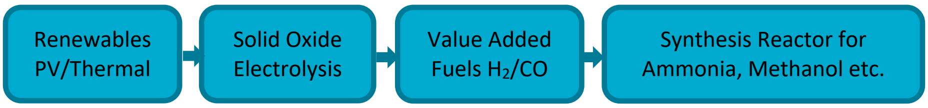
Australia's National Science Agency

CSIRO Solid oxide electrolysis: *Liquid fuels R&D Project*



Efficient sustainable production of value-added fuels and chemicals from CO_2-Steam solid oxide electrolysis and renewables

End of Activity Public Summary Report

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Contents

Project summary and scope

The effects of climate change have been felt globally; in Australia specifically, the temperature has increased on average by 1.44 ± 0.24°C since 1910. The emissions of the primary anthropogenic GHG, carbon dioxide have been increasing since the industrial revolution and the burning of fossil fuels (Brander et al., 2012). This has resulted in estimations that global average atmospheric carbon dioxide levels are currently higher than at any other point within the last 800,000 years (Lindsey et al., 2020)

Hydrogen emits no carbon-di-oxide when burned – thus if the future is hedged on hydrogen, the solid oxide electrolysis (SOE) technology can effectively produce hydrogen from H_2O feedstock by integration with renewables. It can also generate syngas by using H_2O and captured CO_2 from CO_2 intensive industrial processes such as power generation, cement, and steel manufacturing, to produce carbon neutral fungible fuels (Jouny et al., 2018). The stored renewable energy in the form of value-added chemicals and fuels can then be transported over long distances to areas lean in renewables.

Australia's vast renewable energy (RE) generation potential and opportunity for exporting renewable energy are well documented in the National Hydrogen Strategy and various roadmap documents from different federal and state government agencies, and affiliated institutions including CSIRO. Importantly, cost of the renewable energy sources is dropping significantly resulting in its global penetration of the energy sector. SOE technology could help to effectively utilize the renewable energy and overcome the challenges associated with intermittent nature of renewable energy.

Advantageously, the waste heat available in industrial processes or downstream processes to produce hydrogen carriers such as ammonia can be utilized in SOE which could lead to a 30 % reduction in electricity requirements for SOE operation. The efficiency of such a system can be further boosted using low-cost solar thermal heat (<0.5 c per kWh) as a supplement leading to an overall energy conversion efficiency (ratio of energy content of liquid fuel to energy input to SOE process) above 70%.

The major activities during ARENA liquid fuel R&D project were to develop a solid oxide electrolyser device for production of hydrogen, CO or a mixture of both hydrogen and CO (synthesis gas) and its integration concepts from solar energy to liquid fuels. These objectives were achieved through the following outcomes as per the agreement.

1) Development of SOE materials and process optimization for efficient generation of fuel gases such as H_2, CO or syngas from CO_2 and H_2O as a feedstock.

2) Construction and operation of scalable SOE stack (250 W)

3) Integration of CSIRO's tubular SOE with solar thermal/PV at RayGen's site and operation of SOE using high temperature steam from concentrated sunlight from solar furnace test facility.

4) Identification of most suitable fuel (syngas) compositions for downstream processes.

5) Develop concepts for integration by finding the optimal set of conditions for units to run together as an integrated system, cost-benefit analysis, and commercialisation roadmap development.

The areas of involvement and roles of partners to achieve above milestones are listed in Table 1.

Table 1 Areas of Involvement of partners and their roles in the activity

Organisation	Roles
CSIRO	• Design and development of SOE cathode materials • Demonstration of scalable SOE stack with fuel production capacity >3L per hour • Project coordination
Ben Gurion University at Negev	• Development and optimisation of downstream process model and catalysts which can use syngas produced by CSIRO's SOE and convert it into transportable liquid fuels • Provide CSIRO with most optimal syngas composition and -CO to H_2 ratio • Preliminary Technoeconomic model
Johnson Matthey	• Assist CSIRO in the development of SOE cathode materials to understand the solubility limits of various dopants in oxide materials using propriety synthesis and advanced characterisation techniques • Provide catalyst for evaluation in SOE technology
RayGen Resources Pty Ltd	• Build a solar thermal/PV design compatible with CSIRO's tubular SOE • Prepare testbed at RayGen's solar test facility in Melbourne, construct flow circuits and peripherals to test CSIRO SOE

	onsite using concentrated solar thermal energy to provide steam at 800 °C.
Northwestern University	• Advice on the selection of the materials, and testing conditions • Synthesis and supply of selected electrode materials to CSIRO
ABEL Energy, Australia	• Participation in market analysis and development of technology roadmap

1. Key highlights and outcomes

1.1 SOE stack operation and materials development

A major emphasis of this work was on the building and operation of a SOE tubular stack having a capacity of 250 W. To achieve this, tubular 8-cell stack was built with active area of 400 cm^2 (50 cm^2 each tube). During testing, a SOE stack was housed within a specially designed cabinet with data acquisition and power supply. All the safety systems were installed such as heat and gases interlocked with a safety system, capable of shutting the rig down when safety limits are reached.

Steady state operation of the stack was achieved during testing for 350 hours with a fuel production rate greater than 12 L/hour. Notably, the CSIRO SOE stack can be easily scaled up as per the fuel requirements of downstream processes. In addition, it provides flexibility of production of variety of fuels such as H_2, CO and/or syngas as required in downstream processes using H_2O and CO_2 as a feedstock.

The CSIRO SOE stack design is adaptable as it can be integrated with various upstream energy sources and downstream fuel synthesis processes. Some of the additional advantages of CSIRO technology is the simplicity of its tubular design relative to planar designs could provide increased durability while allowing integration with intermittent renewable energy sources. The technology features such as fewer components, with no need for high temperature seals and less equipment operating at high temperature are expected to lead to prolonged life and improved performance.

In parallel to research activities, new cathode materials provided by Johnson Matthey were evaluated for SOE as a part of cathode development work. Notably, SOEC cathodes developed at CSIRO can directly produce fuel gases without requirement of any additional reducing gas such as H_2 or CO in the feed stream. With the state-of-the-art materials, additional supply of the reducing gas such as hydrogen is required during the start and shutdown to prevent oxidation of nickel into nickel oxide which leads to performance degradation. The electrodes require less electrical energy per unit volume of hydrogen or carbon monoxide or a mixture of both (syngas) as compared to traditional Ni-YSZ electrodes (commercially purchased) when tested in our lab using a similar fabrication method and the same test setup.

Advantageously, the same catalyst can be used for both positive and negative electrodes, therefore the time and costs of SOEC fabrication can be reduced. Typically, different materials are used for the fabrication of the negative electrode (Nickel-YSZ composite) and positive electrode ("LSM-YSZ" composite). The temperature used for heat treatment during fabrication process is different when two different materials are used, and as such a two-step processing is required where negative electrode is typically fabricated using heat treatment at 1500 °C followed by positive electrode typically fabricated at 900 to 1100 °C (Zheng et al., 2017). The material developed at CSIRO enables faster fabrication as both positive and negative electrode can be heat treated at the same time. Further, the heat treatment for both electrodes can be carried out at only 800-850 °C (Kaur et al., 2020; Kulkarni et al., 2017).

To demonstrate the concept of SOE operation powered by solar thermal, an SOE testing setup was built and integrated into RayGen's solar furnace test facility. Stable high temperature steam (~ 700 °C) generation was first demonstrated using concentrated solar in the solar furnace. This test validated the functioning of the water/steam circuit and water heater coil, with water pumping flow rates and operating processes refined for optimal operation in preparation for integrating the steam circuit with the electrolyser. Notably, H_2 production via SOE was then demonstrated with solar generated feed steam (topped up) to 800°C. The successful operation of the SOE unit using renewables opens wider options of the production of multiple fuels such as H_2, CO or syngas for downstream processes. Further optimization such as matching the components through the system and longer test periods will be required for further scaleup as work was impacted by COVID-19 restrictions.

1.2 SOE integration and technoeconomic aspects

To determine the benefits of the integration of the technologies in real world conditions we have performed a preliminary techno-economic analysis of producing syngas from a waste stream of CO_2 and H_2O as a feedstock. A known optimised H_2/CO molar ratio for syngas to produce fungible fuels was used as the starting point. The optimal conditions in downstream processes for production of methane, olefins and paraffins were determined with partnership with Ben Gurion University (Kulkarni et al., 2021). Two techno-economic analyses were conducted to obtain values to assess the potential profitability of the plant (net present value NPV and internal rate of return IRR) and to compare to alternative processes (levelized cost of production LCOP).

A plant output of syngas that contains 20,000 tonne H_2/year was assumed and used as the base case. A mass balance was completed from this known molar ratio to determine the amount of steam and CO_2 required as input for a plant to produce syngas that contains 20,000 tonne H_2/year. With the optimised H_2/CO molar ratio of 0.7, this calculates to be a 420,000-tonne of syngas/year plant. Efficiencies for solid oxide electrochemical cell (SOEC) and steam generation from the first RayGen heat exchanger were assumed as 81% and 80%, respectively.

An energy balance was also undertaken from the known electricity consumption of the SOEC (64 Wh/mol) to determine the electricity required to operate the SOEC unit, and the required SOEC capacity, which was determined at 194 MW. A heat balance was completed from the requirements for the process as the SOEC operation was determined to be optimised at 800°C. The duties required were determined utilising ChemCAD software and simulating a low-grade heat exchanger and subsequent concentrated solar thermal heat exchanger to bring the water to steam and then the steam and CO_2 mixture to 100°C and 800°C, respectively.

The first techno-economic analysis to determine the potential profitability of the project was conducted by determining the NPV, the IRR and payback period for the project. The production costs of fossil syngas were set as a selling price for the syngas as an assumption to complete this analysis. A sensitivity analysis was also conducted to assess the effects on the potential profitability of the project due to changes to various parameters.

The second techno-economic analysis was conducted to determine the levelized cost of production, by making some key assumptions regarding the lifetime and output of the project. A sensitivity analysis was also conducted to assess the effects on the levelized cost of production due to changes to various parameters.

The levelized cost of production for syngas produced by co-electrolysis using SOEC and renewable energy was determined as $0.187/kg. The capital costs of the plant have been estimated at $108.8M and the operating costs of the plant estimated at $75.3M/year. The net present value was estimated as $14.5M, with an internal rate of return of 11.5% and payback period of 19.2 years. Sensitivity analysis shows that the process is highly sensitive to changes in the electricity price, and economics of the plant are highly dependent on the carbon-neutral syngas selling price and purchase cost of renewable electricity. However, although the market is not yet developed, the selling price of carbon neutral syngas fuel is expected to attract premium over conventional natural gas. The longer term target of green hydrogen production is set at $16.66/GJ (based on low heating value of H_2 or $2/kg H_2) in the first low emission statements document published by the Australian Government.

1.3 Challenges and lessons learnt

The uneven heat distribution along the length of the furnace have been noticed during the lab experiments which needs to be optimised by designing the furnaces with prolonged heating zones for evaluation of scalable cells at constant temperatures. In addition, long term operation of SOE unit with integration with solar thermal test facilities needs to be conducted in future and process conditions needs to be optimised for higher hydrogen production rates. Due to COVID-19 restrictions and limited availability onsite these experiments will be planned in future.

2. Technology roadmap

Integration of SOE with the steel and ammonia industry is found to be more relevant where waste heat can be utilized immediately in the solid oxide electrolyser and the produced hydrogen can be directly used in various downstream processes. The next stage of development is being planned to be undertaken in partnership with BlueScope Steel at their operating blast furnace facility at Port Kembla. The project aims to demonstrate the operation and durability of SOE with integration with steel blast furnace operating conditions. A source of high-quality steam is available from the Port Kembla blast furnace and the balance of plant design to integrate this with CSIRO's technology will form part of the experimental program. The experimental program will deliver 1-2 kW scale demonstration plant and the operating information to commence manufacturing of larger commercial scale units. BlueScope's engineering capabilities will assist in the design of the BoP to be effectively integrated with the plant.

Once proven, the technology will enable the transition towards green steel production by displacing pulverised coal from the blast oxygen furnace iron-making process. Demand from this application offers potential for a foundation customer for the technology. The IEA has identified the need to develop downstream infrastructure for transport, storage and use as a significant challenge to adopting hydrogen independent of broader competition and policy barriers. Targeting steel and industrial applications with captive demand for hydrogen largely eliminates these challenges.

3. Knowledge sharing activities

ARENA's Survey

All information requested by ARENA has been provided and ARENA surveys have been completed.

Web Articles

1. This project was covered exclusively by Gas World Magazine, a highly reputed UK based industry magazine

https://www.gasworld.com/solid-oxide-electrolysis-grows-up-at-csiro/2018987.article

2. The project also got further coverage on the website of Ammonia Energy Association, a reputed organisation with chapters in Australia and USA

https://www.ammoniaenergy.org/articles/csiro-at-work-on-soec-technology/

(Ammonia energy association's article was not prepared in consultation with CSIRO, rather they pulled information from published interview and journal papers)

Conference presentations

1. *A solid oxide electrolysis for green fuels*, Global technical conference on fuel cell technology, Automotive Research Association of India, July 2020 (online)

2. *An efficient, economical and scalable solution for renewable hydrogen, ammonia and value-added chemicals production*, Positioning Hydrogen 2020: Opportunities and Challenges, Webinar organised by Prism Scientific Australia

3. *Solid oxide electrolysers for sustainable fuels production*, 2nd International Conference on Electrolysis 2019, Loen, Norway

4. *Materials designing for redox stable electrodes for solid oxide electrolysis technology*, 2nd Annual Advanced Water Splitting Technology Pathways: Benchmarking & Protocols Workshop, US DOE, Phoenix, AZ

5. *Efficient Solid Oxide Electrolysis for Syngas Generation, A solid oxide electrolysis technology for efficient syngas generation*, 8th International Conference on Fundamentals and Developments of Fuel cells 2019, Nantes, France.

6. *Three-dimensional microstructure measurements of SOE and batteries: electrode microstructure and long-term durability* CSIRO site seminar by Prof. Scott Barnett

Papers published/submitted

1. *High-performance composite cathode for electrolysis of CO_2 in tubular solid oxide electrolysis cells: A pathway for efficient CO_2 utilization*, Gurpreet Kaur, Aniruddha. P. Kulkarni*, Daniel Fini, Sarb Giddey, Aaron Seeber, Journal of CO_2 Utilization 41, 101271, 2020. https://doi.org/10.1016/j.jcou.2020.101271

2. *Challenges and trends in developing technology for electrochemically reducing CO_2 in solid electrolyte membrane reactors*, HK Ju, G Kaur, AP Kulkarni, S Giddey, Journal of CO_2 Utilization 32, 178-186, 2019. https://doi.org/10.1016/j.jcou.2019.04.003

3. *Techno-Economic Analysis of a Sustainable Process for Converting CO_2 and H_2O to Feedstock for Fuels and Chemicals*, AP Kulkarni, T Hos, MV Landau, D Fini, S Giddey, M Herskowitz, Sustainable Energy & Fuels 5(2), 486-500, 2021. https://doi.org/10.1039/D0SE01125H

4. *A review on synthesis of methane as a pathway for renewable energy storage with a focus on solid oxide electrolytic cell-based processes. S Biswas, AP Kulkarni, S Giddey, S Bhattacharya, Advances in Power-to-X*: Processes, Systems, and Deployment. Frontiers in Energy Research, 8, 570112, 2020. https://doi.org/10.3389/fenrg.2020.570112

5. In *situ synthesis of methane using Ag–GDC composite electrodes in a tubular solid oxide electrolytic cell: new insight into the role of oxide ion removal*, S Biswas, AP Kulkarni, D Fini, S Giddey, S Bhattacharya, Sustainable Energy & Fuels 5 (7), 2055-2064, 2021. https://doi.org/10.1039/D0SE01887B

6. *Catalyst-induced enhancement of direct methane synthesis in solid oxide electrolyser*. Saheli Biswas, Aniruddha Kulkarni, Daniel Fini, Shambhu Singh Rathore, Aaron Seeber, Sarbjit Giddey, Sankar Bhattacharya, Electrochimica Acta, 391, 138934, 2021. https://doi.org/10.1016/j.electacta.2021.138934

7. *A theoretical study on reversible solid oxide cells as key enablers of cyclic conversion between electrical energy and fuel.* Saheli Biswas, Shambhu Singh Rathore, Aniruddha P. Kulkarni, Sarbjit Giddey, Sankar Bhattacharya, Energies 14(15), 4517, 2021 https://doi.org/10.3390/en14154517

Papers submitted to journal or internal CSIRO review

8. *A Critical Review on High Temperature Solid State Technologies for Electrochemical Conversion of CO_2/Steam to Value Added Fuels,* G. Kaur, A. P. Kulkarni, S. Giddey, HyungKuk Ju (to be submitted to Applied Energy, draft can be provided)
9. *Stable high performing $Sr_2Fe_{1.7}Mo_{0.3}O_{6-\delta}$-Ag composite cathode for steam electrolysis in solid oxide cells,* Gurpreet Kaur, Aniruddha. P. Kulkarni, Sarb Giddey, Mark Greaves (to be submitted, draft can be provided)

10. *Fe–$Ce_{0.1}Zr_{0.9}O_{2-\delta}$–Ag electrode for one-step methane synthesis in solid oxide electrolyzer.* Saheli Biswas, Aniruddha P Kulkarni, Aaron Seeber, Mark Greaves, Sarbjit Giddey, Sankar Bhattacharya, 2021, submitted to Solid State Ionics.

Patent Application

1. Novel composite electrode material (Ag-Ceria doped hybrid particles), electrodes thereof, and a one-step method to prepare the composite electrode material for solid oxide cells, Patent drafting by FB Rice.

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Technology Briefs ("pitching slide deck") with some key features of this development work have been sent to following companies who may be interested in partnership for technology development beyond this project. BlueScope steel, Australia is willing for the demonstration of SOE at their Port Kembla site.

1. MSV (Venture capital group)

2. Boeing Corporation, Seattle, USA

3. Bharat Petroleum Corporation Ltd, India

4. WorleyParsons Limited, Australia

5. SGSP Assets Pty Ltd, trading as Jemena

6. BlueScope Steel, Australia

4. Conclusions and next steps

SOE technology has potential to effectively produce value added fuels such as hydrogen, CO and syngas from H_2O and captured CO_2 as the feedstocks which can also be directly utilized for production of various liquid fuels in downstream processes. For SOE operation, the use of low-cost electricity and/or thermal energy from renewables and the utilization of waste heat while integration with downstream processes can boost the energy efficiency of system.

During the research period funded by ARENA, extensive efforts were made on designing, developing, and evaluating the cathode materials and their durability studies in various fuel environments. Cathode materials developed by CSIRO were found to be much more efficient than conventional Ni-YSZ cathodes. Advantageously, same materials can be utilized as anode and cathode reducing the fabrication process and cost of overall system. No protecting gas such as H_2 was used in the feed stream in current studies as required in Nickel -YSZ cathodes to maintain the Nickel in metallic state. This not only avoids the complexities of the system caused by recycling of some of the product to feed stream but also reduces the overall operating cost.

SOE stack was constructed and demonstrated for producing greater than 12 L per hour of fuel gas. The SOE operation at 800°C was also demonstrated at the RayGen site successfully by utilizing high temperature steam generated in the solar test furnace topped up to working temperature. Further optimization such as matching the components through the system and longer test periods will be required for further scaleup.

Detailed technoeconomic analysis performed while considering the optimal set of conditions of upstream and downstream processes to evaluate the potential probability of integration of technologies. The electricity cost is observed to be dominant factor which is almost 52% of overall process. The levelized cost of product for syngas produced by co-electrolysis using SOEC and renewable energy was determined as \$0.187/kg. The selling price of natural gas is generally around \$0.39/kg (assuming long term price of \$7.5/GJ). The capital costs, operating costs and potential profitability for a plant producing 420,000 tonne/year of syngas have been estimated. The capital costs of the plant have been estimated at \$108.8M and the operating costs of the plant estimated at \$75.3M/year. The net present value was estimated as \$14.5M, with an internal rate of return of 11.5% and payback period of 19.2 years. Sensitivity analysis shows that the process is highly sensitive to changes in the electricity price, and economics of the plant are highly dependent on the syngas selling price and purchase cost of renewable electricity.

Future work would involve a techno-economic analysis and potential profitability analysis for other targeted fuels such as diesel, gasoline, and jet fuel by considering integration of various upstream (renewables), SOE (H_2/CO) and downstream processes (fuel synthesis reactor) with optimised conditions.

The technology development roadmap is provided for the pilot scale demonstration of a kW scale SOEC with parallel accelerated research activities for further developments. These include targeting high current densities (>1 A cm^{-2}) and durability analysis of stack in real world conditions up to 2000 hours. To achieve this, external funding with industry partner contribution will support the demonstration and start-up of experimental program and parallel activities for scaling and growth. The onsite demonstration at BlueScope steel at Port Kembla is being discussed which once proven will enable the transition towards green steel production and offers the potential of a foundation customer for the technology.

Abbreviations

RE	Renewable Energy
SOE	Solid oxide electrolyser
SOEC	Solid oxide electrochemical cell
YSZ	Yttria-stabilised Zirconia
LSM	Lanthanum strontium manganite
NPV	Net present value
IRR	Internal rate of return
LCOP	Levelized cost of product
TEA	Technoeconomic analysis

References

1. Brander, M., Davis, G., *Econometrica, White Papers*, 2012. Greenhouse Gases, CO_2, CO_2e, and Carbon: What Do All These Terms Mean?
2. Lindsey, R., Climate Change: Atmospheric Carbon Dioxide, https://www.climate.gov/news-features/understanding-climate/climate-change-atmospheric-carbon-dioxide).
3. Jouny, M., Luc, W., Jiao, F., General Techno-Economic Analysis of CO_2 Electrolysis Systems, Industrial & Engineering Chemistry Research, 57 (2018) pp. 2165-2177. https://pubs.acs.org/doi/abs/10.1021/acs.iecr.7b03514
4. Zheng, Y., Wang, J., Yu, B., Zhang, W., Chen, J., Qiao, J., Zhang, J., A review of high temperature co-electrolysis of H2O and CO2 to produce sustainable fuels using solid oxide electrolysis cells (SOECs): advanced materials and technology. Chem Soc Rev 46 (2017) pp 1427-63. https://doi.org/10.1039/C6CS00403B
5. Kaur, G., Kulkarni, A.P., Fini, D., Giddey, S., Seeber, Aaron., High-performance composite cathode for electrolysis of CO_2 in tubular solid oxide electrolysis cells: A *pathway for efficient CO_2 utilization*, 41 (2020) pp. 101271. https://doi.org/10.1016/j.jcou.2020.101271.
6. Kulkarni, A.P., Giddey, S., Badwal, S.P.S., Efficient conversion of CO_2 in solid oxide electrolytic cells with Pd doped perovskite cathode on ceria nanofilm interlayer. J CO2 Util, 17 (2017) pp. 180-187. https:/./doi.org/10.1016/j.jcou.2016.11.014.
7. Kulkarni, A.P., Hos, T., Landau, M.V., Fini, D., Giddey, S., Herskowitz, M., Techno-economic analysis of a sustainable process for converting CO2 and H2O to feedstock for fuels and chemicals. Sustainable Energy & Fuels 5 (2021) pp. 486-500. https://doi.org/10.1039/D0SE01125H

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