

Scalable reactors for photoelectrochemical hydrogen production

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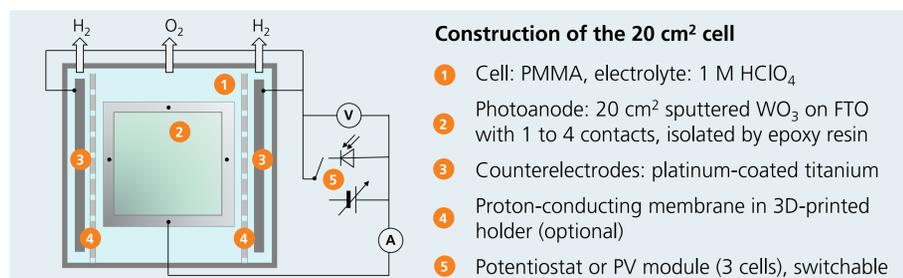
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For a practical application of photoelectrochemical water splitting it is necessary to develop, test and operate large reactors. The scale-up of chemical processes is not a trivial task, and several theoretical and experimental works have described how the size of the photoelectrode affects its efficiency.[1,2,3]. Recently, Domen et al. presented an example for a large photocatalytic reactor, which produces a mixture of hydrogen and oxygen.[4] The authors combined 1.600 reactor units to a 100 m²-photocatalytic solar park and operated it for 3 months. However, large reactors for photoelectrochemical systems with separated H₂/O₂ generation have not been described so far.

Objectives

- Experimental scale-up of electrochemical components and of reactor housing
- Rational design of a scalable reactor for industrial PEC hydrogen production

Experimental setup



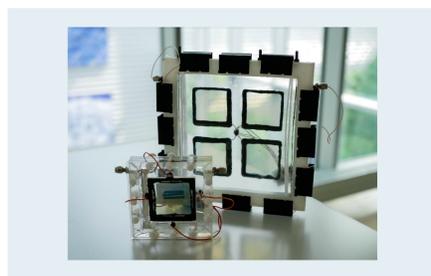
Results

Scaling up the photoanode to 20 cm² results in $J = 500 \mu\text{A cm}^{-2}$, which is approx. 30 % lower than for the same electrode in a commercial 2.5 cm² cell

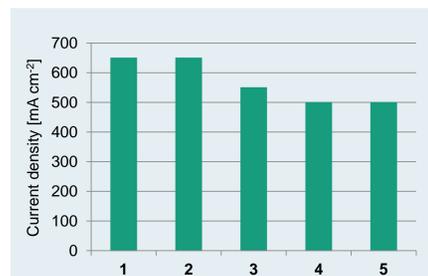
- Gas bubbles reduce the active area significantly (approx. 20 %)
- FTO resistance is responsible for a measurable loss (approx. 10 %)
- Electrolyte and membrane resistances are neglectable

Scaling up to an active area of 80 cm² by multiplication of the photoanodes is possible without significant losses, if characteristic values (e.g., FTO conductor length) remain unchanged. Different construction variants were compared:

- PDMS gaskets and screwed-in connectors seal the cell without leakage.
- Clamps are preferred to screws due to their ease of use and their flexibility.
- Sprayed electrical isolation of larger areas is preferred to other methods.



Photographs of the reactors (front: reactor with active area of 20 cm² for electrode scale-up; back: reactor with active area of 80 cm² for scale-up of reactor components)



Photocurrent density at 1.23 V vs. RHE for different setups (1: reference (2.5 cm²); 2: 1st measurement on 20 cm²; 3 gas equilibrium gas bubbles; 4: with single counter electrode; 5: with membrane)

Design of large-scale reactors

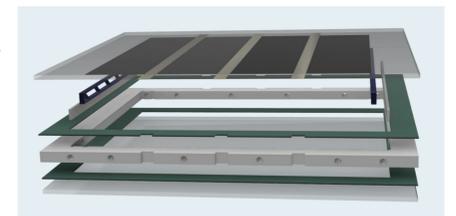
The presented experimental results help to scale up the PEC reactors to a level which allows solar hydrogen production. For these reactors, additional criteria become important and require in constructive changes.

Requirements for large reactors and implications on reactor design

Requirement	Implication on reactor design	Example
Maximal light absorption	Large frontal area and low depth	Flat plate reactor
Mechanical stability	Low volume, materials with similar thermal expansion	Combination of several small cells to larger module
Chemical stability	Non-corroding reactor materials	Reactor: Glass, PVDF Conductor: Ti
Minimal internal resistance	Optimized lengths of FTO, conductor and electrolyte	Segmented absorber with short distance to conductor
Cost-effective production in large numbers	Industrial processing techniques, economical use of expensive materials	Sputtering, injection molding

Based on the experiments and the defined requirements we propose a design for a 30 cm-reactor with an active area of 500 cm²:

- Front glass with sputtered photo-electrodes and sputtered conductors
- Electrical isolation by sprayed acrylates
- Slide-in counter electrodes
- Proton-conducting membranes in 3D printed holders
- A frame made from a polymer (e.g., PVDF) and gaskets from PDMS
- Screwed-in connectors for electrolyte flow; external gas separation
- Industrial metal clamps to close the reactor



Proposed reactor design with active area of 500 cm² (components from top to bottom: front plate with absorber and conductor, membrane holders, counter electrodes, gasket, frame, gasket, back plate)

Conclusion

- Electrode scale up to 20 cm² results in losses of approx. 30 %, mainly due to gas bubbles and FTO resistance
- Reactor components were tested on an 80 cm²-reactor
- Requirements of large reactors are discussed and a design for a 500 cm²-reactor is given

References

- [1] *Energy Storage Mater.* **2018**, 12, 175.
- [2] *Energy Environm. Sci.* **2017**, 10, 346.
- [3] *Sustainable Energy Fuels* **2019**, 3, 2366.
- [4] *Nature* **2021**, 598, 304.

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