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## Analysis and assessment of a continuous-type hybrid photoelectrochemical system for hydrogen production

## Canan Acar<sup>\*</sup>, Ibrahim Dincer

Faculty of Engineering and Applied Science, University of Ontario Institute of Technology, 2000 Simcoe Street North, Oshawa, Ontario, L1H 7K4, Canada

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#### ABSTRACT

In this study, we conceptually develop and thermodynamically analyze a new continuoustype hybrid system for hydrogen production which photoelectrochemically splits water and performs chloralkali electrolysis. The system has a potential to produce hydrogen efficiently, at low cost, and in an environmentally benign way by maximizing the utilized solar spectrum and converting the byproducts into useful industrial commodities. Furthermore, by using electrodes as electron donors to drive photochemical hydrogen production, the hybrid system minimizes potential pollutant emissions. The products of the hybrid system are hydrogen, chlorine and sodium hydroxide, all of which are desired industrial commodities. The system production yield and efficiencies are investigated based on an operation temperature range of 20 °C–80 °C. A maximum energy efficiency of 42% is achieved between the temperatures of 40 °C and 50 °C.

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#### Introduction

One of the major challenges of the twenty-first century is to continue the economic growth and meet the energy demand, due to increasing population and rising standards of living. Currently, 85% of the global energy supply is met by fossil fuels [1]. However, because of their limited nature and nonhomogeneous distribution, fossil fuels are not expected to keep up with the increase in energy demand. In addition to that, since fossil fuel reserves are getting less accessible as the easily accessible ones are consumed, the prices of fossil fuels keep increasing. Along with economic issues, greenhouse (mainly  $CO_2$ ) emissions as a result of fossil fuel utilization, and

their contribution to global warming, have been raising serious environmental concerns. The International Panel on Climate Change (IPCC) declares that above 450 ppm,  $CO_2$ emissions have a potential to cause global warming by more than 2 °C, which potentially damage the entire ecosystem irreversibly. Given the current amount and approximate annual increase of  $CO_2$  emissions, 450 ppm level can be reached in less than 30 years, if no precautions are taken soon [2,3]. Since fossil fuel utilization is the cause of the 99% of  $CO_2$ emissions, switching to a non-fossil fuel energy source could greatly reduce the  $CO_2$ -related emissions and their adverse effect on global warming. Due to their near-zero or zero enduse emissions and continually replenished resources (e.g. sun light, wind, waves, and geothermal heat), renewable

\* Corresponding author.

E-mail addresses: Canan.Acar@uoit.ca (C. Acar), Ibrahim.Dincer@uoit.ca (I. Dincer). http://dx.doi.org/10.1016/j.ijhydene.2014.07.146

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energies are considered as sustainable alternatives to fossil fuels. On the other hand, their intermittent and fluctuating nature raises the need for efficient storage mediums. Hydrogen is an ideal energy carrier because: (i) it has high energy conversion efficiencies; (ii) it can be produced from water with no emissions; (iii) it is abundant; (iv) it can be stored in different forms; (v) it can be transported over long distances; (vi) it can be converted into other forms of energy in more ways than any other fuel; (vii) it has higher HHV and LHV than most of the conventional fossil fuels; and (vii) if produced from renewable energies and water, its production, storage and end use do not harm the environment.

Among the selected possible hydrogen production options presented in Fig. 1, fossil fuel sources are currently the most extensively used commodities to produce hydrogen [5]. However, the transition to hydrogen economy requires it to be produced from renewable or clean and vast sources in order to build a sustainable energy system. There has been a significant amount of research going on to produce hydrogen efficiently at low cost and minimum environmental impact. The methods mentioned in Fig. 1 can be used alone, or together with other alternatives in order to reach this target. Hydrogen from fossil fuels is not considered as sustainable due to their limited and non-renewable nature; yet these methods can be used during the transition to hydrogen economy as the renewable hydrogen production techniques are being developed [4]. Table 1 compares the estimated global power generation capacities of wind, biomass, nuclear, and solar energies. The most suitable hydrogen production pathway depends on various internal and external system characteristics since each method has their own advantages and disadvantages. Table 1 gives that compared to hydro, wind, biomass, and nuclear; solar energy is the only renewable energy source that has a supply 20 TW power generation. Solar energy also does not have as adverse effects on the environment as hydro (harms the aqueous ecosystem), wind (harms the wildlife), biomass (may cause biodiversity loss), and nuclear. However, an efficient solar-to-hydrogen pathway should be developed with minimum environmental effect and increased production yields and rates.

Solar energy, as a renewable and abundant supply, can become a possible sustainable solution to the increasing energy demand of the world. About 30 min of solar radiation incident on the earth surface contains as much energy as the world consumption for one year [8]. Another advantage of solar energy is its relatively low gradual system expansion cost compared to conventional fuels [9]. However, despite its many advantages, solar energy has a sporadic nature, day/ night cycles and cloudy days strongly affect the amount of solar energy reaches to earth's surface. Therefore, solar energy needs to be stored in a different form in order to provide a continuous supply. As a chemical fuel, hydrogen is a promising storage medium due to its high energy storage capacity and ease of transport [10]. Since water is an abundant and easily accessible source of hydrogen, water splitting is a promising pathway for solar-to-hydrogen energy conversion. 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 plenty enough to produce hydrogen via water splitting [11]. Some of the existing pathways for solar hydrogen production are briefly summarized in Table 2. The solar water splitting reaction can be written as follows:

$$2H_2O + \text{sunlight} \leftrightarrow 2H_2 + O_2 \quad \Delta G^\circ = 238 \text{ kJ/mol}$$
 (1)

Photoelectrochemical cells (PEC) convert solar energy to an energy carrier via light stimulated electrochemical processes. In a PEC, solar light is absorbed by one or both of the photoelectrodes and at least one of them is a semiconductor. PECs can produce either chemical or electrical energy. They are also used to treat hazardous aqueous wastes [12–16]. A basic PEC



Fig. 1 – Overview of selected hydrogen production paths categorized by primary energy source and production method.

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