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Innovative technological configurations of photoelectrochemical cells

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Abstract

Solar hydrogen generation from direct photoelectrochemical (PEC) water splitting is the ultimate goal for a sustainable, renewable and clean hydrogen economy. Such electrochemical systems represent a prospective alternative to fossil fuel dependence since the photovoltaic technology may be combined with an electrolysis system to produce hydrogen. The major advantage of this approach is that energy capture, conversion and storage are combined in a single system. The working principle of PEC cells consists of two electrodes, a photoactive semiconductor material and a Pt-wire counter-electrode, both immersed in an electrolyte solution.

Nowadays, much of the research efforts are focused on solving the two main issues related to the photoelectrode materials, i.e. efficiency and stability, giving less attention to the technological problems. The present work aims to study different technological solutions envisaging a global efficiency enhancement of PEC devices, namely: different arrangements of PEC cells for improving H₂ from O₂ separation minimizing overpotentials and different temperatures.

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1. Introduction

The increasing public awareness concerning carbon dioxide emissions and the enhanced depletion of fossil fuel reserves motivates the development of technologies based on alternative energy sources.¹ ¹ With approximately 120 PW continuously striking the surface of the earth coming from the sun, the challenge in converting sunlight into electricity via photovoltaic (PV) solar cells is to reduce dramatically the cost per watt of delivered solar electricity.²

Nevertheless, due to the variability of daily solar radiation, an effective method to store energy for later dispatch is still needed.³ A practical way to convert sunlight into a storable energy form is using photoelectrochemical (PEC) cells for water splitting into hydrogen and oxygen by light-induced electrochemical processes.⁴

The principle of converting sunlight into hydrogen by water photoelectrolysis is illustrated in Figure 1. The photoelectrochemical water-splitting cell consists of a photoelectrode (semiconductor) that absorbs photons with sufficient energy to inject electrons from the valence to the conduction band of the semiconductor, creating electron-hole pairs. The holes oxidize water in the semiconductor surface, while electrons percolate through the
semiconductor layer and reach the counter-electrode, via the external circuit, to promote water reduction at its surface.\(^{[2, 6]}\) In alkaline media, the cycle is then closed when the electrolyte anions generated at the counter-electrode diffuse back to the surface of the semiconductor to recombine with holes. Currently, research efforts have been made on developing and understanding new composite nanostructures that address the challenges of solar photon capture and energy conversion. This approach is motivated by the inherent challenge of finding a single material that meets all the criteria needed to achieve efficient water splitting. However, less attention has been given to the role of different arrangements of PEC cells for improving H\(_2\) from O\(_2\) separation minimizing overpotentials and different temperatures of the cell. The PEC cell performance under these conditions was assessed based on the \(J-V\) characteristics curves in the dark and under simulated sunlight (AM 1.5, 1000 W·m\(^{-2}\)).

![Figure 1. Schematic representation of the relevant processes involved in the photo-hydrolysis of water in alkaline media.](image)

2. Experimental

**Preparation of Si-doped \(\alpha\)-Fe2O3 Photoanodes**

The samples of Si-doped hematite were prepared on F:SnO\(_2\) substrates by spray pyrolysis as described elsewhere.\(^{[7]}\) Briefly, a 10 mM Fe(III)acetylacetone solution in EtOH with 1 wt % TEOS as a dopant was sprayed onto a temperature controlled substrate at 400 °C with an ultrasonic spray nozzle from a distance of 30 cm. A total of 60 sprays (one every 30 seconds) at a flow rate of 12 mL·min\(^{-1}\) (spray length of 5 s) were used corresponding to a final film thickness of about 50 nm. A carrier gas flow (compressed air flow set to 15 L·min\(^{-1}\)) directed the spray towards the substrates.

**Photovoltaic Cell Setup**

For characterizing photoanode samples with a large active area a modular PEC cell was designed and built, made of acrylic material. As shown in Figure 2, the assembled PEC cell, named PortoCell, has two removable windows (front and back) made of black acrylic both screwed to an acrylic part forming the cell. The black acrylic part allows an illumination area of 4 cm\(^2\), crossing a synthetic quartz window (Robson Scientific, England) that is pressed against an o-ring by means of five screws. The total immersed photoanode’s active surface area is 4 cm\(^2\). A sample holder keeps the photoanode vertically aligned and facing the light beam perpendicularly. A 99.9 % pure platinum wire (Alfa Aesar\(^{®}\), Germany) was used as counter-electrode. For Si-doped \(\alpha\)-Fe\(_2\)O\(_3\) photoanode the cell was filled with an electrolyte aqueous solution of 1.0 M NaOH (pH 13.6).
**$I-V$ Measurements**

The photocurrent-voltage ($I-V$) characteristic curves were recorded for the Si-doped $\alpha$-Fe$_2$O$_3$ sample applying an external potential bias to the cell and measuring the generated photocurrent using a ZENNIUM workstation (Zahner Elektrik, Germany). The measurements were performed in the dark and under simulated sunlight (Oriel solar simulator, 150 W Xe lamp, AM 1.5 G, ~1000 Wm$^{-2}$, 25 °C) at a scan rate of 10 mV·s$^{-1}$ from 0.2 $V_{\text{RHE}}$ to 1.8 $V_{\text{RHE}}$. The light beam was calibrated with a c-Si photodiode. A standard three-electrode configuration was used with an Ag/AgCl/Sat. KCl as a reference electrode (Metrohm, Switzerland).

**3. Results and Discussion**

**3.1. Collection of the evolved gases**

The use of PEC cells to produce H$_2$ from solar energy and water represents a promising technology to overcome the fossil fuels dependence since hydrogen can be used as an energy vector. Nevertheless, H$_2$ is not the only product resulting from the water photohydrolysis and O$_2$ is produced simultaneously; it is then necessary to develop a practical approach for collecting these gases separately. This is even more significant for large-scale applications since mixtures of H$_2$ and O$_2$ present a significant explosion danger. In a PEC cell this can be obtained separating both electrodes with a membrane acting as a wall – Figure 3. This configuration takes advantage of the fact that the evolved gases are being produced separately, i.e. H$_2$ evolves from the cathode whereas O$_2$ is produced at the anode. Some studies suggest the use of ion exchange membranes to promote this separation. Nevertheless, these membranes significantly increase the ohmic resistance and the performance of the cell is negatively affected, besides being very expensive. In this work the authors suggest the use of a simple porous Teflon diaphragm, which exhibits a negligible ohmic resistance towards the ions diffusion and keeps the gases bubbles separate. Despite, in this arrangement the dissolved gases can freely cross the diaphragm and meet the opposite electrode.
The photoelectrochemical performances of Si-doped Fe₂O₃ photoanodes with and without a Teflon diaphragm are shown in Figure 4. The generated photocurrent in both cases is similar for the entire range of applied voltage, producing a maximum photocurrent of about 0.8 mA·cm⁻² at 1.45 V_RHE. Thus, as expected, there are no noticeable differences in the photocurrent produced when using the Teflon diaphragm.

3.2. Temperature effect

Under outdoor conditions the PEC cell arrangement is exposed to real atmospheric conditions as temperature, wind and humidity. When exposed to real solar radiation, the temperature of the PEC system should change as a function of the temperature of the air, wind speed and humidity and the solar irradiance. Thus, it is of great importance to know how the cell behaves when exposed as a function of the temperature, ranging from 25 °C to 35 °C. An experimental test bench, sketched in Figure 5, was designed and built. The temperature of the electrolyte was controlled using a water bath, which was continuously pumped in and out of the PEC cell – Figure 5. In the cell the electrolyte temperature and pH were controlled and monitored. The I-V characteristic curves were recorded for two temperatures, 25 °C and 35 °C, and the results shown in Figure 6.
As it can be seen from Figure 6 the overall performance of the cell increases with the temperature. A 10 °C increase originated 8 % increase in photocurrent density at 1.45 VRHE. This enhancement in the generated photocurrent is related to different phenomena occurring within the cell such as the decrease of the band gap energy, the mass transport that is favoured by the increase of temperature and finally at higher temperature the intrinsic carrier population, \( \eta_{\text{int}} \), also increases.[58]

4. Conclusions

It was proposed the separation of the hydrogen and oxygen evolutions using a porous diaphragm of Teflon. The Teflon diaphragm exhibited negligible overpotentials proving to be an attractive approach for keeping the gas bubbles separated. On the other hand, a Nafion membrane can separate as well the gas bubbles but also the dissolved gases but originates significant ohmic overpotential and is very expensive.

Finally, it was observed an 8 % increase on the photocurrent density of the silica-doped hematite photoanode when the temperature was increased from 25 °C to 35 °C.

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