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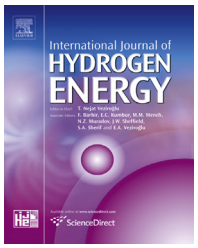

Experimental investigation of hydrogen production in a photo-electrochemical chloralkali processes reactor

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ABSTRACT

This paper develops and analyzes a new photo electrochemical reactor that uses zinc sulfide as a photo catalyst to produce hydrogen, chlorine and sodium hydroxide. The effects of different parameters on the rate of hydrogen, chlorine and sodium hydroxide production are experimentally studied. The parameters include the applied voltage, varied from 4 V to 5 V, amount of catalyst, varied from 1 g/425 mL to 5 g/425 mL and light intensity, varied from 20 W/m^2 to 55 W/m^2. A factorial design of experiments is applied and an analysis of variance (ANOVA) is used to examine the experimental results. Energy and exergy efficiencies are also calculated. An optimization is performed to find the optimal catalyst concentration. At the optimized catalyst concentration, salt water is used to check its effect on the rate of hydrogen production.

Introduction

Among various methods of solar energy conversion, much attention has been given to photocatalytic water splitting because of its potential significance in clean production of hydrogen (H_2) from water. If successfully developed with economic viability, this could be a major technology to address energy and environmental problems together in the future. Conversion of solar energy into chemical energy through light-driven water splitting generates environmentally benign hydrogen gas, a carbon free fuel with a high energy output relative to its molecular weight. The byproduct of water splitting can either be neutralized into oxygen or chlorine and caustic in a chloralkali process.

When water splits into hydrogen, it also produces hydroxyl ions as a byproduct. The half cell water splitting reaction is given as follows:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (1)$$

These hydroxyl ions can be neutralized into oxygen as

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^- \quad (2)$$

and the overall reaction becomes

$$2H_2OH \rightarrow H_2 + O_2 \quad (3)$$

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However, these hydroxyl ions can also be neutralized in a chloralkali process, where OH^- are used to form sodium hydroxide in a salt water reaction. The half cell water reduction reaction is the same as shown in Equation (1)–1. While in the other half, chlorine ions are oxidized to form chlorine gas as follows:

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (4)$$

The sodium ions combine with hydroxyl ions and form sodium hydroxide. The overall reaction is given as follows:

$$2H_2O + 2NaCl \rightarrow Cl_2 + H_2 + NaOH \quad (5)$$

A number of researchers have addressed different aspects of photochemical hydrogen production and membrane cell chloralkali technology. Kamiya et al. [1] have studied the photochemical production of hydrogen from water using solar radiation. They considered the catalytic and energetic requirements of the photochemical and the electron transfer spectra of the catalyst ions [1]. Buehler et al. [2] have reported photochemical hydrogen production with cadmium sulfide suspensions. Their study showed that by using platinum deposition on microcrystals of CdS powders, active photocatalysts for photochemical hydrogen production can be prepared [2]. Reber et al. [3] have studied photochemical hydrogen production with platinized suspensions of cadmium sulfide and cadmium zinc sulfide modified by silver sulfide. The studies showed that the effective hydrogen production can be achieved by irradiating suspensions for platinized CdS in the solutions of the sulphur or sulfide ions [3].

Sakai et al. [4] have studied the homogeneous catalysis of platinum (ll) complexes in photochemical hydrogen production from water. The research showed that the catalytic efficiency of the Pt catalyst is dependent upon a number of different factors, namely metal–metal interactions, coordination environments, steric factors, electron-acceptor capability, and photosensitizing ability [4]. Sakai et al. [5] studied homogenous catalysis of the mixed-valent octa nuclear platinum complexes in photochemical hydrogen production from water. Results showed that an acetimidate-bridged mixed-valent octa nuclear platinum complex has been used as a hydrogen producing catalyst in a photochemical model system containing EDTA as a sacrificial electron donor [5].

Akkerman et al. [6] have studied photo-biological hydrogen production (particularly the photochemical efficiency and bioreactor design). The study showed that biological production hydrogen can be achieved by photoautotrophic or photoheterotrophic organisms [6]. Darwent et al. [7] have studied photochemical hydrogen production using cadmium sulfide suspensions in aerated water. The results showed that suspensions of CdS particles sensitize the photo-reduction of water by the cysteine and ethylenediamine-tetra-acetic acid with a quantum yield of 0.04 mol/Einstein [7]. Striech et al. [8] have studied high-turnover photochemical hydrogen production catalyzed by a model complex of the hydrogenase active site. The work showed that hydrogen has potential as a viable energy carrier of the future, particularly if it is produced in a renewable way, like photochemical splitting of water.

Madeni et al. [9] have investigated the effect of impurities in saturated brine in a chlor-alkali plant. The study showed that the membranes in combination with other treatment methods may be used to decrease the impurities to a desirable level. They used seven different polymeric membranes (FT30, PVD, DOW-PS, TFC-SR, BW30, 37100 and NF45) to treat the saturated brine [9]. Balster et al. [10] have studied the membrane reactors and reviewed the electro-membrane technology (chlor-alkali electrolysis) and polymer-electrolyte fuel cells (FC) as an emerging technology. They showed how the membrane is catalytically effective, as well as how the membrane splits water into protons and hydroxyl ions with the help of bipolar ion-exchange membrane technology [10].

Martel et al. [11] investigated desalination of seawater and its importance and applications in Mediterranean countries and the Canary Islands (Spain). The work showed that chloralkali industry activities have drawbacks and negative impacts on the environment and marine ecosystems, due to the discharge of generated brine into the sea. The research also showed that some changes can be introduced which will be economically viable and effective, not only for the new plants, but also for an existing plant [11]. Kariduraganavar et al. [12] studied the usage of ion-exchange membranes in different industrial processes, i.e., edible salt production in the electrodialytic concentration of seawater, in the desalination of saline water by electro-dialysis, separation of the ionic materials from the non-ionic materials by the electro-dialysis, recovery of acid and alkali from waste acid and alkali solution by diffusion dialysis and the dehydration of water-miscible organic solvent by pervaporation. Zamfirescu et al. [13] have examined a photochemical water splitting reactor with supramolecular catalysts and a proton exchange membrane. Zamfirescu et al. [14] have reported photo-electrochemical chlorination of cuprous chloride with hydrochloric acid for hydrogen production. Zamfirescu et al. [15] have also examined molecular charge transfer and quantum efficiency analyses of a photochemical reactor for hydrogen production. Baniasadi et al. [16] assessed the performance of a water splitting reactor with hybrid photochemical conversion of solar energy. Baniasadi et al. [17] have also investigated oxygen evolving reactor over potentials and ion diffusion in photo-catalytic and electro-catalytic hydrogen production. Baniasadi et al. [18] developed a hybrid photocatalytic water splitting process for an expanded range of the solar spectrum with cadmium sulfide and zinc sulfide catalysts. Also, Momeni and co-coworkers [19–21] have used nanotube composite photoanodes for water splitting with visible light.

These past studies, as discussed above, have been performed separately on electrolysis of salt water and photocatalytic hydrogen production. The aim of the present study is to present a new way of integrating photochemical hydrogen production with electrochemical chloralkali processes in a newly designed reactor. This paper presents a new photo electrochemical reactor configuration that uses zinc sulfide as a photo catalyst to produce hydrogen, chlorine and sodium hydroxide. This reactor is able to extract hydroxyl ions from the hydrogen production unit and neutralize them in a chloralkali process to produce sodium hydroxide. The effects of different parameters are also studied which includes light intensity, voltage, amount of catalyst, etc. Finally, an optimization study is performed for two different objectives to find the optimal parameters.