Australia's National Science Agency

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

Midterm Activity Report

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Project Summary and Scope

This document presents the interim summary of the activities related to the *ARENA liquid fuel R&D project* for public release. The project focuses on the development and integration of key components of a technology suite which once fully developed caters for both generation of renewable hydrogen as well as its conversion to liquid fuels. The major part of the proposed development focuses on the solid oxide electrolyser (SOE) device; however, it also includes crucial activities for matching the SOE characteristics (input power requirements and outlet gas composition) with other key system components to support practical-scale integration. The long-term goals of this work (beyond the life of this current project) are to demonstrate a fully integrated system consisting of Solar Energy Source coupled directly to SOE, and a thermally integrated catalytic reactor for downstream processing of synthesis gas to produce liquid fuels.

Australia's vast potential of renewable energy (RE) generation and opportunity for exporting renewable energy from Australia is well documented in the National Hydrogen Strategy and various roadmap documents from different federal and state government agencies, and affiliated institutions including CSIRO. In the past couple of decades, the cost of production for RE sources has significantly reduced. For example, in the last 10 years, the cost of wind energy (onshore and offshore) has decreased 68%, while solar energy costs have dropped rapidly from 0.378 USD/kWh to 0.045 USD/kWh [1]. Once the electricity from renewable sources is generated, it must either be transported via the electrical grid or transformed into another form. Inherent intermittency and uneven distribution remain the key challenges for the RE supply chain. In several instances, the regions lean in RE supply are the largest consumers of energy. Batteries cater for short term energy localised storage solution, however, strategies for transport and export of RE need to be devised. In response, along with green hydrogen, various hydrogen carriers like ammonia and synthetic hydrocarbons produced using green hydrogen are being evaluated as a media to transport and store RE. Several alternative technologies to produce renewable fuels are under exploration. However, both process cost and capital remain a strong barrier to further acceptance of technologies.

This project proposes the use of SOE technology for production of hydrogen or a synthetic gas by electrolysis of water (steam) or simultaneous electrolysis of steam and waste carbon dioxide. The basic principle of operation for SOE is shown in Figure 1. SOE is an electrochemical device fabricated with ceramic or metal-ceramic composite components. It consists of a dense non-porous oxygen ion-conducting membrane on which electrodes are coated. The electrodes can be connected to the electricity supply. The input feed which can be either steam or CO_2 or a mixture of both is fed at the cathode (-ve electrode). The whole device is heated to the high operating temperatures, typically at 600 to 800℃. Under the influence of the electric field, the oxygen is stripped out from the input feed in ionic form and it emerges as oxygen gas at the anode (+ve electrode).

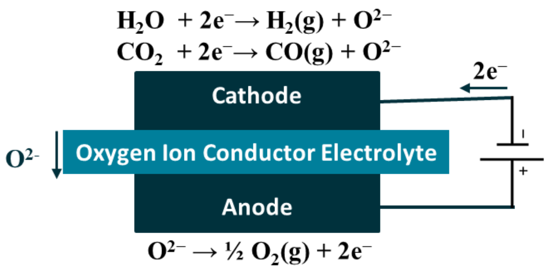

Figure 1 A schematic depicting the working principle of solid oxide electrolyser

The operation of SOE at elevated temperature enables the use of heat energy in a combination with electrical energy. Such operation can reduce the amount of expensive electrical energy required for electrolysis. Further, high temperature also significantly enhances the reaction kinetics and eliminates the need for expensive catalysts for water splitting reaction. Although not yet fully matured, SOE technology has potential to produce hydrogen and hydrogen carrier at substantially reduced costs ($2.14 to 2.74/kg) as compared to energy-intensive and thus expensive alkaline electrolyser (AEL) ($4.78 to 5.84/kg) and polymer electrolyte membrane (PEM) ($6.08 to 7.43/kg) electrolysis [2]. If waste CO_2 from industrial processes or produced from biogenic processes is available, the SOE can split it into carbon monoxide and oxygen. If a mixture of steam and CO_2 is supplied as input feedstock, SOE can produce a syngas (a mixture of H_2 and CO) in a single step without requiring external reformer or processing unit. The syngas thus produced is a potent feedstock which can be easily converted into ready to use liquid fuels using the downstream synthesis process. The heat required for endothermic SOE operation can be obtained from downstream fuel synthesis reaction which utilises syngas from SOE, and as such the integrated operation (Figure 2) results in up to a 30 % reduction in electricity requirements depending upon operating temperature. The efficiency of such a system can be further boosted using low cost solar thermal heat as a supplement leading to an overall energy conversion efficiency (ratio of energy input to the energy content of liquid fuel) above 70%.

The technology can accommodate the supply of RE in thermal and electrical energy forms. This is particularly interesting considering the low cost of renewable solar thermal energy (<0.07 USD/kWh) [3]. Furthermore, it can also be sourced as waste heat from industrial processes like steel, cement and chemical production. Compared to established waste heat utilisation processes, the use of waste heat in SOE can be, in principle, more energy-efficient.

While the focus of current work is on the generation of liquid fuels, gaseous hydrogen carriers such as methane and ammonia could also be produced with some modifications to the SOE system design and using well established downstream processes. It is worth noting that ammonia synthesis and methanation are both highly exothermic processes and as such SOE can be thermally integrated with the well-established Haber Bosch processes or synthetic methane production. While other electrolysers can also be integrated into such processes and are already being tested for such applications at scale, SOE is the only electrolyser which can utilise the heat obtained from the downstream process to reduce the electrical input.

Despite the enormous potential and significant developments, SOE remains an early-stage technology relative to other electrolysis technologies like PEM and AEL electrolysis. High costs, scalability, slower start-up and limited lifetime remain a barrier for the mass scale technology commercialisation. Further commentary on SOE state of the art and development areas is provided in the relevant technology reviews [4–7] and reports related to hydrogen technologies [8,9]. In this work, CSIRO is focusing on the development of novel low-cost materials and on simplifying SOE design which can potentially help to overcome these technical barriers. Further, the project aims at not only the development of SOE, but also developing complete process flow model for a fully integrated system from solar power to liquid fuels along with an optimal set of operating conditions.

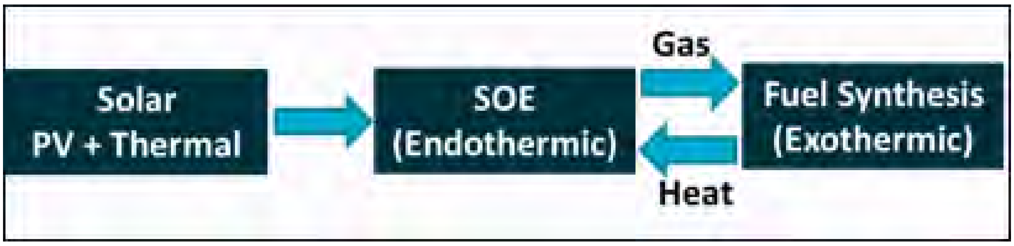

Figure 2 Schematic of an overall process based on SOE

Project design

The design of the project considers both the development requirements of components shown in Figure 1 as well as the challenges of their integration at an early stage, which is important to fast-tracking its commercialisation pathway. This allows developments in solar energy sources, electrolyser, and downstream gas to liquid processing to be addressed in a cost-effective manner, supporting integration at commercial scales. An SOE based liquid fuel generation system can be thought upon as considering three building blocks as shown in Figure 2:

1. Solar (Thermal and Electrical) Energy Source (referred as Solar PV/T)
2. Solid oxide electrolyser (SOE) producing hydrogen /syngas
3. Catalytic reactor for downstream conversion of syngas into liquid fuel.

A Solar PV/T system and downstream fuel synthesis reactors are in the advanced stage of development relative to novel tubular SOE cell and stacks, and hence the major emphasis of this technology (3 years total duration) is on SOE materials development and building a scaled-up SOE stack at CSIRO's Clayton labs. However, matching of Solar PV/T source and downstream fuel synthesis reactor to SOE in an efficient, technically and economically feasible manner is equally crucial for the commercialisation of the technology. Thus, a holistic development plan has been developed and implemented instead of developing these components in silos. A total of 6 organisations are involved in the development of this technology. The project team is working as a small consortium running parallel development programs each looking at different technical aspects but integrated and managed as a single project to ensure project goals and budgets are met. The involvement of partners and roles for this milestone are listed in Table 1.

Table 1 Involvement of partners and their roles in the activity

Organisation	Roles
CSIRO	• Design and development of SOE cathode materials • Development of SOE cell designs and scale-up • Demonstration of lab-scale SOE • Project coordination
Blechner Center for Industrial Catalysis and Process Development, Ben Gurion University at Negev	• Design, development and optimisation of downstream liquid fuel synthesis process and catalyst/s development • Technoeconomic and process flow modelling of integrated process • Technology roadmapping
Johnson Matthey (UK)	• Work with CSIRO for developing SOE cathode materials using propriety synthesis processes, expertise in materials design, and advanced characterisation techniques
RayGen Pty Ltd (Australian company developing large scale solar and allied systems)	• Build a solar thermal/PV design compatible with CSIRO's tubular SOE and test a small CSIRO SOE cell onsite (*Actual testing is planned for FY20-21*) • Development of integration concepts to enable optimal operation of SOE with solar thermal/PV co-generation • Technology roadmapping
Northwestern University (Materials Science & Engineering Department)	• Selection of the material, and testing conditions • Synthesis and supply of selected electrode material/s
ABEL Energy, Australia	• Participation in market analysis and development of technology roadmap

1 Key highlights and progress

The activities to date include the development of new electrode materials for SOE, and lab-scale demonstration of symmetrical tubular solid oxide electrolysis cells using newly developed electrodes and tubular cells, optimization of liquid fuel synthesis process and catalysts, and techno-economic analysis, and preparation of solar testbed at RayGen's site for testing CSIRO SOE.

1.1 SOE materials development and testing

The tubular SOE was tested to produce syngas (a mixture of CO and H_2) by electrolysis of water (steam) and CO_2, and pure hydrogen with steam electrolysis. The cathode and anode electrodes (See Figure 1) are key components of any electrolysis system where the splitting of input fluids (water or CO_2) and evolution of product gases (Hydrogen, CO and oxygen) take place. In the context of SOE, the cathode is one of the challenging components that need further development. A state-of-the-art cathode is a composite of Ni metal with yttria-stabilised zirconia ceramic, commonly referred to as Ni-YSZ. While a well-established fuel cell electrode, Ni-YSZ undergoes limiting degradation under electrolysis conditions reducing lifetime [10]. Further, the operation with Ni-YSZ requires to maintain the low oxygen partial pressure in the cathode chamber. This is typically achieved by operation under high current conditions or recirculating part of produced hydrogen back into SOE. Such approaches either reduce the lifetime or the efficiency of the system. In this phase of the project, a major emphasis of work at CSIRO was on developing an alternative cathode material. Based upon a comprehensive literature survey including insights from materials modelling and computation techniques we tested several cathode materials as an alternative to Ni-YSZ. Both in-house prepared, as well as commercially available cathodes, were evaluated using standard protocol to compare the performance under identical conditions. The performance of all the cathodes is evaluated in scalable and cost-effective tubular electrolyte-supported cells, so the scale-up and technology demonstration can be fast-tracked after an optimal cathode material is chosen. A testbed approach was taken meaning the developed materials were directly put to test for the electrolysis of dry CO_2 which is the most energy-intensive process, and selected materials were further tested for steam electrolysis and later for syngas generation with target ratio of 70 vol% carbon monoxide and 30 vol% hydrogen. Non-confidential work, along with details of experimental work are either submitted to journals or will be submitted this FY (20-21) or presented in various scientific conferences (*See knowledge sharing section of this report*). After comprehensive testing, a novel composite electrode design was conceived and developed. A unique feature of the development is the same material can be used as both a positive and negative electrode i.e. as anode and cathode. As the same electrodes can be used for both positive and negative electrode, the time in SOE fabrication can be reduced. Further, the heat treatment for both electrodes can be carried out at only 800-850°C. This is rather interesting considering the typical heat treatment of anode requires a very high temperature of about 1400°C and for cathode, it is typically above 1000°C [11]. The newly developed electrodes enable hydrogen or syngas production without requiring recirculation of hydrogen. In the preliminary tests, the electrodes demonstrated promising performance with only 35 kWh of electrical energy input required per kg of hydrogen, and only 2.5 kwh per kg of carbon monoxide. It should be noted that heat energy required to heat the furnace to SOE operating temperature is excluded as it can be obtained with a combination of heat generated in the cell due to internal Joule heating and heat from downstream fuel synthesis process topped with solar thermal.

Besides issues with the cathode material, a cell and stack design of SOE plays a crucial role in deciding cost and lifetime. A flat planar design typically used in the state of the art SOEs requires high temperatures gas sealing and involves complex manifolding to bundle or “stack” cells together. To simplify the cell fabrication and stacking, CSIRO undertook the development of simple tubular cell design and developed a new cell fabrication method which enables faster production and at scale.

1.2 Downstream process for liquid fuel synthesis

The downstream catalytic process for the conversion of syngas was designed and a complete process model was developed by The Blechner Center for Industrial Catalysis and Process Development of Ben Gurion University at Negev in Israel. The unique process developed by Blechner Center is based upon an inexpensive and mass-producible iron-based catalyst. The liquid fuels produced can be directly blended with gasoline fuels used in IC engines and vehicles without any modifications. The optimal ranges of the inlet syngas compositions (different H_2 to CO ratios) were identified for the process, and CSIRO’s SOE was optimised and tested to produce this composition of syngas. Unlike typical renewable liquid fuel synthesis processes which rely either on pure hydrogen or hydrogen-rich syngas, the Blechner process utilises syngas lean in hydrogen, and thereby enables a substantial reduction in the cost of liquid fuels. A comprehensive techno-economic analysis of the process shows overall energy efficiencies up to 70% can be achieved realistically. The sensitivity analysis shows the cost of liquid fuels depends upon the cost of renewable electricity and decreases with the size of the plant. Details of the analysis and results will be published in a peer-reviewed journal (*submitted to RSC Sustainable Energy & Fuels*).

1.3 Solar testbed preparation

For the preparation of the next phase of the project, CSIRO's SOE was moved to RayGen Pty. Ltd. site in Melbourne. RayGen's solar testbed capable of producing high-temperature steam (800°C) was modified and tailored to accommodate CSIRO's SOE. RayGen operates a solar furnace test facility to test the behaviour of new system component designs and to investigate new concentrating solar applications. This testbed enables laboratory testing of equipment under a focussed solar beam in a controlled and safe manner. The flexibility offered by this facility permits detailed diagnostic monitoring and performance of new equipment and technology to be assessed under high solar intensity loads which are representative of full-scale plant conditions.

1.4 Additional work

The focus of this work is on the production of hydrogen carriers in the form of liquid fuels, however, materials and designs of solid oxide electrolysis cells developed in this work were found to be very relevant to the synthesis of gaseous fuels like synthetic methane using renewable energy. Based upon the promising SOE results, we also carried out a review and energy balances for application of SOE to produce synthetic methane and compared it with the state of the art electrolysers like AEL and PEM electrolysers as applied to the production of synthetic methane or synthetic natural gas. We also reviewed the status of the electrolytic methane synthesis process. A review article came out of this work and is now accepted for publication in a journal as described in knowledge sharing section below.

2 Work in progress and commercialisation prospects

In the second phase of this project (already commenced at the beginning of this FY), the activities will be focused on:

1. Testing of CSIRO SOE at RayGen's Melbourne test site will commence evaluating the performance of SOE under realistic operating conditions.
2. A major emphasis of the next phase will be on the building of a larger capacity stack with multiple tube cells. The SOE stack will then be tested for 300 hours (minimum).
3. The current electrode materials and cell designs meet the stipulated performance targets. However, to make the technology more relevant to the hydrogen market, materials and cell design development will continue.
4. The performance data will be used to estimate the capital costs for the complete system from solar to liquid fuels production as well as pure hydrogen production in Australia.

Technology commercialisation roadmap

The final objective of this work involves the creation of a Roadmap document in consultation with industry and academic partners as well as potential customers and stakeholders including ARENA. As with any emerging energy technology, the demonstration of the technology in a relevant industrial environment is key for the early adaptation of the technology by industry sector. The SOE is a multifunctional technology capable of accepting different feedstocks and can produce different fuels or speciality chemicals for different industries. Thus, technology has multiple potential industrial use cases for both current and future applications. Identification of the first use case where the technology can provide the most significant competitive advantage will be important for the technology progression. CSIRO and partners will be working together in developing use cases, and the proposals for pilot plants will be discussed with the prospective partners. CSIRO has secured additional funding (*Innovation Acceleration Fund from CSIRO Commercialisation*) to hire a specialist consultant who will be assisting CSIRO and partners in identifying ideal uses cases and developing market entry strategy at the end of the current project lifecycle. *Innovation Acceleration Fund* also commits a seed fund for pilot project CAPEX along with the partners.

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 by Gas World Magazine (web), a reputed UK based industry magazine

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

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

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

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.

Papers published/submitted

1. *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
2. *High-performance composite mixed ionic electronic conductor cathode for electrolysis of Carbon dioxide in symmetrical Solid Oxide Electrolysis Cells compared with Ni-YSZ cathodes*, Gurpreet Kaur, Aniruddha. P. Kulkarni*, Daniel Fini, Sarb Giddey, Aaron Seeber, Accepted for publication in Journal of CO_2 Utilization, https://www.sciencedirect.com/science/article/pii/S2212982020305746?dgcid=author
3. *A Review on Synthesis of Methane as a Pathway for Renewable Energy Storage with a focus on Solid Oxide Electrolytic Cell based Processes*, Saheli Biswas, Aniruddha P Kulkarni, Sarbjit

Giddey, Sankar Bhattacharya, accepted for publication Frontiers in Energy Research, Open Access. https://www.frontiersin.org/articles/10.3389/fenrg.2020.570112/abstract

4. Techno-Economic Analysis of a Sustainable Process for Converting CO_2 and H_2O to Feedstock for Fuels and Chemicals, Submitted to Sustainable Energy & Fuels

Papers to be submitted to peer-reviewed journals this FY

1. *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, H. K. Ju (to be submitted)
2. Evaluation of B-site titanium doped ferrites for water and CO_2-H_2O co-electrolysis in solid oxide electrolysis cells
3. Syngas production with cobalt infiltrated MnO_2 based electrodes in solid oxide electrolysis cells
4. Efficient ferrite-based electrodes for steam electrolysis in solid oxide cells

Abbreviations

AEL	Alkaline electrolyser
PEM	Polymer electrolyte membrane
PV/T	Photovoltaic-thermal
RE	Renewable electricity
SOE	Solid oxide electrolyser
YSZ	Yttria-stabilized zirconia

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