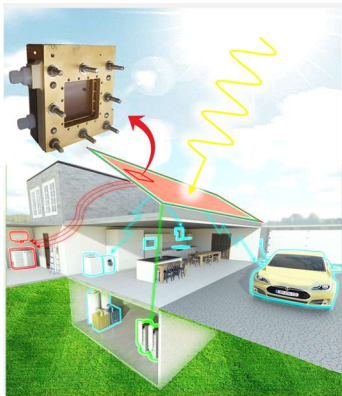


## Solar redox flow cell: cutting-edge technology for the production of cost-competitive solar fuels

ORAL/POSTER  
Ph.D. Student: N  
Journal: NONE

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A solar redox flow cell (SRFC) allows the conversion of sunlight into electrochemical storable energy and heat. These solar fuels can easily release the stored energy at a redox flow battery (RFB) as electrical power. The singularity of SRFCs to display overall energy conversion efficiencies of *ca.* 80 % is not achievable by any other technology. Although the use of a photoelectrochemical (PEC) cell is very attractive, since it uses a simple semiconductor | electrolyte junction, the truth is that SRFC devices remain at a low Technology Readiness Level (TRL) due to the low semiconductor efficiency, system durability, and lack of validated demonstrators. This talk will present the latest developments in the field: i) stable and efficient earth-abundant photoabsorber and catalyst materials; ii) high energy density redox pairs matching with the energy levels of the semiconductors; iii) optimized cell architectures suitable for large-scale solar fuels production; and iv) standardized methods for benchmarking device performance and stability.

### Introduction

The world needs a disruptive technology to quickly decarbonise the energy sector; the success of this technology critically depends on its social acceptance, sustainability, low-cost and fast implementation. Imagine a storing technology that mimics the energy strategy of the plants, *i.e.* harvests sunlight and stores it by driving thermodynamically uphill redox processes, providing a source of chemical energy in the form of electrochemical fuels. A solar redox flow cell (SRFCs) promises to be this technology, using a semiconductor-liquid junction photoelectrochemical (PEC) cell for solar charging redox pairs dissolved in liquid electrolytes.[1] Therefore, compared with other PEC devices (water splitting and CO<sub>2</sub> reduction), the SRFCs display the following advantages: i) the redox energy levels of the electrolytes can be tuned to fit the energy levels of the photoabsorber, rendering the system more efficient; ii) non-aqueous based electrolytes can be used to improve the stability and the stored energy density; iii) allows the simultaneous conversion of sunlight to an electrochemical fuel and thermal energy; iv) the electrochemical fuel-to-electricity efficiency at a redox flow battery (RFB) is much higher when compared *e.g.* with H<sub>2</sub> at a PEMFC; v) allows reducing CO<sub>2</sub> to chemical fuels, *e.g.* CO, ethylene or ethanol.[2]

It was only very recently that the full potential of SRFC technology was realised, though its background goes back to the 80s.[3] In 2020, Li *et al.*[4] reported a buried-junction SRFC using a tandem perovskite/silicon cell, displaying a maximum of *ca.* 19.7% solar-to-power conversion efficiency and a current density of *ca.* 15.8 mA·cm<sup>-2</sup>. Despite research efforts have seen progresses in the development of semiconductor materials and redox couples for increasing the solar-to-fuel conversion efficiency, little-to-no attention has been given

to experimental standardization, device architecture and photoelectrode upscaling, which is equally important in fuelling the development of SRFCs.

In this work, disruptive devices were designed, low-cost and stable photoelectrodes were upscaled, and standardized methods were proposed for measuring their (photo)electrochemical performance under dark and illuminated conditions and using two- and three-electrode configurations.

### Material and Methods

$\alpha$ -Fe<sub>2</sub>O<sub>3</sub> ultrathin films were prepared by ultrasonic spray pyrolysis (USP) following a previously reported in-house developed procedure[5]. USP and photolithography were used to produce substrates with high surface area and good electrical conductivity; higher surface areas were achieved by micro-structuring the glass substrate through laser ablation and chemical etching techniques - Figure 1.

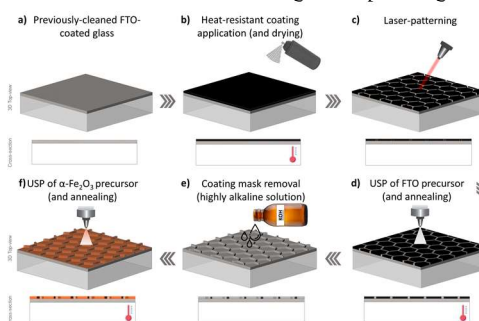


Figure 1. Schematics of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> films prepared.

Antraquinone-2,7-disulfonic acid disodium salt (2,7 AQDS, 97 %) and sodium hexacyanoferrate(II) decahydrate (98.5 %) were used to prepare the catholyte and anolyte aqueous solutions, respectively. Sodium

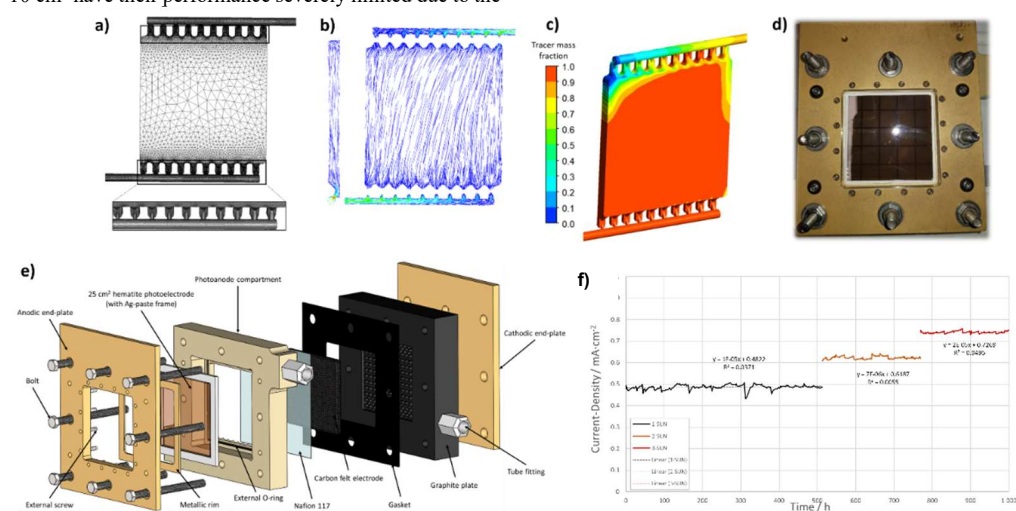
hydroxide solution (1 M) was the supporting electrolyte for the catholyte, and a 1 M sodium sulfate ( $\geq 99\%$ ) aqueous solution was chosen for the anolyte.

### Results and Discussion

To design a SRFC capable of the large-area photocharging of redox pairs, three main goals were set: i) the device should allow the photoelectrode to be used as a window of the cell and backside illuminated, for a maximized radiation absorption by the semiconductor; ii) an optimized and continuous electrolyte recirculation should be promoted to ensure effective diffusion and convection of the reacting molecules; iii) the counter-electrode and membrane should be positioned as close to the photoelectrode as possible, guaranteeing minimal ionic resistances. Figure 2 shows the optimized cell with an active area of  $25\text{ cm}^2$  - SolarFlow25.

Upscaling such devices is also a challenging task; e.g., only few deposition techniques can reliably produce photoelectrodes with uniform morphology. In addition, when the uniformity of the light-absorbing layer is not an issue, photoelectrodes with photoactive areas beyond  $10\text{ cm}^2$  have their performance severely limited due to the

high ohmic losses imposed by the transparent conductive oxides (TCOs) commonly used as substrates/current collectors. An increase in surface area is made possible by microstructuring the glass substrate, while conductivity is improved by using highly conductive fluorine-doped tin oxide (FTO) lines as stable current collectors. The width and geometry of such lines were optimized using a computational simulator until substrate conductivity and transparency were maximized. The PEC performance of ultrathin  $25\text{ cm}^2$  hematite photoelectrodes prepared using these substrates was evaluated through  $J$ - $V$  characteristic curves. A photocurrent density of ca.  $0.60\text{ mA}\cdot\text{cm}^{-2}$  (at  $1.45\text{ V}_{\text{RHE}}$ ) was recorded, which is ca.  $82\%$  of the photocurrent density of a similar  $0.52\text{ cm}^2$  photoelectrode. This optimized large-area photoelectrode remained stable for more than 1000 h under continuous PEC operation under different concentrated sunlight (up to 3-sun). This impressive result surpasses any previously reported current collector's stability by over 10-fold, avoiding the use of expensive and prone-to-corrosion metallic materials.



**Figure 2.** Details of the SolarFlow25 cell: a) mesh of the fluid body inside the cell, b) uniform upward electrolyte flow path, c) simulated tracer test results, d) prepared hematite sample assembled, e) expanded view of all cell components, f) stability test over 1000 h.

### Conclusions

The applicability of SRFC was demonstrated in a 1000 h stability test using the optimized  $25\text{ cm}^2$  hematite photoelectrode to photocharge a ferrocyanide/anthraquinone chemistry. These studies provided important guidelines to build the first upscaled SRFC ever – SolarFlow25 cell. The device was architected to minimize electronic and ionic transport resistances commonly found in large-area PECs, showing an unprecedented solar-to-output-electricity-efficiency and stability. The present communication will also present other emerging strategies to overcome the SRFC challenges, paving the way for their commercialization.

### Acknowledgements

P. Dias, T. Lopes, and F. Francisco are grateful to FCT for funding (references: CEECIND/02862/2018, SFRH/BD/146338/2019, and SFRH/BD/147426/2019, respectively). This work has received funding from Project ASAPFuels - PTDC/EQU-EQU/4225/2021 funded by FEDER, through COMPETE2020 and by national funds, through FCT; and by LA/P/0045/2020 (ALiCE), UIDB/00511/2020 and UIDP/00511/2020 (LEPABE), funded by national funds through FCT/MCTES (PIDDAC).

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