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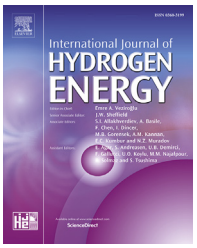

Influence of design and operating conditions on the performance of tandem photoelectrochemical reactors

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ABSTRACT

Solar-driven photoelectrochemical water splitting technology is a promising avenue for a sustainable hydrogen production. In this work, a comprehensive 2-dimensional model is developed and numerically simulated with hematite (α-Fe_2O_3) as the principal photoelectrode. The model evaluates light absorption, charge transport and electrochemical reactions to elucidate the effects of light transmitting materials, electrolyte height and electrolyte velocity on hydrogen and oxygen gas production. Results indicated that major losses in photocurrents are attributed to the transparent conducting oxide while losses due to the electrolyte increase with its height. Gas concentrations increase with increasing photocurrent densities and also in the direction of the flow. Gas bubbles however decrease with increasing electrolyte velocity. From these results, light reception in the reactor is uneven and poses a bigger challenge due to the bias in gas bubble distribution. Prospects of upscaling tandem schemes hence not only lie in the semiconductor material combinations but rather in the proper integration of system components and operating conditions.

Introduction

The world today is predominantly reliant on conventional energy systems whose resource base continues to diminish due to the finite nature of majority of them. Most of these resources are also associated with the uncovering of the long buried carbon which causes detrimental impacts on the environment due to the release of carbon dioxide (CO_2) when oxidized. Alternative energy supply systems such as the renewable energy systems which seek to counter this dilemma are also ridden with other challenges associated with their intermittency. Hydrogen (di-hydrogen) is the smallest molecule and one of the most abundant element on earth that could open new frontiers for future energy systems. The most unfortunate fact however is that it does not exist in its natural form but rather is imbedded in other materials [1] requiring its extraction before use.

Sustainable hydrogen production can be achieved through photobiological conversion of biomass [2], photocatalysis, photoelectrochemical and also through solid state hydrolysis reaction of hydrides [3,4] processes. Indeed the latter has the potential of coupling both production and storage of hydrogen in one-step regenerative cycle [5–8]. Photoelectrochemical (PEC) hydrogen production using solar energy as a driving

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force to split water is a promising way of delivering hydrogen as an energy carrier. The combination of solar energy and water makes the best regime which is purely free of emissions and has minimal anticipated supply uncertainties in the foreseeable future. Besides, only a single conversion device is required, making the system more compact and easier to focus on its efficiency improvements.

The decomposition of water into hydrogen and oxygen is rather straightforward, where under neutral conditions, the associated reactions at the electrodes (anode and cathode) and the overall reaction can be expressed as follows;

Self ionization of water $H_2O \Leftrightarrow OH^- + H^+$ (1)

Anode $2OH^- \rightarrow H_2O + \frac{1}{2}O_2 + 2e^- (E^0 = 0.81V)$ (2)

Cathode $2H^+ + 2e^- \rightarrow H_2 (E^0 = -0.42V)$ (3)

Overall $H_2O \rightarrow \frac{1}{2}O_2 + H_2 (E = 1.23V)$ (4)

Under standard conditions, the minimum photon energy (or the net work done) required to decompose water into oxygen and hydrogen is 1.21 eV for a closed cell (where V, T = constant) or 1.23 eV for an open cell (where P, T = constant). The two are respectively equivalent to the change in Helmholtz's free energy ΔA° = 233.1 kJ/mol and Gibb's free energy $\Delta G^\circ = +237.2$ kJ/mol [9]. In the case of a PEC, the reactor is usually an open system and the second case applies. The change in Gibb's free energy can be expressed in terms of electrical energy from, $\Delta G^\circ = -nFE$, where, F is the Faraday's constant (96,485 C/mol) and E is the ideal potential difference which translates to an equivalent of 1.23 V [10] considering that two electrons are involved in the reaction process. Thermodynamically however, a minimum voltage of 1.48 V based on enthalpy change (ΔH° = 285.8 kJ/mol) at standard conditions of 1 bar and 25 °C would be required to overcome the associated high entropies.

From a semiconductor point of view, one or more suitable semiconductor material can provide this minimum required voltage when illuminated by sunlight. However, most semiconductor materials are not properly aligned to easily achieve water splitting. As one of the principal requirements, the semiconductor's conduction band edge should be more negative than the reduction potential of H^+/H_2 (0 V vs RHE) while the valence band edge should lie more positive than the oxidation potential of H_2O/O_2 (1.23 V vs RHE) [11,12]. This requirement limits the use of small bandgap semiconductors which can absorb most of the visible spectra of the incoming solar radiation. Secondly, most relatively stable medium bandgap semiconductor materials corrode in aqueous environments. As such, most PEC cells work with some form of external or internal bias [13] with conventional electricity being the main source. This fact makes the efforts of decoupling PEC technology from CO_2 emissions a challenge.

A combination of two semiconductor materials as shown in Fig. 1 could eliminate external biasing making PEC operation completely free of CO_2 emissions. This concept has been employed in tandem bi-photoelectrode (D4) systems to overcome the external voltage compensations.

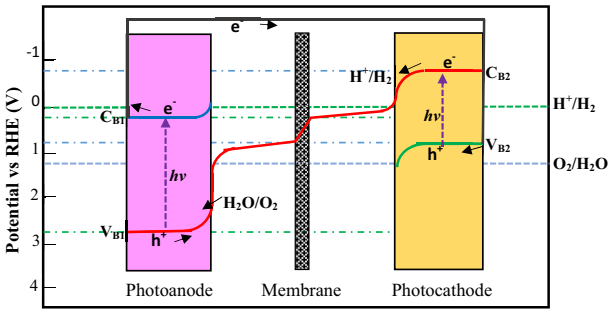

Fig. 1 – Energy level diagram of a bi-photoelectrode or tandem D4 PEC. C_B = conduction band edge energy, V_B = valence band edge energy, hv = photon energy and e^- = electron flow.

A wide range of semiconductor materials have been studied so far with photoanodes (n-type photoelectrodes) dominating most of the studies mainly because of their stability in aqueous conditions. The pioneer semiconductor material and most studied, titanium dioxide (TiO_2) coined by Fujishima and Honda [14] is highly handicapped due to its high bandgap (3.0–3.2 eV) and as such, only absorbs UV light which is only 4% of solar irradiation [10,15,16] resulting in very low efficiencies. Among other considerably studied photoanode semiconductor materials are, zinc oxide (ZnO), tungsten trioxide (WO_3), hematite (α-Fe_2O_3), bismuth vanadate ($BiVO_4$), tantalum oxynitride (TaON), tantalum nitride (Ta_3N_5) [17–23]. Hematite (α-Fe_2O_3) is particularly attractive because it has a small bandgap (2.1 eV), is abundant, environmentally friendly, cheap, stable, has high absorption efficiency [24–26] and is versatile in applications [26,27].

On the other hand, non-metal oxide semiconductor materials mainly derived from solar PV applications such as silicon (Si), indium phosphate (InP), gallium phosphide (GaP), gallium indium phosphide (GaInP), cuprous oxide (Cu_2O), cadmium telluride (CdTe), etc., are the major photocathodes (p-type photoelectrodes) known to date. These semiconductors offer high efficiencies due to their narrow bandgaps but they unfortunately suffer from photoelectrochemical corrosion under aqueous conditions [19,20,22,28,29]. Other semiconductor materials such as strontium titanate ($SrTiO_3$), potassium tantalate ($KTaO_3$), zinc sulphide (ZnS), gallium nitride (GaN), silicon carbide (SiC), among others have band edges that straddle the water redox potential [15,18,22] making them capable of splitting water without any form of biasing.

A considerable amount of numerical work has been demonstrated by several research groups albeit with many challenges. The works of Carver et al. gave a very thorough theoretical background to PEC simulation and design work [30]. Variations in potential across the electrode surface, associated electrode resistance and improvement strategies, reactor geometry design for effective electrolyte flow, effects of bubble formation have also been explored by several teams [30–33]. Key design considerations focusing on electrolyte height for both back-to-back series/tandem and side-by-side/parallel duo photoelectrodes have been explored by Haussener et al. [34]. Insights into transport phenomena, effects of

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