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The Australian National University & University of Wollongong Hydrogen Generation Project:

Hydrogen Generation by Electro-Catalytic Systems

Research & Development Project

Funded under the Renewable Hydrogen for Export Program by the Australian
Renewable Energy Agency

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End of Activity Report

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1. Executive Summary

This document corresponds to the 'End of Activity' report for the Australian National University (ANU) and University of Wollongong (UoW) Hydrogen Generation Research and Development Project: *Hydrogen Generation by Electro-Catalytic Systems*. The project aimed to use biologically inspired catalysts with gas permeable electrode surfaces to develop a simpler and more efficient hydrogen generating electrolysis technology than any known to operate from pure water and renewable electricity.

The key thesis was to develop high performance catalysts with components that mimic those of the natural water oxidation catalyst of photosynthesis, namely, the *Photosystem II Oxygen Evolving Centre* (PSII-OEC). These were then to be deposited on specially designed gas permeable electrodes to achieve 'bubble-free' water splitting in the same way that occurs in photosynthesis. The hypothesis was that such a system should offer a more efficient hydrogen generating electrolysis technology than any known to date using water of near-neutral pH. The ability to avoid the very high or low pH's normally required in water electrolyzers offers a potentially important commercial advantage in green hydrogen production. For example, it allows green hydrogen production without notable corrosion.

The project has achieved all of the aims, including all of the milestones and deliverables, it set out to accomplish. It has successfully demonstrated the hypothesis on which it was based, namely, that an Earth-abundant, bio-inspired catalyst undertaking bubble-free hydrogen generation could convert near-neutral water into hydrogen at a high level of efficiency. Thus far, project work has resulted in 9 research publications (7 published, 2 submitted).

The final outcome of the project has been the development of a prototype - a highly efficient, multi-cell hydrogen generating electrolyser, operating from water under mild chemical conditions and employing low-cost abundant-earth materials. The prototype allows for a detailed analysis of the commercial potential of the technology, including product costings, business model and preliminary market assessment, which will be carried out next by the lead investigators. The prototype will also provide a working example of the system for potential future investors. A patent application protecting the technology has been filed.

2. Introduction

This document corresponds to the 'End of Activity' report for the Australian National University (ANU) and University of Wollongong (UoW) Hydrogen Generation Research and Development Project: *Hydrogen Generation by Electro-Catalytic Systems*.

This is a public report and contains no commercially confidential information.

3. Project Summary & Scope

Many non-fossil fuel energy production methods (solar, wind etc.) yield electricity but are fundamentally intermittent. Hydrogen is recognized as the ideal clean, high capacity, chemical medium for storage of energy from non-constant sources, capable of achieving stable energy continuity and providing an alternative energy source to help to decarbonize other sectors. Electrolytic hydrogen generation, using cheap and abundant inputs (sunlight and water) is the preferred approach, if the process can be made sufficiently economical and energy efficient.

A future hydrogen economy will likely depend on hydrogen produced by water electrolysis using renewable energy. Renewable, or green, hydrogen may find applications in seasonal storage, as a transportation fuel, and as a chemical feedstock. It is likely that a low-cost, energy-efficient electrolyser will form an important part of a future hydrogen economy.

Electrolysis of water involves passing an electric current through a water solution, by means of two electrodes. The positive electrode generates oxygen (O_2) and the negative electrode generates hydrogen (H_2). The process is well known, but presently suffers from two major difficulties:

- i) The formation of hydrogen and oxygen bubbles during traditional electrolysis represents an impediment to the realisation of low-cost, energy-efficient electrolysers. Bubbles require energy to form, and partially block electrode surfaces, reducing the active area available for gas evolution reactions. Furthermore, the gases generated at the two electrodes must be separated from solution. The problem of bubble coverage is typically overcome by pumping liquid over the electrodes. However, pumps add to system cost, lower system efficiency due to their power consumption, require maintenance, and compromise reliability. Furthermore, the bubble-laden liquids must be piped to gas-liquid separators. Thus, bubbles not only reduce the energy efficiency of electrolysers, but they also add significant cost and complexity to their design, fabrication, operation, and maintenance.
- ii) Another impediment to the realisation of low-cost, energy-efficient electrolysers is the traditional use of strongly acidic or strongly alkaline electrolytes necessitating the use of expensive, high-quality materials such as Pt electrodes due to the corrosive

environment. Since biochemical reactions in nature mostly occur at mild pH, the pursuit of biomimicry would permit the use of cheaper, lower quality materials.

With these impediments in mind, the project aimed to use biologically inspired catalysts with gas permeable electrode surfaces to develop a simpler and more efficient hydrogen generating electrolysis technology than any known to operate from pure water and renewable electricity. Of relevance is the well-known, naturally occurring Oxygen Evolving Complex (OEC) within Photosystem II (PSII) which contains a Mn_4CaO_5 cluster that catalyses the oxidation of water to oxygen. The development of oxygen evolution electrocatalysts based on Earth-abundant Mn and Ca has been motivated by the high activity and low overpotential of the Mn_4CaO_5 cluster for the oxidation of neutral water.

The objective was to develop high performance catalysts with components that mimic those of the natural water oxidation catalyst of photosynthesis, namely, the OEC. These were then to be deposited on specially designed gas permeable electrodes to achieve 'bubble-free' water splitting in the same way that occurs in photosynthesis. The hypothesis was that such a system should offer a more efficient hydrogen generating electrolysis technology than any known to date using water of near-neutral pH. The ability to avoid the very high or low pH's normally required in water electrolyzers, offers a potentially important commercial advantage in green hydrogen production. For example, it allows green hydrogen production without notable corrosion that occurs in highly acidic or alkaline environments.

The project has successfully demonstrated the hypothesis on which it was based, namely, that an Earth-abundant, bio-inspired catalyst undertaking bubble-free hydrogen generation could convert near-neutral water into hydrogen at low energy. The final outcome of the project has been the development of a prototype - a highly efficient, multi-cell hydrogen generating electrolyser (16 cm² electrodes in each cell) at Technology Readiness Level (TRL) 4, operating from water under mild chemical conditions and employing low-cost abundant-earth materials. The prototype allows for a detailed analysis of the commercial potential of the technology, including product costings, business model and preliminary market assessment, which will be carried out next by the chief investigators.

4. Outcomes

Outcome 1. *Identification of the best performing electrolyser water oxidation catalysts (from either a-biological or bio-mimetic materials) for bubble-free operation on Gortex, under mild pH conditions.*

We demonstrated a functioning assembly of the bubble-free electrode system (see **Figure 1**) with both i) a-biological and ii) bio-inspired catalytic surfaces operating at mild pH. The 1 cm² bubble-free electrode system comprises a gas permeable, hydrophobic Polytetrafluoroethylene (PTFE) membrane (Gortex), which supports a PTFE interlayer, with the catalyst binder layer on top (with conducting Ni mesh current collector). The catalyst layer

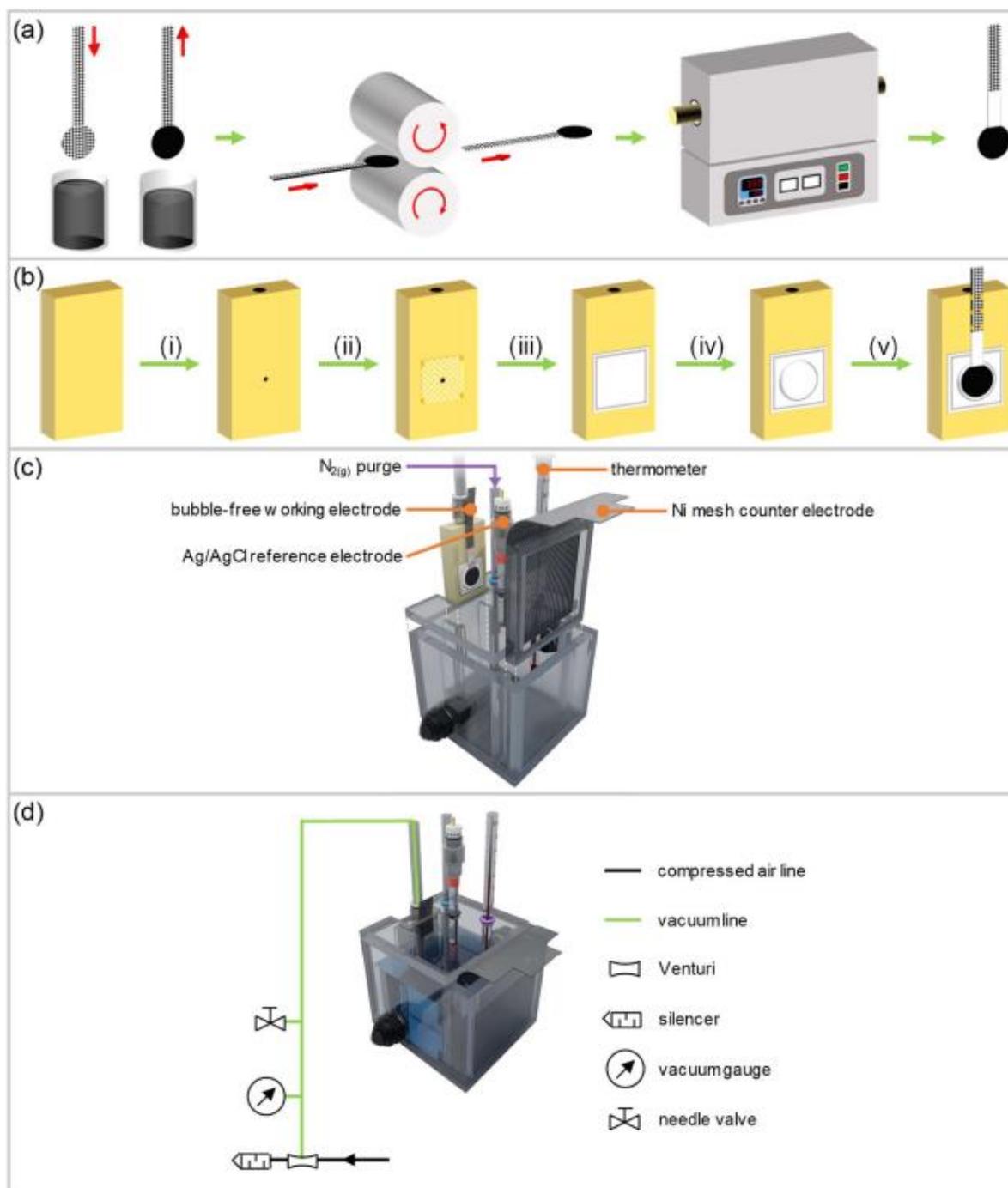


Figure 1. Bubble-free electrode assembly. **a)** Schematic of catalyst-binder layer preparation. From left to right: dip-coating of Ni mesh current collector in ink containing catalyst (Raney Ni) and binder (PTFE), rolling, heat-treatment, and masking. **b)** Schematic of breathable electrode preparation. The starting point was a poly(propylene) (PP) block. (i) Drilling of holes to allow application of vacuum behind ePTFE membrane. (ii) Thermal tacking of PP spacer. (iii) Thermal welding of ePTFE membrane. (iv) Drop casting of PTFE interlayer dispersion. (v) Wet lamination and thermal tacking of catalyst-binder layer. **c)** Schematic of (unfilled) 3-electrode electrochemical cell. **d)** Schematic of testing system with pressure differential (ΔP) control.

contains the catalyst species, immobilised within a PTFE matrix (binder). For the a-biological system i), the metal catalyst species included various combinations of Ni (Raney), Mn and Ca. In the case of the bio-inspired catalyst ii), the edge-functionalised graphene (EFG) was included to mimic the metal-binding local protein environment, and the tyrosine residue, in the OEC of PSII, while MnO_x and Ca^{2+} were incorporated to mimic the Mn_4CaO_5 cluster.

- i) The a-biological catalyst Raney Ni/Polytetrafluoroethylene (PTFE), with and without edge-functionalised graphene (EFG), deposited on Gortex, operated bubble-free under near neutral conditions (pH 12). The performance of this catalyst exceeded that of the Pt noble metal control at all current densities. At 10 mA/cm^2 , this catalyst, without EFG, operated for 2 h at $\leq 2.5 \text{ V}$. This equates to an energy efficiency of at least 59 % HHV.
- ii) The bio-inspired catalyst $\text{Ca}+\text{MnO}_x+\text{EFG}$ on Raney Ni/PTFE, deposited on Gortex, operated bubble-free under near neutral conditions (pH 12). The performance of this catalyst exceeded that of the Pt noble metal control at all current densities. At 10 mA/cm^2 , this catalyst operated for 2 h at $\leq 2.3 \text{ V}$. This equates to an energy efficiency of at least 64 % HHV. Interaction between EFG, MnO_x , and Ca^{2+} resulted in a significant, 130 mV fall in the overpotential required to drive electrocatalytic oxygen evolution at 10 mA/cm^2 , compared to the electrode without these biomimetic components. Importantly, both the experimental and computational results (see below) agree on the catalytic importance of Ca, as in the natural water oxidising site.

Of particular significance is the performance of the bio-mimetic system, whose catalyst layer uses EFG as the metal co-ordinating organic substrate, with Mn and Ca sequentially incorporated. This mimics the componentry and general geometry of the OEC which is the natural, oxygen evolving electro-chemical water splitting site in Photosystem II, the most efficient such catalyst known. The bio-mimetic catalyst operates with around 64 % anodic efficiency under mild alkaline conditions, corresponding to the best overall performance of any of the catalyst systems studied.

Outcome 2. *Detailed theoretical understanding (through computational chemistry) of the water oxidation chemical pathway on the bio-mimetic catalysts relevant to the Activity.*

The coordination of oxo-manganese clusters to edge-functionalised graphene (EFG) offers a potential route to advanced water oxidation electrodes with exceptional electrochemical surface area and electron transport properties. Accordingly, parallel computational studies, using density functional theory, were undertaken on catalytic assemblies relevant to the project, to identify the molecular geometries and likely reaction pathways at the catalyst surface. Initially, a broad survey of candidate attachment geometries for metal oxide clusters on edge-functionalized graphene (EFG) surfaces was examined. This study identified reliable, computationally convenient, substrate/metal cluster models suitable for detailed mechanistic examination of anodic water oxidation pathways. It also revealed how the Mn ions co-ordinated to the EFG through oxo bridging (see **Figure 2**) and confirmed the functional

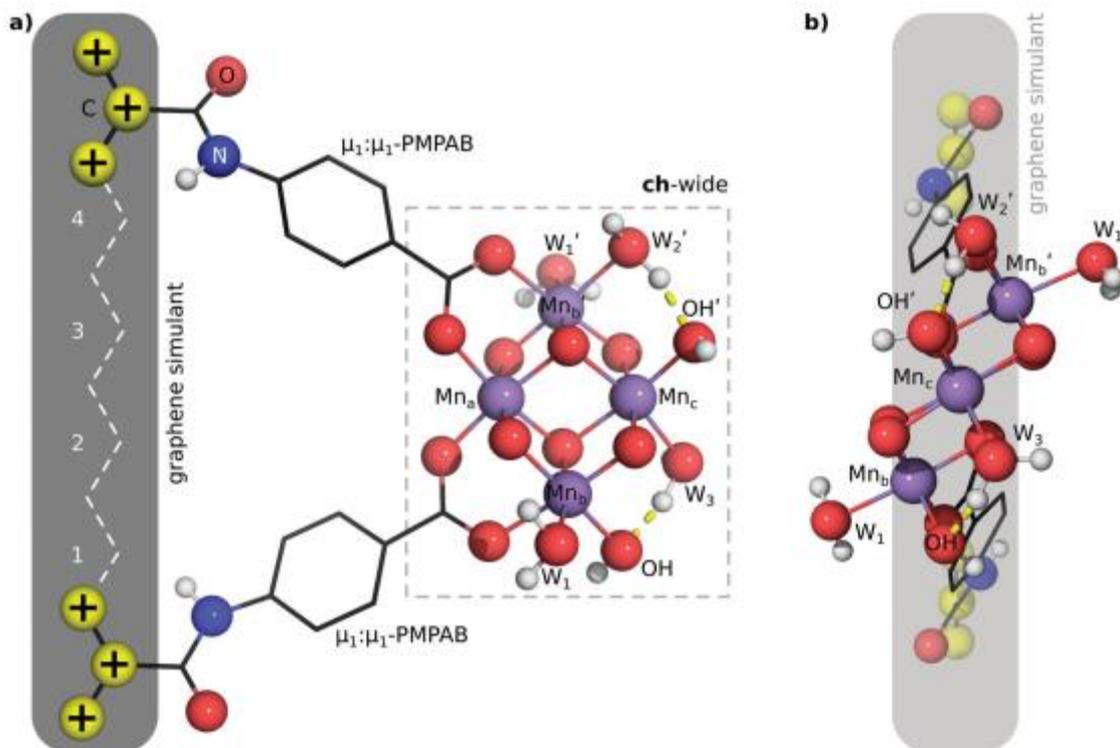


Figure 2. Modelling of oxomanganese cluster binding to graphene surface. **a)** Side angle, illustrating coordination of ch-wide fragment by 4-(2-methylprop-2-enamido)benzoate (PMPAB) ligands simulating edge-functionalised graphene with a separation of 4 rings. Cartesian constraints are indicated with yellow balls marked with +. **b)** The same structure viewed edge-on.

importance of Ca, as in the natural water oxidising site. Specifically, the coordination of Ca^{2+} was shown to reduce the activation energy of dioxygen release from the metal oxide cluster. Subsequent calculations on the most likely models of the catalytic surface explored potential molecular reaction pathways leading to O-O bond formation from metal oxide cluster bound water molecules (see **Figure 3**). It produced results, in terms of inferred electrode overpotentials, that were almost quantitatively consistent with the experimental results.

Because of the various interruptions in 2020 (see Key Highlights & Difficulties below), an internal decision was made to concentrate the computational work on the bio-mimetic EFG/Mn/Ca system, which was the best performing system experimentally. The calculations proved more time consuming than originally expected and precluded studies on a-biological, Ni or Mn based systems, which lacked the EFG as a metal co-ordinating component.

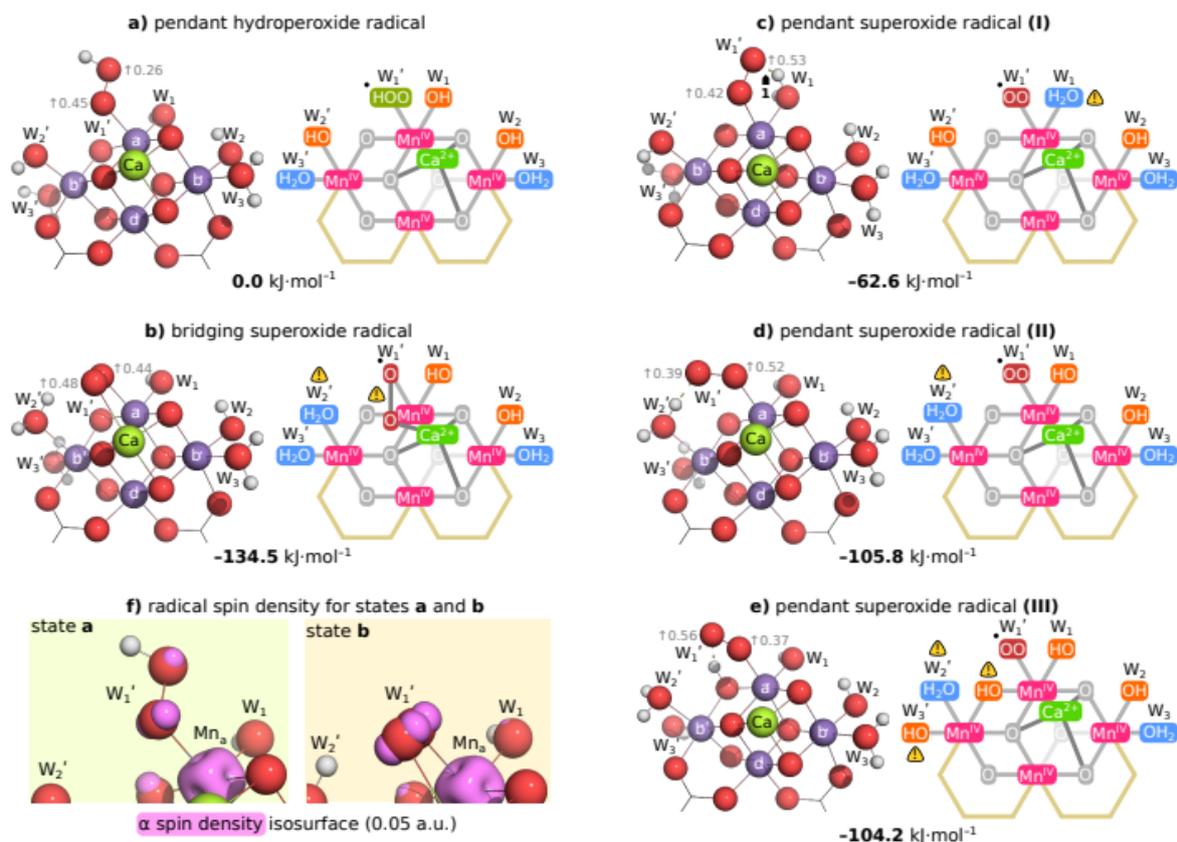


Figure 3. a) to e) Scheme depicting dispositions of hydroperoxide and superoxide ligands attached to Mn in the cw cluster model. All Mn ions are in the +4 oxidation state and are mutually ferromagnetically coupled ($Q = +1$, $M_s = 14$, $4 \times d^3$ (high spin)). Constrained benzoate terminals have been elided for clarity. **f)** Unpaired α spin density isosurfaces for pendant hydroperoxide and bridging superoxide radicals. All other states possessed analogous spin density structures. β spin density was negligible in each case. 1) hydrogen bond between superoxide radical and hydroxide. Grey numbers beside hydroperoxide/superoxide oxygen atoms indicate Löwdin atomic spin density.

Outcome 3. *Development of a prototype, multi-cell electrolyser which incorporates the best catalyst materials on bubble-free Gortex electrodes, operating at near-neutral pH.*

The prototype multi-cell electrolyser builds on our earlier work (see Outcome 1) where we demonstrated ‘bubble-free’ oxygen evolution at mild pH using an electrocatalyst that mimicked photosystem II and whose efficiency exceeded that of current noble metal catalysts. The 1 cm² bubble-free electrode included a gas-extracting Gortex membrane. Edge-functionalised graphene (EFG) was included to mimic the metal-binding local protein environment, and the tyrosine residue, in the oxygen evolving complex (OEC) of PSII, while MnO_x and Ca²⁺ were incorporated to mimic the Mn₄CaO₅ cluster.

In search of improved bubble-free performance, we employed a recently developed ‘capillary-fed’ electrolysis cell concept (see **Figure 4**) over the use of gas-extracting Gortex membranes. In this electrolysis cell, the bottom end of a hydrophilic, porous separator is dipped in a reservoir, resulting in upward, in-plane flow of electrolyte. Hydrophilic, porous

electrodes are placed on either side of the separator, above the level of the electrolyte, and electrolyte flows into them laterally. The application of sufficient voltage between the electrodes results in the electrolysis of water, which is continuously replenished by water flowing up through the separator from the reservoir. Thus, the capillary-fed electrolysis cell concept results in inherently bubble-free water electrolysis and promises improved voltage efficiency. In addition, the movement of product gases away from the separator and normal to the flow of reactant water avoids the mass transport limitation associated with counter multiphase flow inherent in traditional water electrolyzers.

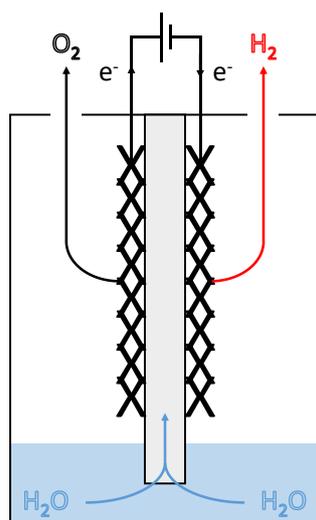


Figure 4. Schematic of capillary-fed electrolysis cell concept.

We have demonstrated a 16 cm², multi-cell, bubble-free electrolyser prototype based on the ‘capillary-fed’ electrolysis cell concept integrating the same EFG, MnO_x, and Ca²⁺ catalyst on the oxygen-evolving anode developed above (see **Figure 5**). It employs low-cost construction materials and operates at pH 12, which represents greater than 3 orders of magnitude lower OH⁻ concentration compared to commercial alkaline electrolyzers.

The two-cell electrolyser showed close to 100 % Faradaic efficiency, and displayed steady voltage during operation at 10 mA/cm² (160 mA) for 8 hrs. It required 4.12 V to operate at 10 mA/cm² (160 mA), which equated to 2.06 V per cell. Although this 2.06 V included losses due to the OER, HER, and separator, it was 160 mV lower than the previously reported 2.22 V required to drive the OER alone at the same current density using a gas-extracting Gortex membrane. This vindicated our selection of the capillary-fed electrolysis cell concept over the use of gas-extracting Gortex membranes.

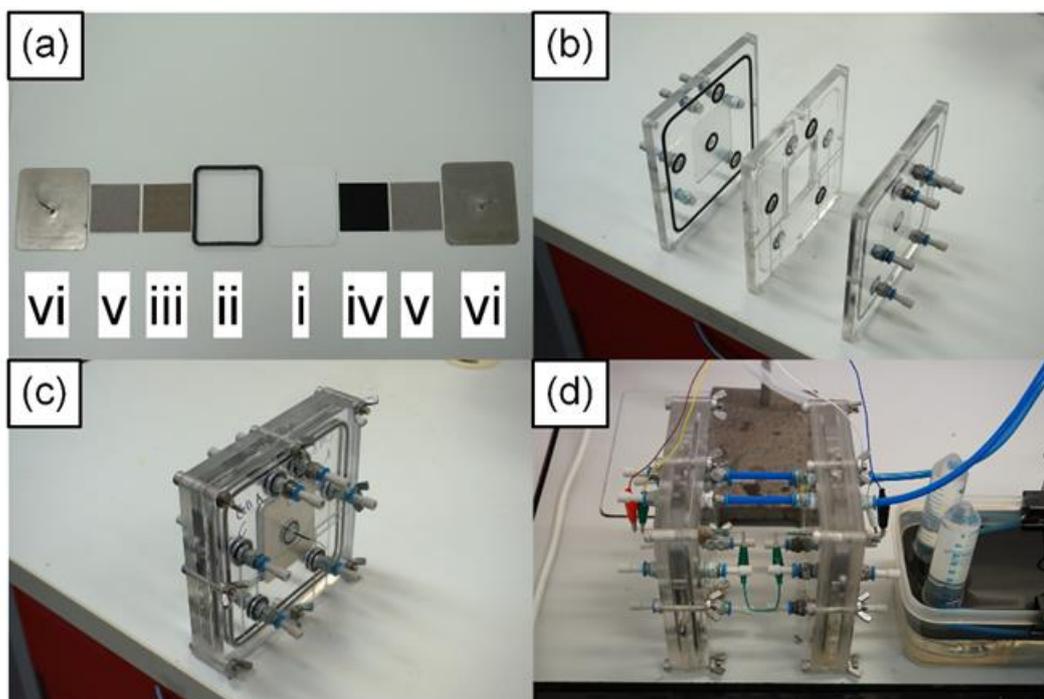


Figure 5. Photographs of **(a)** Internal components of the capillary-fed electrolysis cell: (i) polyethersulfone separator, (ii) acrylic insert, (iii) Ni mesh/galactomannan-bound edge-functionalised graphene/MnO_x/Ca²⁺ oxygen-evolving anode, (iv) Pt/C on carbon fibre paper hydrogen-evolving cathode, (v) Ni foam inserts, (vi) Ni plates with soldered wires. **(b)** Acrylic housing comprised of centre plate and end plates. **(c)** Assembled 16 cm² cell charged with electrolyte. **(d)** 16 cm², two-cell electrolyser ready for electrochemical testing.

The results demonstrate highly efficient hydrogen production from a near-neutral aqueous solution using a bio-inspired, bubble-free system that exceeds the performance of any man-made system under similar conditions. While a state-of-the-art commercial alkaline electrolyser will produce around 1,500 mA/cm² or more at an energy efficiency of 64 % HHV (i.e. it will have about 150-times the output of hydrogen), the more extreme pH necessitates a far higher cost of construction, operation, and maintenance. For example, all of the pumps, valves, tanks, scrubbers, and other components of the balance-of-plant must be capable of handling the extremely corrosive alkaline electrolyte used. Our bubble-free system using pH 12 electrolyte, avoids the need for expensive, corrosion-resistant components. Moreover, the bubble-free nature of the system sees the gas collected directly in the cell, thereby avoiding the need for most of the pumps, valves, tanks, scrubbers, and other components that are usually required. Accordingly, to make a proper comparison of the two systems, a detailed techno-economic comparison that takes into account the relative trade-offs, is needed to discern which is the more attractive economically. The co-investigators plan to undertake such an analysis.”

In summary, the project achieved all of the aims, including all of the milestones and deliverables, it set out to achieve. The thesis behind the project has therefore been proven.

5. Key Highlights & Difficulties

The three key breakthroughs in the project were:

- a) the development of a bio-inspired water oxidation catalyst whose activity proved to be within the same order of magnitude as the PSII-OEC in mild pH conditions, using only simple, earth-abundant materials, including MnO_x , Ca^{2+} , and graphene. This catalyst outperformed Pt, which is the industry standard water oxidation precious metal catalyst.
- b) the use of a new cell architecture, known as a 'capillary-fed' electrolysis cell to realise highly active bubble-free water electrolysis. The new cell was developed separately by the chief investigators in separate ARENA-funded project (Project number 2018/DM015 RND009, entitled "Ammonia production from renewables").
- c) Computational studies using density functional theory identified the most likely metal oxide cluster geometries and attachment modes of the $\text{MnO}_x/\text{Ca}^{2+}$ catalyst to the graphene surface of the electrode as well as molecular reaction pathways leading to O-O bond formation from the metal oxide cluster bound water molecules.

Three factors impacted progress over the course of the project. The first was the ACT fires and hailstorms early in 2020, which closed the ANU laboratories due to smoke interference and roof damage. The second was the COVID-19 interruption in mid-2020, which resulted in campus-wide closure at ANU for nearly three months. As a result, a time extension for the project was granted. Research meetings were held online, which worked well. The third was the COVID-19 interruption in 2021 which affected the University of Wollongong campus and again resulted in laboratory closure or severely limited access for essentially six months. As a result, a further extension of project time was granted to compensate for this loss.

6. Commercialisation Prospects

The final outcome of the project has been the development of a prototype, multi-cell electrolyser (16 cm^2 electrodes in each cell) at Technology Readiness Level (TRL) of 4 (see **Figure 5**). The electrolyser achieves highly efficient hydrogen generation from a near-neutral aqueous solution using a bio-inspired, bubble-free system that exceeds the performance of any man-made system under similar conditions.

The prototype allows for a detailed analysis of the commercial potential of the technology, including product costings, business model and preliminary market assessment, which will be carried out next by the lead investigators. The prototype will also provide a working example of the system for potential future investors. Other novel electrolysers have also been successfully commercialised (e.g. Hysata electrolyser), which provides a precedence for this project. A patent application protecting the technology has been filed.

7. Knowledge-Sharing Activities Completed

The knowledge-sharing activities conducted since the commencement of the project are as follows:

a) Journal Publications

- 1) A. Gagrani, M. Alsultan, G. F. Swiegers, T. Tsuzuki, *Photo-Electrochemical Oxygen Evolution Reaction by Biomimetic CaMn_2O_4 Catalyst*, Applied Sciences, **2019**, *9*, 2196-2206.
- 2) A. Gagrani, M. Alsultan, G. F. Swiegers, T. Tsuzuki, *Comparative Evaluation of the Structural and Other Features Governing Photo-Electrochemical Oxygen Evolution by Ca/Mn Oxides*, Catalysis Science and Technology, **2020**, *10*, 2152-2164.
- 3) R. N. L. Terrett, G. Tsekouras, T. Tsuzuki, G. F. Swiegers, R. J. Pace, R. Stranger, *Electronic Structure Modelling of Edge-Functionalisation of Graphene by MnOx Particles*, R. Terrett, Physical Chemistry Chemical Physics, **2020**, *23 (1)*, 514-527.
- 4) G. Tsekouras, R. N. L. Terrett, Z. Yu, Z. Cheng, G. F. Swiegers, T. Tsuzuki, R. Stranger, R. J. Pace, *Insights into the Phenomenon of 'Bubble-Free' Electrocatalytic Oxygen Evolution from Water*, Sustainable Energy and Fuels, **2021**, *5*, 808-819.
- 5) G. Tsekouras, R. N. L. Terrett, A. Walker, Z. Yu, Z. Cheng, D. L. Officer, G. G. Wallace, G. F. Swiegers, T. Tsuzuki, R. Stranger, R. J. Pace, *Interaction of graphene, MnOx, and Ca^{2+} during biomimetic, 'bubble-free' electrochemical oxygen evolution at mild pH*, International Journal of Hydrogen Energy, **2021**, *46*, 28397-28405.
- 6) G. F. Swiegers, R. N. L. Terrett, G. Tsekouras, T. Tsuzuki, R. J. Pace, R. Stranger, *The Prospects of Developing a Highly Energy-Efficient Water Electrolyzer by Eliminating or Mitigating Bubble Effects*, Sustainable Energy and Fuels, **2021**, *5*, 1280-1310.
- 7) R. N. L. Terrett, G. Tsekouras, T. Tsuzuki, G. F. Swiegers, R. J. Pace, R. Stranger, *Towards a Computational Understanding of Water Oxidation at Graphene-Bound Mn_xO_y and $\text{Mn}_x\text{O}_y\text{M}^{2+}$ Particles*, Sustainable Energy Fuels, **2022**, *6*, 2276-2288.

b) Papers Submitted for Publication

- 8) D. Boskovic, R. N. L. Terrett, M. S. M. Basheer, P. Wagner, R. J. Pace, R. Stranger, G. F. Swiegers, *A bioinspired water oxidation catalyst that is approximately one-tenth as active as the Photosystem II Oxygen Evolving Center at neutral pH*.
- 9) G. Tsekouras, R. N. L. Terrett, G. Ryder, A. Walker, A. Hodges, A. L. Hoang, C-Y. Lee, K. Wagner, Z. Yu, D. L. Officer, G. G. Wallace, G. F. Swiegers, T. Tsuzuki, R. Stranger, R. J. Pace, *A 16 cm^2 , two-cell, biomimetic, 'bubble-free', 'capillary-fed' water electrolyser operating at mild pH*.

c) Patent Applications

Patent title “Biomimetic Water Oxidation Catalysts” (Pace et al., International PCT patent application WO2019119044 which was filed in the USA as US Patent Application 16/955997 on 23 June 2020)

8. Conclusion & Next Steps

The project has successfully demonstrated the hypothesis on which it was based, namely, that an Earth-abundant, bio-inspired catalyst undertaking bubble-free hydrogen generation could convert near-neutral water into hydrogen at a high level of efficiency.

The final outcome of the project has been the development of a prototype - a highly efficient, multi-cell hydrogen generating electrolyser (16 cm² electrodes in each cell) at Technology Readiness Level (TRL) 4, operating from water under mild chemical conditions and employing low-cost abundant-earth materials.

The next stage to be undertaken by the chief investigators involves a detailed analysis of the commercial potential of the technology, including product costings, business model and preliminary market assessment, followed, if appropriate, by full commercialisation (initially in niche markets).