

Dry hydrogen production by photoelectrochemical tandem cell (O-16H-V)

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1. Introduction

Photoelectrochemical hydrogen production is one of the most popular research subjects because it promises an effective route for converting solar energy and storing it as chemical energy in the form of hydrogen. Theoretically, 1.48 V (thermoneutral potential) are necessary to split water by electrolysis; however much higher voltages and expensive electrocatalysts are necessary. In this sense, water splitting by photoelectrolysis [1] is a very promising approach since it necessitates much lower electric bias or even none.

To achieve high solar to hydrogen (STH) conversion efficiencies [2] the choice of photoelectrodes and cell configuration (tandem or with dark electrode), in design of photoelectrochemical (PEC) cells [3], is of great importance.

For what concerns the backing layer of the top high-energy gap photoanode of the PEC cell, the main requisites are a high transmittance in combination with a high conductivity and proper work function. Usually, the anodic semiconductors are deposited on a conductive transparent glass: fluorine-doped tin oxide (FTO), indium-doped tin oxide (ITO) or antimony-doped tin oxide (ATO). Whereas, regarding the bottom photocathode backing layer, the most important requirements are high conductivity and proper work function if the intention is to use direct illumination only and no diffusive light. Thus, in this case, it is possible to use a dark metallic-type substrate with proper work-function to avoid junction effects [4].

This work addresses the use of a porous hydrophobic backing layer in a PEC cell to allow direct production of dry hydrogen.

2. Experimental

2.1 Photocathode substrates

A porous carbon paper named Spectracarb 2050A-1550 and a non-woven carbon paper containing a microporous layer that was made of 5 wt% polytetrafluoroethylene (PTFE) and carbon black named Sigracet 35BC were utilized.

Both Spectracarb and Sigracet are hydrophobic, however, for both substrates a further hydrophobisation treatment, with fluorinated ethylene propylene (FEP), was carried out to understand how this process could influence the electrical and wettability characteristics.

The procedure for the carbonaceous backing layer waterproofing consisted of different steps, particularly, the diving of the sample in a FEP solution, one layer (for Sigracet, the side with MPL) or both layers (full), for 1 min or 2 min or 5 min.

Afterwards, the obtained substrates were investigated in terms of electrical conductivity to preliminarily evaluate the effective possibility of using them as cathodic backing layers.

The most promising substrate, Sigracet, originally containing 5% of PTFE (subsequently named 0% of FEP) and further hydrophobised by a FEP treatment showing thus different FEP uptakes (e.g., 7% and 15% of FEP) were investigated in a complete tandem cell configuration. To compare these results with the state of the art, an FTO glass cathodic substrate was also examined.

2.2 Photoelectrochemical cell configuration

For the investigated PECs, only the cathode substrate was varied while the other components remained unchanged.

The tandem cell architecture thus consisted of:

1. photoanode: glass + FTO + Fe₂O₃ + NiFeO_x + ionomer
2. electrolyte: transparent FAA-3 anionic solid polymer membrane
3. photocathode: ionomer + CuO + conventional backing layer (FTO + glass) or porous hydrophobic backing layer (Sigracet) or (Sigracet + FEP addition)

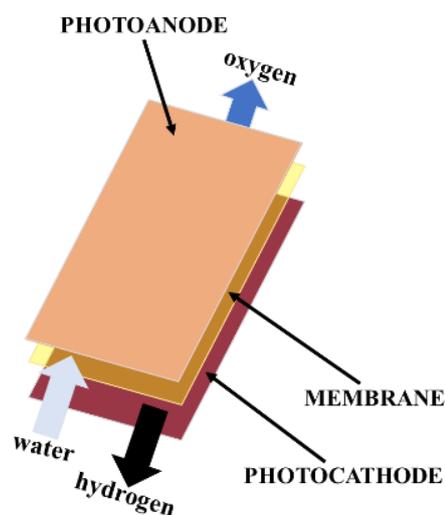


Fig. 1. Schematic sketch of the photoelectrochemical cell (PEC).

3. Results and Discussion

3.1 Photocathode substrates characterisation

Figure 1 shows a plot of electrical conductivity vs diving time.

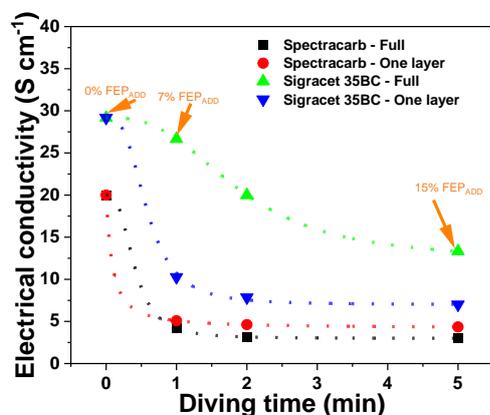


Fig. 2. Electrical conductivity vs diving time of different gas diffusion layers under different hydrophobisation conditions.

For the Spectracarb sample, the electrical conductivity was 20 S cm^{-1} without any treatment (0 min). After treatment with FEP, it was registered an important decrease of conductivity to about 5 S cm^{-1} , quite independently from immersion time, both for full and for one-layer immersion, whereas, for the Sigracet substrates, the conductivity decreased from about 30 S cm^{-1} , in the one-layer immersed sample, to about 10 S cm^{-1} , quite independently from the immersion time. In the full-immersed sample, the conductivity decreased to 27 S cm^{-1} after 1 min of immersion time, 20 S cm^{-1} after 2 min of immersion time and 13 S cm^{-1} after 5 min of immersion time.

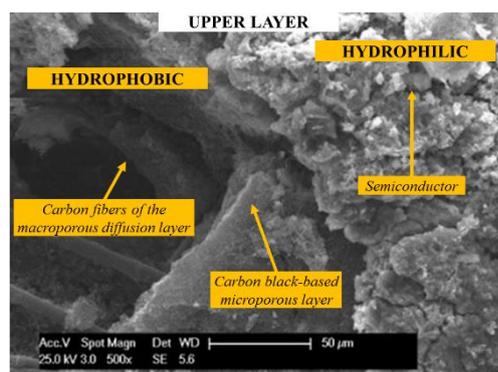


Fig. 3. SEM images of the upper layer of CuO semiconductor on a Sigracet 35BC gas diffusion layer containing 7% FEP.

The morphological characteristics of the backing layer based CuO photocathode are shown in Figure 3. Three different layers are clearly distinguishable from the inner to the outer parts: carbon fibers-based macroporous diffusion layer (hydrophobic layer), microporous carbon black layer (MPL) and CuO semiconductor layer (hydrophilic layer).

3.2 Photoelectrochemical cell characterisation

Figure 4 shows the photocurrent, $I_{\text{light}} (\text{AM } 1.5) - I_{\text{dark}}$, density variation as a function of the cell potential for the

complete photoelectrolysis tandem cells based on FTO and various porous hydrophobic carbonaceous backing layers as substrates for the photocathode.

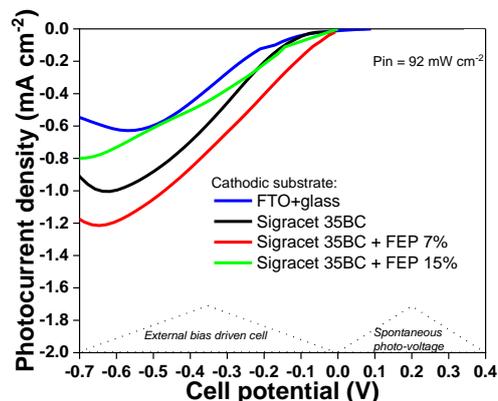


Fig. 4. Photocurrent density vs cell potential between -0.7 and 0.4 V in the photodiode representation mode an applied bias corresponds to a negative cell potential.

The photocurrent trend as a function of cell potential in Figure 4 shows the occurrence of a maximum photocurrent at a cell potential bias of about -0.6 V . It is evident that in the case of Sigracet + FEP 7% the level of photocurrent (-1.2 mA cm^{-2}) was the highest among the various samples throughout the entire range of interest.

A chronoamperometric test was carried out for the best performing PEC based on the Sigracet + 7 wt% FEP GDL with proper cell hydration (Figure 5). The cell was polarised at -0.6 V and the relative current density was recorded by varying the illumination conditions. The steady-state current density in the dark was less than $-20 \mu\text{A cm}^{-2}$ at -0.6 V , while it was about -1.1 mA cm^{-2} under illumination. The very low dark current suggests no side reactions are occurring at relevant extent. An appropriate stability was observed. Passing from dark to light and vice versa, the current variation shows a slight mismatching with light conditions due to the sampling range.

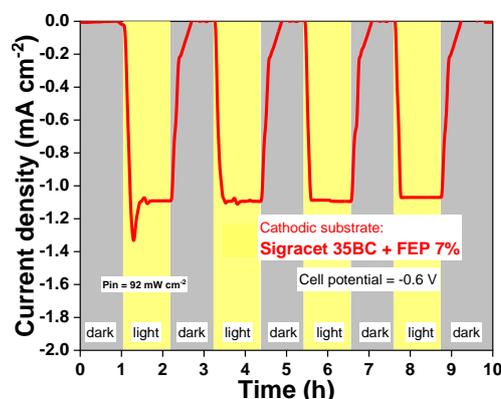


Fig. 5. Chronoamperometric test (applied cell bias of -0.6 V) of the PEC cells based on the hydrophobic backing layer.

To further validate the possibility of producing almost dry hydrogen in the output stream, we have placed a small piece of filter paper below the hydrophobic layer during the reported chronoamperometric test (Figures 6a,b). No traces

of humidity have been detected (Figure 6c).

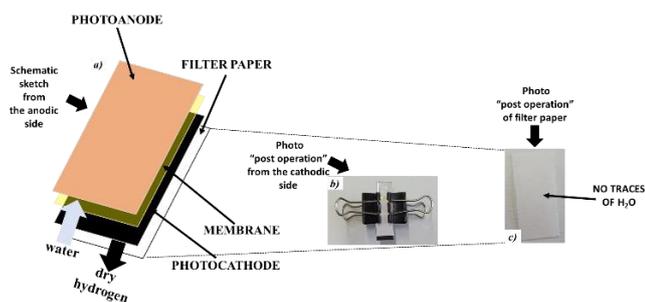


Fig. 6. Schematic sketch (a) and photograph (b) of the photoelectrochemical cell (PEC) with carbonaceous gas diffusion layer as cathode substrate and filter paper to highlight any traces of water (left); (c) photograph of filter paper “post operation”.

4. Conclusions

The concept of a porous hydrophobic carbonaceous backing layer as a photocathode substrate in a photoelectrolysis cell to get dry hydrogen is here demonstrated.

Two different carbonaceous gas diffusion layers based on low-cost carbon paper and carbon black, were hydrophobised and studied to achieve the best compromise between hydrophobicity and electrical conductivity.

These new porous hydrophobic substrates were demonstrated as cathodic gas diffusion layers in tandem n-Fe₂O₃ / transparent FAA-3 membrane / p-CuO photoelectrolysis cells.

A short-term durability test indicated a good stability of the cell as long as a good hydration of the membrane is assured.

The produced hydrogen appeared dried; no traces of humidity have been detected.

This concept was used for the design and construction of a 1 m² photoelectrochemical panel.

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