

SELECTIVE SUN-DRIVEN OXIDATION OF CELLULOSIC BIOMASS DERIVATIVES FOR THE SYNTHESIS OF ADDED VALUE CHEMICALS



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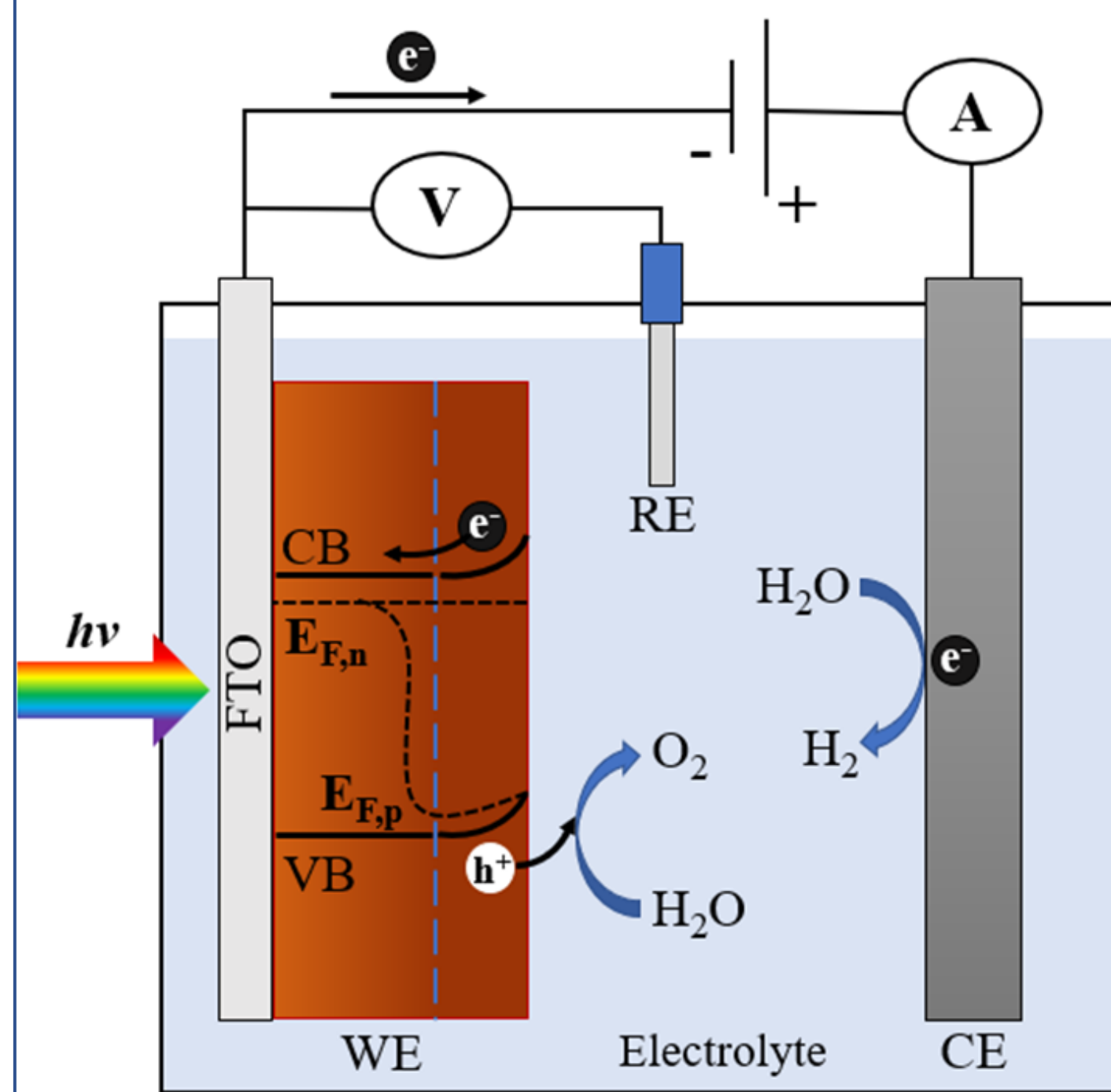
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This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101006839

Solar energy and photoelectrosynthetic cells



Sun-driven oxidative chemistry aimed at the preparation of high-value chemicals of industrial or pharmaceutical interest is one of the most interesting applications of photoelectrosynthetic cells.

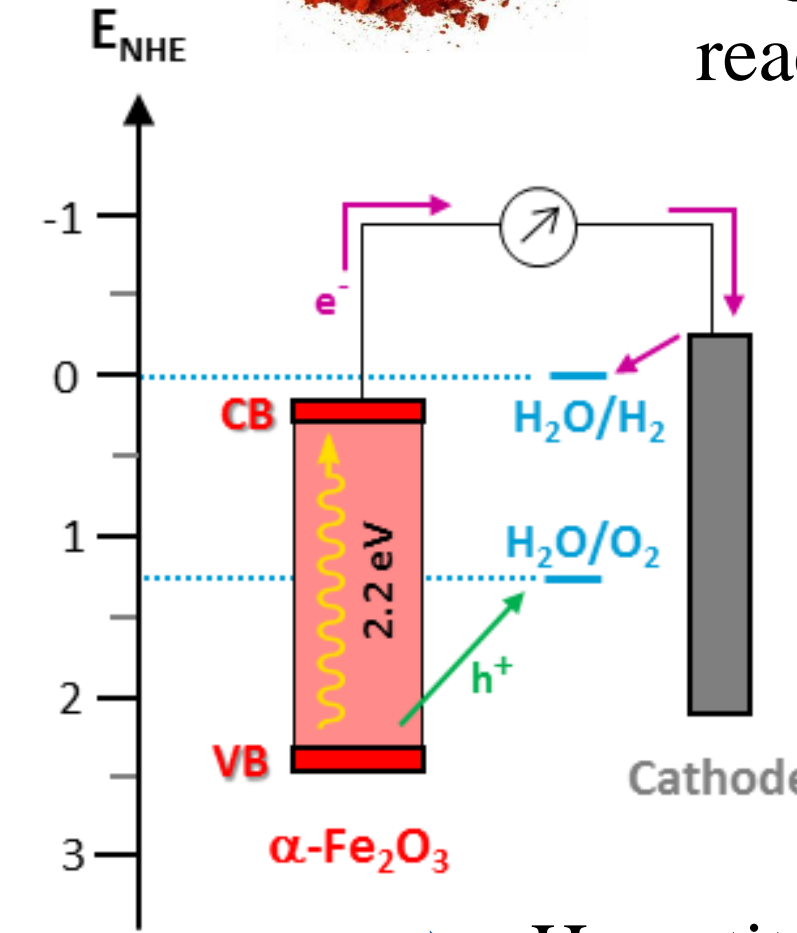
Semiconductor-based devices can be exploited to promote different redox processes, and, among them

transformations of organic molecules for the synthesis of high-value products under less drastic conditions than traditional organic synthesis methods.

Hematite and oxidation reactions



Hematite ($\alpha\text{-Fe}_2\text{O}_3$) is an n-type semiconductor that exhibits the target characteristics of a photoanodic material for oxidation reactions



- ✓ Band gap of 2.1 eV, which allows for visible-light absorption
- ✓ Stability in aqueous basic environment
- ✓ Made of non-toxic, earth-abundant elements
- x Slow hole-transfer dynamics
- x Charge recombination phenomenon

Hematite photoelectrodes are able to oxidize biomass and have been used by us in HMF photo-electro oxidation into FDCA driven by Cobalt phosphate-modified Ti:Fe₂O₃ photoanodes.

Hematite photoanodes: synthesis and performances

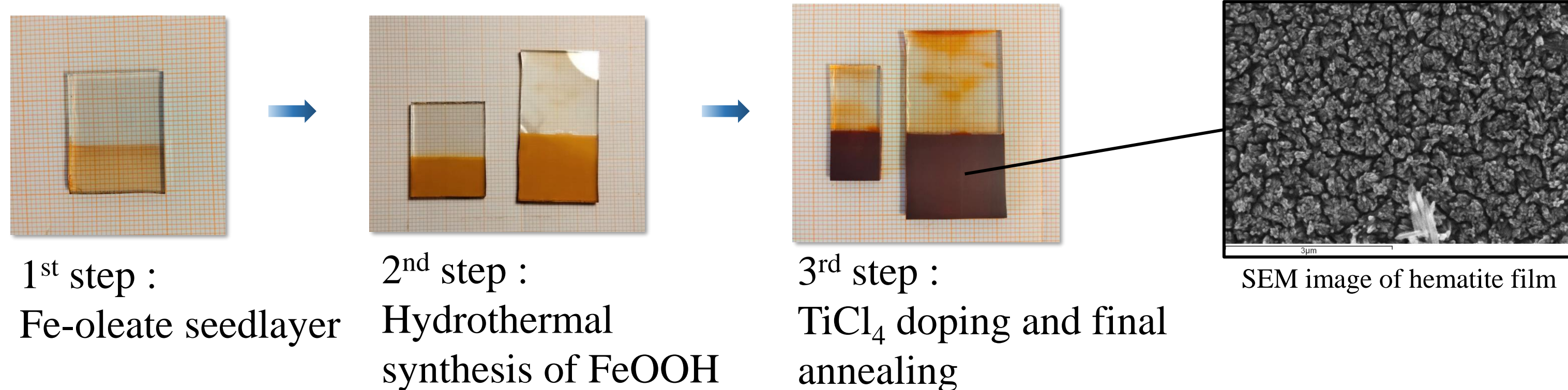
Synthesis

Deng *et al.* hydrothermal synthesis to produce nanostructured thin films of hematite

- Variation of time, temperature and pressure
- Additives in the autoclave solution
- Seedlayers/underlayers



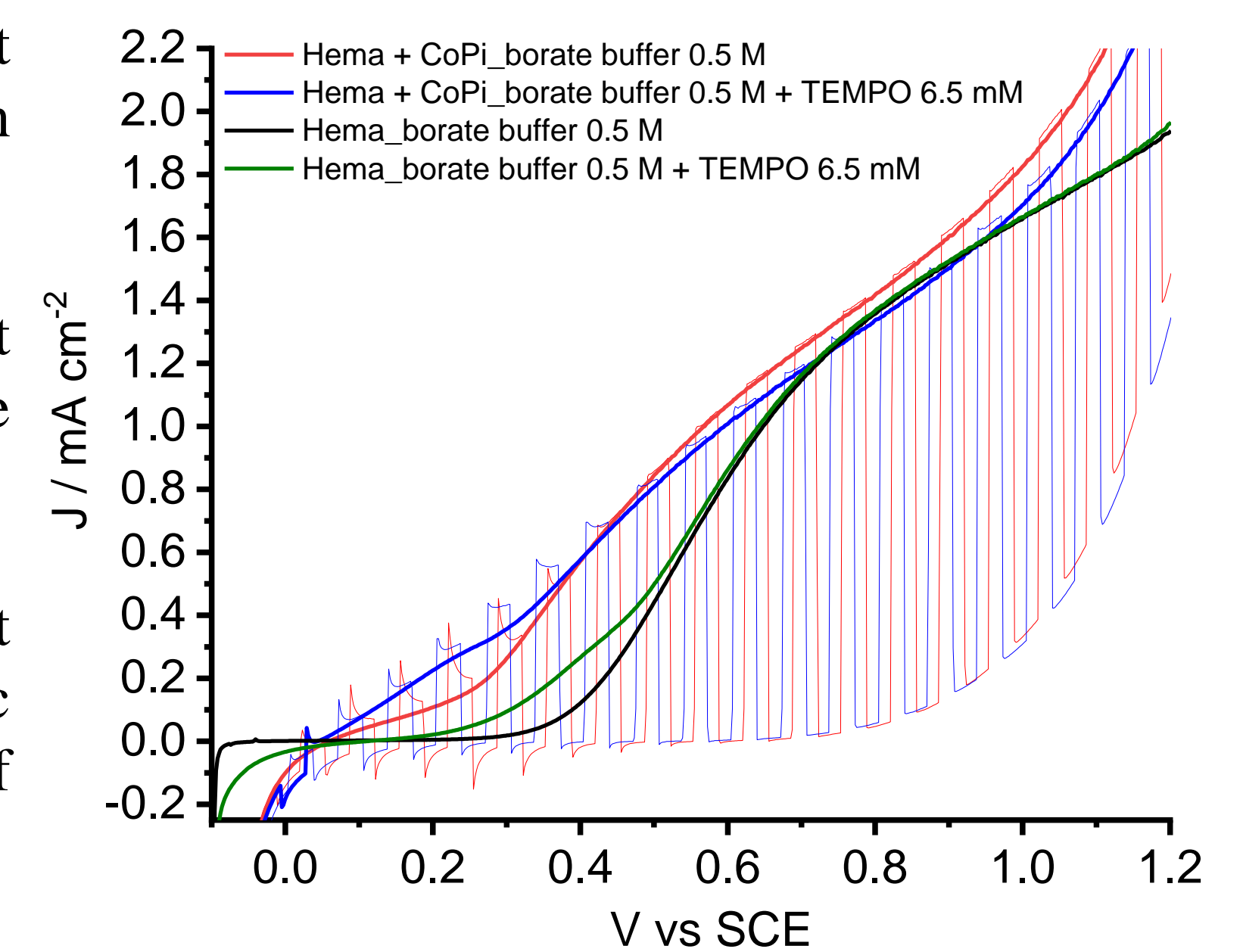
Can affect **thickness** and **morphological growth** of hematite film



CoPi electrodeposition and photoelectrochemical performances

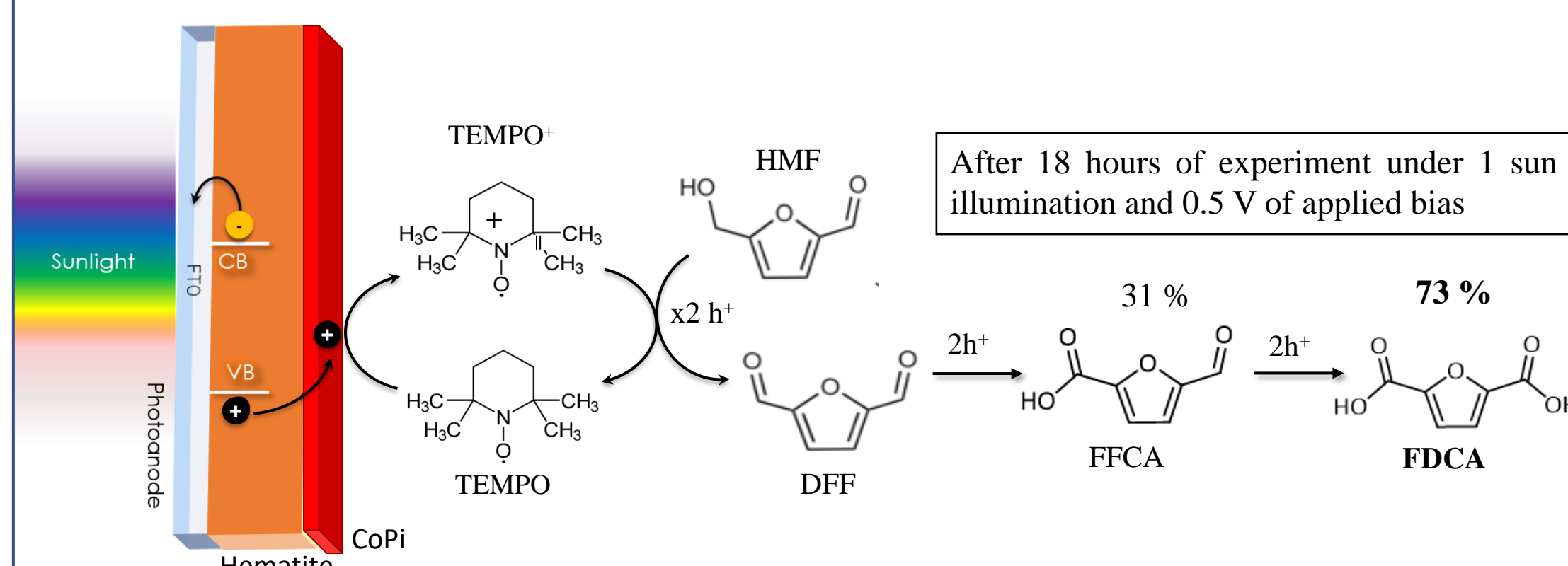
CoPi is a Cobalt (III) oxide catalyst with coordinated phosphate, known as a catalyst for water oxidation

- Increased photocurrent at intermediate potentials in the presence of CoPi (red curve)
- Significant shift of photocurrent onset and decrease of cathodic spikes in the presence of TEMPO (blue curve)



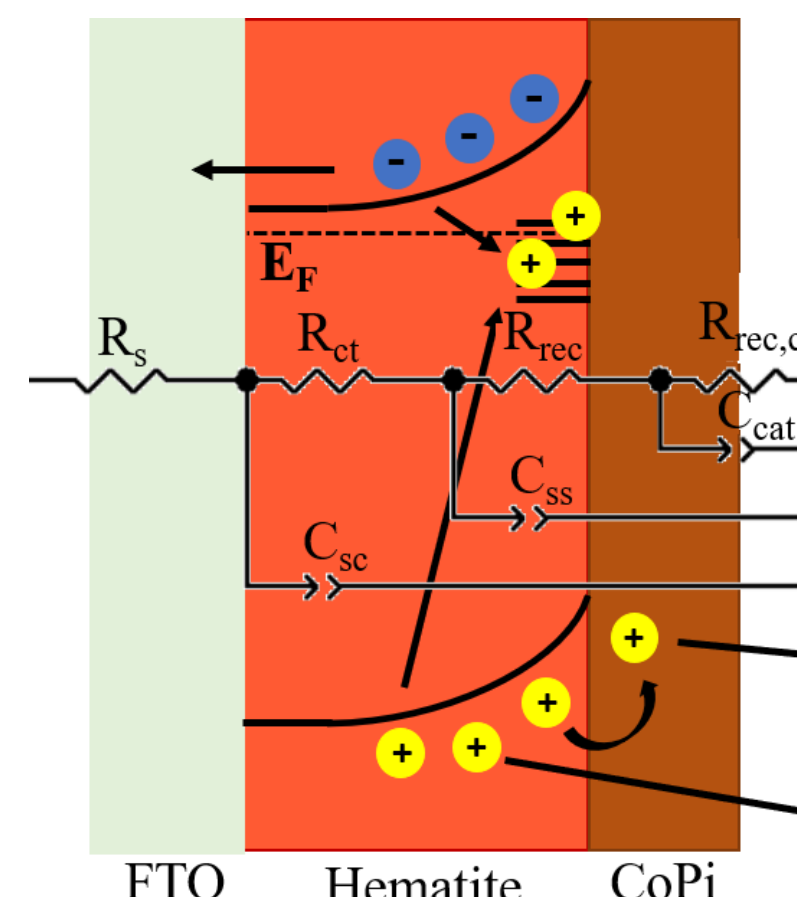
Evaluation of charge transfer dynamics trough EIS

Ti:Fe₂O₃/CoPi photoanodes for biomass oxidation



HMF photo-electro oxidation into FDCA driven by Cobalt phosphate-modified Ti:Fe₂O₃ photoanodes.

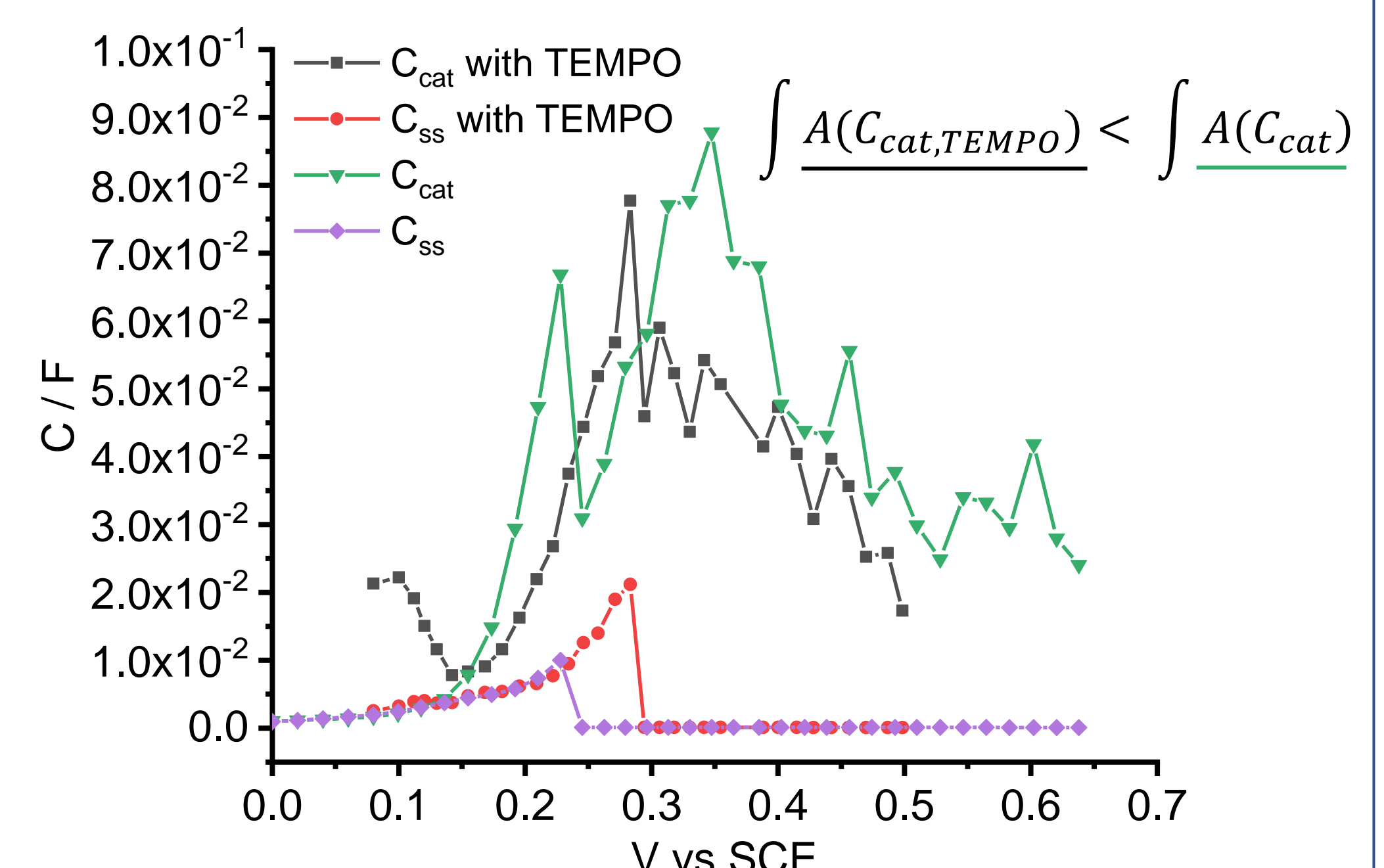
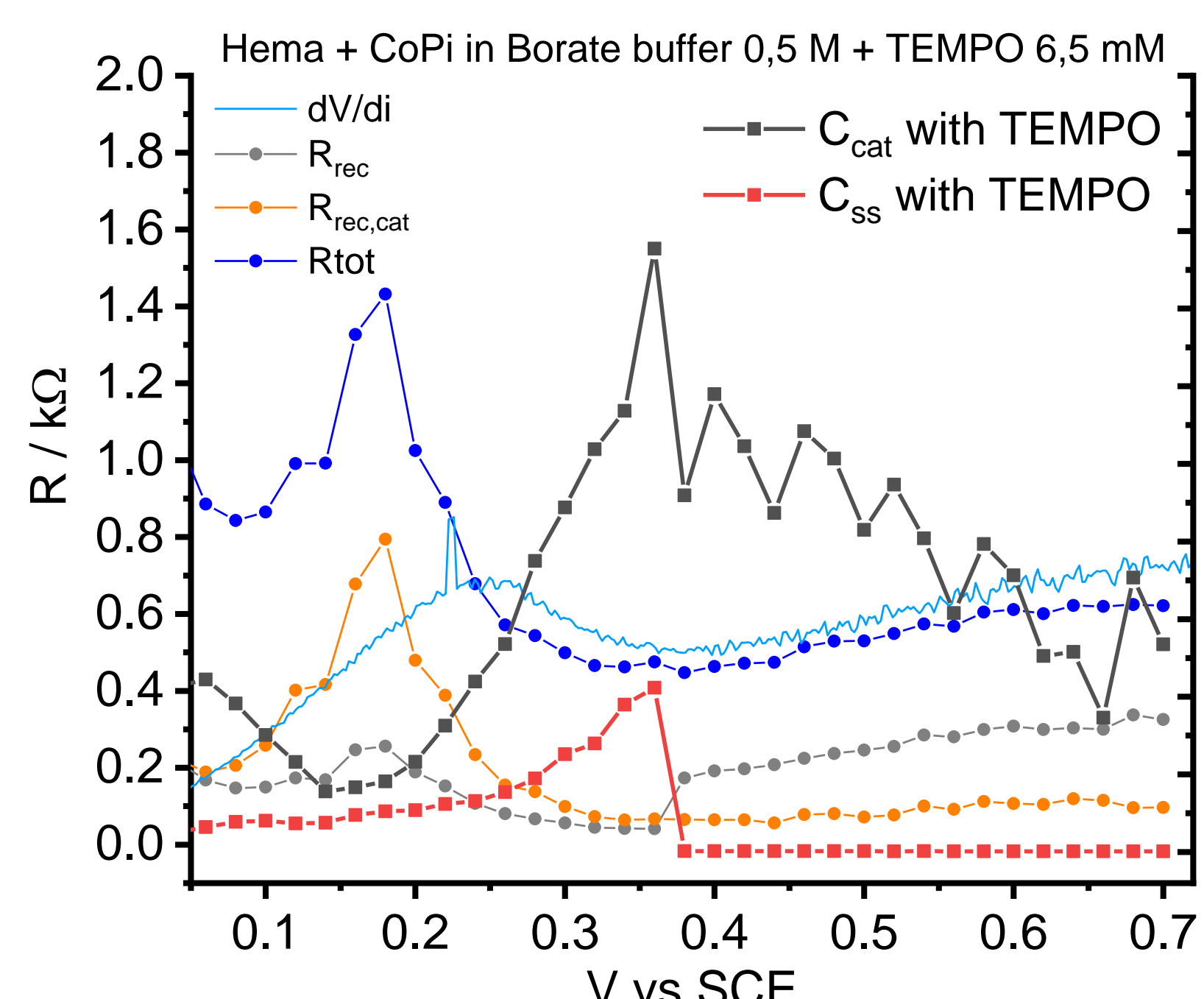
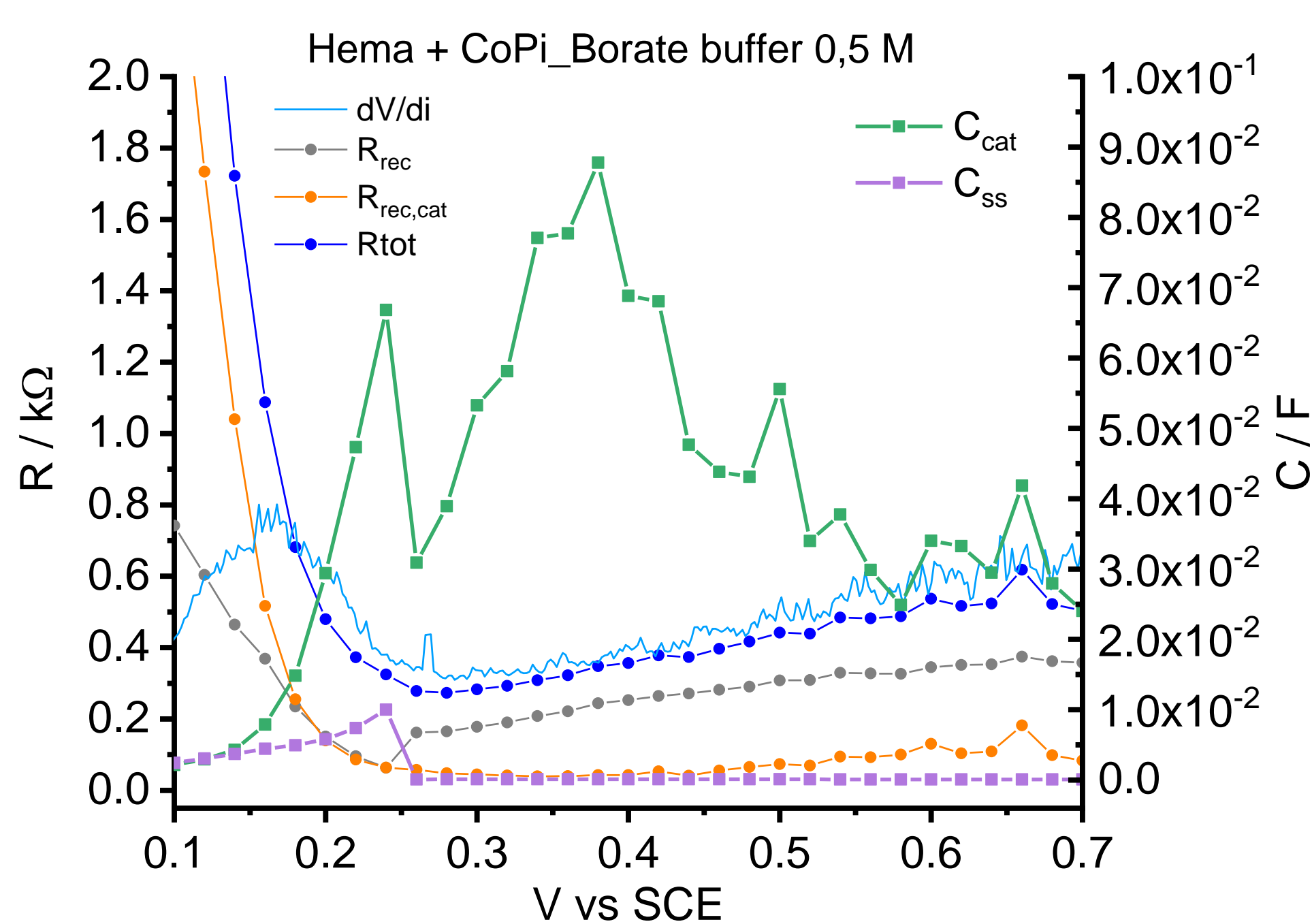
Charge transfer dynamics have been studied trough EIS.



EIS study and equivalent circuit

Electrochemical impedance spectroscopy allowed us to extract and compare charge transfer dynamics in Ti:Fe₂O₃/CoPi photoanodes for water and HMF oxidation.

- R_{ct} and C_{sc}: charge transfer processes in the bulk of hematite.
- R_{rec} and C_{ss}: processes involving surface states, recombination and accumulation of photogenerated h⁺ in them, respectively.
- R_{rec,cat} and C_{cat}: charge transfer through the CoPi layer.



When hematite electrodes are modified with CoPi, photogenerated holes accumulates preferentially on CoPi surface rather than on hematite superficial states ($C_{cat} > C_{ss}$).

Adding TEMPO to the electrolyte mixture, that's a redox mediator who starts the reaction, the ability of the catalyst to accumulate charges decreases, $\int A(C_{cat,TEMPO}) < \int A(C_{cat})$.

In the presence of TEMPO charge transfer processes become faster, demonstrating that, compared with water oxidation, CoPi is selective toward TEMPO-mediated oxidation of biomass.

Results and conclusions

Electrode	Time of the exp (h)	Total charge passed (C)	HMF consumed (%)	Conv HMF exp in DFF (%)	Conv HMF exp in FFCA (%)	Conv HMF exp in FDCA (%)	Faradaic efficiency for FDCA (FE%)
Hema+CoPi	18	117	100	0	31	73	54
Hematite	19	83	100	0	57	43	43

- The table highlights the effect of CoPi on hematite electrodes: it compares conversion rate and faradic efficiency for FDCA in the absence (second row) and in the presence of CoPi on hematite surface (first row).
- Because of the competition with OER, a full conversion of HMF to FDCA is not completely achieved. However, the presence of CoPi on the hematite surface enhances the selectivity towards FDCA, increasing the reaction yield from 43 % to 73 % of conversion into the target product.
- The reaction it's been conducted in basic aqueous conditions at room temperature, under sunlight illumination with the application of a low bias, milder and environmentally friendly conditions with respect to the traditional industrial production processes of FDCA.