

Solar hydrogen production via pulse electrolysis of aqueous ammonium sulfite solution

Cunping Huang

University of Central Florida, Florida Solar Energy Center, 1679 Clearlake Road, Cocoa, FL 32922-5703, USA

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Abstract

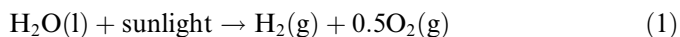
A long-standing challenge for hydrogen production via solar water splitting is the efficiency of converting solar energy to hydrogen chemical energy. Thermolysis, photocatalysis and electrolysis are three basic solar water splitting processes that utilize solar thermal, photonic and electrical energies. A technology using a combination of these processes can utilize a wider spectrum of solar radiation, thereby enhancing the efficiency of solar energy conversion. Due to the simplicity and maturity of photovoltaic (PV) cells and electrolyzer cells, solar hydrogen production via PV cells plus water electrolysis has been implemented and widely used as a bench mark process. The present study focuses on solar hydrogen production via direct current pulse electrochemical oxidation of aqueous ammonium sulfite solutions, one important step in solar sulfur–ammonia (S–NH₃) thermochemical water splitting cycles. The results show that pulsating electrolysis enhances the efficiency of hydrogen production. The effects of pulsating parameters (such as pulsating on time and off time, frequency and duty cycle) on hydrogen evolution rates are discussed in detail.

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1. Introduction

Solar water splitting for hydrogen production is a renewable and carbon free process that can produce ultra pure hydrogen gas according to:



The total energy (ΔH) required for water splitting can be separated into thermal energy ($T\Delta S$) and Gibbs free energy (ΔG , useful work) as:

$$\Delta H = \Delta G + T\Delta S$$

where $\Delta G_{298\text{K}}^\circ = 237 \text{ kJ/mol}$; $\Delta S_{298\text{K}}^\circ = 163 \text{ J/mol/K}$ and $\Delta H_{298\text{K}}^\circ = 285 \text{ kJ/mol}$.

At ambient conditions more than 80% of the total enthalpy (ΔH) for water decomposition must be provided

as Gibbs free energy (ΔG) in the form of electrical energy or photonic energy.

1.1. Solar water splitting processes

There are basically three processes that can be used for solar H₂ production via water splitting: (1) thermal chemical process (thermolysis), (2) electrochemical process (electrolysis) and (3) photochemical process (photocatalysis). Concentrated solar irradiation provides an ideal high temperature thermal energy ($T\Delta S$) for water splitting (Nakamura, 1977; Liu et al., 2008). As temperature increases, the change of Gibbs free energy (ΔG) for water splitting decreases and water is gradually decomposed into H₂ and O₂. To achieve a significant H₂ yield, the reaction temperature must be greater than 2500 °C. Solar irradiation can be converted into electrical energy via a photovoltaic cell for water electrolysis operating at an ambient temperature.

E-mail address: cunp_huang@hotmail.com

In comparison with high temperature direct water thermochemical splitting, the operational cost for water electrolysis is greatly reduced. Corresponding to 237 kJ/mol of Gibbs free energy, the minimum potential needed for water electrolysis is 1.23 V. When energy losses are taken into account, the total potential (minimum potential plus over potential) of water electrolysis must be greater than 1.8 V or 2.0 V (Zeng and Zhang, 2010). The major expenses for this process are photovoltaic cells and electrolyzers. Water electrolysis can be carried out under either alkaline (Zeng and Zhang, 2010) or acidic conditions (Barbir, 2005). Under an alkaline condition no noble metal based electrodes are needed, thereby reducing electrolyzer costs. However, alkaline electrolyzers normally are larger in size and lower in efficiency compared to proton exchange membrane (PEM) based electrolyzers. Because electrodes are operated under highly acidic conditions, PEM electrolyzers require noble metals (Pt, Pd, Ir, etc.) as electrode catalysts. The efficiency of solar H₂ production via PV + electrolysis can be estimated as 7–12% based on the product of 10–15% photovoltaic cell efficiency and 70–80% water electrolysis efficiency. Of all water splitting technologies, this process has been commercialized due to the maturity of the technology. The photocatalytic process integrates the solar photovoltaic cells and electrolysis into one process and each single photocatalyst particle (semiconductor) serves as one micro-scale, complete photovoltaic cell and electrolyzer system. The major obstacle to the photocatalytic process is the identification of an ideal photocatalyst (Osterloh, 2008; Kudo and Miseki, 2009).

Water splitting is an energy intensive process. Any single process (thermolysis, electrolysis or photocatalysis) is ineffective in achieving greater efficiency for solar H₂ production. The key to achieving increased efficiency is to use as much solar spectrum energy as possible. This is because total H₂O splitting energy (ΔH) is a weak function of temperature. The amount of useful work needed for water splitting decreases with the increase of temperature. From this viewpoint, processes that can use solar thermal energy to reduce the need for Gibbs free energy can effectively increase solar to H₂ efficiency. Water splitting via multiple-step thermochemical cycles has achieved much higher solar to H₂ efficiencies (>35%) (Abanades et al., 2006; Sakaba et al., 2007). The basis of this process is to employ two or more chemical reactions to form a closed chemical reaction cycle, with a net reaction of water decomposition. Because the major energy used in thermochemical water splitting cycles (TCWSCs) is thermal heat, concentrated high temperature solar thermal energy provides one of the most desirable renewable energy sources.

The fundamental concept of a TCWSC is to break down the overall water splitting into several steps, accomplished by separated reactions (Fig. 1). Thus, one high energy and low efficiency direct water splitting process is replaced by two or more low energy intensive but higher efficiency steps. In the case of reported solar TCWSCs, high energetic photonic energy (i.e. near UV and visible photons) in the

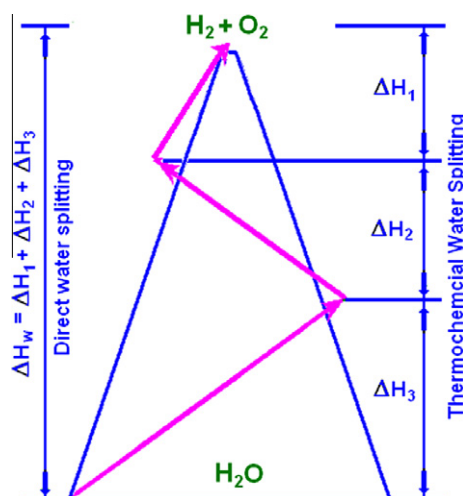
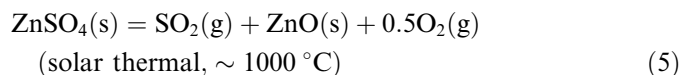
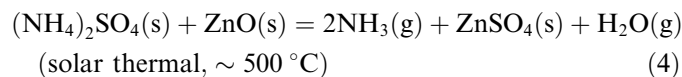
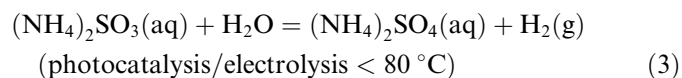
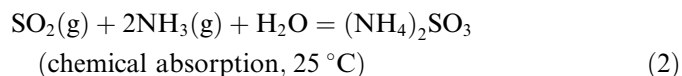


Fig. 1. Energy diagram for thermochemical water splitting.

solar spectrum is often degraded to thermal heat prior to its use in a cycle. Furthermore, some TCWSCs require very high temperatures (>1200 °C), significantly limiting the choice of materials and increasing heat loss during solar energy concentration.

At Florida Solar Energy Center, we have developed pure solar driven sulfur ammonia (S–NH₃) based TCWSCs in which high photonic energy ($\lambda < 525$ nm) is used for the photocatalytic production of H₂ based on the photochemical oxidation of aqueous SO₃²⁻ ions. The remaining portion of the solar thermal energy ($\lambda > 525$ nm) is utilized to produce O₂ via decomposition of metal sulfates (MSO₄) or metal pyrosulfates (K₂S₂O₇ for example) (Huang and T-Raissi, 2004; Huang et al., 2007, 2008a, 2011; T-Raissi et al., 2007; Yao et al., 2011; Huang et al., 2008b; Mao et al., 2011). The photochemical H₂ production of the S–NH₃ TCWSCs is based on:



Reaction (3) can also be carried out electrochemically with less than 1/10 of the potential required for water electrolysis ($\Delta E = 0.11$ V vs. NHE). The remaining water splitting energy is derived from a solar thermal process used for O₂ production. The advantages of these TCWSCs are: Firstly, the use of both solar thermal and photonic energy fundamentally enhances the efficiency of the process. Secondly, electrolysis for hydrogen production under low potential requirements makes the process easier and

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