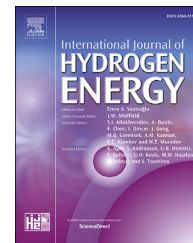




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Thermodynamic analysis and experimental investigation of a unique photoelectrochemical hydrogen production system

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ABSTRACT

In this study, we thermodynamically analyze and experimentally investigate a continuous type hybrid photoelectrochemical H₂ generation reactor. This system enhances solar spectrum use by employing photocatalysis and PV/T. Additionally, by replacing electron donors with electrodes to drive the photocatalysis, the potential of pollutant emissions are minimized. In this study, the present reactor is tested under electrolysis operation during which the present reactor is investigated under three different inlet mass flow rates (0.25, 0.50, and 0.75 g/s) and four different operating temperatures (20, 40, 60, and 80 °C). Some parametric studies are run by varying the environmental temperature between 0 and 40 °C. In addition, the impact of coating the membrane electrode assembly of the reactor with Cu₂O is investigated. The present results show that the highest energy and exergy efficiencies occur at the environmental temperature of 20 °C which is about 60% and 50%, respectively. The Cu₂O coated membrane gives a lot higher current readings, meaning that the coating makes the membrane more conductive and increases H₂ production by permitting ions at a higher rate.

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Introduction

With the continuous worldwide increase in population and standards of living, meeting the ever-increasing global energy demand in an affordable, clean, reliable, and sustainable manner has become one of the most challenging tasks of the twenty first century. As a consequence of their restricted supply and non-homogeneous resource distribution, fossil fuels are not anticipated to keep pace with the growing energy

needs. Along with that, while fossil fuel resources are becoming harder to extract while the easily accessible reserves are exhausted, the fossil fuel prices continue rising. In conjunction with financial matters, GHG (mainly CO₂) emissions as a consequence of fossil fuel consumption, and their influence on global warming, have been causing significant worries [1].

Meeting the significantly escalating global energy requirements with no or minimal environmental damage and fossil fuel dependence can only be accomplished by

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employing clean energy systems. These systems can present substantial environmental, energetic, financial, and societal advantages. To be considered actually sustainable, an energy system ought to meet these conditions: (i) insignificant or zero undesirable environmental or societal influence; (ii) negligible or no natural source exhaustion; (iii) capable of meeting the present and forthcoming population's energy requirements; (iv) reliable, affordable, and effective fashion; (v) air, land, and water safety; (vi) minor or zero net GHG emissions; and (vii) well-being at present with no burden to prospect generations [2].

Hydrogen is recognized as an essential energy carrier for these subsequent reasons: (i) it possesses good energy exchange effectiveness; (ii) it could be generated from water with zero emissions; (iii) it is plentiful; (iv) it could be stored in various arrangements (i.e., gaseous, liquid, or solid phase storage); (v) it could be transferred across extended distances with minimal loss; (vi) it could be transformed into additional energy forms in more methods than the existing fuels; (vii) it contains greater HHV and LHV than the majority of the traditional fossil fuels; (viii) if it is generated from renewable energy sources and water, its manufacture, storing, transport and finale usage do not pose an environmental and/or health risk. However, the majority of the hydrogen production methods are not well-established, causing elevated production cost and/or low efficiencies [3].

Hydrogen is a great and useful energy carrier which has a potential to become one of the key components to turn the dream of a CO₂-free energy infrastructure dream into reality. When it is utilized in fuel cells, H₂ is converted to water and it emits very low or zero greenhouse gas emissions. In order to have successful H₂ energy systems, it needs to be produced in an affordable, clean, reliable, and sustainable way.

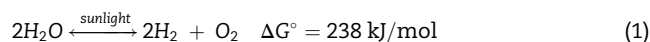
There is noteworthy volume of publications in the literature on hydrogen energy systems with an objective of generating hydrogen effectively in an affordable and reliable manner with lowest environmental damage. The approaches stated to this point could be employed alone, or in conjunction with additional options with the intention of reaching this objective. Fossil fuel based hydrogen is not regarded as sustainable; however, these techniques could be utilized while the renewable hydrogen generation methods are getting more technologically advanced [4].

The most appropriate hydrogen generation method selection depends on numerous internal and external system features given that every technique has both benefits and drawbacks. Resource accessibility, affordability and reliability, geographic position, population and climate, and compatibility with the current infrastructure are some of the criteria to bear in mind when selecting the most advantageous hydrogen generation path. Fossil fuels are estimated to meet a 25–30 TW energy utilization for at least a few centuries [5]; consequently, they are anticipated to be utilized as the principal hydrogen resource while the required infrastructure is being developed to generate hydrogen from renewables in TW level [6,7].

Solar energy, by means of a renewable and plentiful source, could turn out to be a probable sustainable resolution to the growing global energy demand. Approximately 30 min of solar irradiation reaching to the Earth's surface comprises

as much energy as the worldwide annual energy consumption [8]. An additional benefit of solar energy is its comparatively small continuing system scale up price relative to traditional fuels [9]. Regardless of many of its significant benefits, solar energy possesses an intermittent character; day and night cycles and hazy days greatly influence the quantity of solar energy gets reaching to the Earth's surface. For that reason, solar energy necessities to be stored in an altered fashion with the intention of providing a constant energy supply. Because it is a chemical fuel, hydrogen appears to be a favourable solar energy storage medium attributable to its high energy storing capability and easiness of transportation [10].

Given that water is a reliable and easily manageable resource of hydrogen, water dissociation is a favourable path for solar to hydrogen energy transformation. A photon in the visible light portion of the solar spectrum has minimum and maximum energies of 1 eV (100 kJ/mol) and 3 eV (300 kJ/mol), respectively, which is sufficiently adequate to generate hydrogen through water dissociation [11]. Solar hydrogen generation could be achieved by means of various methods, such as artificial photosynthesis, PV-electrolysis, and photo-electrolysis, and thermochemical, photocatalytic and PEC water dissociation. Every method possesses particular benefits and drawbacks. When affordability, dependability, and environmental influence are taken into consideration, PEC hydrogen generation technique appears to be a favourable option amongst the existing solar hydrogen paths [12]. The solar energy driven water dissociation reaction is generally shown as



Numerous published major books [3,11,13,14] and review articles [15–18] consist of outstanding analyses of the essential theories of PEC. Within PEC structures, arriving photons ($h\nu$) produce electrons (e^-) and holes (h^+). The photogenerated electrons and holes are disconnected afterwards and pass through the semiconductor in reverse ways. The holes power the oxygen evolution reaction (OER) at the surface of the semiconductor working electrode. At the same time, the electrons are transported to the surface of the counter electrode to run the hydrogen evolution reaction (HER). Minimum possible voltage required to dissociate water (ΔE°) is 1.23 V.

Second law of thermodynamics related losses through the photogenerated electrons and holes should be taken into account as well [9,10,18]. The actual powering force for water dissociation is presented as photovoltage (V_{ph}). As a consequence of the losses happening due to several reasons, such as spontaneous emission, partial light absorbing, and electron-hole recombination [18], V_{ph} is always less than the band gap of the semiconductor. Additional circumstances for example non-ideal band assembly configuration could further decrease accessible photovoltage [19].

The underlying motivation of this work is the potential for taking advantage of water electrolysis in a hybrid photo-electrochemical reactor to improve the solar spectrum utilization and hydrogen production yield. For this purpose, a system consisting of a photoactive ion selective membrane is developed as a medium for solar fuel generation. For this reason, in this study, a novel hybrid photoelectrochemical

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