INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–10

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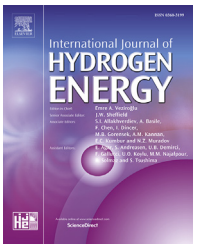

Energy and exergy analyses of hybrid photocatalytic hydrogen production reactor for Cu–Cl cycle

Tahir Abdul Hussain Ratlamwala [a,b,*], *Ibrahim Dincer* [a]

[a] *University of Ontario Institute of Technology, Faculty of Engineering and Applied Science, Department of Mechanical Engineering, 2000 Simcoe Street North, Oshawa, Ontario, L1H 7K4, Canada*

[b] *National University of Sciences and Technology, Islamabad, Pakistan*

ARTICLE INFO

Article history:
Received 27 October 2017
Received in revised form
21 December 2017
Accepted 24 December 2017
Available online xxx

Keywords:
Hydrogen production
Electrochemistry
Energy
Exergy
Efficiency
Exergoeconomics

ABSTRACT

The present paper concerns electrochemical, energy, exergy and exergoeconomic analyses of a hybrid photocatalytic-based hydrogen production reactor which is capable of replacing the electrolysis sub-system of the Cu–Cl thermochemical cycle. Several operating parameters, such as current density, reactor temperature, ambient temperature and electrode distance, are varied to study their effects on the hydrogen production rate, the cost of hydrogen production and energy and exergy efficiencies. The present results show that the voltage drops across the anolyte solution (sol 1), catholyte solution (sol 2), an anode, cathode, and cation exchange membrane vary from 0.005 to 0.016 V, 0.004–0.013 V, 1.67–2.168 V, 0.18–0.22 V and 0.06–0.19 V, respectively with an increase in current density from 0.5 to 1.5 A/cm^2. The energy and exergy efficiencies of the hybrid photocatalytic hydrogen production reactor decrease from 5.74 to 4.54% and 5.11 to 4.04%, respectively with an increase in current density.

Introduction

Photocatalytic hydrogen production methods have recently gained considerable interest due to their potential of converting solar light into electrical and chemical energies. Researchers during the past decade have focused on the development of a two half-cell reactor separated by a membrane. This two-half-cell reactor uses a photocatalyst and an electron donor to separate water molecule and produce hydrogen. The photocatalysts available for use are divided into two categories: (a) homogeneous and (b) heterogeneous photocatalysts.

The homogenous photocatalysts work on the principle of supramolecular complexes in which there are different sections; namely (a) the light absorbing unit, (b) the electron relay unit and (c) the electron collector unit [1–3]. In a homogeneous photocatalyst, the process starts at the terminal ligand where it receives an electron from the electron donor, which is then transferred to the electron collector unit with the help of the bridging ligand. The water is then introduced into the solution at the electron collector unit to reduce its bond to hydrogen gas and hydroxyl ion [4]. Schulz et al. [5] studied the role of the bridging ligand in photocatalytic supramolecular assemblies for the reduction of protons and carbon dioxide. A solar energy

* *Corresponding author*. National University of Sciences and Technology, Islamabad, Pakistan.
E-mail address: tahir.ratlamwala@pnec.nust.edu.pk (T.A.H. Ratlamwala).

https://doi.org/10.1016/j.ijhydene.2017.12.138
0360-3199/

conversion study for photocatalytic hydrogen production from water using mixed-metal supramolecular complexes was performed by Rangan et al. [6]. Recently, Brewer and Elvington [7] have introduced a new homogenous photocatalyst consisting of ruthenium (Ru) and rhodium (Rh) for solar energy based hydrogen production. In this new homogenous photocatalyst, dimethylaniline (DMA) and dimethylformamide (DMF) are used as an electron donor and the solvent, respectively [8]. However, homogenous photocatalysts are too expensive and are currently limited to lab-scale use only.

On the other hand, the heterogeneous photocatalysts provide an option of a solid catalyst that can be used either as a powder or a solid electrode, which is cheaper than homogeneous photocatalysts. In heterogeneous photocatalysts, the catalyst exists in a different phase as that of the reactant. When solar or other forms of light carrying energy greater than that of the energy gap between the valence and conduction band is focused on such photocatalysts, it excites the electrons carried by the valence band and forces it to travel from the valence band to the conduction band where they react with water to produce hydrogen and hydroxyl ions. In a study, Buehler et al. [9] found that an active solar hydrogen production photocatalyst can be obtained simply by depositing platinum on cadmium sulfide (CdS) microcrystal. A study presented by Reber and Rusek [10] concluded that by irradiating suspensions for platinized CdS in the solutions of the sulfur or sulfide ions, an effective photocatalytic hydrogen production can be achieved. Reber and Meier [11] found that an effective hydrogen production can be achieved by suspending ZnS in multiple electrolyte solutions such as Sz, So-, S2O-, and H_2PO. Hydrogen production was achieved under visible and ultraviolet light irradiation by splitting of the water molecule in the presence of a band-controlled cadmium-zinc sulfide solution as reported by Xing et al. [12]. The major difference between the homogeneous catalyst and heterogeneous catalysts is that the quantum yield of the earlier one is approximately 0.01 (Richter and Brewer [13]) as opposed to 0.9 (Xing et al. [12]) for the later one.

The titanium dioxide based catalysts are considered as another group of catalysts which can be very useful in producing hydrogen using photocatalytic hydrogen production reactors. Wu et al. [14] used a Pd-Gardenia-titanium dioxide photocatalyst for solar driven hydrogen production. Parayil et al. [15] in their study showed that carbon-modified titanium dioxide composite materials can enhance the photocatalytic water splitting capability of titanium dioxide based photocatalysts. An improved hydrogen production rate by using titanium dioxide–Zinc oxide mixed oxides photocatalysts was achieved by Perez-Larios et al. [16]. A study carried out by Matos et al. [17] showed that titanium dioxide based catalysts can also be used to produce hydrogen in visible light if these catalysts are prepared to form a gold-titanium dioxide activated carbon photocatalyst.

The present paper proposes a hybrid photocatalytic hydrogen production reactor capable of replacing electrolysis sub-system of the Cu–Cl cycle. Comprehensive electrochemical, energy, exergy and exergoeconomic analyses of the hybrid photocatalytic reactor are performed to provide the reader with the knowledge of working principles of the proposed reactor. A parametric study is also carried out to study the effect of different operating parameters such as current density, reactor temperature, electrode distance and ambient temperature on hydrogen production rate, the cost of hydrogen production and energy and exergy efficiencies of the reactor. The main differences between the current study and the previous studies are that this study presents comprehensive electrochemical, energy, exergy and exergoeconomic analyses of a novel, newly developed, hybrid hydrogen production reactor for the Cu–Cl cycle capable of replacing the conventional electrolysis system in the Cu–Cl cycle for generating hydrogen while consuming lesser electricity and using solar energy as opposed to the previous studies which focus on using electrolysis system for hydrogen generation.

System description

The use of solar energy in generating hydrogen comes with the benefits of low greenhouse gas emissions and low operation cost. The hybrid photocatalytic hydrogen production reactor studied in this paper is shown in Fig. 1. The hybrid photocatalytic hydrogen production reactor consists of two half-cells. The first half-cell is the anode side of the reactor and the second half-cell is the cathode side. A mixture of CuCl, HCl, and water are fed to the anode half-cell. In the anode half-cell, the breaking of the mixture into $CuCl_2$, water, and positive hydrogen ions take place when a voltage is supplied with the help of photocatalyst. The titanium dioxide is used as an electrode in the anode half-cell to act as a solid photocatalyst. As a result, of this breaking of bonds, two electrons, and positive hydrogen ion are released. The positive hydrogen ions and electrons pass through the membrane and electrical circuit, respectively and enter the second half-cell of the hybrid photocatalytic hydrogen production reactor (cathode side). The overall reaction taking place in the reactor is given as follows:

$$2Cl(aq) + 2HCl(aq) \rightarrow 2CuCl_2(aq) + H_2(g) \quad (1)$$

Here, the CuCl is in the aqueous phase, HCl is in the aqueous phase, $CuCl_2$ is in the aqueous phase and hydrogen is in the gaseous phase.

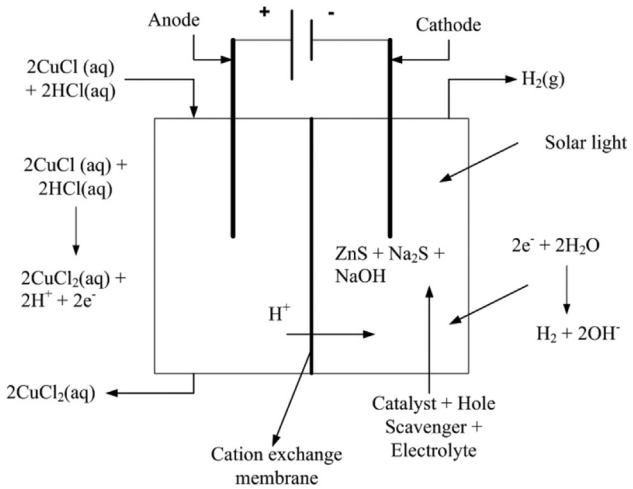

Fig. 1 – Schematic of the hybrid photocatalytic hydrogen production reactor.

Please cite this article in press as: Ratlamwala TAH, Dincer I, Energy and exergy analyses of hybrid photocatalytic hydrogen production reactor for Cu–Cl cycle, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2017.12.138