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## Thermodynamic Analysis of the Efficiency of Photoelectrochemical CO<sub>2</sub> Reduction to Ethanol

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### Abstract

Over the last decades, long-term fossil fuel shortage and growing global demand for energy ignited an interest in developing alternative and “green” approaches for fuel production. One promising way to generate solar fuels is photocatalytic or photoelectrochemical (PEC) CO<sub>2</sub> reduction. Although various research efforts were undertaken to improve the efficiency and stability of PEC devices, many questions remain that have not been adequately answered due to lack of understanding of the reaction mechanisms and underlying limiting factors. In this study, we illustrate the thermodynamics of single or double-junction photo-absorbing materials. Finally, this research work investigated the efficiency limits of solar-driven CO<sub>2</sub> conversion into ethanol as a two-step process with formate as intermediate.

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## 1. Introduction

Global population and economical growth have led to an enormous growth for energy demand. Fossil-based fuels such as coal, oil and natural gas currently supply the majority of world's energy needs. However, dramatic changes in climate throughout the world have been primarily attributed to the increased anthropogenic carbon dioxide (CO<sub>2</sub>) emissions produced by burning of fossil fuels [1]. This has put the focus on exploring alternative energy resources and employ net-zero-CO<sub>2</sub> emission processes. Conversion of CO<sub>2</sub> into fuels using solar energy is a very promising approach to simultaneously address both global warming and increased energy demand.

Photocatalytic and photoelectrochemical (PEC) CO<sub>2</sub> reduction systems, also known as artificial photosynthetic cells, mimic natural process of plants that use CO<sub>2</sub> and water as a raw materials and energy from sunlight to carry out the energy-requiring reactions [2]. In artificial photosynthetic systems, photo-absorbing materials are considered the most crucial components [3] because they generate electron-hole pairs under illumination that drive oxidation and reduction reactions. A large number of photo-absorbing materials have been investigated since Halmann [4] in 1978 reported the first PEC cell based on a p-type gallium phosphide photocathode through which CO<sub>2</sub> was converted into fuels. Although many research efforts have been focused on the development of highly active semiconductor-based photocatalysts [5, 6], solar-driven CO<sub>2</sub> reduction efficiencies are still very low. Generally, the photo-absorbing material must have a suitable band gap not only large enough to provide electrons but also small enough to enable efficient visible light absorption. Moreover, the potential of the conduction band must be more negative than the CO<sub>2</sub> reduction potential, while the valence band must be more positive than the water oxidation potential [2]. Thus, one of the most critical issues in this field is to find the optimal band gap of a photo-absorbing material or a combination of photo-absorbing materials for multi-junction cells [7].

In this study, the main objective was the calculation of the thermodynamic solar-to-fuel (STF) and applied bias solar-to-fuel efficiencies of CO<sub>2</sub> reduction to fuels as a function of band gaps of photo-absorbing materials. Specifically, we focused on PEC CO<sub>2</sub> reduction to high-energy fuels such as ethanol because it is considered a very promising approach to an ethanol-based economy [8]. In addition, the optimal band gap that is required to achieve maximum CO<sub>2</sub> photo-reduction to ethanol for single or double junction photo-absorbers was identified. The thermodynamic efficiency limits for a single-step 12-electron transfer CO<sub>2</sub> photo-conversion into ethanol was investigated and compared with a two-step process with formate as intermediate. In this way, it was highlighted the importance of a deeper understanding of CO<sub>2</sub> photo-reduction mechanism and reaction pathways.

## 2. Methodology

For this study, a web-based model (WBM) of Seger and co-workers was used to perform our calculations [9, 10]. This software focuses on the photocatalyst performance and simulates the thermodynamic performance of PEC systems for several light-driven reactions such as water splitting and CO<sub>2</sub> reduction. This modelling tool allows the simulation of the thermodynamic behaviour of semiconductor-liquid junction cell using diode equation. Besides the optical properties and bandgap of the photoabsorber, this software provides the option to input several electrochemical parameters for the calculation of the STF efficiency limits. The following equation, which is the basis of this model, shows that a photoelectrochemical reaction is possible only if the potential provided by the photocatalyst is equal or greater than the thermodynamic potential ( $E_{Therm}$ ) plus any other losses:

$$\sum_1^n E_{PV}(j) \geq E_{Therm} + \eta_{Red}(j) + \eta_{Ox}(j) + E_{Ionic,Res}(j) + E_{Elec,Res}(j) - E_{Bias}(j) \quad (1)$$

where  $n$  denotes to number of photoabsorbing materials,  $j$  is current density (A cm<sup>-2</sup>),  $\eta_{Red}$  is the reduction overpotential (V),  $\eta_{Ox}$  is the oxidation overpotential (V),  $E_{Ionic,Res}$  is the losses due to ionic resistance (V),  $E_{Elec,Res}$  is the losses due to electric resistance (V), and  $E_{Bias}$  represents any additional external bias used (V) [9]. In this study, the current density is calculated by the diode equation [9, 11]:

$$j = j_{Limit} - j_0 \times \left( \exp\left(\frac{q(V + j\Omega_{Series})}{kT}\right) - 1 \right) - \frac{(V + j\Omega_{Series})}{\Omega_{Shunt}} \quad (2)$$

where  $j_0$  is defined as:

$$j_0 = M_{user} \times qA \frac{2kT}{h^3 c^2} \times \left( E_g^2 + 2kTE_g + (kT)^2 \right) \times \left( \exp\left(\frac{-E_g}{kT}\right) \right) \quad (3)$$

In equations (2) and (3),  $J_{Limit}$  represents the maximum theoretical photocurrent density for a given amount of absorbed photons ( $A \text{ cm}^{-2}$ ),  $j_0$  is the dark saturation current density ( $A \text{ cm}^{-2}$ ),  $q$  is equal to elementary charge ( $1.602 \times 10^{-19} \text{ C}$ ),  $V$  is the photovoltage (V),  $\Omega_{Series}$  and  $\Omega_{Shunt}$  represent the series and the shunt resistance respectively ( $\text{Ohm cm}^{-2}$ ),  $M_{user}$  represents a factor equal to multiple of the minimum theoretical dark saturation current,  $A$  is an indicator of the number of the emitted surfaces of a material ( $A=2$  for a material because it has two sides),  $k$  is the known Boltzmann's constant ( $8.617 \times 10^{-5} \text{ eV K}^{-1}$ ),  $T$  is the temperature (K),  $h$  is the constant of Planck ( $4.136 \times 10^{-15} \text{ eV s}$ ),  $c$  is the speed of light ( $3 \times 10^8 \text{ m s}^{-1}$ ) and  $E_g$  is the band gap (eV).

Finally, the STF efficiency is calculated from the current using the following equation:

$$STF(E_g) = \frac{j \times E_{Therm} \times FE}{P_{in}} \times 100\% \quad (4)$$

where STF is the cell efficiency at a given band gap ( $E_g$ ),  $E_{Therm}$  is the thermodynamic potential needed for the electrochemical reaction, FE is the faradaic efficiency and  $P_{in}$  is the incident solar power. To determine the theoretical limits of STF efficiencies of photoelectrochemical  $\text{CO}_2$  reduction cells, the following conditions and parameters were assumed:

- Illumination with the AM 1.5G standard spectrum
- Temperature of 298 K
- Electrolyte resistance is ignored
- Negligible ohmic resistance, anodic and cathodic overpotential and ionic losses
- Unity Faradaic Efficiency for each product
- It was selected a purely theoretical approach option for the photo-absorber
- It was used diode equation for the photovoltage calculation
- Complete absorption of all photons above the band gap of the semiconductor
- Ideal position of conduction and valence band in perfect match with reduction and oxidation potentials of each electrochemical reaction

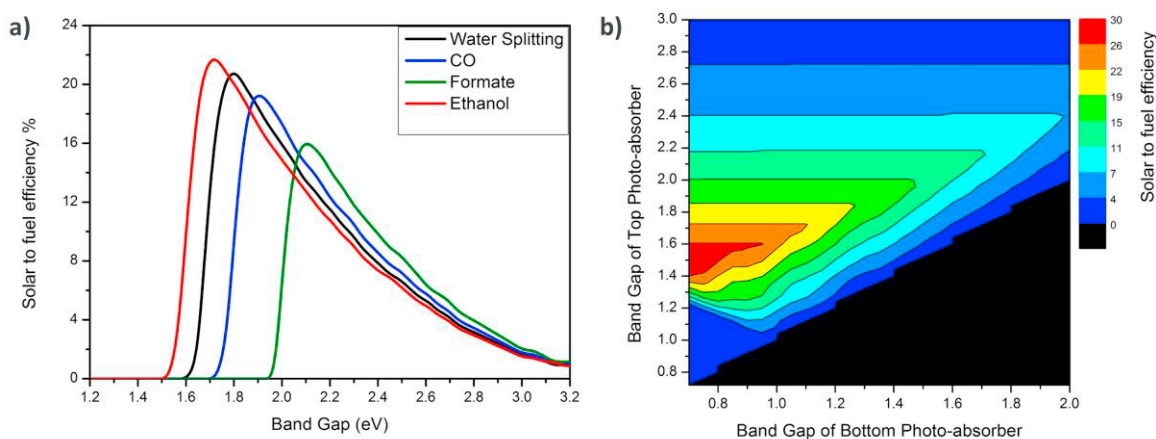
Table 1. Standard potentials related to  $\text{CO}_2$  reduction and water oxidation with reference to Normal Hydrogen Electrode (NHE) at  $\text{pH}=0$  [12].

Reaction	$E^0$ vs. NHE at $\text{pH} = 0$	Eq.
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0 V	(5)
$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{e}^- + 4\text{H}^+$	-1.23 V	(6)
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOO}^- + \text{H}^+$	-0.31 V	(7)
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}$	-0.11 V	(8)
$2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \rightarrow \text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O}$	0.08 V	(9)

### 3. Results and Discussion

#### 3.1. Theoretical limits of CO<sub>2</sub> reduction to ethanol via a single-step multi-electron transfer

Thermodynamically, the energy needed for converting CO<sub>2</sub> and H<sub>2</sub>O into ethanol is 1.15 V, which was calculated using Eq. (6) and (9) of Table 1. An approach with a single photo-absorber was investigated for CO<sub>2</sub> reduction to CO, formate and ethanol. It was found that an optimal band gap photo-absorber of 1.73 eV can achieve STF efficiency of 21.9% as shown in Fig 1a. The energy required for converting CO<sub>2</sub> to ethanol is lower than that needed to convert CO<sub>2</sub> to formate (1.54 V) and CO (1.34 V). Thus, theoretical limits of STF efficiency for formate and CO formation reach 19.4% and 16.2%, respectively. Additionally, Fig. 1b shows the thermodynamic STF efficiency for a PEC CO<sub>2</sub> reduction to ethanol system using an ideal double junction photo-absorber. In this case, the maximum STF efficiency of 29.6% is obtained with top and bottom photo-absorber's band gaps of 1.48 eV and 0.75 eV, respectively.



**Fig. 1** a) Theoretical limits of STF efficiency vs band gap for a single multi-electron transfer step of CO<sub>2</sub> reduction into several fuels in comparison with water splitting reaction. b) Theoretical limits of STF efficiency of CO<sub>2</sub> reduction to ethanol via a single 12-electron step as a function of band gaps of an ideal double junction photo-absorber.

#### 3.2. Theoretical limits of CO<sub>2</sub> reduction to ethanol via a two-step multi-electron transfer

However, CO<sub>2</sub> reduction to Ethanol is a 12-electron reaction and it is considered a multi-step process involving multiple reaction intermediates and pathways. Thus, multi-step CO<sub>2</sub> reduction process via formation of intermediates is more realistic. So far, several mechanisms have been proposed and investigated in experimental and computation CO<sub>2</sub> reduction studies. Although there are still controversies regarding the mechanisms of CO<sub>2</sub> reduction into alcohols, the formation of the following three intermediates has been proposed in the literature as the initial 2-electron mechanistic steps [13-16]:

- Carbon monoxide (CO\*) intermediate - Redox mechanism
- Formate (HCOO\*) intermediate – Formate mechanism
- Carboxylic acid (COOH\*) intermediate – Carboxylic acid mechanism

A plausible route for the formation of ethanol is that its formation is initiated after some formate is already formed via a 2-electron reduction step (Eq. 10). Then, formate in turn can be further reduced to ethanol via multi-electron uptake step (Eq. 13). In parallel, water serves as electron and proton donor (Eqs. 11 and 13). Thermodynamically, the energy needed for 2-electron CO<sub>2</sub> conversion to formate is 1.54 V (Eq. 12), while the overall reaction for 8-electron formate conversion into ethanol requires 0.95 V (Eq. 15). In addition, half-reduction and oxidation reactions of the overall two-step process are presented analytically in Table 2.

Table 2. Proposed mechanistic steps for CO<sub>2</sub> photoreduction to ethanol assuming that formate is main intermediate product. Standard potentials related to CO<sub>2</sub> reduction and water oxidation with reference to Normal Hydrogen Electrode.

Reactions	E <sup>0</sup> vs. NHE at pH = 0	Eq.
<i>A first step where CO<sub>2</sub> is reduced to HCOO<sup>-</sup></i>		
Half Reaction (Reduction) : 2CO <sub>2</sub> + 4H <sup>+</sup> + 4e <sup>-</sup> → 2HCOO <sup>-</sup> + 2H <sup>+</sup>	-0.31 V	(10)
Half Reaction (Oxidation) : 2H <sub>2</sub> O → O <sub>2</sub> + 4H <sup>+</sup> + 4e <sup>-</sup>	-1.23 V	(11)
Overall Reaction : 2CO <sub>2</sub> + 2H <sub>2</sub> O → 2HCOO <sup>-</sup> + O <sub>2</sub> + 2H <sup>+</sup>	-1.54 V	(12)
<i>A second step where HCOO<sup>-</sup> is further reduced to C<sub>2</sub>H<sub>5</sub>OH</i>		
Half Reaction (Reduction) : 2HCOO <sup>-</sup> + 10H <sup>+</sup> + 8e <sup>-</sup> → C <sub>2</sub> H <sub>5</sub> OH + 3H <sub>2</sub> O	+0.28 V	(13)
Half Reaction (Oxidation) : 4H <sub>2</sub> O → 2O <sub>2</sub> + 8H <sup>+</sup> + 8e <sup>-</sup>	-1.23 V	(14)
Overall Reaction : 2HCOO <sup>-</sup> + H <sub>2</sub> O + 2H <sup>+</sup> → C <sub>2</sub> H <sub>5</sub> OH + 2O <sub>2</sub>	-0.95 V	(15)

The maximum theoretical solar to fuel efficiency of the two-step process simulation (CO<sub>2</sub> → HCOO<sup>-</sup> → C<sub>2</sub>H<sub>5</sub>OH) is 1.7% for a single photo-absorber with band gap of 2.12 eV, as shown in Fig. 2a. Nevertheless, there is one way to increase the theoretical STF efficiency of the PEC system. Breaking up the CO<sub>2</sub> reduction process into separate steps offers the option to perform each reaction step on different photocatalyst and different operation conditions such as temperature, pH and pressure etc. Thus, a photo-reactor with two subsequent chambers can allow running each multi-electron transfer step of the aforementioned reaction on two different photo-absorbers. In the best case scenario of a photo-absorber with a band gap of 2.08 eV for the first reaction chamber (CO<sub>2</sub> → HCOO<sup>-</sup>) and a photo-absorber with band gap of 1.72 eV for the second reaction chamber (HCOO<sup>-</sup> → C<sub>2</sub>H<sub>5</sub>OH), the overall solar to fuel efficiency reached 3.6%. Finally, it was investigated the effect of additional bias on the efficiency. Specifically, WBM program can be used for the calculation of the maximum efficiency as a function of photo-absorber's band gap by subtracting the applied external voltage from the required thermodynamic potential of a given reaction. In Fig. 2b, it can be clearly seen that the application of an external bias enables efficient PEC CO<sub>2</sub> conversion into ethanol for photo-absorbing materials having a wider range of band gap.

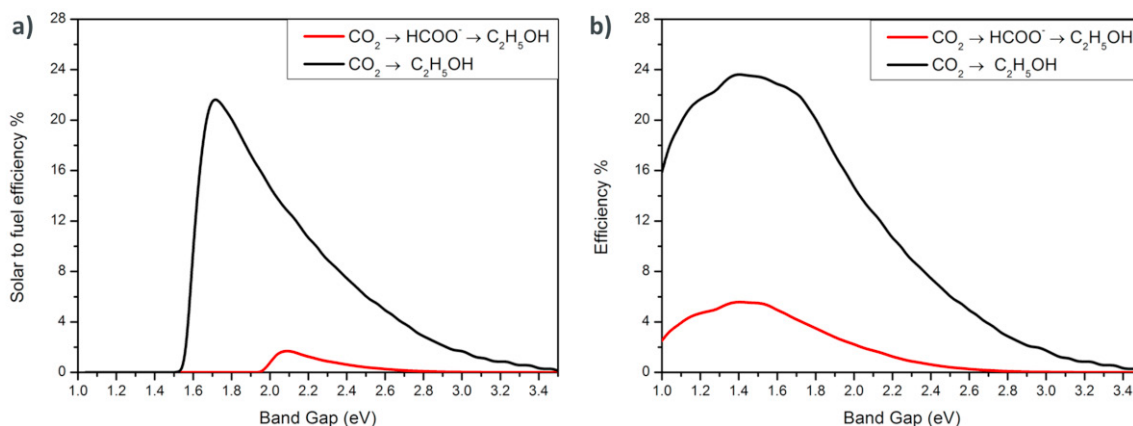


Fig. 2. a) Theoretical limits of STF efficiency vs band gap for CO<sub>2</sub> reduction to ethanol assuming that formate is the only intermediate product without and b) with applied bias.

#### 4. Conclusions

Although solar-driven CO<sub>2</sub> reduction into fuels such as ethanol attracts more and more attention, a little progress has been done in the clarification of the fundamental mechanisms and reaction pathways of this process. Thus, the main aim of this study is to provide a starting point of thermodynamic hypotheses that will assist in a deeper understanding of the highly endothermic reaction steps of CO<sub>2</sub> conversion into fuels. In summary, it was presented

the thermodynamic STF efficiencies of single or double-junction photo-absorbers under ideal conditions for CO<sub>2</sub> conversion into ethanol. Finally, we illustrated a study of the efficiency limits of PEC CO<sub>2</sub> conversion into ethanol of a proposed two-step multi-electron transfer process with formate as intermediate with and without external applied bias.

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