Thermodynamic Analysis of a Photoelectrochemical Hydrogen Production System

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Abstract
Hydrogen is regarded as a potential energy carrier for the future. There exist several methods to produce hydrogen from various sources. One promising method is photoelectrochemical (PEC) decomposition of water into hydrogen and oxygen. In this study, the thermodynamic analysis of PEC hydrogen production is performed for air mass 1.5 insolation. Because the energy required for splitting water decreases as temperature is increased, heating the system by using the long wavelength energy will increase the system efficiency.

As the energy band gap of the photoelectrode increases, the induced photocurrent is decreased. If photons absorbed are all excited, the maximum photocurrent is 63.75 mA/cm$^2$. For TiO$_2$ (~3.2 eV) and Fe$_2$O$_3$ (~2.1 eV), the maximum photocurrent is respectively 0.68 mA/cm$^2$ and 10.43 mA/cm$^2$. The maximum power conversion efficiency of a PEC cell is 44.07%. For TiO$_2$ and Fe$_2$O$_3$, the power conversion efficiency is 2.8% and 21.9%, respectively.

Keywords: photoelectrochemical, efficiency, hydrogen production

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>$E$</td>
<td>Energy</td>
</tr>
<tr>
<td>$E_s$</td>
<td>Spectral solar energy</td>
</tr>
<tr>
<td>$E_g$</td>
<td>Energy band gap</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday constant</td>
</tr>
<tr>
<td>$FF$</td>
<td>Fill factor</td>
</tr>
<tr>
<td>$h$</td>
<td>Planck’s constant (=6.626x10^{-34}Js)</td>
</tr>
<tr>
<td>$c$</td>
<td>Speed of light</td>
</tr>
<tr>
<td>$I$</td>
<td>Current</td>
</tr>
<tr>
<td>$I_{mp}$</td>
<td>Maximum power point of current</td>
</tr>
<tr>
<td>$I_{sc}$</td>
<td>Short circuit current</td>
</tr>
<tr>
<td>$n$</td>
<td>Mole of electrons for splitting per mole of water</td>
</tr>
<tr>
<td>$P$</td>
<td>Power</td>
</tr>
<tr>
<td>$P_{mp}$</td>
<td>Maximum point of power</td>
</tr>
<tr>
<td>$P_{in}$</td>
<td>Solar irradiation power</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
</tr>
<tr>
<td>$V$</td>
<td>Voltage</td>
</tr>
<tr>
<td>$V_{H2O}$</td>
<td>Voltage for splitting water at standard state</td>
</tr>
<tr>
<td>$V_{mp}$</td>
<td>Maximum power point voltage</td>
</tr>
<tr>
<td>$V_{oc}$</td>
<td>Open circuit voltage</td>
</tr>
<tr>
<td>$H^+$</td>
<td>Ion</td>
</tr>
<tr>
<td>$h^+$</td>
<td>Hole</td>
</tr>
<tr>
<td>$v$</td>
<td>Frequency</td>
</tr>
<tr>
<td>$e^-$</td>
<td>Electron</td>
</tr>
<tr>
<td>$\eta_p$</td>
<td>Power conversion efficiency</td>
</tr>
<tr>
<td>$\eta_{p,max}$</td>
<td>Maximum power conversion efficiency</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength</td>
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</tbody>
</table>

Introduction
Solar energy driven water splitting combines several attractive features for energy utilization. The energy source of the sun and the reactive media of water are readily available and renewable, and the resultant fuel of hydrogen and reactant fuel of water are each environmentally clean. Since Fujishima and Honda [1] proved that water can be effectively cleaved into its constituents on a photoelectrode covered with n-type TiO$_2$ semiconductor, considerable attention has been devoted to the photodecomposition of water as an alternative solar energy conversion process leading to a non-polluting fuel.

The operating principle [2] is simple. A photoelectrochemical (PEC) cell consists of a semiconductor anode and a metal counter cathode immersed in an aqueous electrolyte. When light is incident on the semiconductor, it absorbs part of the light and generates free electrons ($e^-$) in the conduction band and free holes ($h^+$) in the valence band. The electrons and holes are separated due to the energy from the solar incident at the interface of semiconductor and electrolyte. The holes stay at the surface of anode and react with water to produce oxygen. The electrons travel through the external circuit and arrive at the surface of cathode to combine with the ions (H$^+$) to generate hydrogen. The complete reaction is absorption of the photons and splitting of water into hydrogen and oxygen. The complete reaction is as below:

\[
\text{Solar : } 2hv \rightarrow 2h^+ + 2e^- \tag{1}
\]

\[
\text{Anode : } 2h^+ + H_2O_{(aq)} \rightarrow \frac{1}{2}O_2(g) + 2H^+_{(aq)} \tag{2}
\]

\[
\text{Cathode : } 2e^- + 2H^+_{(aq)} \rightarrow H_2(g) \tag{3}
\]

Solar photons having energy greater than the energy band gap, $E_s$, are absorbed by the semiconductor and generate free electrons ($e^-$) in the conduction band and free holes ($h^+$) in the valence band. The electrons and holes are separated due to the energy from the solar incident at the interface of semiconductor and electrolyte. The holes stay at the surface of anode and react with water to produce oxygen. The electrons travel through the external circuit and arrive at the surface of cathode to combine with the ions (H$^+$) to generate hydrogen. The complete reaction is absorption of the photons and splitting of water into hydrogen and oxygen.

Licht [3, 4] recently proposed a model to increase the hydrogen production efficiency. While the short wavelength energy from the sun is used for PEC conversion, the long wavelength energy is used for heating the reactor to lower the water-splitting potential. This provides a process of highly efficient elevated temperature solar electrolysis of water to hydrogen fuel. The semiconducting material is characterized by the energy band gap [5]. Only that part of incident solar radiation having energy higher than the energy band gap
can be absorbed by the semiconducting material. Therefore, the spectral distribution of solar insolation should be taken into account along with electrode material when designing a PEC cell.

However, most studies on PEC production of hydrogen have focused on the development of photoelectrode materials. Little attention has been paid to the study of thermodynamics in photon-to-electron, theoretical power conversion efficiency and photocurrent density from the sun. It is the purpose of this work to investigate these effects of a PEC hydrogen generation and provides some guiding principle for designing the PEC system.

### Analysis and Results

**Analysis of the thermodynamics combined with electrochemistry for water splitting**

Fig. 1 shows the electrochemical potential of the splitting of water into hydrogen and oxygen as function of temperature and pressure. At the standard state, the potential needed to dissociate water is $V_{\text{H}_2\text{O}} = 1.229\text{V}$. The potential for splitting water is obtained as [6]:

$$V = \Delta G/nF$$

(4)

where $\Delta G$ is the Gibbs free energy change and $F$ is the Faraday constant. For $V_{\text{H}_2\text{O}} = 1.229\text{V}$, $\Delta G$ is 237.1 kJ/mole.

As the cell temperature and pressure are increased, $V_{\text{H}_2\text{O}}$ is decreased. At the critical point of water ($p = 221\text{bar}$, $T = 647\text{K}$ and $\Delta G = 186.76\text{kJ/mole}$), $V_{\text{H}_2\text{O}}$ is decreased to 0.968V. Thus, the maximum increase in efficiency by raising the temperature and pressure is 21.2% compared to that at the standard state.

**Analysis of the energy loss during the process of solar-to-electrons**

The energy used for splitting water is calculated from the spectral solar energy of AM1.5 [7]. It is integrated as below:

$$E = \int_\lambda E_{\lambda}\text{d}\lambda$$

(5)

There is an interesting physics during the process of solar-to-hydrogen. For photons with energy higher than the energy band gap, $E_g$, they can be absorbed by the photo-anode to split water. However, the excess energy, $E - E_g$, will be lost. This excess energy is called "relaxes" [8]. Unless some physical process can be used to hold the electrons at the excited state, this excess energy is usually converted into heat on the electrode surface.

Figure 2 shows the total and effective excited energy from solar irradiation for different energy band gap materials. As the value of band gap is increased, the excited energy is decreased. The value of the total excited energy is 615.7 W/m² for 1.5eV, 366.5 W/m² for 2.0eV, 179.9 W/m² for 2.5eV and 61.5 W/m² for 3.0eV. In contrast, the value of the effective excited energy is 434.7 W/m² for 1.5eV, 292.0 W/m² for 2.0eV, 155.5 W/m² for 2.5eV and 55.7 W/m² for 3.0eV. The relaxes can be used to heat the reactor and should be taken into account in thermal analysis of PEC cell.

The total excited energy can be viewed as a thermodynamically “internal energy” and the effective energy as the “Gibbs energy”. Therefore, only a fraction of the total excited energy can be converted into electric energy. This is part of the reason why the potential of a PEC cell is never as high as the band gap potential.

**Effect of the I-V curve in the PEC cell**

The solar induced current-voltage characteristic of a PEC cell is shown in Fig. 3. The spectral solar energy is calculated from AM1.5. The output power of the PEC cell is the product of current and voltage. The fill factor [9] of the PEC cell is defined as:

$$\text{Fill Factor} = \frac{I_{sc}V_{oc}}{(I_{mp}V_{mp})}$$

(6)

where $I_{sc}$ and $V_{oc}$ are the current and voltage at the maximum power point, and $I_{mp}$ and $V_{mp}$ are the short circuit current and the open circuit voltage.

The solar power conversion efficiency is defined as [9]:

$$\eta_p = \frac{P_{mp}}{P_{in}N_{sun}}$$

(7)

where the maximum efficiency is defined as $\eta_{p,max} = \frac{P_{mp}}{P_{in}}$. For the maximum efficiency, the operating point of the PEC cell should be close to the maximum power point of Fig. 3, which corresponds to the band gap of 1.12eV. The maximum power conversion efficiency, $\eta_{p,max}$, is 44.07%. For the case of TiO₂ (~3.2eV) and Fe₂O₃ (~2.1eV), the power conversion efficiency is respectively 2.8% and 21.9%. Therefore, materials with a band gap close to 1.12eV would give higher $\eta_p$.

**Analysis of the maximum photo-current density from the sun (AM1.5)**

The number of solar photons from the sun (AM1.5) at each wavelength and the corresponding integrated photo-current density are shown in Fig. 4. The solar photons are absorbed by the photo-anode up to the energy band gap and converted into one electron per photon in the external circuit. Thus, the maximum photocurrent density with the different energy band gap can be calculated as in Fig. 4.

If every absorbed photon produces one electron, the maximum photo-current is 63.75 mA/cm². For TiO₂ (~3.2eV) and Fe₂O₃ (~2.1eV), the maximum photocurrent density is respectively 0.68 mA/cm² and 10.43 mA/cm². In comparison, Cao et al. [10] studied the nanoporous TiO₂ film electrodes under 250 W xenon lamp with pH = 13.22 NaOH solution. The photo-current was measured to be 0.11 mA/cm². Kay et al. [11] used a thin film of silicon-doped Fe₂O₃ under illumination of AM 1.5 sunlight of 1000 W/m² in 1 M NaOH, the photocurrent was measured to be 2.2 mA/cm².

Because the conversion efficiency of photon-to-electron (also called quantum efficiency) is usually low, measured photo-current density is often smaller...
experimentally than theoretical values. Thus, the most effective way to increase the photo-current is to increase the quantum efficiency.

**Conclusion**

The thermodynamic analysis of a photoelectrochemical hydrogen production system has been investigated theoretically. Effects of several characteristics from solar on a PEC cell are studied.

As the cell temperature and pressure are increased, the potential for splitting water could be decreased. The maximum increase in efficiency is to be 21.2% compared to that at the standard state. The energy loss during the process of solar-to-electrons should be paid to attention. As the value of band gap is decreased, the relaxes energy are increased. This energy should be considered to heat the PEC cell.

For the power conversion efficiency and photo-current density, the maximum power efficiency and photo-current of a PEC cell is 44.07% and 63.75 mA/cm\(^2\). For the case of TiO\(_2\) and Fe\(_2\)O\(_3\), the maximum power conversion efficiency is 2.8% and 21.9%, and maximum photo-current is 0.68 mA/cm\(^2\) and 10.43 mA/cm\(^2\), respectively.

![Figure 1](image1.png)  
**Figure 1** Electrochemical potential of water splitting to hydrogen and oxygen with different temperature and pressure

![Figure 2](image2.png)  
**Figure 2** Total and effective excited solar energy with different energy band gap, and the free energy of water with different temperature

![Figure 3](image3.png)  
**Figure 3** The solar current-voltage characteristics of a PEC cell. The maximum power conversion efficiency is 44.07% at band gap of 1.12eV.

![Figure 4](image4.png)  
**Figure 4** Number of photons from the sun (AM1.5) [7] and the corresponding integral photo-current density with different wavelength
Reference


