

Optimization and scaling-up of a photoelectrochemical cell for hydrogen production (O-14H-V)

C. Lo Vecchio^{1**}, S. Trocino¹, G. Giacoppo¹, O. Barbera¹, V. Baglio¹, M. I. Díez-García², M. Contreras², R. Gómez², A. S. Aricò¹

¹ Consiglio Nazionale delle Ricerche, Istituto di Tecnologie Avanzate per l'Energia "Nicola Giordano", CNR-ITAE, Via Salita Santa Lucia sopra Contesse 5, 98126 Messina, Italy

² Departament de Química Física i Institut Universitari d'Electroquímica, Universitat d'Alacant, Apartat 99, E-03080 Alicante, Spain

(*) Pres. author: carmelo.lovecchio@itaecnr.it

(**) Corresp. author: carmelo.lovecchio@itaecnr.it

Keywords: low-cost semiconductors, tandem cell, solar to hydrogen efficiency, Ni-based co-catalysts, PEC

1. Introduction

Nowadays, fossil fuels cover most of the world's energy demand worldwide. These fuels supply the energy needed by our industry and transportation sectors and provide energy for residential applications[1,2]. However, it is clear that these resources are not sustainable in the long term and cause climate change issues such as global warming through greenhouse gas emissions. Thus, there is an increasing interest in renewable energy sources' role in the future.

Photoelectrochemical (PEC) water splitting (WS) is considered the most promising solar process for hydrogen production and represents a proper backup solution to store energy[3,4]. The research on PEC WS relies on semiconductor electrodes that exhibit appreciable photogenerated charge separation at the solid/liquid interface when illuminated by sunlight. To the best of our knowledge, studies on PEC cells were conducted, even recently, in a liquid electrolyte, thus requiring post-processing energy to separate evolved gas from water splitting. Furthermore, the facile scalability of a PEC device could also be helpful for hydrogen-powered vehicles, which shall complement battery-powered vehicles, especially for long-range journeys.

In our recent works, tandem PEC cells were constituted by a solid polymeric membrane, acting as both gas separator and electrolyte, sandwiched between a photoanode (PA) and a photocathode (PC)[5–8]. Attention was focused on investigating non-critical raw materials (non-CRM) for the European Union (EU) in a 0.25 cm² PEC cell.

The most suitable tandem couple, achieved in a small cell area, was based on n-type P- and Ti-doped Fe₂O₃ photoanode and p-type CuO photocathode, including ionomer coatings as protective layers.

An anion-exchange membrane was optimized for PEC WS applications in a low-cost tandem cell. Furthermore, the use of a hydrophobized gas diffusion layer (GDL), as a substrate for the CuO photocathode, produced a relevant increase in efficiencies, doubling the performance of the conventional FTO photocathode substrate-based cell.

Herein, the pros and cons of scalable production of the main components of PEC cell, constituted of a PVC case, internal connectors, gaskets, photocathode/GDL, membrane, photoanode/drilled FTO, glass frame, current slab, and closure frame is reported.

2. Experimental

2.1 Synthesis of Photoelectrodes

Hematite-based photoanodes were prepared by a chemical bath deposition procedure followed by a thermal treatment. The modification with Ti was achieved by dip-coating and successive thermal annealing at 650 °C for 1 h in air. This treatment leads to a Ti-doped α -Fe₂O₃/FTO.

The optimized procedure for CuO/GDL photocathode was obtained in three steps: 1) spray deposition of metallic Cu over GDL; 2) chemical oxidation and 3) thermal treatment at 300 °C.

Home-made metallic Ni and NiCu were deposited on the CuO/GDL using a doctor blade technique. The photocathode was subjected to a second heat treatment at 300 °C for 1 h before ionomer deposition.

2.2 Assembly of the PEC cells

An anion exchange Fumasep membrane (FumaTech), with a geometric area of 1.1 x 1.1 cm² was assembled between photoanode and photocathode. Before the cell assembly, the membrane and photoelectrodes were soaked in pure water, thus providing the necessary water content for the photoelectrochemical reaction. A black insulating tape was used so that the photoactive area was 0.25 cm². Finally, the assembled cell was clamped with two paper clips for each side to provide sufficient pressure to secure all of the cell components. The PEC cell was tested in a solar simulator (Oriel) in a vertical position at 1.5 AM, corresponding to a power density of 92 mW cm⁻², as measured by a calibrated photovoltaic cell.

For the scaling up, current collectors were previously inserted into the plastic case; the H₂ gasket, the porous hydrophobic photocathode and the membrane were stacked. A drilled TCO glass supporting the photoanode and the relative gasket was settled down with the hematite electrode facing the membrane. Finally, a top gasket for preventing water/O₂ leakage was applied and compressed on the other stacked components through the plastic frame closure. The PEC was compressed using a torque wrench; the imposed torque was lower than 1 Nm per bolt.

2.3 Physicochemical Characterization

X-ray diffraction (XRD) patterns for powder co-catalysts were acquired with an X'Pert 3710 X-Ray diffractometer using a Cu-K α source operating at 40 kV and 20 mA. The morphology of the co-catalysts was studied by scanning electron microscopy (SEM) with a FEI-XL 30 SEM microscope.

2.4 Electrochemical Tests

Polarization tests were carried out by sweeping the potential between the open circuit potential (OCP) value up to a bias of -1.3 V, recording the current density of the PEC in the dark and under illumination.

Impedance spectra were performed in the bias-assisted region at -0.6 V under illumination to evaluate the kinetic and electrochemical effect of the PEC in comparison with the scalable prototype.

3. Results and discussion

3.1 Polarization measurements in 0.25 cm² PEC cell

To obtain suitable performance for the WS, the approach of using a co-catalyst based on Ni or NiCu at the cathode side was employed. Polarization curves illustrated in Figure 1 were carried out in the dark (dashed lines) and under illumination (continuous lines). Loadings of 8 or 12 $\mu\text{g cm}^{-2}$ were used for metallic Ni, and loading of 8 $\mu\text{g cm}^{-2}$ was tested for the NiCu alloy as a compromise between cost-effectiveness and performance. The bare PEC, without a co-catalyst, was investigated for comparison and was characterized by a lower value of the photocurrent density J_{ph} (difference between current density under illumination and in the dark) than those obtained with a Ni co-catalyst-based PEC.

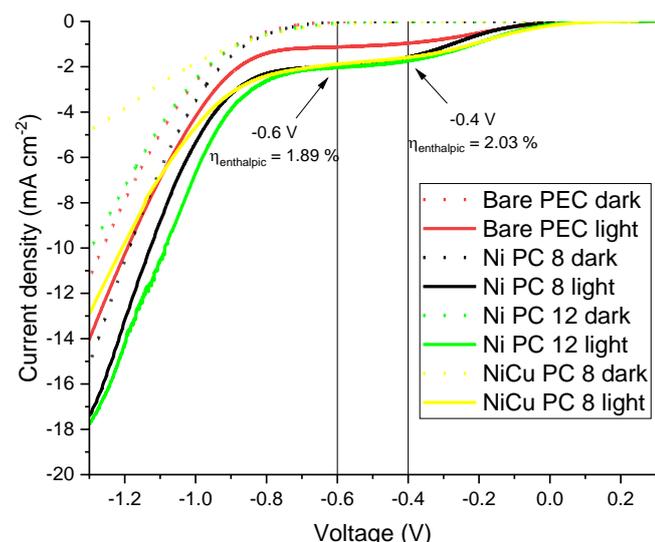


Fig. 1. Polarization curves in the dark and under illumination from 0.3 to -1.3 V.

Table 1 summarizes data of the photocurrent (J_{ph}), enthalpy (η_{enth}), and throughput ($\eta_{\text{throughput}}$) efficiencies for the best-performing cell, where a 12 $\mu\text{g cm}^{-2}$ Ni co-catalyst was added to the hydrophobized CuO/GDL photocathode. J_{ph} increases from 1.73 to 7.33 mA cm^{-2} in the potential range

from -0.4 V to -1.225 V. The enthalpy efficiency at -0.4 V reaches a maximum value of 2.03% and then decreases to 1.89% at -0.6 V as a result of the balance between the larger photocurrent and lower bias potential (E_{bias}). The throughput efficiency is a ratio between the power output and the overall power input (solar + electric) supplied by an external source; thus, it increases in the function of a larger J_{ph} achieving a maximum calculated at -1.225 V of 10.75%.

Table 1. Photocurrent density (J_{ph}), enthalpy efficiency (η_{enth}), and throughput efficiency ($\eta_{\text{throughput}}$) achieved by the addition of Ni co-catalyst to the photocathode.

V_{bias} (V)	J_{ph} (mA cm^{-2})	η_{enth} (%)	$\eta_{\text{throughput}}$ (%)
-0.4	1.73	2.03	2.76
-0.6	1.97	1.89	3.13
-1.225	7.33	2.03	10.75

3.2 Scaling up of the main components

A 25 cm² prototype was realized and electrochemically tested in the dark (dashed lines) and under illumination (continuous lines). The photocurrent and consequently the efficiency were in this case about 10 times lower than the 0.25 cm² lab cell. The main issues appear to be related to charge transfer at the photo-electrodes/electrolyte interfaces. A very high polarization resistance (R_p) for the 25 cm² PEC compared to the 0.25 cm² reference cell was displayed in EIS measurements. The final revision of the unit cell prototype was based on the GEMA concept (Glass Electrode Membrane Assembly). This approach improved the interfacial contact between membrane and photoelectrodes with a simplified current collection in the module.

4. Conclusions

A small amount of homemade Ni-based co-catalysts was deposited onto a CuO/GDL-based photocathode of a photo-electrochemical cell formed by Ti-and-P-doped hematite photoanodes and an anionic exchange membrane, used as a gas separator between the two electrodes. It appears that the use of the co-catalyst promotes hydrogen evolution under illumination with the achievement of 10.75% in throughput efficiency at -1.225 V. Pros and cons of the scalability for PEC prototype are presented and discussed.

Acknowledgements

The authors gratefully acknowledge funding from the European Union's Horizon 2020 research and innovation program under grant agreement no. 760930 (FotoH2 project).

References

- [1] Acar C, Dincer I. Investigation of a novel photoelectrochemical hydrogen production system. *Chemical Engineering Science* 2019;197:74–86. <https://doi.org/10.1016/j.ces.2018.12.014>.

- [2] Osterloh FE, Parkinson BA. Recent developments in solar water-splitting photocatalysis. *MRS Bulletin* 2011;36:17–22. <https://doi.org/10.1557/mrs.2010.5>.
- [3] Saravanan P, Khan MR, Yee CS, Vo DVN. An overview of water electrolysis technologies for the production of hydrogen. *New Dimensions in Production and Utilization of Hydrogen*, Elsevier; 2020, p. 161–90. <https://doi.org/10.1016/B978-0-12-819553-6.00007-6>.
- [4] Ferrero D, Santarelli M. Investigation of a novel concept for hydrogen production by PEM water electrolysis integrated with multi-junction solar cells. *Energy Conversion and Management* 2017;148:16–29. <https://doi.org/10.1016/j.enconman.2017.05.059>.
- [5] Lo Vecchio C, Carbone A, Trocino S, Gatto I, Patti A, Baglio V, et al. Anionic exchange membrane for photo-electrolysis application. *Polymers (Basel)* 2020;12:1–12. <https://doi.org/10.3390/polym12122991>.
- [6] Trocino S, Vecchio C lo, Zignani SC, Carbone A, Saccà A, Baglio V, et al. Dry hydrogen production in a tandem critical raw material-free water photoelectrolysis cell using a hydrophobic gas-diffusion backing layer. *Catalysts* 2020;10:1–23. <https://doi.org/10.3390/catal10111319>.
- [7] Lo Vecchio C, Trocino S, Giacoppo G, Barbera O, Baglio V, Díez-García MI, et al. Water splitting with enhanced efficiency using a nickel-based co-catalyst at a cupric oxide photocathode. *Catalysts* 2021;11. <https://doi.org/10.3390/catal11111363>.
- [8] Lo Vecchio C, Trocino S, Zignani SC, Baglio V, Carbone A, Díez-García MI, et al. Enhanced photoelectrochemical water splitting at hematite photoanodes by effect of a nife-oxide co-catalyst. *Catalysts* 2020;10. <https://doi.org/10.3390/catal10050525>.