Australian National University

Efficient Solar Hydrogen Generation

Mid-Term Activity Report

Prepared by Professor Kylie Catchpole

ANU College of Engineering & Computer Science

REIMAGINE

This project received funding from the Australian Renewable Energy Agency (ARENA) as part of ARENA's Research & Development Programme. The views and opinions expressed in this report are those of the author and do not necessarily reflect the official policy or position of ARENA.

Lead organisation: The Australian National University
Project commencement date: 1 August 2018
Completion date: 28 March 2022
Reporting Period: 1 August 2018 to 30 September 2020
Contact name: Professor Kylie Catchpole
Email: kylie.catchpole@anu.edu.au
Phone: 02 6125 0874

CRICOS Provider: 00120C
ABN: 52 234 063 906

Table of Contents

Contents **3**
Executive Summary **4**
Project Overview **5**
Project Summary 5
Project Scope 5
Outcomes 6
Transferability 6
Conclusions and next steps 7
Lessons Learnt **8**
Lessons learnt report: Solar hydrogen research 8

Executive Summary

The aim of this project is to design, fabricate and integrate low-cost semiconductors and catalysts for direct solar-to-hydrogen production systems. Achieving a high solar-to-hydrogen (STH) conversion efficiency based on durable low-cost materials is crucial to promote commercial adoption of solar hydrogen systems. However, the STH efficiencies demonstrated till now with low-cost materials remained relatively low with poor operational stability.
When two semiconductors with complementary light absorption abilities (i.e., one absorbing the blue part and the other absorbing the red part of the solar spectrum) are configured in tandem, they could exploit a larger fraction of the solar spectrum, providing high STH efficiencies necessary for practical implementation. Perovskite and Si are low-cost semiconductors suitable to construct a tandem cell for carrying out direct solar hydrogen production at high efficiencies when integrated with Ni-based catalysts.

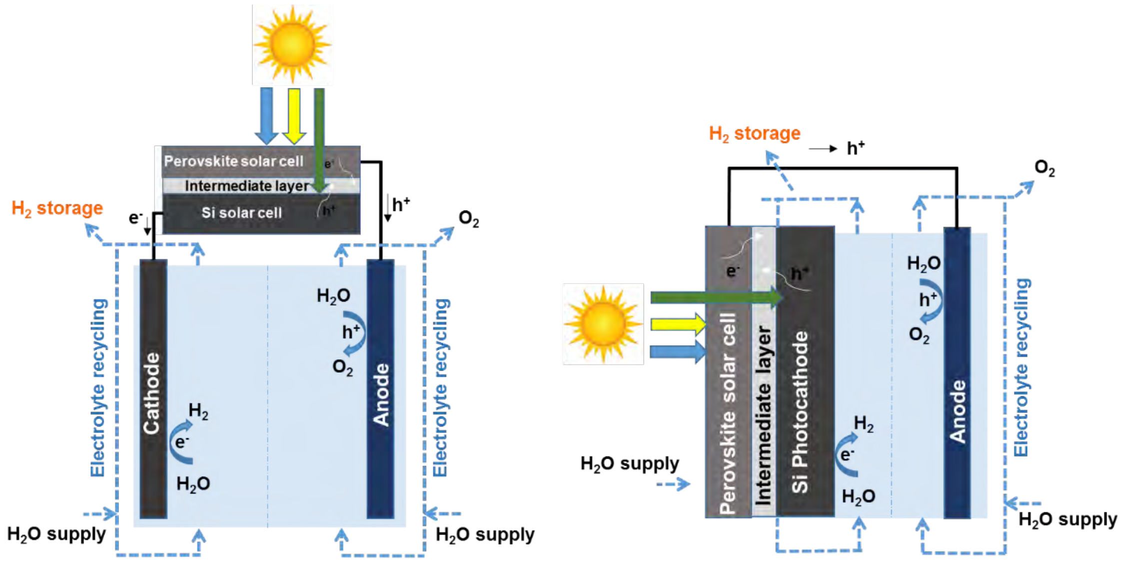
The project focusses on the design and development of robust integrated solar-driven water splitting systems with >18% STH conversion efficiency at ambient conditions using all low-cost materials (perovskite/Si tandem cell and Ni-based catalysts), advancing the commercial prospects of low-cost solar hydrogen production.

Project Overview

Project Summary

At the mid-term point of the project, the main goal was to integrate perovskite and Si tandem cells with earth-abundant low-cost catalysts enabling direct solar hydrogen production via both photovoltaic (PV)-electrolysis and photoelectrochemical (PEC) routes (see Figure 1). In the PV-electrolysis route, the tandem PV cells were coupled with earth-abundant Ni-based catalyst electrodes, to realise a direct solar hydrogen generation. The advantage of this system is the simplified integration and flexibility of the architecture. The major development effort went towards designing custom configurations of solar cells that can then be used to drive water splitting, while at the same time achieving a high system efficiency.

In a PEC tandem cell, perovskite PV is integrated with a Si photoelectrode and coupled with a counter electrode. The advantages of PEC method is its simplified two-component architecture, which could result in reduced costs, and the ability to utilize waste heat from the photovoltaic conversion, which could increase the rate of catalysis. Si photocathodes were developed with an improved performance by optimising material designs, adopting light management strategies, and catalyst integration. A high performing perovskite cell was developed to combine with the Si photocathode. The tandem photocathode was then combined with a counter electrode to realise high efficiency solar hydrogen generation.



PV-Electrolysis Route **PV-PEC Electrolysis Route**

Figure 1: Configurations that are investigated in this project a) PV-electrolysis, in which a photovoltaic tandem cell is electrically connected to water splitting electrodes and b) PV-PEC electrolysis, where a tandem photocathode is connected to an anode to form an integrated system.

Project Scope

Cost and efficiency are two major bottlenecks to the widespread commercial production of solar hydrogen. This project addresses both the challenges by developing abundant and readily available materials and assembling them into inexpensive, robust, and highly efficient solar hydrogen systems. The STH efficiency of the systems using only a single semiconductor is severely limited as the semiconductor can only absorb a limited portion of the solar spectrum. In this project, tandem semiconductors with complementary bandgaps are used, which can utilise a larger proportion of the solar spectrum to generate the necessary voltage from sunlight to drive the water splitting reactions.

This results in a much higher STH efficiency, which is essential for low overall system cost. The project utilises Si as the bottom absorber, taking advantage of its low cost and dominant market position. Perovskite is used as the top absorber because of its potential for low-cost fabrication and high-efficiency.

A further goal of the project involves the development of highly efficient, low-cost electrocatalysts based on earth-abundant metal composites and incorporating the new catalysts in the individual components and full systems. Low-cost, robust Ni-based binary composites (e.g., $NiFe(OH)_x$ and $NiMo_x$) are developed to drive the oxygen-evolution reaction and hydrogen-evolution reaction at high catalytic efficiencies. The developed catalysts are integrated onto surface-modified Si substrates (for PEC approach) or three-dimensionally interconnected porous Ni foams (for PV-electrolysis approach) for enhancing water-splitting performance.

Finally, the integration of the components developed is carried out to realise high-efficiency, bias-free water splitting via perovskite/Si tandem PV integrated electrolysis and perovskite/Si tandem PEC system. Ultimately, this project targets to achieve STH efficiencies above 18% for the integrated water splitting systems.

Outcomes

To minimise the overpotential losses of catalyst materials, we optimised NiMox and NiFe(OH)x catalysts by tuning their compositions, morphology and synthesis processes. In particular, we prepared NiMox catalysts for hydrogen evolution reaction with an innovative flower-stem morphology affording increased active surface area and low reaction overpotential. We also optimised the performance of Si photocathodes by adopting buried p-n junction architecture and decoupled reaction and light harvesting interfaces, resulting in a greatly improved photocathode performance. These results paved the way for realising both the PV-electrolysis and PV-PEC systems for solar-driven water splitting with impressive STH efficiencies > 16%.

Through the optimisation of catalyst performances and Si photocathode device architecture, we were able to develop solar-driven hydrogen production systems with efficiencies exceeding the milestone requirements (achieved >16%, milestone >13%). These are amongst the best results reported to date for direct solar-to-hydrogen generation. In addition, the performance of the NiMox catalyst, requiring an overpotential of 6 mV at a current density of 10 mAcm-2, is the best reported performance for the hydrogen evolution reaction. Similarly, the applied-bias photocathode efficiency of 14% achieved for Si photocathodes developed in this project is one of the highest reported value for Si photoelectrodes.

While further work is still needed to improve the STH efficiency to 18%, as well as achieve the desired operational stability, these results represent significant technological advances made in enabling high efficiency stand-alone solar water splitting systems.

Transferability

Though the innovations made and challenges addressed in this project are more specific to solar hydrogen production systems, they are broadly applicable to PV cells and electrolysers. For example, the devices engineering approaches developed are useful to fabricate various PV devices. Similarly, the developed low cost Ni-based catalysts can find use in alkaline electrolysers.

Knowledge sharing within the project occurs through regular meetings, seminars, as well as internally produced documents that detail specific processes. The project partners participate in regular meetings to discuss new results and specific challenges. The chief investigators and other researchers involved in the project regularly attend conferences, visit research institutions, and give talks at a variety of forums for both specialist and non-specialist audiences. One of the project members is also scheduled to give a public webinar in November this year, hosted by the Energy Change Institute at ANU.

In addition, significant outcomes are shared with general public through news articles. To date, our research findings have been covered in various news articles by RenewEconony, ANU News, PV magazine, Electronics Weekly, New Atlas etc.

Conclusions and next steps

The project has so far been successful in advancing direct solar hydrogen technologies achieving >16% STH efficiency by optimising and integrating perovskite/Si tandem and low-cost catalysts. However, there are still many remaining challenges towards commercial adoption, including further improvements in the efficiency and operational stability of the material systems. Our current work to address these challenges is focussed on understanding the degradation mechanism of catalysts and solar cells, and tuning of material properties towards obtaining a stable performance. To better inform future work on this technology, we are also undertaking technoeconomic feasibility studies of the developed solar water splitting systems.

Ultimately, the benefit of the project will be to facilitate and accelerate the development of commercial technologies for solar hydrogen generation by developing robust integrated stand-alone systems with >18% STH conversion efficiency, providing widespread potential for renewable hydrogen exports from Australia.

Lessons Learnt

Lessons learnt report: Solar hydrogen research

Project Name: *Low-Cost Perovskite/Silicon Semiconductors Integrated with Earth Abundant Catalysts for Efficient Solar Hydrogen Generation*

Knowledge Category:	Technical
Knowledge Type:	Technology
Technology Type:	Solar Hydrogen
State/Territory:	ACT

Key learning

The project faced difficulties in reproducing the device performances. This is due to the dependence of the project on the use of a range of synthesis and fabrication equipment which are also shared by other researchers for many other purposes. The recent laboratory closedowns due to hail damage and COVID-19 also contributed to this issue, resulting in nonconformity of the state of the equipment.

Implications for future projects

It is imperative in future projects to better estimate these risks and develop rigorous standardisation criteria for the individual processes.

Knowledge gap

N/A

Background:

Objective or process requirements

Through this stage of the project, we aimed to develop integrated solar water splitting systems with all low-cost materials achieving >13% STH efficiency. To meet the requirements of this stage, we have undertaken 1) design and fabrication of low-cost tandem solar module architectures specifically for water splitting applications, 2) discovery of new catalysts by material innovation and optimisation of the structure-performance and reaction mechanisms, and 3) development of new methods for integrating highly efficient, low-cost solar hydrogen modules with high STH efficiency and robustness.