



How to achieve the desired performance of solar water splitting with voltage biases



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ABSTRACT

This work demonstrates how to set efficiency benchmarks in photo-electrochemical measurements for solar water splitting with assistance of voltage biases. We modify the applied bias photon-to-current efficiency to circumvent the existing limitations for precisely estimating the energy transformation efficiency under valid conditions. The light sources, surface area of counter electrodes, and oxygen content in electrolytes, and photo-anode materials are changed to investigate their impact on the energy transformation efficiency. This work clarifies that a larger counter electrode surface area results in the enhancement of the oxygen reduction reaction, reducing the applied bias voltage but also reducing the hydrogen generation rate. Furthermore, positive potential biases on the photo-anode and removal of dissolved oxygen molecules in the electrolyte are effective to promote the hydrogen generation rate because of efficient electron/hole separation and the ORR elimination. Due to the high photocurrent generated by the ultraviolet light source, the consumption of photocurrents by the ORR is generally negligible. Therefore, a balance between photocurrent and applied potential bias on the photo-electrochemical cell is proposed to achieve the desired energy transformation efficiency.

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1. Introduction

Splitting water into hydrogen and oxygen via the renewable energy sources such as solar energy, wind power, wave power, *etc.* is an ideal way to transform these energy sources into chemical energy. From a comparison of these energy forms, solar water splitting directly converting the solar energy into chemical energy without additional steps of energy transformation is considered an advantage although the efficiency of solar-to-hydrogen energy transformation is generally low [1,2]. Therefore, hydrogen evolution involving photocatalytic (PC) and photo-electrochemical (PEC) cells are still at the stage of fundamental research. In addition, separation of electron–hole pairs generated on the photo-anode subjected to solar radiation has been found to be enhanced by voltage biases [2,3], which makes the feasibility of solar water splitting into hydrogen and oxygen although the applied electricity has to be carefully considered.

Solar water splitting has been widely investigated for hydrogen generation since Fujishima and Honda demonstrated this process with the assistance of potential bias for solar hydrogen production in 1972 [4]. In order to promote the separation of electron–hole pairs produced in the charge-pair generation step, minority

charge carriers generated under illumination are driven to the n-type semiconductors/aqueous solution interface as a result of the electric field formed at the semiconductors/aqueous contact. In addition, majority carriers recombine at ohmic contacts that connect the photo-electrodes, or are transferred to a metal/anode and carry out the complementary photo-electrolysis step [2]. Therefore, these electrons are continuously moved to the cathode to generate hydrogen under potential biases. The left positively charged holes in the valence band are more positive than the equilibrium potential of oxygen evolution and can oxidize water to evolve oxygen [2,5]. Therefore, one of/both the electrode processes are accelerated by the applied voltage in order to meet the practical demand.

Through massive PEC studies, several equations corresponding to the photo-energy conversion efficiency for solar water splitting have been established. However, to date, researchers have not reached an agreement on estimating the energy transformation efficiency. The PEC studies consist of several uncertain operation and environment factors, including artificial light sources [6], light absorption in electrolytes [7], illumination areas and angles [8], *etc.* Consequently, a lot of energy transformation efficiency indeed are overestimated due to the above uncertainties. It is important to build reasonable benchmarks for efficiency estimation to precisely compare/relate to other works (see Supporting Information on “Equations for estimating the solar energy transformation efficiency”).

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With applying a voltage bias on the PEC cell, an energy-conversion efficiency index, e.g., applied bias photon-to-current efficiency (ABPTCE, Eq. (1)), has been proposed to gain the energy conversion information [9].

$$ABPTCE = \left[\frac{|j_{ph}(\text{mA cm}^{-2})| \times (1.23 - |V_b|)(V)}{P_{total}(\text{mW cm}^{-2})} \right] \times 100\% \quad (1)$$

where j_{ph} is the photocurrent under an applied voltage bias, V_b . This equation does not consider the Faradaic efficiency even though a modified equation in the literature mentioned an undefined Faradaic efficiency of hydrogen evolution (η_F) [10]. Hence, j_{ph} would be counted as the water splitting current for hydrogen generation. This assumption is practically unsuitable because the ORR is a thermodynamically favorable competition reaction on the cathode, especially when the photocurrent generated under the solar irradiation is low.

This work proposes a “modified applied bias photon-to-current efficiency” (denoted as mABPTCE) to accommodate the above issues of efficiency overestimation, voltage/potential bias application, light source, and photo-current, etc.

$$\begin{aligned} mABPTCE &= \frac{(j_{ph} - i_d) \times 1.23 - j_{ph} \times V_b}{P_{total}} \times 100\% \\ &= \frac{j_{ph} \cdot \eta_F \times 1.23 - j_{ph} \times V_b}{P_{total}} \times 100\% \end{aligned} \quad (2)$$

where i_d is the diffusion current density of the ORR and $\eta_F = (j_{ph} - i_d)/j_{ph}$ (Faradaic efficiency of hydrogen evolution). Since oxygen molecules from the air and generated from the anode are always present in the solution, leading to photocurrent consumption, the Faradaic efficiency on the cathode has to be carefully considered to correctly estimate the energy transformation efficiency in the PEC process. Although the usage of an ion-exchange membrane between the anode and cathode can avoid the ORR effect due to dissolved oxygen from the anode, the iR drop becomes an additional issue. Hence, the porous diaphragm film is a preferable separator but cannot prohibit the diffusion of dissolved oxygen molecules. Since the onset potential of the HER is much more negative than that of the ORR, the relatively small current for hydrogen generation can be simply considered to be $j_{ph} - i_d$. On the other hand, if the photocurrent is equal to/lower than the ORR diffusion current (i_d), there is no photocurrent available for hydrogen generation, which is suitable for the photo-catalytic degradation of organics [11,12] but not for the water splitting process. In this work, four variables: light source, exposed surface area of Pt cathode, dissolved oxygen in the electrolyte, and photo-anode materials are changed to demonstrate the impact of PEC variables on the evaluation of ABPTCE and mABPTCE, which are very important for practical PEC cell design and process evaluation.

2. Results and discussion

2.1. Photo-electrochemical characteristics of a TiO_2/Pt system

Fig. 1 clearly demonstrates the PEC characteristics of a photo-anode of TiO_2/Ti and Pt1 as the working and counter electrodes, respectively under the standard solar light irradiation. In Fig. 1a, visible photocurrents are obtained on the solid line as photo-electrode potentials are more positive than -0.02 V (*versus* RHE) comparing with the background current measured under dark (dash line). The photocurrents are exponentially increased with the positive polarization between -0.02 and 0.3 V; and gradually increased with the positive shift in the electrode potential, reaching *ca.* $370 \mu\text{A}/\text{cm}^2$ at 1.6 V. From curve 2 in Fig. 1b, the measured cell voltages are negative when the electrode potentials of TiO_2/Ti are negative than 0.07 V, due to the very positive electrode potentials of Pt (see curve 1). This positive electrode potential is due to

the formation of Pt oxy-hydroxide because of the exposure of Pt in air after cleaning and aqueous media. Since all Pt electrodes have been pre-cleaned at 2.0 V and -0.4 V for 3 times, active superficial Pt atoms are easy to react with oxygen and/or water [13]. With the continuous supply of electrons, Pt oxy-hydroxide is gradually reduced, resulting in the negative shift of the Pt electrode potential. The shoulder visible on curve 1 from 0.7 to 0.5 V is attributed to the reduction of $\text{Pt}(\text{OH})_2$ [14], further supporting the above statement. An unobvious shoulder on curve 1 is also visible between 0.3 and 0 V, reasonably attributable to the hydrogen adsorption on Pt [15]. Then, hydrogen evolution starts at *ca.* -0.2 V and a slightly negative shift in the electrode potential on Pt with the positive shift of the photo-anode potential is visible. Accordingly, the generated photocurrents are used to reduce the superficial Pt oxy-hydroxide and render the under potential deposition (UPD) of hydrogen atoms before hydrogen evolution. Because of the above reduction reactions with the positive shift of the photo-anode potential, the cell voltage (see curve 2) is gradually increased from -1.25 V to *ca.* -0.6 V and a shoulder wave is visible at *ca.* -0.5 V, corresponding to the reduction of $\text{Pt}(\text{OH})_2$ on curve 1. Most importantly, hydrogen evolution commences at an applied cell voltage of *ca.* 0.24 V which is much lower than the thermodynamic equilibrium voltage of water splitting (1.229 V at 25°C). Accordingly, solar irradiation is effective to reduce the electric energy required for water splitting. Moreover, due to the very high activation overpotential of oxygen evolution in water electrolysis (e.g., *ca.* 0.35 – 0.45 V on RuO_2 , NiCo_2O_4 , etc. [16,17]), the above photo-electrochemical water splitting process should save more energy in comparison with the process of water electrolysis.

Fig. 1c shows the dependence of ABPTCE on the applied cell voltage since the electrolyte has been pre-purged with nitrogen gas for 1 h before the photo-electrochemical measurement. Therefore, consumption of photocurrents by the ORR is negligible. Note that when the photocurrents start to generate hydrogen, the APTCE value becomes meaningful. When the cell voltages are larger than 1.23 V, the APTCE values become negative. Accordingly, the APTCE values are given in the cell voltage range from 0.24 to 1.23 V. From Fig. 1c, the APTCE value starts from 0.022% at a cell voltage of 0.24 V, reaches a maximum value of 0.115% at the applied cell voltage of *ca.* 0.65 V, and then decays gradually with the increase of the cell voltage. Also note that the maximum APTCE occurs at the cell voltage of 0.65 V, corresponding to the photo-anode potential of 0.3 V (*versus* RHE). Due to the exponential increase in the photocurrent with the positive shift in photo-anode potentials from -0.02 to 0.3 V (see Fig. 1a), the increase in photocurrents is more effective than the decrease in the difference between 1.229 V and the applied cell voltage before reaching the maximum ABPTCE. Therefore, if the PEC water splitting process is conducted under the maximum APTCE condition, the hydrogen generation rate is about $190 \mu\text{A}/\text{cm}^2$ (based on TiO_2/Ti) which is much lower than that at a cell voltage of 1.23 V (*ca.* $280 \mu\text{A}/\text{cm}^2$, corresponding to *ca.* 0.65 V *versus* RHE for the photo-anode).

Fig. 1 shows the ideal situation of electrochemical photocatalytic water splitting and four variables: light source, surface area of Pt cathodes, without and with dissolved oxygen molecules in the electrolyte, NaOH concentration, and photo-anode materials (*i.e.*, TiO_2/Ti and ZnO/FTO), are investigated to correctly estimate the solar energy transformation efficiency. An index, “mABPTCE” is proposed to correctly evaluate the solar energy transformation efficiency from the PEC process.

2.2. PEC performances of a TiO_2/Pt system

Fig. 2a shows the potential-photocurrent curves measured under AM 1.5 G solar light illumination by LSV, in which curves 1 and 2 refer to the measurements where the cathodes are Pt1 and Pt2,

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