



Clean hydrogen and power from impure water



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HIGHLIGHTS

- A new photoelectrochemical (PEC) H₂ production system is introduced.
- The system provides clean water, H₂, electricity, heat, and industrial chemicals.
- Solar energy is employed as a clean source.
- The system is investigated experimentally and theoretically.

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ABSTRACT

This paper presents a new photoelectrochemical (PEC) H₂ production system which is capable of providing clean energy and water, and multi-generation of H₂, electricity, heat and industrial chemicals from a single clean, abundant and renewable source: sun. This novel system maximizes solar spectrum utilization and increases system efficiencies by generating more outputs from solar energy alone. The hybrid PEC-chloralkali system, coupled with PV/T (Photovoltaic Thermal), is capable of producing H₂, Cl₂, electricity, and heat simultaneously. Incoming solar light is split into high-energy photons (with wavelengths lower than 400 nm) and low-energy photons. The high-energy portion is used to generate photocurrent in the reactor, and the remaining part is sent to the PV/T. This PV/T supports the electricity needs of the system and also provides electricity output for the end user. Moreover, the heat recovered from PV/T is a system output. The findings suggest that this system is capable of producing H₂ and Cl₂ as well as heat and electricity with higher efficiencies than the reported PV electrolysis and PEC-based H₂ production efficiencies in the literature.

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1. Introduction

The development of cleaner alternative energy systems to replace existing fossil fuel sources is becoming increasingly important [1]. This is evident through worldwide efforts to stabilize carbon dioxide concentration in the atmosphere, and other greenhouse gas emissions [2,3]. It is desirable for H₂ to be more widely adopted as a clean fuel, provided it can be produced by utilizing sunlight, a primary energy source, and can be safely stored and transported [4].

There are various potential H₂ generation methods; among them, fossil fuel based methods are at present the most heavily

used [5]. However, to make a shift to a H₂ economy viable, it is necessary to develop a sustainable energy pathway, and this means H₂ must be produced from renewable or clean and vast sources [6].

Numerous past studies have examined a range of hydrogen production methods from various sources including fossil fuels, renewable energies, nuclear, and biomass. Boyano et al. [7] conducted exergoenvironmental analyses to investigate the exergetic and environmental impact performance of conventional and advanced steam methane reforming methods for H₂ production. Life cycle assessment studies of various hydrogen production methods have been performed by Cetinkaya et al. [8]. Christopher and Dimitrios [9] and Dincer and Acar [4] have reviewed the exergetic performance levels of renewable energy based hydrogen generation techniques. Demirci and Miele [10] provided a summary of emerging and traditional hydrogen generation methods. A comprehensive review and evaluation of hydrogen production

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methods for better sustainability in terms of global warming and acidification potentials, social costs of carbon dioxide, energy and exergy efficiencies, and production costs were presented by Acar and Dincer [11].

A comprehensive classification, discussion, assessment, and comparison of green methods for hydrogen production was presented by Dincer [3] along with some illustrative examples and case studies. Dincer and Zamfirescu [12] comparatively discussed sustainable hydrogen production options in terms of efficiency, environmental impact, and sustainability. Bicakova and Straka [6] presented an overview of various renewable based hydrogen production technologies. Another review analyzed and discussed the development of industrial processes and emerging techniques for hydrogen production from renewable and sustainable sources [13].

Solar energy is an abundant and renewable source of energy. Approximately half of an hour of solar irradiation on the surface of the earth contains enough energy to supply the global energy demand for one year [14]. A further benefit of solar energy is its relatively small incremental cost relative to traditional fuels [15]. A promising method of solar to hydrogen energy conversion is water splitting, as water offers a widely available and easily accessible source of hydrogen. A visible light photon has a minimum and maximum energy of 1 eV and 3 eV (or 100 kJ/mol and 300 kJ/mol) respectively, which is more than adequate to generate hydrogen by means of water splitting [16].

There are various ways to harness solar energy to generate H₂. Direct utilization of solar energy to split water into H₂, namely photo-based H₂ production, has a potential to address aforementioned clean energy issues when integrated with sustainable energy systems. Xing et al. [17] have summarized the fundamentals of photochemical and PEC systems, and provided an overview of a variety of photoreactor designs and development for solar H₂ production from water splitting. Acar et al. [18] have compared visible light-powered heterogeneous photocatalysts for H₂ generation in terms of technical, ecological, and financial measures. Recent progress in enhancing the solar-to-H₂ efficiency has been summarized by Chen et al. [19].

Joshi et al. [20] have classified solar H₂ production systems based on their energy (i.e. photonic, thermal, and/or chemical energy) and material (i.e. water, natural gas, coal, oil, etc.) inputs. They have comparatively assessed various methods (including electrolysis, reforming, gasification, cracking etc.) in terms of exergy efficiency and sustainability. Past authors performed a detailed exergy and sustainability assessment of various solar H₂ production methods using different solar collector types (i.e. flat plate, vacuum tube, concentrating, field mirror, and parabolic) [21]. A large inventory of H₂ production from solar energy by considering energy, environmental, and economic aspects was conducted by Ngoh and Njomo [22]. Yadav and Banerjee [23] expanded this review by including a detailed comparative assessment of solar thermochemical processes for H₂ production.

The primary focus of this study is photocatalytic and PEC based H₂ production, taking advantage of the appropriate energy spectrum of solar energy for clean and efficient H₂ production. Preethi and Kanmani [24] reported the efficiency of different photoactive materials for photocatalytic H₂ production based on a comprehensive literature review (results are reported to be collected from 200 articles). In the recent literature, there are numerous reviews and discussions of semiconductor materials for photochemical splitting of water for H₂ production by photocatalysis [25–27].

In this paper, a hybrid PEC-chloralkali system is experimentally investigated and thermodynamically analyzed. The primary aim of this study is to develop a new H₂ production system where efficiency is maximized and waste is minimized. The proposed integrated system produces H₂ via water splitting and converts the

by-products into useful industrial products, namely Cl₂ and NaOH. Furthermore, this system maximizes the utilized solar spectrum by combining photochemical and electrochemical processes. There is further potential for the system when it is connected to a desalination unit, as it can produce fresh water from brackish or impure water. The system is experimentally tested at four temperatures (20, 40, 60, and 80 °C) and three light settings (no light, 600 W/m², and 1200 W/m²).

2. System description and analyses

The system used in this study is developed based on a batch scale design proposed and analyzed by Rabbani et al. [28]. Rabbani et al. [28] have used various heterogeneous photocatalysts (e.g., CdS/ZnS) in their system. Acar and Dincer [29] have conceptually developed the design in a continuous type operation and conducted thermodynamic analysis of the system. Energy, exergy and economic analyses and assessments of the system have been performed by Acar et al. [30]. To our knowledge, there has been no previous experimental testing of a continuous type hybrid PEC reactor with a photoactive membrane and investigation of a hybrid reactor integrated with a solar spectral splitter and PV/T in prior archival literature. The originality of this research is both experimental and theoretical analyses of a continuous type hybrid PEC reactor in an integrated system which is capable of producing H₂, Cl₂, electricity, heat, and clean water.

In the thermodynamic analysis of this system, the following assumptions are made:

- The environmental temperature (T₀) and pressure (P₀) are 20 °C and 1 atm, respectively.
- The reactants and products are at the reaction temperature and pressure and these values are constant during reactions.
- All processes take place at steady state steady flow conditions.
- The changes in kinetic and potential energies are negligible.
- The H₂ and Cl₂ gases are ideal.
- The heat losses to the environment are neglected.
- The auxiliary components are well insulated and capable of conducting electricity with no losses.
- The spectral splitting system is evaluated from the procedure reported by Zamfirescu and Dincer [31].

For the integrated multigeneration system, a hypothetical location is chosen where sufficient solar irradiation exists. This is presumed to be 1 kW/m² with AM1.5G solar spectrum. The number of annual operational sunlight hours is taken as 2000 h.

2.1. Experimental setup

The experimental setup has a hybrid dual half-cell reactor with a cation exchange membrane used for PEC-chloralkali based H₂ production. During this process, Cl₂ gas leaves the reactor from the anode. Gaseous H₂ and NaOH solutions are produced in the cathode. Fig. 1 presents the process flow diagram of the experimental setup. PEC-chloralkali experiments are conducted under 600 and 1200 W/m² irradiation levels. NaCl and NaOH solutions are used as the anolyte and catholyte, respectively. It is tested at three different flow rates and four different temperatures.

From Fig. 1, it can be seen that the experimental setup has eight main components, namely: (I) reactor; (II) electrolyte feed tanks; (III) electrolyte dump tanks; (IV) peristaltic pumps; (V) water displacement cylinder; (VI) heaters; (VII) potentiostat; and (VIII) solar simulator. In all cases, where specified, additional (a) and (b) terms are used for the anolyte and catholyte, respectively.

During the experimental studies, the anolyte feed is saturated

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