 1367 \text{ W/m}^2$. Solar radiation reaching the earth is equivalent to blackbody radiation for a temperature of 5779 K. The spectral distribution of extraterrestrial radiation is composed of three spectral regions, ultraviolet 6,4% ($\lambda < 0.38 \mu m$), visible 48% (0.38 $\mu m < \lambda < 0.78 \mu m$) and infrared 45,6% ($\lambda > 0.78 \mu m$) of total radiation. But the distance from the sun to the earth varies due to the elliptical motion of the earth, so the extraterrestrial flux also varies, which can be calculated by the equation:

$$I_n = I_{sc}(1 + 0.033\cos\left(\frac{360n}{365}\right)) \tag{1}$$

Where "n" is the day of the year counted from the first day of January in a year, for utilization of solar energy, a study is required to be carried out of radiations received on the earth's surface. Indeed solar radiation passes through the atmosphere and is subjected to scattering and atmospheric absorption. Some definitions are required to study terrestrial solar radiation:

Some empirical equations for estimating the availability of solar radiation exist, for example for determining the amount of sunshine at a given location:

$$\frac{H_g}{H_o} = a + b(\frac{D_L}{D_{max}}) \tag{2}$$

where H_g = monthly average of daily global radiation on a horizontal surface at a given location, in MJ/m²/day, D_L = monthly average measured solar day length, in hours D_{max} = monthly average of the longest day-length, in hours, a and b = constants for the location, H_o = monthly average of daily extraterrestrial radiation that would fall on a horizontal surface at the given location, in MJ/m²/day.

Further.

$$H_o = \frac{24}{\pi} I_{sc} (1 + 0.033 \cos\left(\frac{360n}{365}\right)) (\omega_s \sin\phi \sin\delta + \cos\phi \cos\delta \sin\omega_s)$$
 (3)

Where I_{sc} = solar constant per hour = 1367 W/m² in SI units, ω_s = sunset hour angle

The daily diffuse to global radiation ratio can be correlated with the daily global to extraterrestrial radiation ratio. It was expressed by a cubic equation:

$$\frac{H_d}{H_g} = 1.390 - 4.027 \frac{H_g}{H_o} + 5.531 \left(\frac{H_g}{H_o}\right)^2 - 3.108 \left(\frac{H_g}{H_o}\right)^3 \tag{4}$$

Where H_d = monthly average for daily diffuse radiation on a horizontal surface, in kJ/m²/day.

The equipment used for the experiments is the Solar Photovoltaic Training Kit of INSIGHT SOLAR. It's composed of two adjustable photovoltaic modules with regulated lamps and a main controller to connect the terminals and take the readings. So the sunlight will be simulated by halogen lamps.





Figure 1: The Control Panel (left) and the PV modules I and II (right) used for this investigation

The characteristics of the modules are: polycrystalline, $P_{mpp} = 40$ W, $V_{oc} = 21,90$ V, $I_{sc} = 2,45$ A, $V_{mpp} = 17,40$ V, $I_{mpp} = 2,30$ A, which represents voltage at open circuit (OC) and current at short circuit (SC) along with V-I at maximum power point (MPP). Power specification is measured at standard test condition insolation: 1000 W/m^2 , 25°C (Cell temperature).

The Power curves for the modules with varying light intensity have been discussed further.

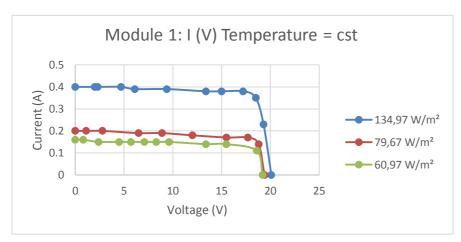


Figure 2: Radiation has a big influence on the short circuit current, the current increases while the radiation increases. However its influence on the open circuit voltage is very low but the effect is the same, the voltage increases while the radiation increases.

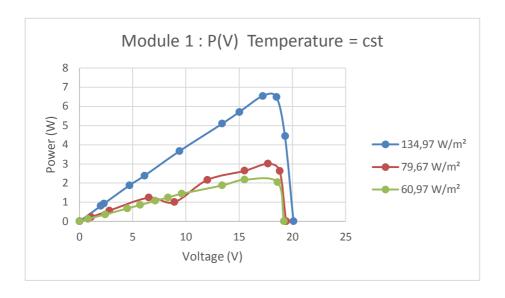


Figure 3: Observing increase in power when the radiation grows, confirming if voltage and current increases then the power will increase.

The results of experiments confirm the theory of module characteristic. In order to obtain a maximum power from a PV module the radiation has to be maximal and the temperature of the module should be minimal as possible. Panel tilts were not interfered and was kept parallel to the ground surface as show in figure 1.

A good way to evaluate the efficiency of a PV module is to calculate its Fill Factor (FF) with the followed expression:

$$FF = \frac{Imp*Vmp}{Isc*Voc} \tag{5}$$

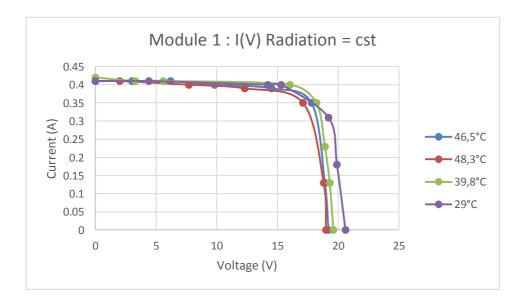


Figure 4: Temperature has an influence on the open circuit voltage, it decreases while the temperature increases, whereas the short circuit current is very little influenced.

Set	Imp (A)	Vmp (V)	Isc (A)	Voc (V)	FF
Set 1	0,38	17,2	0,4	20,1	0,813
Set 2	0,17	18	0,2	19,4	0,789
Set 3	0,13	16,5	0,16	19,2	0,698
Set 4	0,37	17	0,41	19,2	0,799
Set 5	0,37	16,5	0,41	19	0,784
Set 6	0,38	17,5	0,42	19,6	0,808
Set 7	0,36	17	0,41	20,6	0,725

Table 2: FF (Fill Factor) for different set of experiments

For PV systems the storage component usually includes batteries for storing and discharging electrical energy as needed¹⁰. However, every time a battery is charged or discharged, energy in some form is lost from the system. Parameters by which batteries vary are: depth of discharge, life, rate of charge and types¹¹. Lead acid batteries are the most common type of batteries used. Charge controllers are involved in the flow of electricity from the battery, loads and the array¹². Appropriate charge control algorithms and charging currents must be matched with the battery. Inverters and converters are integrated with the system to account for direct current (DC) to alternate current (AC) conversion, and energy losses are accounted here as well¹³.

3. The Electrolysis of Water

The laws of electrolysis were first reported in 1833-1834 by the Yorkshire born English scientist Michael Faraday. He established the quantitative relationship between the amount of electricity q passing through the electrode/electrolyte interface¹⁴ and the mass m of substances involved in the electrolysis (redox) process:

$$m \frac{1}{4} k_e q;$$
 (6.1)

Here $k_e = M/nF$ is the electrochemical equivalent in kg/C h kg/(Amps s); M in kg/mole is the molar mass of substance produced at the interface; n is the number of electrons involved in the electrochemical reaction; F = 96,485.3 C/mole is the Faraday's constant

Regarding water electrolysis, when the steady (stationary) electric current "I" and time period "t" had been given, the theoretical (maximum) amount of hydrogen (or oxygen) produced can be calculated using:

$$V_{\text{theor.}} = \frac{k_{\text{e}} I t}{r} \tag{6.2}$$

Where V_{theor} is the theoretical volume of gas evolved in m^3 , I in Ampere is the total current, t in seconds is time; r in kg/m^3 is the gas density

Throughout the most recent decades, new uses of hydrogen as energy carrier, for instance, in the capacity of vitality acquired from renewable energy sources¹⁵, were found. Water electrolysis can be utilized for the direction of electrical lattices. The coupling of extensive scale high-temperature water Electrolyzers with atomic power plants (utilizing electrical power and waste heat of high-temperature helium reactor) is viewed as one of the key advancements for hydrogen creation inside the system of hydrogen-nuclear vitality¹⁶.

Also, the generation of hydrogen by electrolysis is appropriate for frameworks in view of renewable vitality (solar based, wind, tides, and so on.) that are not coordinated into the system¹⁷. In such cases, hydrogen can gather the energy to deliver power and heat for the eras when the renewable source does not create power³⁹. Electrolyzers are likewise utilized as a part of applications, for example, the analytical instruments (hardware for gas chromatographs), remedy frameworks for water-chemistry⁴⁰ modes of atomic reactors¹⁸, high-immaculateness metals and composites metallurgy, the generation of high-virtue materials for the electronics business and hydrogen welding¹⁹.

3.1. Thermodynamics of Water Splitting

In standard conditions (298 K, 1 bar), the water split-ting reaction is as follows:

$$H_2O_{(l)} \rightarrow H_{2(g)} + \frac{1}{2}O_{2(g)}$$
 (6.3)

Assuming that the chemical reaction is performed along a reversible path under isothermal conditions, then:

$$\Delta G(T) = \Delta H(T) - T\Delta S(T) \tag{6.4}$$

Where; $\Delta H(T)$ in J/mol is the enthalpy change associated with reaction (a); $\Delta H(T)$ is positive up to 2250 C (the water splitting reaction is endothermic); $\Delta H(T)$ is the total amount of energy that must be supplied to the electrolysis cell to dissociate water into H_2 and O_2 . $\Delta S(T)$ in J/mol/K is the entropy change; $\Delta S(T)$ is positive because 1 mole of water dissociates into 1.5 mol of gases. T in K is the absolute temperature. $T\Delta S(T)$ is positive. $\Delta G(T)$ in J/mol is the Gibbs free energy change; $\Delta G(T)$ is positive (reaction (a) is a nonspontaneous process) up to 2250°C because for such defined temperature range, the enthalpy term is significant over the change in entropy²⁰. $\Delta G(T)$ represents the amount of electricity that must be supplied to the electrolysis cell in addition to the $T\Delta S(T)$ amount of heat to dissociate water²¹. In standard conditions (25°C), $\Delta G^0 = 237.23$ kJ/mol (2.94 kWh/Nm³ H_2), $\Delta H^0 = 285.83$ kJ/mol (3.54 kWh/Nm³ H_2), $\Delta S^0 = 163.09$ J/mol/K.

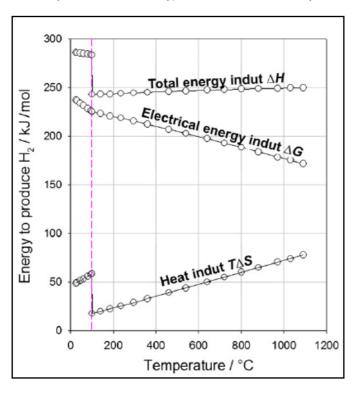


Figure 5: Dependence on Temperature of main thermodynamic parameters for water electrolysis.

3.2. Water Splitting Kinetics & Efficiencies

At equilibrium conditions, water splitting reaction takes place at slow rates, a situation of any practical interest. To split water into hydrogen and oxygen, the cell voltage U applied to the electrolysis cell should be significantly greater than the thermodynamic voltage in order to let a vast current density flow across the cell and minimize capital expenses²². Main resistances to current flow are (1) charge transfer over voltages at both anode/electrolyte (h_a) and cathode/electrolyte (h_c) interfaces and (2) the resistivity of the electrolyte²³.

During water electrolysis, the anodic over-voltage happens mainly for the charge transfer associated to the oxygen evolution reaction (OER) and the cathodic over-voltage is due to the transfer of charges²⁴ related to

the hydrogen evolution reaction (HER). Both terms are a function of operating current density which is in line with the Butlere Volmer theory of charge transfer. At a current density j, the cell voltage U(j) is given by:

$$U(j) = E + \eta_{c}(j) + \eta_{a}(j) + JR_{el}(j)$$
(6.5)

Another such important electrolysis cell characteristic is the current (faradic) efficiency which is defined as the ratio of the volume of gas produced over a period of time²⁵ interval to the theoretical volume that should be produced during that same time:

$$\eta_{\rm F} = rac{V_{
m actual}}{V_{
m theor.}}$$
(6.6)

Usually, efficiency is 1 but significantly lower values are sometimes obtained. There are several reasons for such deviations to occur; firstly the energy consumption used for the electrolysis of impurities which are present in the electrolyte²⁶; secondly, the spontaneous recombination of reaction end products i.e. hydrogen and oxygen which are not appropriately separated during operation²⁷. Several studies suggest that the calculation of the overall efficiency of an electrolysis cell should take into account the efficiency of the electrical source²⁸. Generally, the efficiency of thermal power stations is less than 50%, and therefore, the overall efficiency of the hydrogen production process is approximately 40%, for to incorporate graphene electrodes integrated with Solar PV changes the overall chemistry²⁹.

4. Graphene and Renewable Electrolysis

Graphene comprises of a flat monolayer of carbon molecules firmly stuffed into a two-dimensional (2D) honeycomb cross section, also, is a fundamental building block for graphite-based materials of all other dimensionalities³⁰. The structure can be wrapped up into 0D fullerenes, moved into 1D nanotubes or stacked to form 3D graphite³¹. Theoretically, graphene (or '2D graphite') has been studied for seventy years, and is broadly utilized for depicting properties of different carbon-based materials.

Known as an important part of 3D materials, graphene was assumed to not have existed in the free-state, being depicted as a "academic" materials what's more, was accepted to be unstable as for the arrangement of bended structures³², for example, fullerenes, soot and nanotubes. All of a sudden, the vintage display transformed into reality, when stable graphene graphene was startlingly discovered fourteen years ago and particularly when the subsequent experiments confirmed that its charge transporters were in fact massless Dirac fermions³³. Thus, the graphene utilization era has begun.

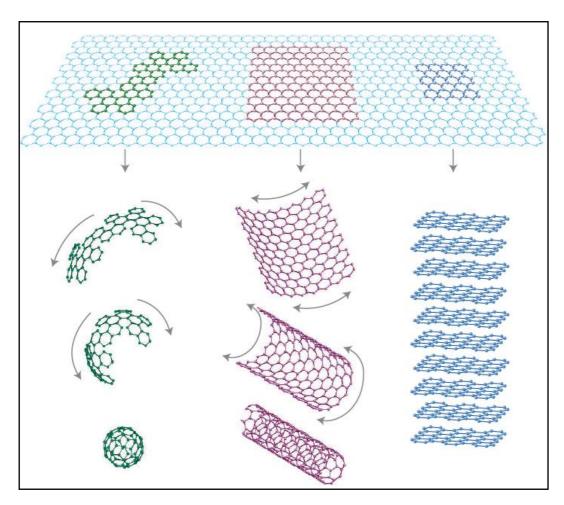


Figure 6: In all the graphitic forms, Graphene can be wrapped into 0D buckeyballs, rolled into 1D nanotubes, or stacked into 3D graphite³¹ (Permission given)

There has additionally been a little number of endeavors to develop graphene. The same approach as for the most part utilized for the development of carbon nanotubes so far just delivered graphite films thicker than ≈ 100 layers³⁴. Then again, single-and few-layer graphene have been developed epitaxially by chemical vapor³⁶ deposition of hydrocarbons on substrates of metals³⁷ and by heat treatment of SiC (Silicon Carbide).

Without quality graphene wafers, most test gatherings are at present utilizing tests got by micromechanical cleavage of mass graphite, a similar strategy that permitted the detachment of graphene surprisingly 35 . After fine-tuning, the strategy presently gives top notch graphene crystallites up to $100 \, \mu m^{31}$ in estimate, which is sufficient for most research purposes 38 . And the same mechanism was utilized to make the graphene discs that were used in the experiments with Solar PV.

4.1. Renewable Electrolysis using Graphene as electrodes

The following setup has been made for the experimentation and it was found that when graphene electrodes were in contact, water splitting was achieved.

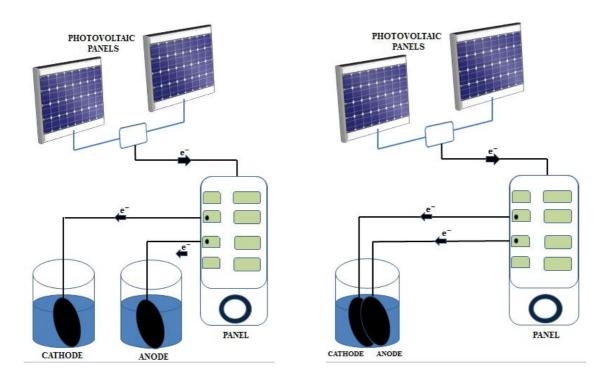


Figure 7: The setup on the left was initially tested but had no response, the setup on the right reports electrolysis when the graphene discs were in contact, thereby eliminates membrane requirement

The general features of Graphene water electrolysis cells are pictured in Figure 7. Two electrodes are pressed against each other thus forming a so-called membrane electrode assembly (MEA). The MEA is immersed in pure (18 MU cm) water³¹. Mobile protons species remain confined inside the graphene membrane.

Oxygen evolution tales place at the anode:

$$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^- (E^\circ = 1.229 V \text{ at } 25 \text{ °C})$$
 (6.7)

The hydrogen ions are transported across the ion-exchange membrane (SPE) and hydrogen is generated at the cathode:

$$H^+ + 2e^- \rightarrow H_2 \ (E^\circ = 0 \ V \ at \ 25 \ ^\circ C \)$$
 (6.8)

The overall reaction is:

$$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^- (E^\circ = 1.229 V \text{ at } 25 \text{ °C})$$



Figure 8: Electrolysis of water using contact anode and cathode of Graphene

In this investigation the feasibility of using graphene for electrolysis has been studied however this study does not report the specific elemental parameters associated with the process, the Solar PV modules were studied at a maximum voltage of 19.9 V and the V-I characteristics are given below in Figure 9.

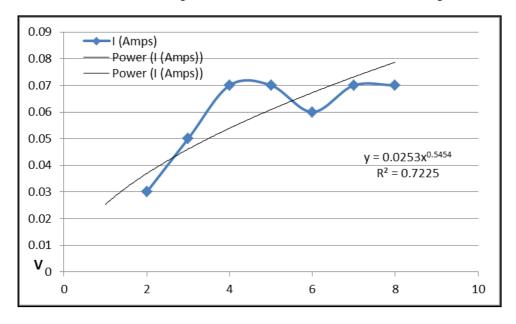


Figure 9: V-I (Voltage Current) characteristics of the Solar PV modules when electrodes are attached

5. Conclusion

Electrolysis of water is a well-established technology that has been used for a significant amount of time for miscellaneous application in the industry (food industry, metallurgy, power plants, etc.). Presently, it is also regarded as a key process that can be used for the production of high-purity hydrogen from water and renewable energy sources. Expected results from this field in the near future will involve water electrolyzers that will occupy an increasingly prominent place for the decentralized production of hydrogen, such as, for hydrogen-fueling stations. Thus, in spite of its long industrial history, this is still the focus of several ambitious R&D programs and worldwide investments. There are different water electrolysis technologies. The difference between them comes from the operating temperature and related parameters. Coupled with graphene, the most significant nanomaterial, a seemingly ultra-thin with unique electronic properties ought to help bring down the cost of renewable hydrogen fuel. Also, that can be a leap forward for hydrogen energy based electric vehicles.

With lower handle costs, it is relied upon to see more hydrogen fuel stations controlled by on location renewable vitality, and the way would likewise be cleared for huge scale energy to-gas frameworks driven by solar based, tidal or even wind energy.

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