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PECSYS Virtual Workshop
5th November 2020

WP 2: Silicon based photovoltaic integrated alkaline water electrolysis

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Disclaimer

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Workpackage objectives and main tasks

Objective: Upscaling of thin film silicon (TF) and silicon heterojunction (SHJ) based approaches, improve efficiency and stability

Task description
T 2.1 (FZJ) Improve stability and efficiency of TF silicon based integrated device on < 10 cm^2
T 2.2 (FZJ) Incorporate gas separation membrane and upscale TF silicon approach to 10 cm × 10 cm
T 2.3 (HZB) SHJ PV-EC device with EC electrodes stuck to the rear of the PV part
T 2.4 (HZB) Scalable and stable PV-EC using SHJ approach with ion separator
T 2.5 (HZB) Simulation of electrical current distribution, thermal management and mass transport phenomena of prototypes for SHJ approach
T2.6 (HZB) Perform computational fluid dynamics (CFD) computations of possible SHJ based on demonstrator configurations

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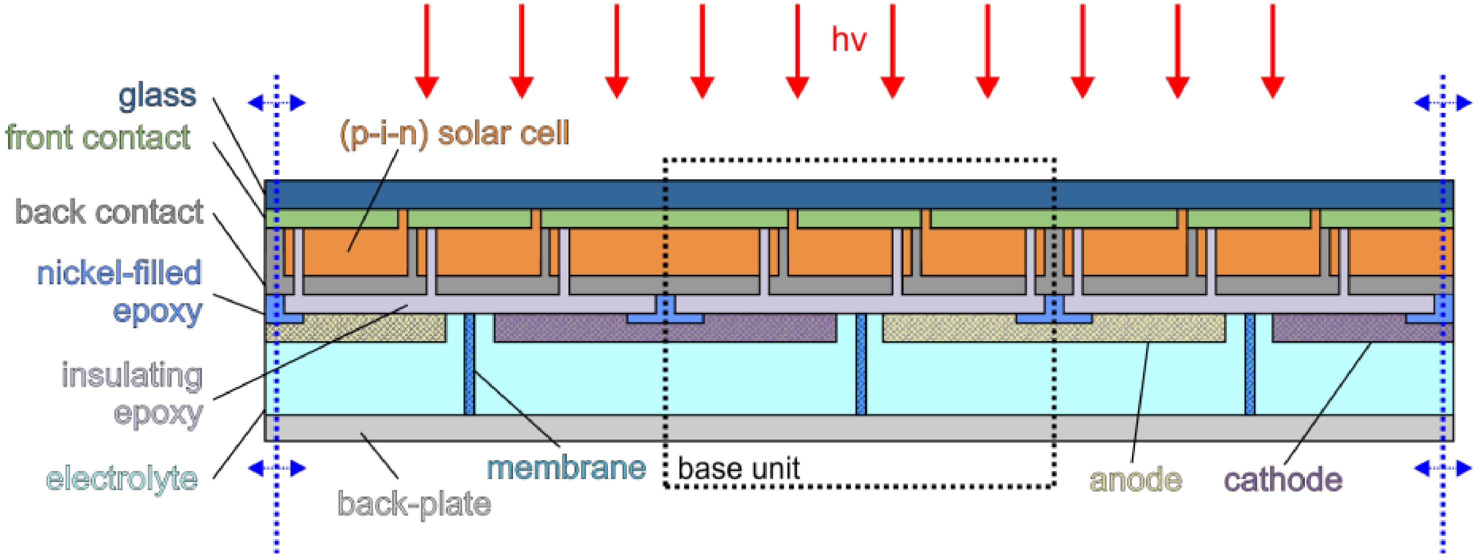
Explanation of the concept (FZJ)



- TF Si PV and transition-metal electrocatalysts
- Side by side series connection for voltage adjustment
- Continuous mirroring of a base unit
- Neighboring base units share electrodes
- No wiring
- Compatible with many types of thin film solar technologies

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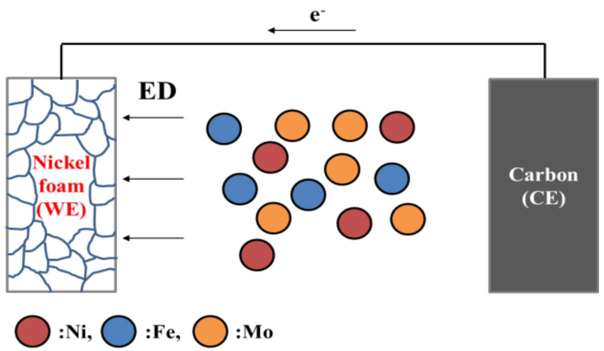
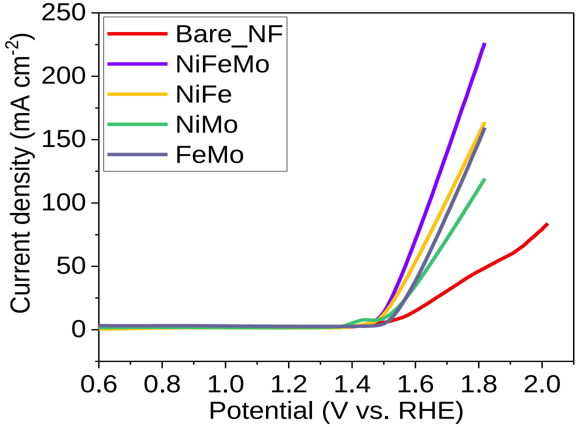
Development of efficient bifunctional catalyst (FZJ)

All except a) in 1.0 M KOH at room temperature

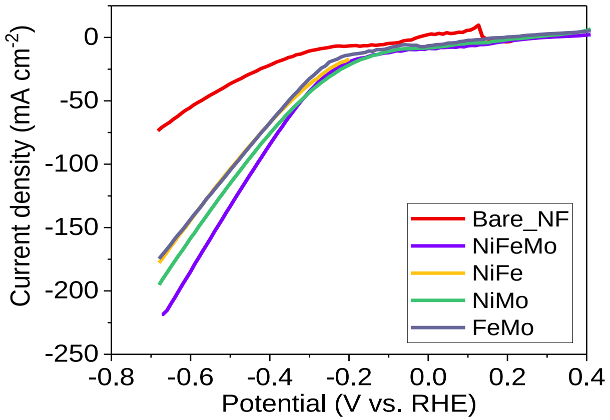
a) *Scheme*



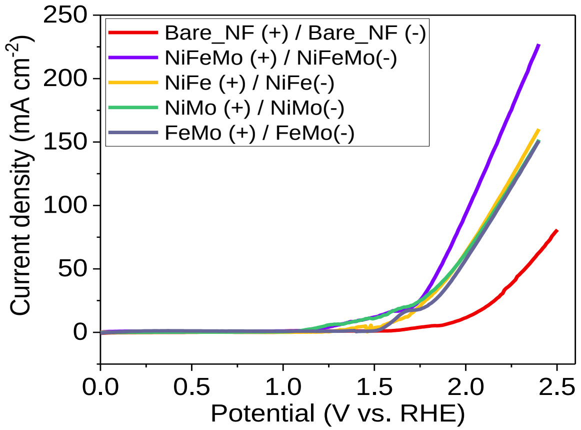
b) *IV: OER*



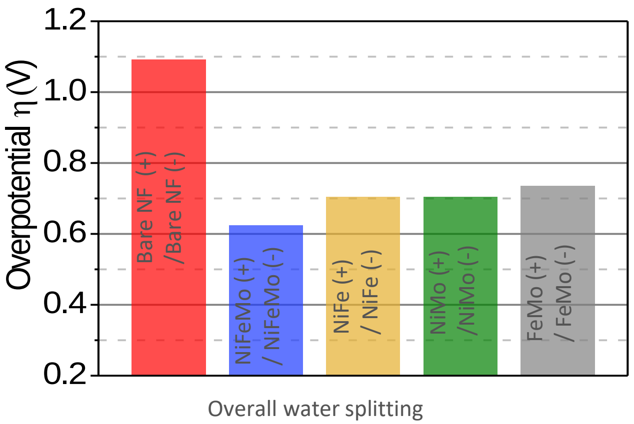
c) *IV: HER*



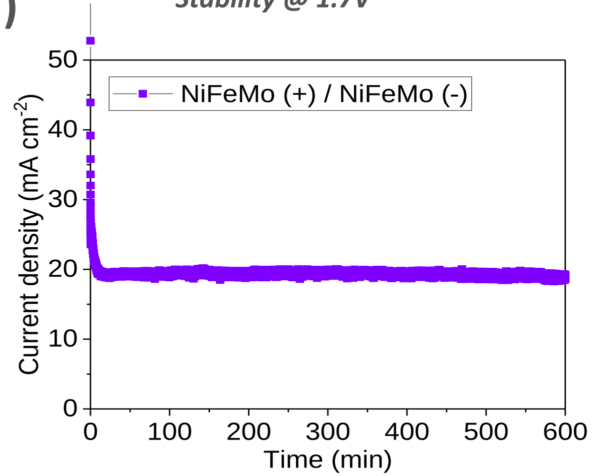
d) *2 electrode*



h) *Overpotential @ 50mA cm-2*



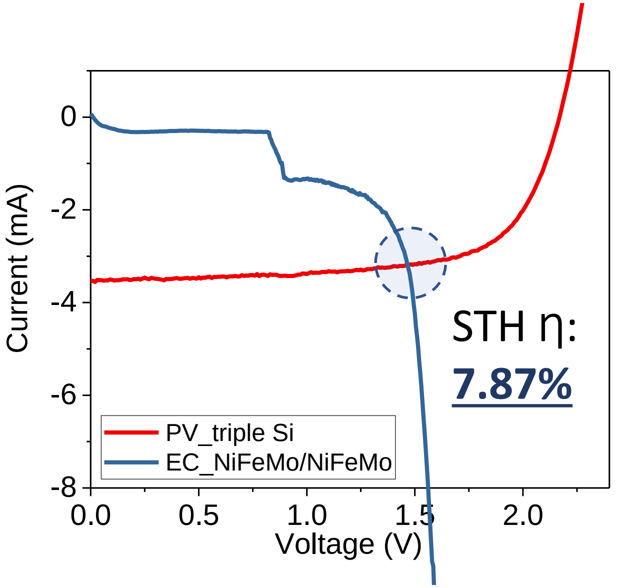
i) *Stability @ 1.7V*



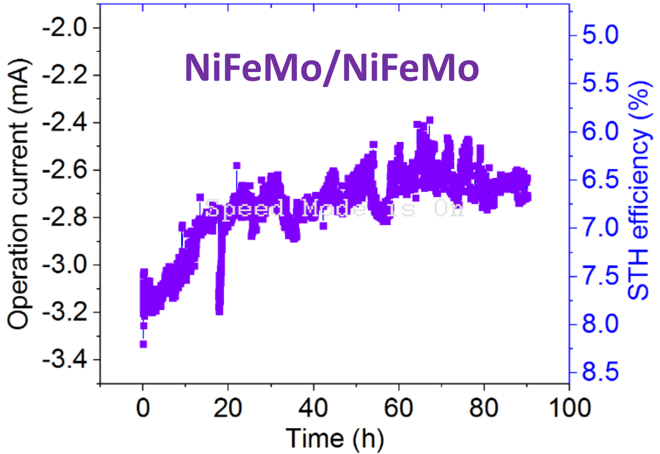
[1] M. Lee et al., Adv. Sustain. Syst., 2020, p. 2000070, doi: 10.1002/adsu.202000070

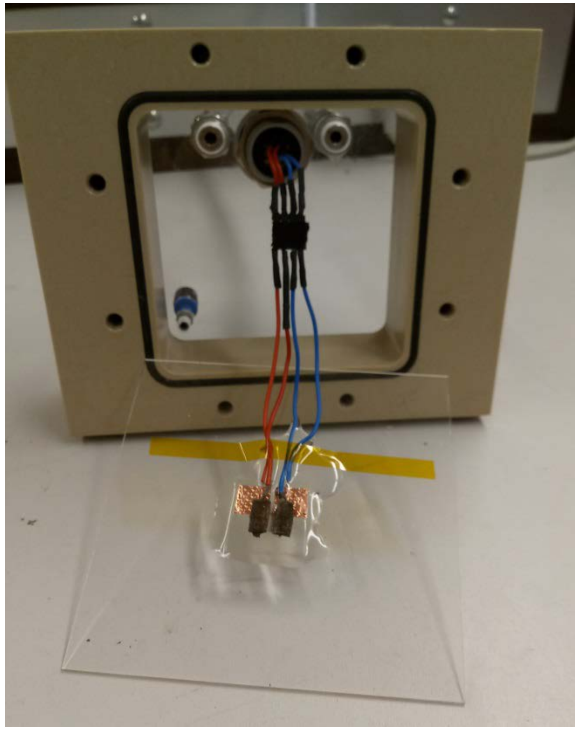
T2.1 - Small area device performance (FZJ)

- PV based on thin film silicon triple cell made of a-Si:H/a-Si:H/μc-Si:H
- PV area 0.5 cm²
- Bifunctional catalysts made of NiFeMo
- Catalyst area 0.5 cm² each (HER and OER)
- Measurement performed in 10 cm ×10 cm sample holder



STH η:
7.87%





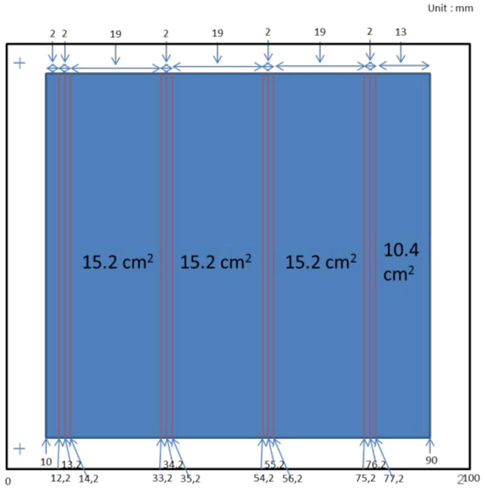
0 ~ 1h Ave. 7.72%

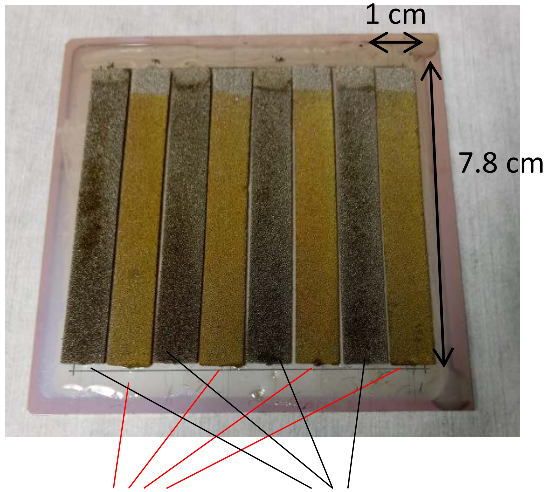
Last 1h Ave. 6.57 %

[1] M. Lee et al., Adv. Sustain. Syst., 2020, p. 2000070, doi: 10.1002/adsu.202000070

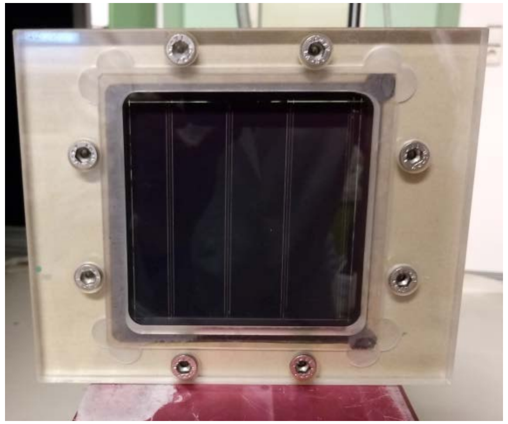
T 2.2 – Upscaling thin film silicon (FZJ)

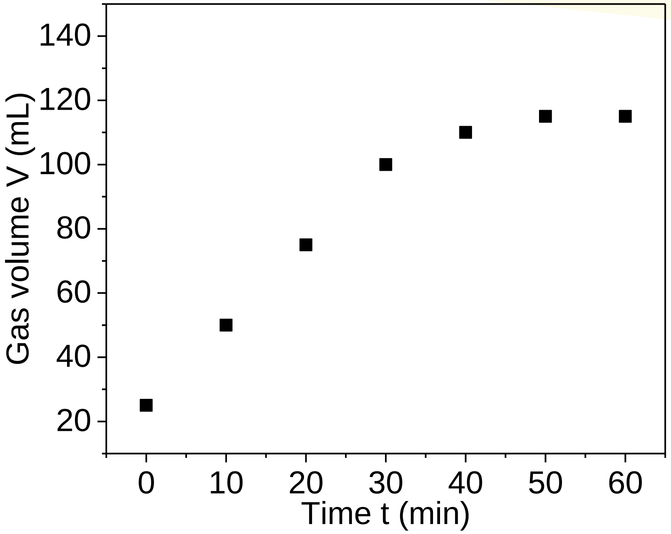
- Arrangement design on Large device

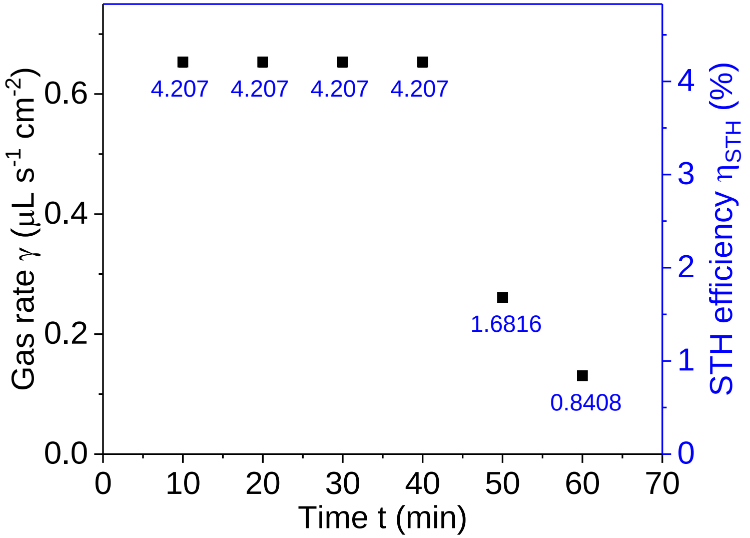




OER:NiFe, HER:NiMo







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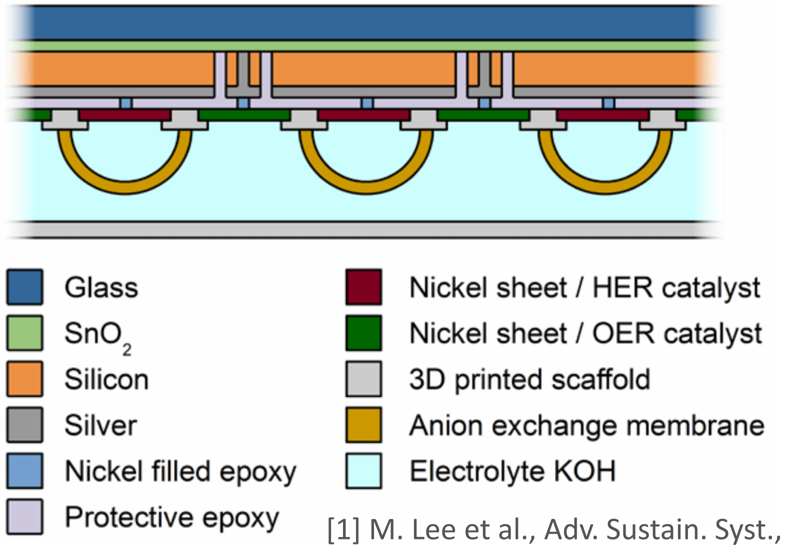
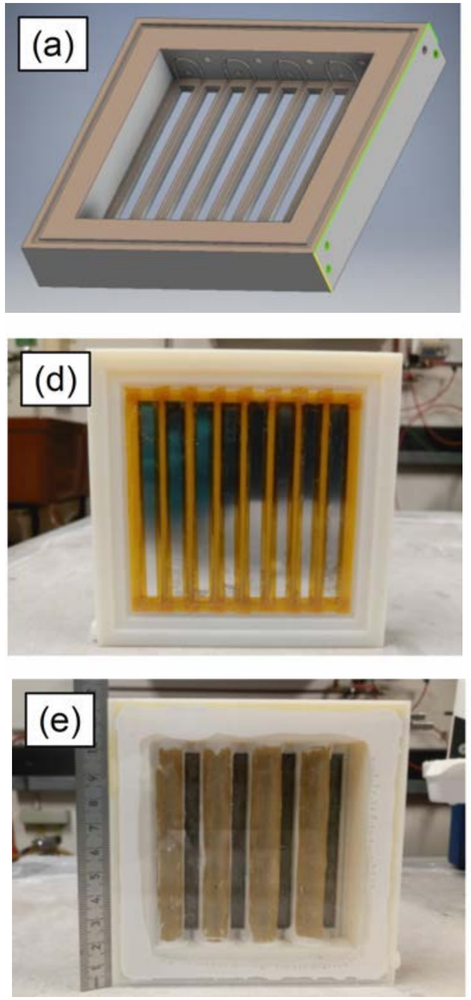
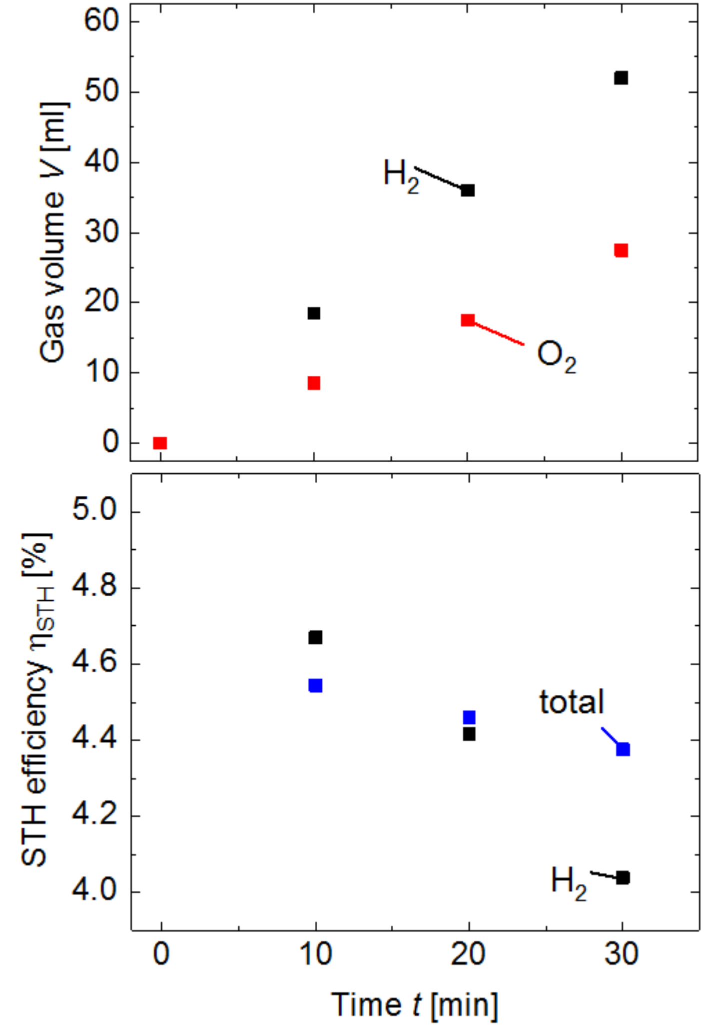
T 2.2 – Upscaling thin film silicon (FZJ)

- Upscaling of device on 10 cm × 10 cm substrate size
- Repetition of base unit
- Incorporation of bent AEM
- Replaced nickel foam with nickel sheets







[1] M. Lee et al., Adv. Sustain. Syst., 2020, p. 2000070, doi: 10.1002/adsu.202000070

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Explanation of the HZB concept

Task 2.3 SHJ PV-EC device with EC electrodes stuck to the rear of the PV part

1. Low cost materials for both photovoltaics (PV) and electrolysis cells (EC)
   - Photoabsorber using silicon heterojunction (SHJ) solar cells
   - Alkaline electrolysis using Ni-foam electrodes coated with $NiFeO_x$ (OER, anode) and NiMo (HER, cathode)
   - Photovoltaic modules and electrolyser cells made in-house in HZB
2. Series-connected SHJ cells directly (electrically and thermally) coupled to alkaline electrolyser (EC)
3. Heat exchange though the back of the PV to the electrolyser via the electrolyte to boost hydrogen production

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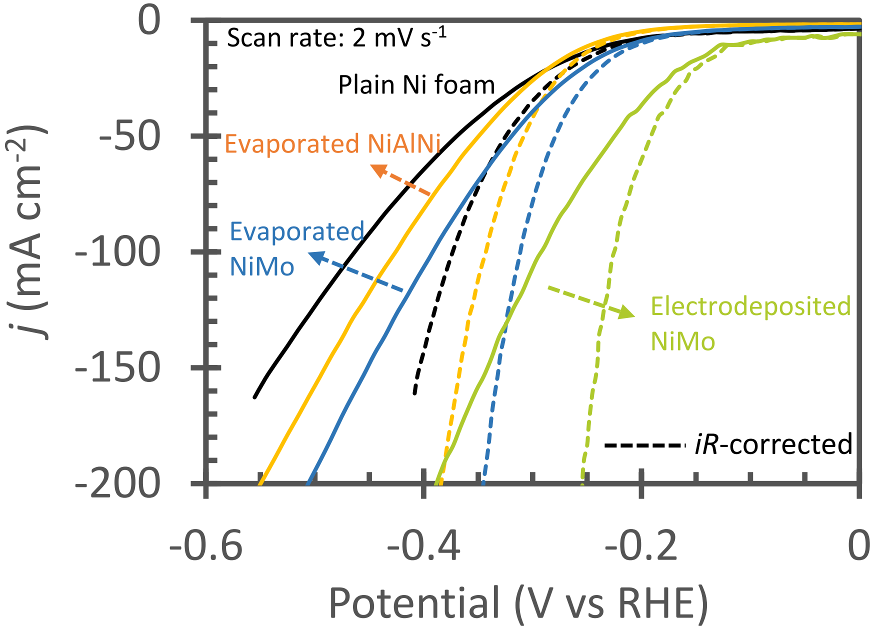
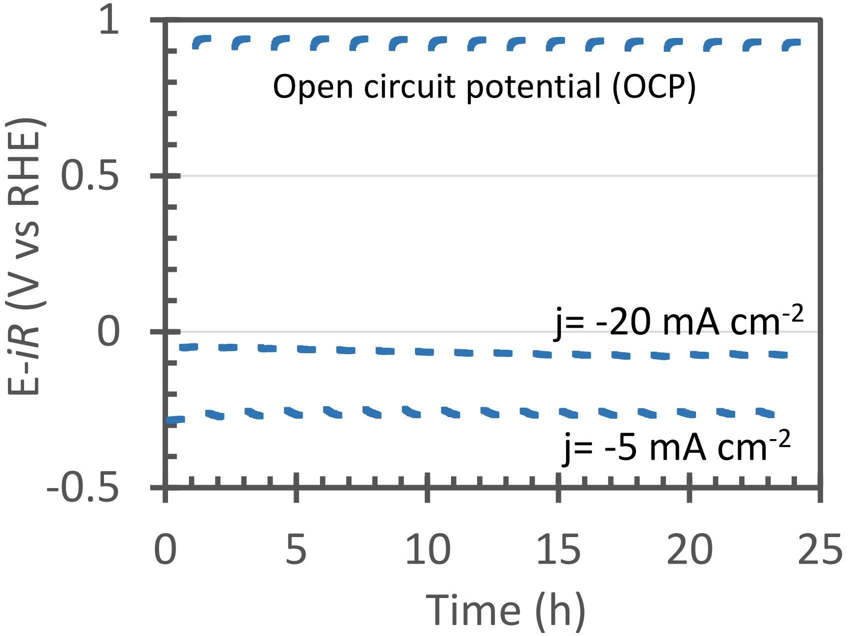
HER electrocatalysts (HZB)

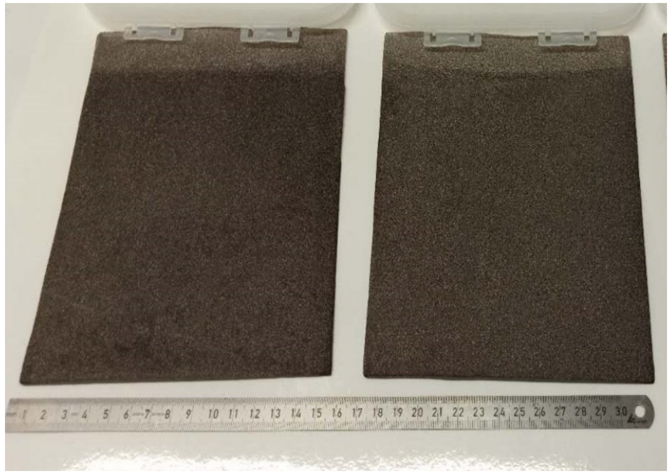
Comparison of HER catalysts



Stability of electrodeposited NiMo



15 cm×15 cm electrodeposited NiMo



Test conditions:

- 1.0 M KOH
- Three-electrode configuration
- Hg/HgO reference electrode
- Electrode size: 1 cm × 5 cm (ca. 1 cm × 1 cm immersed)
- Scan rate: 2 mV s^{-1}

Electrodeposited NiMo showed the best HER performance and was stable over 24 h test

- NiMo film (1 cm × 1 cm): **overpotential 104 mV@ -10 mA cm^{-2}**
- short-term stabile under the cycling potential conditions for 24 hours (for -20 mA cm^{-2} the overpotential stabilized at ~270 mV during the stability test).
- 15 cm× 15 cm size NiMo/Ni foam samples were prepared via electrodeposition.

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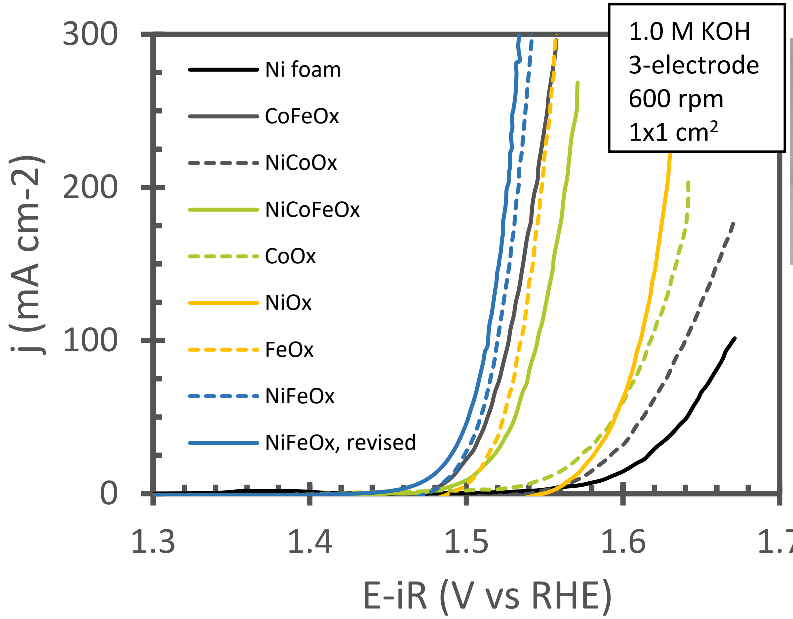
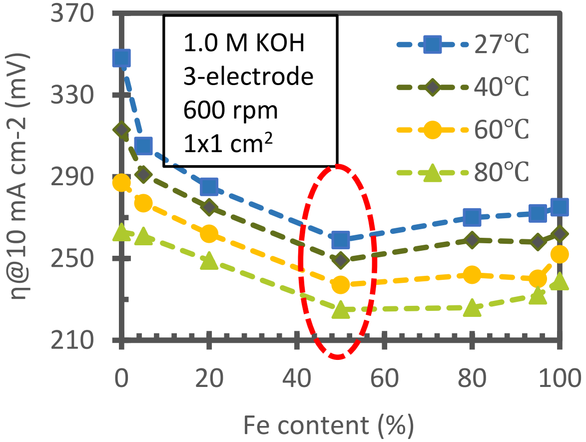
OER electrocatalysts (HZB)

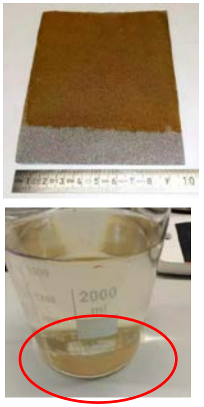
Various electrodeposited OER catalysts



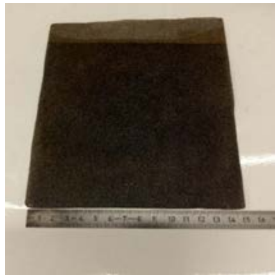
Ni/Fe ratio, optimum Fe 50%

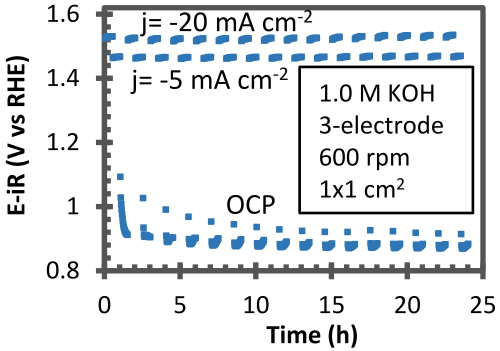


Up-scaled NiFeO$_x$ (Fe 50%)



Electrodeposited NiFeO$_x$, revised recipe





Electrodeposited NiFeO$_x$ the best OER catalyst, stable over 24 h test

- Several transition metal based materials were electrodeposited on Ni foam.
- The optimal Fe content was confirmed to be 50% (**259 mV overpotential @ 10 mA cm^{-2}**), but it suffered from catalyst detachment.
- Revised recipe improved both the OER activity (**247 mV overpotential @ 10 mA cm^{-2}**) and stability under the cycling potential conditions for 24 hours

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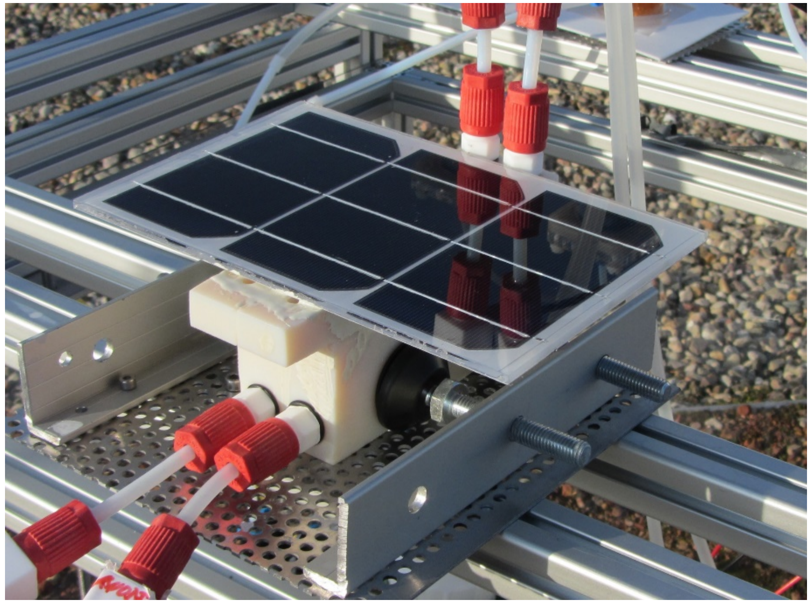
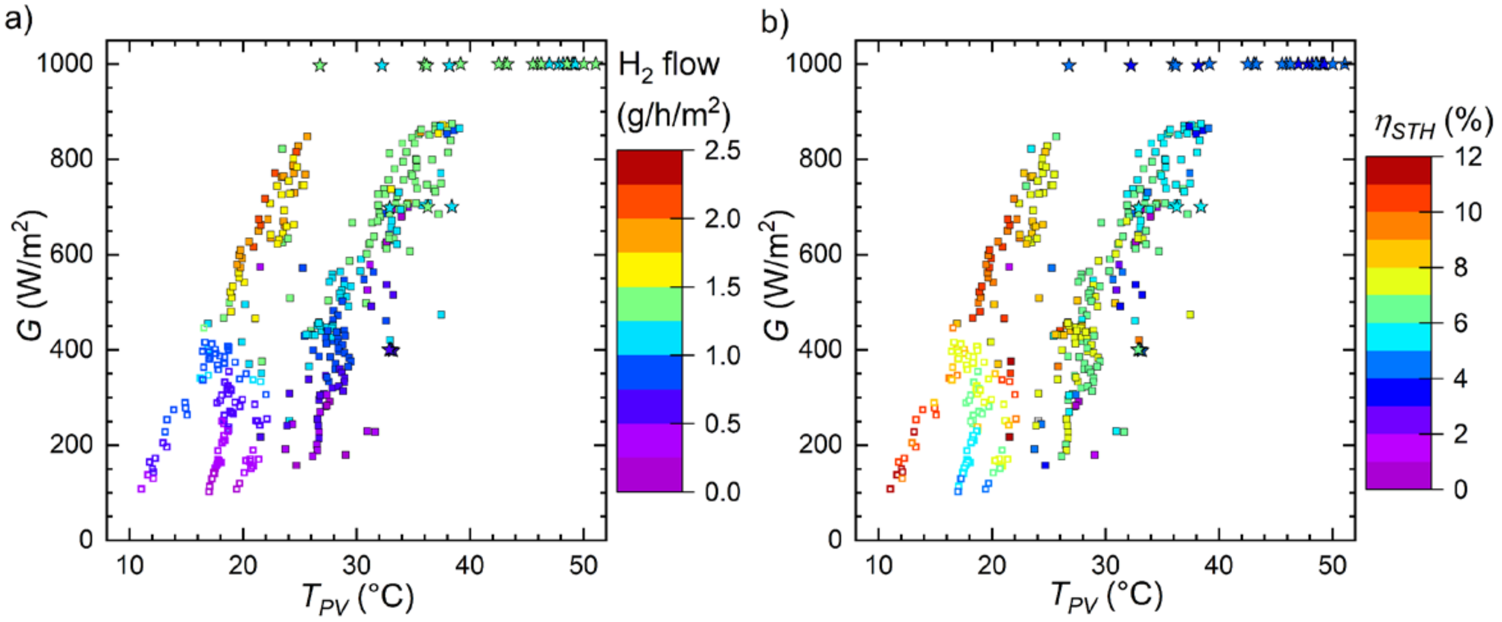
T 2.3 – Device performance (HZB)

- PV area = 294 cm^2; EC electrode area = 50 cm^2
- Device tested outdoors (square markers) and in solar simulator (stars)
- 3-5 % in solar simulator under 1000 W/m^2





STH efficiency strongly dependent on PV/ambient temperature

[2] E. Kemppainen *et al.*, *Sustain. Energy Fuels*, 2020, 4:4831, doi: 10.1039/D0SE00921K

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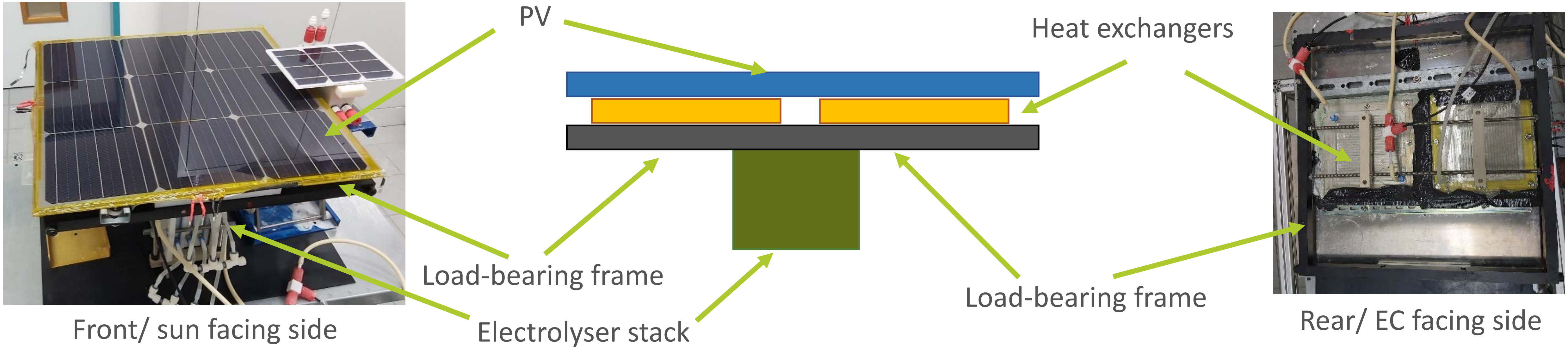
Scale up and enhanced thermal integration (HZB)

1. Scale up for increased hydrogen production capacity
    1. 9 × SHJ cells resulting in **50 cm × 50 cm** photocollection area
    2. 3 × EC with electrode area of each increased to **15 cm × 15 cm**
2. Heat exchanger incorporated **to improve heat transfer** between the PV module and the electrolyte
    1. Maintains high photovoltage at high irradiances and/or ambient temperatures
    2. Increases operating temperature of electrolyser



Front/ sun facing side

Rear/ EC facing side

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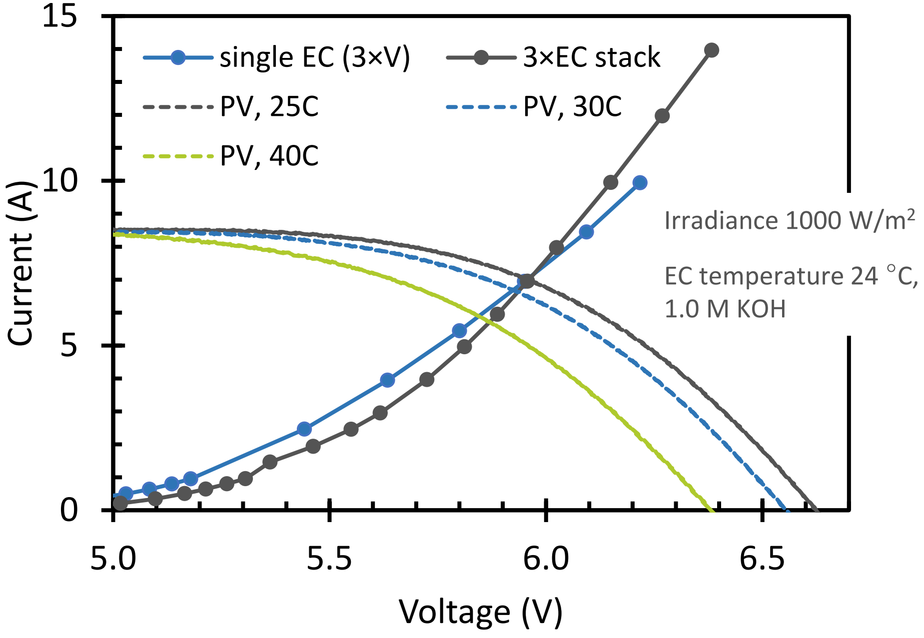
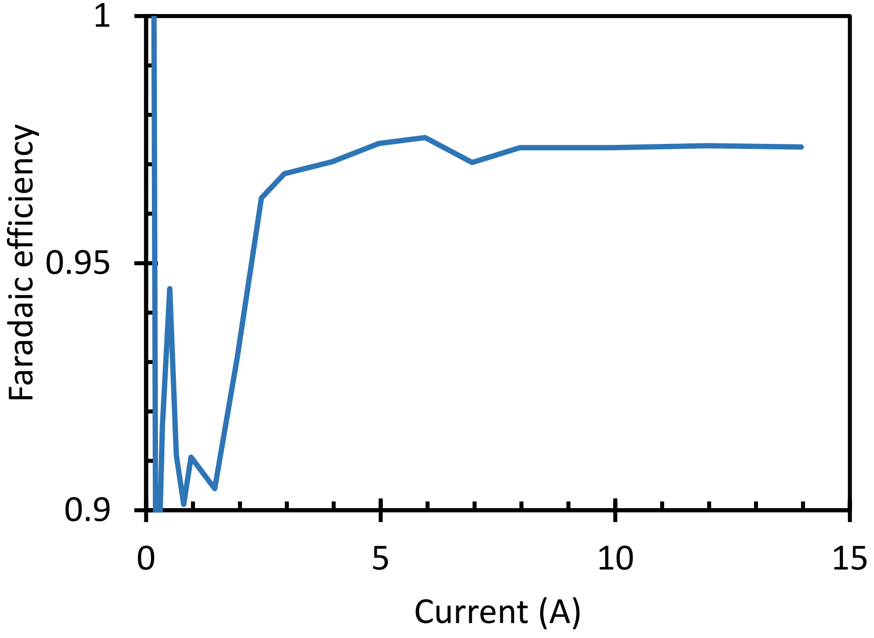
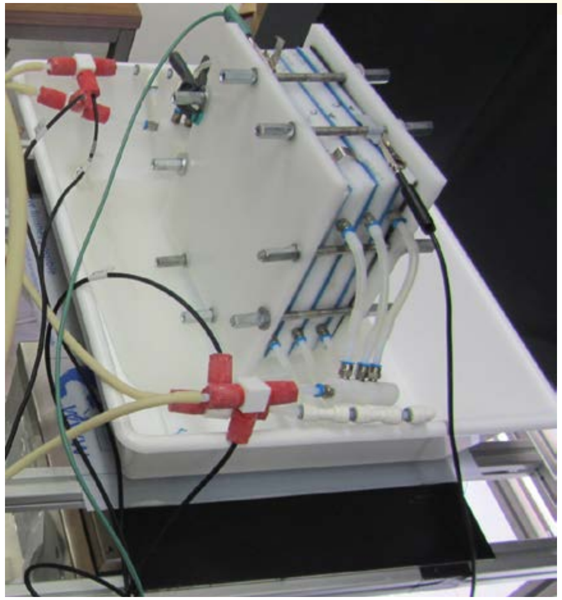
PV and electrolyser characterization (HZB)







Single-cell performance transferred to stack, faradaic efficiency 97%

Comparison with PV module indicates ~7 A initial current (~10 % STH), if both at room temperature and connection losses negligible

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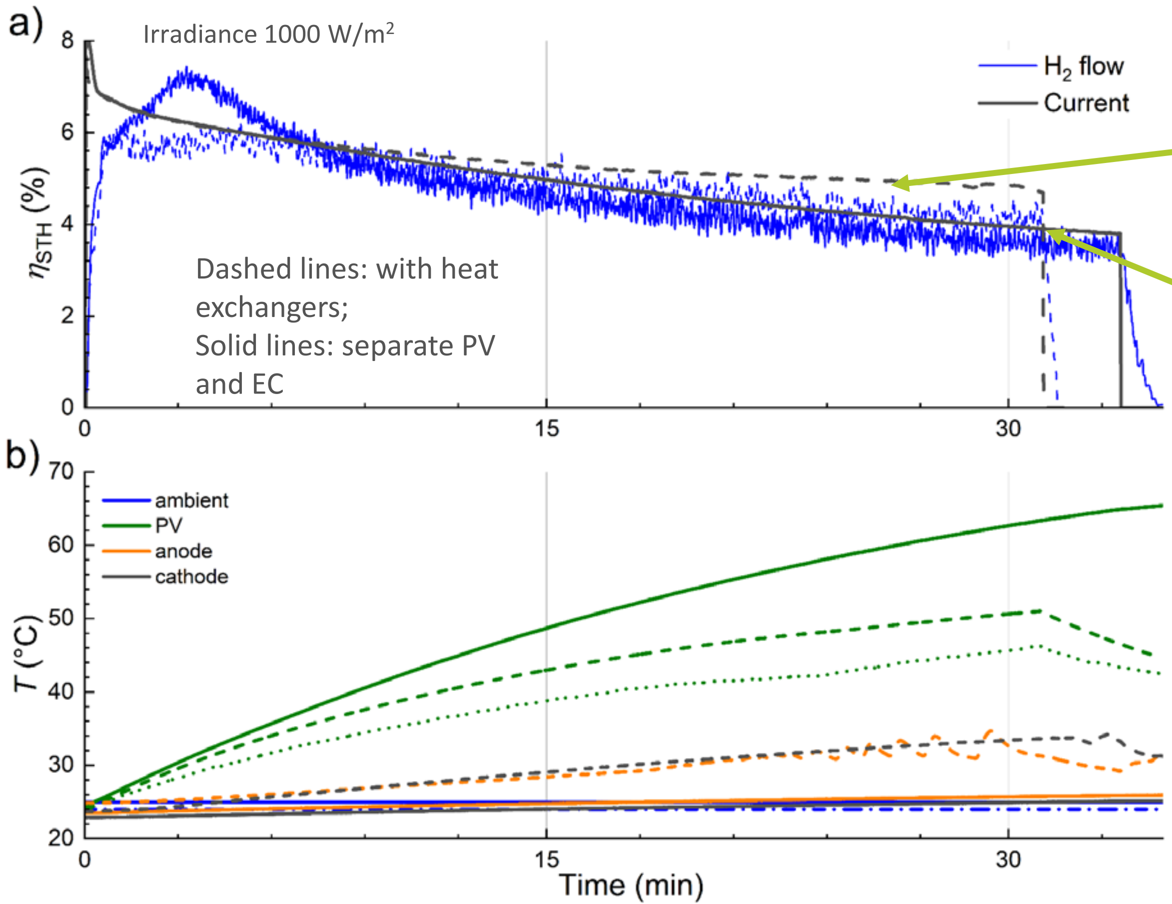
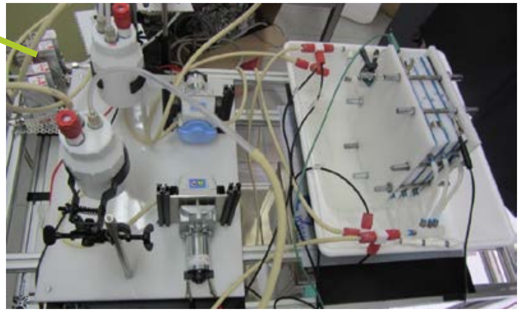
T 2.4 – Performance and heat transfer (HZB)

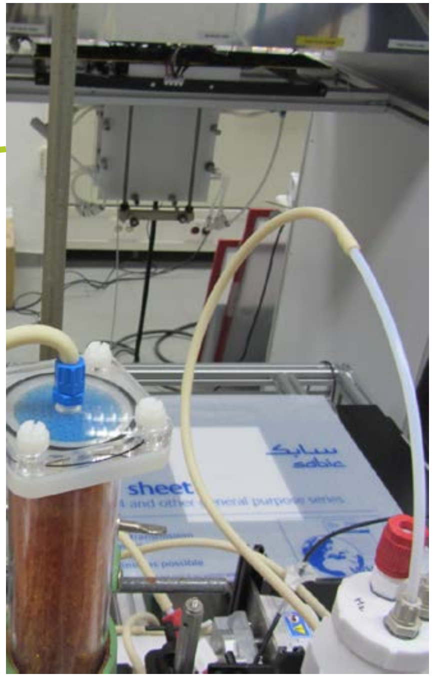
- Quantification of heat exchange and its effect on performance compared to separate PV and EC
- Same initial performance (~6 A current), but heat exchangers reduce PV temperature and increase H_2 production rate after ~10 minutes (compared to separate PV and EC)



Irradiance 1000 W/m^2

Dashed lines: with heat exchangers;
Solid lines: separate PV and EC





Thermal integration increases H_2 generation rate at 30 min by 17 % to 70 mL/min and STH to 4.5 %

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Progress beyond state of the art and impact

Thin film silicon approach

1. Photoelectrochemical operation using thin film silicon absorbers on up to 64 cm² active area demonstrated with inherent scalability
2. Lessons and knowledge can be used to inform scale-up of other PEC technologies

Silicon heterojunction approach

1. Large-area PV-EC with heat exchange, approaching square meter size achieved
   - Only 2 larger integrated devices (with lower STH efficiency) reported in literature [3]
2. Direct measurement of electrolyte and PV temperatures
   - Understanding of device state and operation
3. Qualitatively demonstrated the positive effect of heat transfer on solar to hydrogen efficiency

[3] Kim et al., Chem. Soc. Rev., 2019, 48:1908, doi: 10.1039/C8CS00699G

Conclusions and Outlook

- Upscaled devices achieved about 4.5 % STH and 1.7 mL/min H_2 generation rate with TF-Si and 4.5 % and 70 mL/min with SHJ approach
  - SHJ improved from smaller device and approaching 6% target
- Electrodeposited NiMo, $NiFeO_x$, NiFeMo were the best tested electrocatalysts in alkaline conditions
  - Stability of active catalysts can be a concern
- Operation of PV-EC devices is sensitive to device temperatures
  - Development and improvement of heat transfer crucial for high-efficiency operation

- Outlook
  - Longer term measurements planned of the SHJ based prototype, if possible also outdoor before the end of 2020 (and the project)

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Publications and conference presentations

- Publications
  - E. Kemppainen *et al.*, “Effect of the ambient conditions on the operation of a large-area integrated photovoltaic-electrolyser,” *Sustain. Energy Fuels*, 4 (9), pp. 4831–4847, 2020, doi: 10.1039/D0SE00921K.
  - M. Lee et al., “A Bias-Free, Stand-Alone, and Scalable Photovoltaic–Electrochemical Device for Solar Hydrogen Production,” Adv. Sustain. Syst., pp. 2000070, 2020, doi: 10.1002/adsu.202000070.
- Conference presentations
  - E. Kemppainen, et al. „Performance Limits and Trends of an Integrated Photovoltaic-Electrolyser System, 69th Annual Meeting of the International Society of Electrochemistry“, 5 Sept 2018, Bologna, Italy. (oral presentation)
  - E. Kemppainen et al., „Mass flow: geometry and voltage losses in a PV-electrolyser“, ModVal 2019, 12.-13.3.2019, Braunscweig, Germany (oral presentation)
  - S. Calnan et al., „Silicon photovoltaic integrated alkaline electrolyser prototype using earth abundant active materials“, International Bunsen Discussions Meeting: Fundamental and Application of (Photo)Electrolysis for Efficient Energy Storage, 1.-5.4.2019, Taormina, Italy (oral presentation)
  - E. Kemppainen et al., „Geometry and mass transport losses in a PV-integrated electrolyser”, International Bunsen Discussions Meeting: Fundamental and Application of (Photo)Electrolysis for Efficient Energy Storage, 1.-5.4.2019, Taormina, Italy (poster)
  - S. Calnan, et al., „Sustainable Hydrogen Production Using Water By a Photovoltaic Integrated Electrolyser with Active Area Exceeding 100 cm^2“. 235th Electrochemical Society (ECS) Meeting, 26-31 May 2019, Dallas, TX, EEUU.
  - S. Calnan, et al., „From cm^2 to dm^2: Up-scaled photovoltaic integrated electrolyser for water splitting.“ EFCF 2019- Low-Temperature Fuel Cells, Electrolysers & H_2 Processing Fundamentals and Engineering Design, 2 - 5 July 2019 Luzerne, Switzerland.
  - S. Calnan, at al., „Machbarkeitsstudien für Solare Wasserstofferzeugung: Zentralisierte und Autarke Systeme (Das PECSYS Projekt)“, CLEANTECH Initiative Ostdeutschland, 16 Sep 2019, Hochschule Stralsund, Germany.
  - S. Calnan, “PECSYS - Technology demonstration of large scale photo-electrochemical system for solar hydrogen production”, Programme Review Days 2019, Brussels, Belgium.
  - Fuxi Bao *et al.*, “Understanding the Hydrogen Evolution Reaction Kinetics of Electrodeposited Nickel–Molybdenum in Acidic, Near-Neutral, and Alkaline Conditions,” 71st Annual Meeting-International Society of Electrochemistry, 31.8. – 4.9.2020, Belgrade/online (poster)
- More comprehensive list (other WPs) at https://www.helmholtz-berlin.de/projects/pecsys/

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HZB Helmholtz Zentrum Berlin PVcomB

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