Light assisted solar fuel production by artificial CO_2 Reduction and water Oxidation

Deliverable D5.3

Full Photoelectrochemical Cell

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EXECUTIVE SUMMARY

This public report, Full Photoelectrochemical Cell, is a deliverable of the LICROX Project which is funded by the European Union's H2020 Program under Grant Agreement No. 951843 and contains information about the coupling of the best photoanodes containing molecular water oxidation catalysts and organic photovoltaic cells (BVO-WOC-OPV) obtained in the project together with the best dark cathodes containing a combination of Cu-nanocubes and molecular Fe porphyrins as CO_2 reduction catalysts. We describe the main PEC parameter that successfully work with just sunlight in the absence of any other external bias, together with a qualitative analysis of products generated. Finally, an electrode scale up, up to a size of 10 cm^2 (5 cm x 2 cm) was also performed. Specific structures are not provided due to confidentiality issues, but a full description is to be found in the final confidential report.

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WP5. PEC implementation & validation

In WP5 the catalysts, semiconductors and light trapping strategies developed in WPs 2, 3 & 4 respectively, will be assembled together to build and test the performance of different PEC configurations. The implementation of the activities in this WP targets:
i) Assembly of the materials and optimal light trapping configurations into one single device by multi-layering or by stacking and connection through conductive materials;
ii) Assessment of the current output of the device upon simulated sun illumination; and
iii) Quantification of the chemical products obtained from the current output and determination of Faradaic efficiencies and solar to chemical energy efficiency.

The present report describes the Full Photoelectrochemical Cell achieved within the LICROX project. Report on the performance and comparison of the three Full PECs fabricated within Task 5.4 with configuration photoanode/OPV/photocathode. Unfortunately, the low stability of the photocathodes prevents its use in the device and therefore the device described here on is based on the photoanode/OPV/dark cathode configuration.

1. Structure and performance of the best dark cathode

The low stability of the photocathode prevented its incorporation into the Cell so that the best performing Cell was assembled using a dark cathode that was composed of two types of catalysts: a) Cu nanocubes (Cu-NC) combined with b) Fe-benzoporphyrins (Fe-TBTPP)[1] that are shown on the left hand side of Figure 1. The performance of this hybrid material Cu_{cub}/Fe-TBTPP with regard to the CO2R reaction as a function of the applied potential is shown in the right-hand side of Figure 1. As it can be observed at potentials close to -1.0 V vs. RHE, the hybrid electrode generates ethylene with close to 40% selectivity which is one of the targets of LICROX.

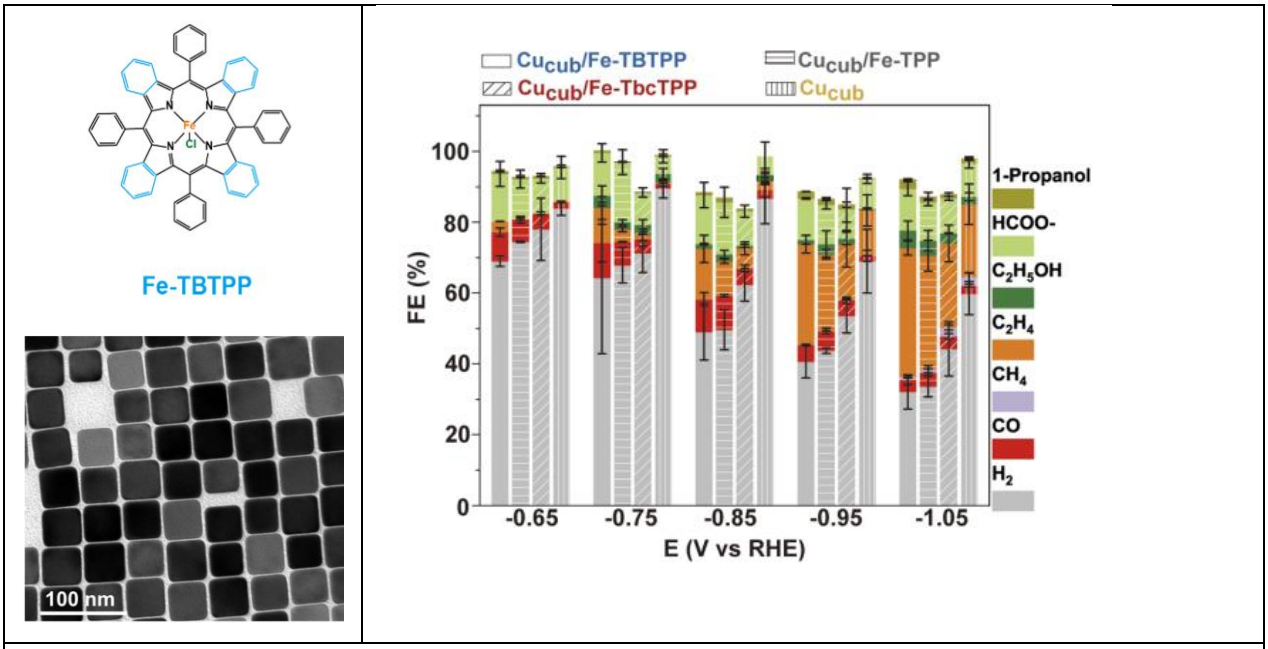

Figure 1. Left top, structure of the porphyrin molecular catalyst, Fe-TBTPP. Left bottom, Microscopy picture of the Cu nanocubes, Cu_{cub}. Right, CO_2 reduction product distribution as a function of applied potential for a series of Cu_{cub}/Fe-TBTPP.

2. Assembling the complete PEC cell: photoanode/OPV/dark cathode and its performance

The PEC measurements were carried out with custom methacrylate photoelectrochemical cell fabricated at ICFO workshop. This cell allows to control perfectly the intensity of the light that reaches the photoanode surface, putting no element in the light path aside of a quartz window and the liquid. Its modular construction consists of two compartments separated by Selemion AMVN membrane in a perpendicular direction to the light propagation path.

Next the performance of the whole cell was evaluated first taking into account the performance of the photoanode and the cathode independently. Finally, the coupled photoanode and cathode including the tandem cells were allowed to work under 1 sun illumination with no additional external bias and the results are shown in Figure 4. The gases generated at the headspace of the cathode after 4000 s were analyzed by GC (TCD for H_2 and FID for CO) showing the presence of H_2 and CO. A test with a rigorous gas-tight cell will be carried out to quantify them.

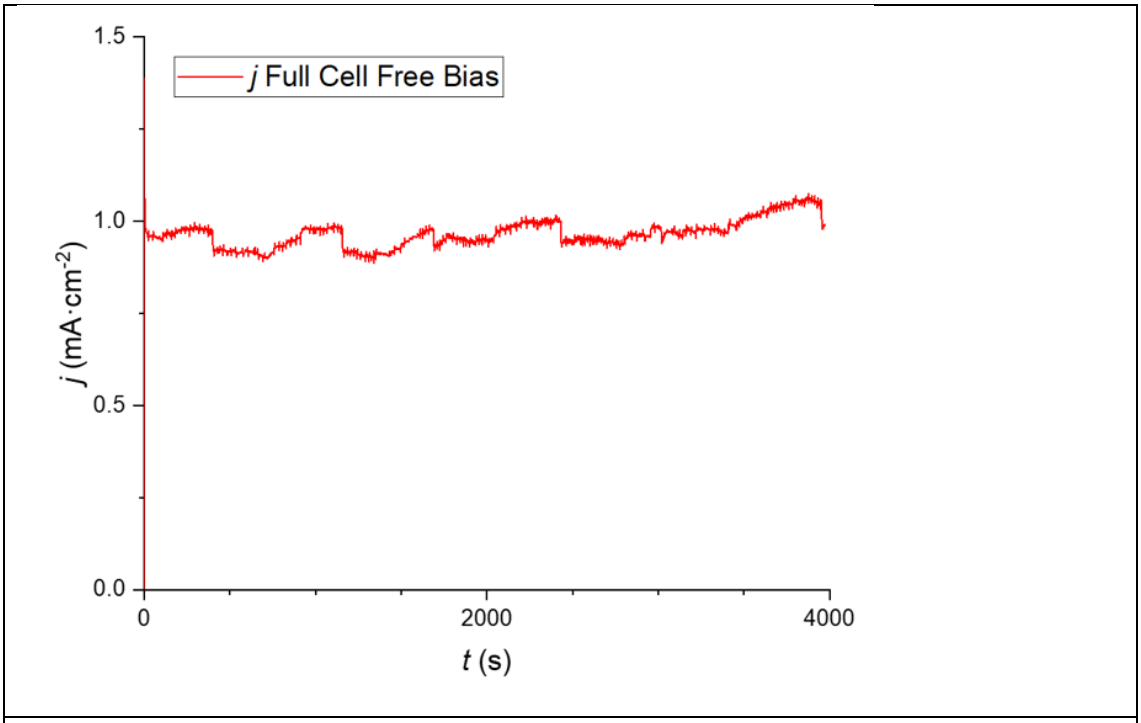

Figure 2. CPE at 0V (unbiassed) for 4000s with a two-electrode configuration under 1 sun illumination. Cathodic compartment: $KHCO_3$ 0.1M. Anodic compartment: phosphate buffer (I = 0.1M) pH 7.

3. Scale up of photoanodes and dark cathode

Both photoanodes BVO-WO_3, Mo-BVO and the dark cathodes Cu_{cub}-FeTBTPP were scaled up to 10 cm^2 (5 cm x 2 cm) displaying basically the same properties as the initial 1cm x 1cm materials as displayed in Figure 5 for the dark-cathode.

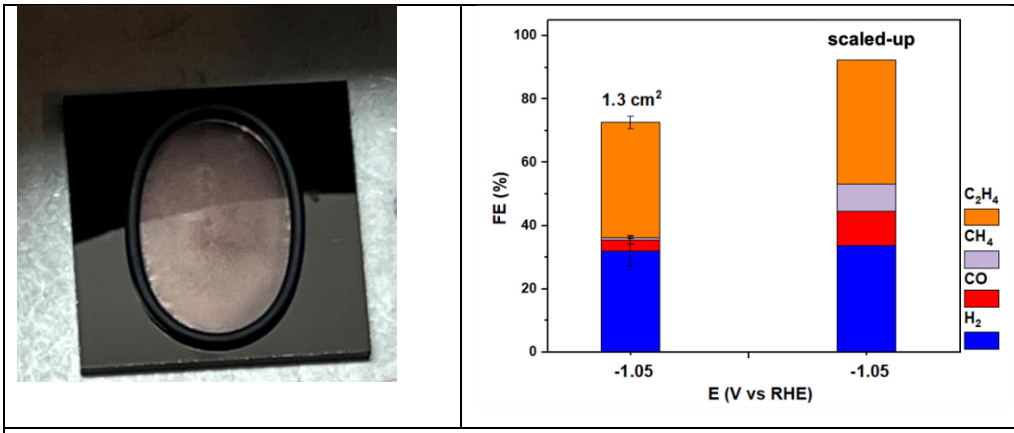

Figure 5. Left, photo of the scaled-up cathode evidencing the achieved homogeneity of deposition, which is important for reproducible performance. Right, CO_2 reduction product distribution for Cu_{cub}/Fe-TBTPP for the standard and for the scaled-up electrode. Both electrodes were prepared by dropcasting 20 ug/cm^2 of catalyst on glassy carbon via slow evaporation from THF.

4. Conclusions and future prospects

We have built a PEC based on the photoanode/OPV/dark cathode configuration that successfully works with sunlight in the absence of any external bias. In the presence of 1 sun it generates a steady current of 1 mA/cm^2 that generates H_2 and CO (they need to be quantified).

The performance of the cell can be improved by simply using a set of OPV that generate a 1.5 V cathodic shift at the photoanode. In this way the anodic part of the PEC will be perfectly aligned with the cathodic side to maximize the production of ethylene, that is one of the main objectives of LICROX.

5. References

[1] M Wang, V Nikolaou, A Loiudice, I D Sharp, A Llobet, R Buonsanti, *Chem Sci*. **2022**, 13, 12673-12680.