



Arrow Innovation Support

Client: Rubbish Energy

Project: Evaluating the effectiveness of wastewater electrolysis for the generation of renewable hydrogen

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Executive Summary

The existing electricity grid is being put under considerable pressure due to increasing energy demands resulting from the electrification of heating and transportation, coupled with the integration of renewable energy sources. To help reduce the strain on the grid when there is a surplus of electricity, wind farms are curtailed. Rubbish Energy aim to provide flexibility services to the power grid by converting excess renewable energy into green hydrogen via the electrolysis of wastewater.

Industrial hydrogen production by electrolysis uses fresh/ pure water as feedstock due to the water purity requirements of existing electrolysis technologies. Given that water is becoming an increasingly scarce resource, an alternative feedstock for electrolysis is required. Wastewater poses as an attractive alternate electrolysis feed as it is cheap, abundant, and available throughout the year. However, the presence of contaminants and impurities within wastewater raises several questions as to its suitability for green hydrogen production via electrolysis: What are the products of wastewater electrolysis? Is hydrogen production hindered by the contaminants present in wastewater? Are electrolyser components fouled during the electrolysis of wastewater? Can fouled electrolyser components be rejuvenated to extend the lifetime of the system?

The aim of the Arrow project was to provide Rubbish Energy with an overview of the feasibility of wastewater electrolysis by reviewing the published literature, with guidance from Prof Anh Phan of Newcastle University's School of Engineering.

Wastewater effluent may contain trace microorganisms, heavy metals, inorganic chemicals, micropollutants, organic carbon, halogens, and dissolved gasses such as carbon dioxide, nitrogen, and oxygen. The presence of such contaminants has been reported as making electrolysis of wastewater an energy-intensive and low-yield process.

The review found that hydrogen can be evolved from raw wastewater, anaerobic sludge, and anaerobic effluent. Relative to electrolysis of distilled water, 74 % hydrogen was evolved during the Alkaline electrolysis of untreated wastewater – we view this as a good yield and a promising finding (Chauhan and Ahn, 2023). The greater the amount of treatment wastewater had undergone, the greater the amount of hydrogen evolved when effluent was electrolysed (Chauhan and Ahn, 2023). Chauhan and Ahn (2023) did not investigate what other gases were evolved or the effect of side-products on electrolyser components, representing a gap in current understanding. Hydrogen production via electrolysis of domestic wastewater in a 100 L Microbial Electrolysis Cell decreased over a 12-month period, likely due to electrode fouling (Heidrich *et al.*, 2014).

Electrolysis of wastewater can result in the formation of unwanted side-products. Halide evolution reactions outcompete the Oxygen Evolution Reaction resulting in the formation of halide ions which can corrode the electrodes and other

components of the electrolysis cell (Becker *et al.*, 2023; He *et al.*, 2023). OH^- , produced during the Hydrogen Evolution Reaction, can cause Mg^{2+} and Ca^{2+} to precipitate and form hydroxides which deposit on the cathode (Tong *et al.*, 2020). Electrode decomposition was observed following electrolysis of wastewater containing nickel or copper (Cokay and Gurler, 2020).

Cationic impurities, such as Na^+ and Mg^{2+} , can be exchanged for protons in the membrane of Proton Exchange Membrane electrolysis cells, resulting in a reduction of membrane conductivity and overall membrane stability (Becker *et al.*, 2023). Organic contaminants and metal cations were found to adsorb on the catalyst, reducing the electrochemically active surface area and thus catalytic activity (Becker *et al.*, 2023).

Fouled electrolyser components may be rejuvenated thereby increasing the lifetime of the system. Light carbonates adsorbed to the surface of the cathode may be removed as carbon dioxide at high voltages (Becker *et al.*, 2023). Halide ions and organic contaminants may be removed from the catalytic surface via oxidation at high potentials (Becker *et al.*, 2023). Flushing of the electrolysis cell to adjust the pH may solubilise metallic and salt impurities, allowing for their subsequent removal (Becker *et al.*, 2023). Research is currently focussed on the re-design of electrolysis cells to minimise fouling, for example by modifying the electrode with a coating or film (Hassen, Siraj and Wong, 2016).

In conclusion, it is possible to produce hydrogen through the electrolysis of raw wastewater, anaerobic sludge, and anaerobic effluent. Fouling of the electrolyser components and membrane degradation pose the greatest challenges to wastewater electrolysis. Whilst there are reported methods for the rejuvenation of fouled components of the electrolysis system, the lifetime of electrolyzers using wastewater as feedstock remains to be determined. Rubbish Energy could develop a model to estimate the cost: benefit of wastewater electrolysis using different technologies which would allow for unsuitable technologies to be quickly ruled out. The findings of the review support the initiation of feasibility studies of wastewater electrolysis using off-the-shelf electrolyzers.

Background

Rubbish Energy, incorporated on 01 July 2022, is investigating whether an off-the-shelf electrolyser can be used to generate green hydrogen via the electrolysis of wastewater. Increasing energy demands coupled with the integration of renewable energy sources has put the existing electricity grid under significant strain. Wind farms may be shut down during periods when electricity is in surplus, to relieve pressure on the grid. Rubbish Energy aims to supply electricity flexibility services to the power grid by converting excess renewable energy into hydrogen by electrolysing wastewater. Rubbish Energy are developing software to link electricity network requests and the initiation of electrolysis for hydrogen production.

Currently, pure water is used in the industrial production of hydrogen via electrolysis due to existing technologies having water purity requirements. Increasing water scarcity necessitates the use of an alternative water source as feed for electrolysis. Wastewater poses as an attractive alternative to fresh water due to it being cheap, abundant, and available throughout the year. Given that wastewater contains contaminants and impurities, a number of questions are raised as to its suitability for use in electrolysis. By reviewing the published literature, the project will provide Rubbish Energy with insight into the feasibility of wastewater electrolysis for green hydrogen production. The review will explore the products of wastewater electrolysis and the effects these can have on electrolyser components.

The literature review was conducted by Dr Hannah Gibson, with direction from Prof Anh Phan of Newcastle University's School of Engineering. The suggestions made in the report are based on published research and experience in working in process development. The hypotheses have not been tested by the authors.

Aims

The aim of the project was to gain an understanding of the feasibility of wastewater electrolysis for green hydrogen production by reviewing the published literature. The literature review aims to identify the products generated from wastewater electrolysis and explore their potential effect on electrolyser components. Methods by which fouled electrolyser components can be rejuvenated are outlined.

The project aims to provide Rubbish Energy with a consolidated, evidence-based report on current understanding within the field, which may inform the future development of a Minimal Viable Product.

Literature Review

Introduction

In the push for the UK to reach net zero by 2050, challenges have arisen in the transition from fossil fuels to the integration of intermittent renewable energy sources into the power grid (Rusmanis *et al.*, 2022). Significant stresses have been placed on the existing electricity grid due to increased demand resulting from electrification of heat and transport coupled with variable electricity production from renewable energy sources (Rusmanis *et al.*, 2022). Flux in production and demand of electricity has resulted in renewable energy sources, such as wind, producing surplus electricity necessitating the temporary shutdown of subsets of wind turbines to alleviate pressure on the system (Rusmanis *et al.*, 2022).

Figure 1 shows the curtailment rates of British onshore and offshore wind farms in 2021. In 2020, 3.5 TWh of wind generation was curtailed in Britain (Drax, 2022). There were lower curtailments of 2.3 TWh in 2021, due to low wind output levels and a surge in energy demand following easing of COVID-19 restrictions (Drax, 2022). The curtailed wind generation across 2020 and 2021 would have been sufficient to power 800,000 homes each year (Drax, 2022). The UK Government has an ambition of achieving 50 GW of off-shore wind capacity by 2030 which, without significant grid improvements, would result in an increase in the amount of energy being curtailed (Drax, 2022; Giampieri, Ling-Chin and Roskilly, 2023).

The storing of excess renewable energy in chemical bonds, particularly hydrogen, would have several benefits, including long-term storability and the ability to transfer renewable electricity into the heat and transport sectors and into chemical industry (Schmidt *et al.*, 2017).

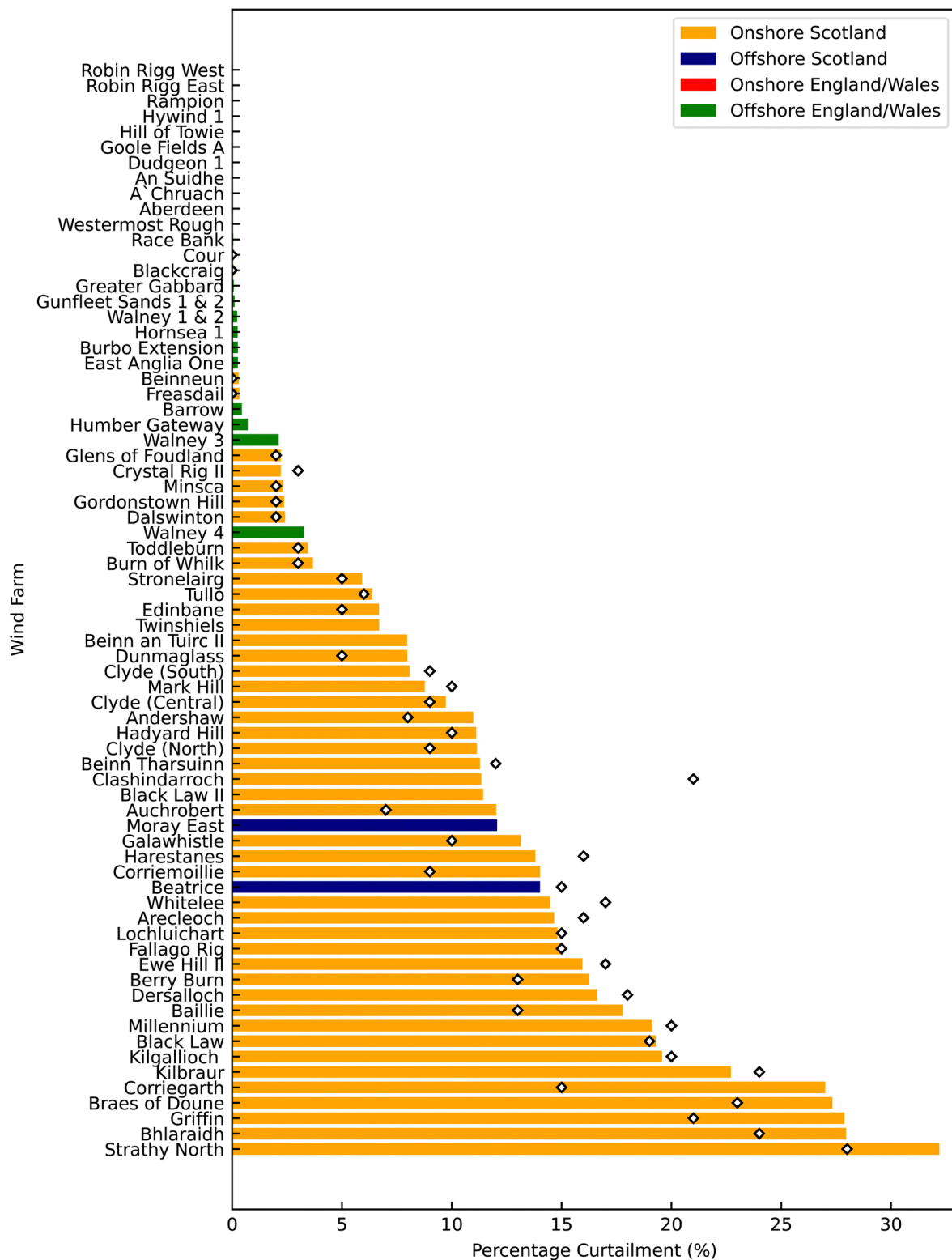


Figure 1. Curtailment of British wind farms in 2021. Bars represent the curtailment percentage (%) of British wind farms in 2021 (Atherton *et al.*, 2023). Bar colours represent the farm type and location, diamonds represent renewable Energy Foundation values, which were only available for some wind farms. Figure obtained from Atherton *et al.*, 2023.

Water electrolysis is a clean alternative technology for hydrogen production (Cartaxo *et al.*, 2022). Electrolysis of pure water can give rise to large volumes of pure (99.999 vol %) hydrogen without emission of gaseous pollutants (Cartaxo *et al.*, 2022). Hydrogen produced without directly releasing CO₂, such as through water splitting, is categorised as green hydrogen (Chauhan and Ahn 2023). The splitting of water is an endothermic reaction, with the required energy being provided by electric current through an electrochemical cell.:

Cathode (-): $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$

Anode (+): $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$

Overall: $\text{H}_2\text{O} + \text{energy} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2$.

A cell voltage of 1.48 V is required to split water whilst overcoming the ohmic resistance of the electrolyte and the cell components of the electrolyser (Shiva Kumar and Lim, 2022).

Water electrolysis technologies include Alkaline Electrolysis cells, Proton Exchange Membrane Electrolysis cells and the emerging Solid Oxide Electrolysis cells (Schmidt *et al.*, 2017). Water purity (typically > 1M Ω cm) is an essential requirement for hydrogen evolution in both Alkaline Electrolysis and Proton Exchange Membrane Electrolysis cells, meaning that fresh water is required in vast quantities to produce green hydrogen on an industrial scale (Becker *et al.*, 2023; Chauhan and Ahn 2023; Schmidt *et al.*, 2017). Theoretically, 45 kg of pure water needs to be hydrolysed to produce 5 kg (~ 166 kWh_{HHV}) of hydrogen (Becker *et al.*, 2023). Mayyas *et al.*, (2019) reported that deionisation of water for Proton Exchange Membrane electrolysis contributed to 32 % and 22 % of the total balance of plant cost of 200kW and 1 MW systems, respectively. The energy use associated with water purification impacts operational costs of electrolysers, with 0.2 kW of energy estimated to be required to produce high purity water for every 5 kg of hydrogen gas generated via electrolysis (Becker *et al.*, 2023).

Given the prediction that 6 billion people will be suffering from water scarcity by 2050, an alternative to fresh water for green hydrogen production is required (Boretti and Rosa, 2019). Wastewater from municipal and industrial settings could be utilised as a resource for green hydrogen production through electrolysis.

The following literature review evaluates the effectiveness of wastewater electrolysis for the generation of renewable hydrogen. The review aims to consolidate current understanding of the impact electrolysis of domestic wastewater has on electrolyser components and whether these can be rejuvenated to increase longevity of the system.

Wastewater

Yearly global wastewater generation is currently 380 billion m³ and is expected to increase by 51 % by 2050 (Qadir *et al.*, 2020). Wastewater is considered a promising source of hydrogen due to its abundance and ease of access (Aydin *et al.*, 2021). Whilst wastewater treatment technologies are necessary for society, they are also energy intensive – the conventional activated sludge process requires 0.3–0.65 kWh per m³ of wastewater (Gikas, 2017). Therefore, the application of systems that can produce hydrogen whilst treating wastewaters are important for recovering the energy spent on treatment and reducing greenhouse gas emissions (Aydin *et al.*, 2021).

Domestic wastewaters consist of human waste and wastewater from household appliances and fixtures (Zaibel, Arnon and Zilberg, 2021). Domestic wastewaters are composed of nutrients, biodegradable organic matter, microorganisms and organic micropollutants, such as pharmaceuticals and personal care products (Zaibel, Arnon and Zilberg, 2021). Industrial wastewater and urban run-off can contain inorganic chemicals, heavy metals, pesticides, and dyes (Zaibel, Arnon and Zilberg, 2020). High levels of chemical oxygen demand (COD), biological oxygen demand (BOD), total organic carbon (TOC), nitrogen, phosphorus, and microorganisms within wastewaters are reduced through a series of treatment processes (Barghash *et al.*, 2022).

Briefly, preliminary treatment of wastewater consists of the removal of solid particles (> 3 mm) via screening. Wastewater is subsequently transferred to settlement tanks where the settled solids form sludge (Zaibel, Arnon and Zilberg, 2021). Advanced primary treatment may involve filtration and/ or chemical addition to remove organic matter and suspended solids (Zaibel, Arnon and Zilberg,

2021). Primary effluent is transferred to an aeration tank in which bacteria utilise food waste and faecal contaminants (Barghash *et al.*, 2022). The secondary effluent is transferred into another settlement tank, where bacteria settle to form a sludge which is returned to the secondary treatment stage. Tertiary treatment involves elimination of colloids, turbidity, and dissolved ions using filters, ion exchange and desalination (Ghangrekar, 2022). Disinfection may be performed using chlorination, ultra-violet irradiation or ozonation (Zaibel, Arnon and Zilberg, 2021).

To summarise, wastewater treatment effluent may contain trace phosphorus, chlorine, bromine, organic carbon, sulphates, inorganic chemicals, heavy metals, organic micropollutants, and microorganisms (El-Shafle, 2023; Zaibel, Arnon and Zilberg, 2021). Dissolved gasses such as argon, nitrogen, oxygen, and carbon dioxide may also be present (Becker *et al.*, 2023). With each successive treatment process, the amount of contaminant present in effluent will be reduced.

Electrolysis technologies

The review will first consider the working principle of water electrolysis technologies as applied to pure water before exploring the current understanding of wastewater electrolysis.

Water electrolysis technologies have undergone continuous development as part of their use in industrial applications (Shiva Kumar and Lim, 2022). As a result, different types of electrolysis have been introduced based on the operating conditions, electrolyte, and ionic agents (OH^- , H^+ , O_2^-) (Shiva Kumar and Lim, 2022). The characteristics of these different electrolysis technologies are summarised in table 1 and are described in detail below.

Table 1. Comparison of electrolysis technologies, as applied to pure water.

Electrolysis technology	Investment cost (US\$/ kW)	Lifetime (hours)	Efficiency (%)	H ₂ purity (%)	Energy consumption (kWh/kg H ₂)	References
Alkaline electrolysis	270-1000	60,000	50-78	99.5-99.9998	47-66	Daoudi and Bounahmidi, 2024; El-Shafie, 2023; Shiva Kumar and Lim, 2022
Proton Exchange Membrane electrolysis	400	50,000-80,000	50-83	99.9-99.9999	47-63	El-Shafie, 2023; Shiva Kumar and Lim, 2022
Solid Oxide electrolysis	>2000	20,000	89 (in laboratory setting)	99.9	-	El-Shafie, 2023; Shiva Kumar and Lim, 2022

Alkaline Water Electrolysis

Alkaline Electrolysis is a well-developed technology which has been commercialised for industrial hydrogen production, up to the multi-megawatt range (Shiva Kumar and Lim, 2022). Alkaline Electrolysis has proved the most popular method of water splitting due to it being low cost, stable, durable, and not requiring platinum group metal-based catalysts (Chauhan and Ahn 2023).

Figure 2 is a schematic diagram of the working principle of Alkaline Water Electrolysis. Briefly, at the cathode water is reduced to produce hydrogen, which is released from the cathodic surface, and hydroxyl ions that diffuse through the ion-exchange membrane to the anode (Shiva Kumar and Lim, 2022). At the anode, hydroxyl ions recombine to form water and an oxygen molecule (Shiva Kumar and Lim, 2022).

Alkaline Water Electrolysers operate at low temperatures (30–80 °C) with a concentrated alkaline solution (typically 5M KOH/ NaOH) and electrodes composed of nickel coated perforated stainless steel (Shiva Kumar and Lim, 2022). Electrolytes provide ionic conductivity between the electrodes and within the porous catalysts (Cavaliere, 2023). Thus, electrolytes must have a suitably high level of ionic conductivity and be non-corrosive to the electrodes (Cavaliere, 2023). Electrolyte impurities such as carbon, chlorine, magnesium, silicon, and sulphur impact upon the performance of Alkaline Electrolysis cells (Thissen *et al.*, 2023). Alkaline electrolytes are typically replaced once or twice a year and, as such, are not considered to be a major cost associated with maintaining the electrolyser (US Department of Energy, 2022). Once neutralised by addition of a strong acid (e.g., nitric acid), the alkaline solution can be disposed of without generating any hazardous material (US Department of Energy, 2022).

The ionic charge carrier OH^- (from NaOH/ KOH) has limited motility resulting in low current densities (0.1–0.5 A/cm²) (Shiva Kumar and Lim, 2022). A further disadvantage of Alkaline Electrolysis is the reaction of KOH with atmospheric CO_2 to form K_2CO_3 which decreases the number of available hydroxyl ions and ionic conductivity. The K_2CO_3 salt can block the pores of the diaphragm of the electrolysis cell, reducing ion transferability and, thus, hydrogen production (Shiva Kumar and Lim, 2022).

Alkaline Water Electrolysis systems have an investment cost of 270–1000 US\$/kW, with a system lifetime of 60,000 hours (Daoudi and Bounahmidi, 2024). Alkaline Water Electrolysis has an efficiency of 50–78 % when applied to pure water, generating hydrogen gas with 99.5–99.9998 % purity (Shiva Kumar and Lim, 2022). The maturity of the technology has meant that some electrode packages have a lifetime of more than 5 years with negligible changes in performance guaranteed (Thissen *et al.*, 2023).

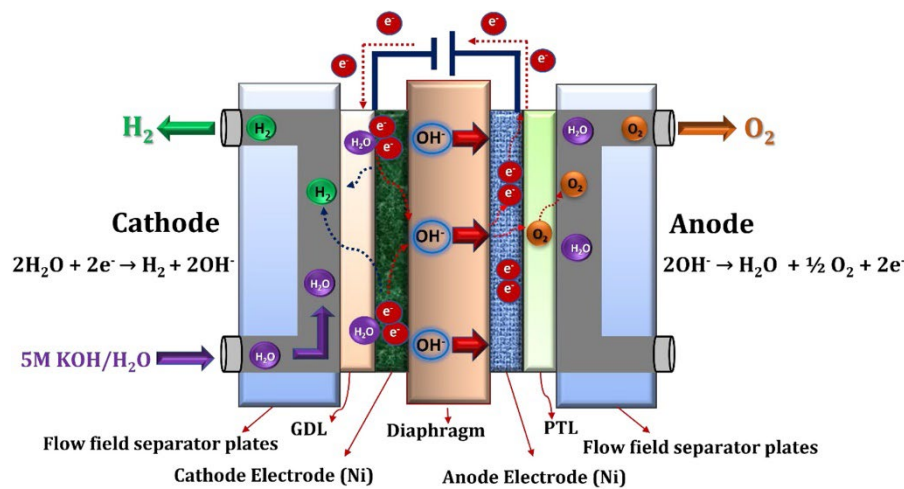


Figure 2. Schematic diagram of the working principle of Alkaline Electrolysis. Figure obtained from Shiva Kumar and Lim, 2022.

Proton Exchange Membrane Electrolysis

In Proton Exchange Membrane electrolysis cells solid polysulphonated membranes, typically perfluorosulphonic acid (PFSA), are used as an electrolyte (Shiva Kumar and Himabindu, 2019). The most common PFSA used in Proton Exchange Membrane Electrolysis is Nafion®, which consists of a semi-crystalline polytetrafluoroethylene backbone and randomly tethered polysulfonyl fluoride vinyl ether sidechains that are covalently bonded via SO_3^- ions linked to a specific backbone counterion (Perovic *et al.*, 2023). Nafion® has excellent ion and solvent transport properties due to the phase-separated morphology of the covalently linked backbone and sidechains (Perovic *et al.*, 2023). Furthermore, Nafion® has high proton conductivity, high water permeability and a long lifetime due to good chemical and

mechanical resistance (Perovic *et al.*, 2023). However, Nafion® is expensive and there are high costs associated with its disposal due to fluorine being a backbone component (Perovic *et al.*, 2023).

Proton Exchange Membrane electrolysis operates under low temperatures (20–80 °C) and high current densities ($>2 \text{ A/cm}^2$) (Shiva Kumar and Himabindu, 2019). A disadvantage of Proton Exchange Membrane electrolysis over Alkaline Electrolysis, is the use of expensive noble metals as catalysts. Platinum or palladium are used as cathodic electrocatalysts for the Hydrogen Evolution Reaction, whilst iridium oxide or ruthenium oxide are the anodic catalysts of the Oxygen Evolution Reaction (Shiva Kumar and Himabindu, 2019). Protons generated by the splitting of water at the anode travel to the cathode via the proton conducting membrane (Figure 3) (Shiva Kumar and Himabindu, 2019).

Platinum-group metals (platinum, palladium, rhodium, ruthenium, and iridium) have been listed as critical raw materials by the European Commission (2023). South Africa is the main global supplier of iridium, platinum, ruthenium, and rhodium (European Commission, 2023). Whilst the annual world production of platinum (the main global supplier of which is Russia) could suffice for the scale up of water electrolysis technologies, iridium is a far scarcer resource and could limit hydrogen production via electrolysis at scale (European Commission, 2023; Salonen, Petrovykh and Kolen'ko, 2021). A 10 MW Proton Exchange Membrane electrolyser operating at 1 A/cm^2 requires ~15 kg of iridium with assumed catalyst loading of 2–3 mg/cm^2 (Shiva Kumar and Lim, 2022). In August 2021, iridium was valued at 196,119 US\$/ kg demonstrating the considerable costs associated with Proton Exchange Membrane electrolysis (Shiva Kumar and Lim, 2022). Current research is focused on the replacement of platinum-group metals with transition metals to improve the cost-efficiency of the technology (Shiva Kumar and Lim, 2022). Strategies to reduce the use of platinum include alloying platinum with non-noble metals and supporting platinum on more abundant and cost-effective substrates (Salonen, Petrovykh and Kolen'ko, 2021).

Proton Exchange Membrane electrolysis is a commercialised technology, with investment costs of 400 US\$/ kW (Shiva Kumar and Lim, 2022). When applied to pure water, Proton Exchange Membrane electrolysis has an efficiency of 50–83 %

and generates hydrogen gas of 99.9–99.9999 % purity (Shiva Kumar and Lim, 2022).

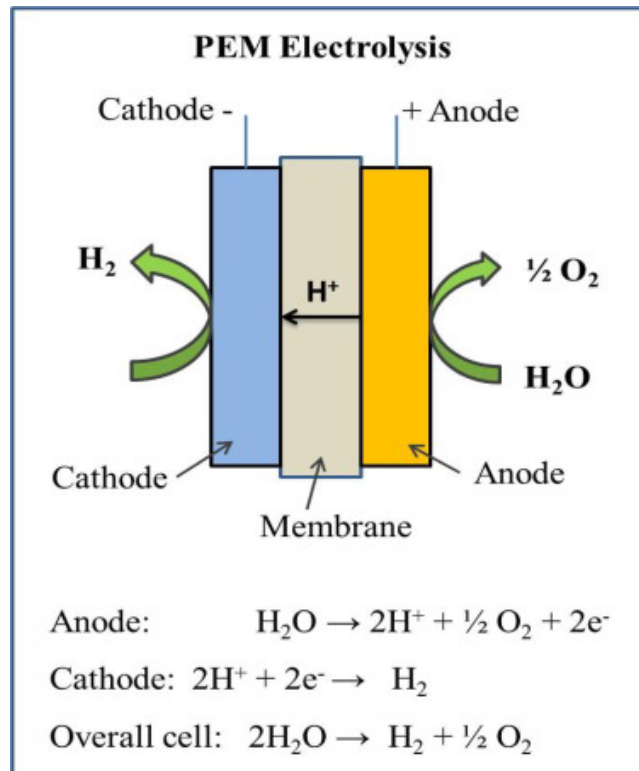


Figure 3. Schematic diagram of the working principle of Proton Exchange Membrane electrolysis. Figure obtained from Shiva Kumar and Himabindu, 2019.

Solid Oxide Electrolysis

Solid Oxide Electrolysis cells consist of two porous electrodes separated by a dense pure oxide ion conducting electrode, commonly yttria-stabilised zirconia (Wolf *et al.*, 2023). Solid Oxide Electrolysis cells operate at much higher temperatures than the other technologies discussed – typically between 600 and 900 °C – which results in lower ohmic losses and advantageous kinetics and thermodynamics (Wolf *et al.*, 2023). By operating at such high temperatures Solid Oxide Electrolysis consumes less power to split water thereby increasing the energy efficiency of the process (Shiva Kumar and Lim, 2022). A further advantage is that noble metal electrocatalysts are not required (Shiva Kumar and Lim, 2022).

The cathode is a ceramic metal formed of nickel and yttria-stabilised zirconia (Shiva Kumar and Lim, 2022). The anode is typically composed of perovskite materials such as LSCF, a mixed ionic material with high electrical and ionic conductivity and high oxygen diffusion properties (Shiva Kumar and Lim, 2022).

At the cathode, a water molecule (in the form of steam due to the high operating temperatures of the system) is reduced to hydrogen and an oxide ion (O^{2-}). The hydrogen is released from the cathodic surface whilst the oxide ion migrates to the anode via the ion-exchange membrane (Shiva Kumar and Lim, 2022). At the anode, the oxide ion is further reduced to generate oxygen, which is released from the anodic surface, and electrons which migrate to the cathode (Figure 4) (Shiva Kumar and Lim, 2022).

Solid Oxide Electrolysis has not yet been commercialised due to the insufficient stability of the electrolyte – currently only 20,000 hours (Shiva Kumar and Lim, 2022). In a laboratory setting, Solid Oxide Electrolysers have an 89 % efficiency when applied to pure water and generate hydrogen gas of 99.9 % purity (Shiva Kumar and Lim, 2022). The investment costs of Solid Oxide Electrolysis are > 2000 US\$/ kW, owing to the technology still being in the research and development phase (Shiva Kumar and Lim, 2022).

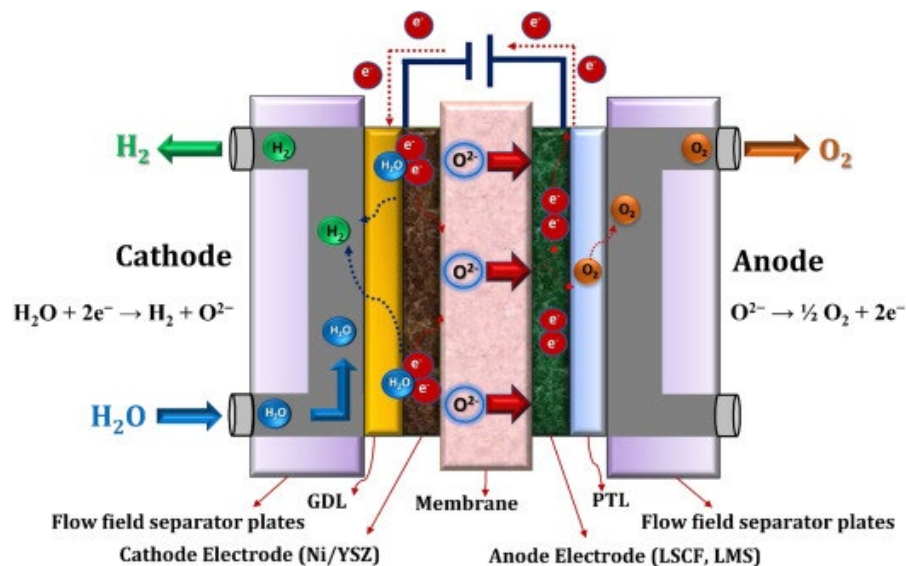


Figure 4. Schematic diagram of the working principle of Solid Oxide Electrolysis.

Figure obtained from Shiva Kumar and Lim, 2022.

Microbial Electrolysis Cells

Microbial Electrolysis Cells are modified versions of microbial fuel cells and are considered as promising bioprocesses for the recovery of resources, such as hydrogen, whilst simultaneously treating wastewater and waste (Aydin *et al.*, 2021; Zakaria *et al.*, 2019). Microbial Electrolysis Cells utilise anode-respiring bacteria which facilitate the long-distance electron transfer to the anode through an extracellular electron transport mechanism (Zakaria *et al.*, 2019). Exoelectrogenic bacteria at the anode oxidise organic matter to produce electrons, protons, and carbon dioxide (Chen *et al.*, 2019). The electrons are transferred to the cathode and subsequently used to reduce the protons to produce hydrogen (Figure 5) (Lu and Ren, 2016). Microbial Electrolysis Cells require a much lower voltage (0.2–0.8 V) to be applied to the electrodes than other water electrolysis technologies (Lu and Ren, 2016). Various carbon sources, including domestic and industrial wastewaters, can be used in Microbial Electrolysis Cells to produce hydrogen whilst simultaneously lowering the Chemical Oxygen Demand of the feed water (Chen *et al.*, 2019).

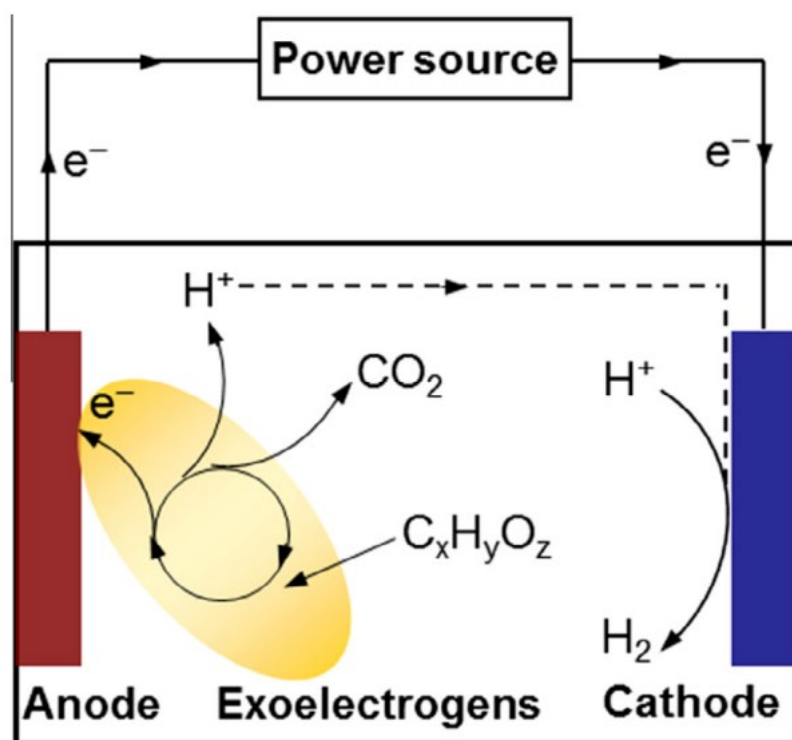


Figure 5. Schematic diagram of the working principle of Microbial Electrolysis Cells. Figure obtained from Lu and Ren, 2016.

Electrolysis of wastewater

Whilst Alkaline electrolysis of wastewater is possible, it is not yet popular for the reasons outlined as follows. The use of industrial wastewater for hydrogen production is an energy intensive and low-yield process due to the wastewater consisting of particulates and dissolved organic and inorganic constituents which hinder hydrogen yield and the specific hydrogen production rate (Cartaxo *et al.*, 2022; Chauhan and Ahn, 2023). As such, electrolysis of wastewaters is still very much in the research and innovation phase with limited studies having been conducted using municipal wastewater as a substrate for hydrogen production via Alkaline electrolysis (Chauhan and Ahn, 2023).

Chauhan and Ahn (2023) investigated hydrogen generation via Alkaline electrolysis using wastewater effluents collected from municipal wastewater treatment plants. Hydrogen production from low-grade water (raw wastewater, primary effluent, secondary effluent, tertiary effluent, and surface water) was assessed under varying parameters and compared to the hydrogen generated by splitting high-grade water (distilled and tap water). The lowest amount of hydrogen was evolved from raw wastewater (19.18 ± 0.15 mL/h/cm² representing 74.18 ± 2.31 % hydrogen, compared to distilled water) (Chauhan and Ahn, 2023). The greater the amount of treatment the wastewater had undergone, the greater the amount of hydrogen evolved – for example, more hydrogen was evolved from tertiary effluent (82.18 ± 0.94 % hydrogen, compared to distilled water) than from secondary effluent (79.12 ± 1.46 % hydrogen compared to distilled water) (Chauhan and Ahn, 2023). For all wastewater effluents tested, KOH was a better electrolyte than NaOH and there was a positive correlation between electrolyte dosage (5M, 7M and 10 M) and hydrogen generation (Chauhan and Ahn, 2023). Chauhan and Ahn (2023) did not investigate whether other gases are evolved or whether electrolyser components are fouled during electrolysis of wastewater, representing a gap in current understanding.

Heidrich *et al.*, (2014) built and ran a 100 L Microbial Electrolysis Cell for 12 months to evaluate hydrogen production from domestic wastewaters at low temperatures. Whilst hydrogen gas was produced continuously for the 12 months until the

Microbial Electrolysis Cell was decommissioned, the amount produced declined throughout the year (Heidrich *et al.*, 2014). The systems overpotential was thought to have increased over the year as a result of inactive biomass build-up at the anode and fouling of the membrane and wire connectors (Heidrich *et al.*, 2014). 41.2 % of the hydrogen that could theoretically be produced based on the currents used was captured (Heidrich *et al.*, 2014). There were substantial losses during hydrogen recovery, with the plastic tubing and connectors used known to be permeable to hydrogen (Heidrich *et al.*, 2014). Hydrogen gas evolved at the cathode was consistently pure (98–99 %) and whilst there was no methane detected in the cathode gas, 0.8 % methane was present in the anode gas (Heidrich *et al.*, 2014). Chemical Oxygen Demand of the wastewater was reduced by 44 % following electrolysis, however, this was insufficient to reach UK discharge standards (Heidrich *et al.*, 2014). Whilst there was 38.4 % less sulphate present in the wastewater following electrolysis, there was not any substantial removal of other anions (chloride, nitrate, phosphate, acetic acid, and propionic acid) present (Heidrich *et al.*, 2014). The work conducted by Heidrich *et al.*, (2014) highlighted the areas in which further research and development was required for hydrogen production from wastewater via Microbial Electrolysis Cells to be successful at scale.

Waste anaerobic sludge was subjected to a range of DC voltages (0.5–5V) through aluminium electrodes by Kargi, Catalkaya and Uzuncar (2011). 2V was the optimum voltage applied, with 94.3 % hydrogen gas evolved from the anaerobic sludge and an energy efficiency of 74 % (Kargi, Catalkaya and Uzuncar, 2011). The majority of the hydrogen gas evolved was due to electro-hydrolysis of the anaerobic sludge, with <20 % of the hydrogen gas formed resultant of water electrolysis (Kargi, Catalkaya and Uzuncar, 2011). A similar level of Chemical Oxygen Demand removal (84 %) was observed for the control (no voltage applied) as for the range of voltages tested, suggesting that Chemical Oxygen Demand removal can be attributed to natural anaerobic digestion of the sludge (Kargi, Catalkaya and Uzuncar, 2011).

In brief summary, hydrogen gas can be generated from anaerobic sludge, anaerobic effluent and treated wastewater.

Products of wastewater electrolysis

The splitting of water via electrolysis produces hydrogen and oxygen. Chauhan and Ahn (2023) propose that oxygen generated during electrolysis of wastewater could be used during aerobic sludge digestion of municipal wastewaters. The average power required to produce Advance Treated Water in wastewater treatment facilities is $875 \text{ kW/m}^3/\text{s}$ (Chauhan and Ahn, 2023). Given that the supply of oxygen for aerobic digestion accounts for 50–60 % of the total power requirement of wastewater treatment facilities, utilising oxygen produced via electrolysis would help the facilities to reach carbon neutrality (Chauhan and Ahn, 2023). Furthermore, pure oxygen has higher absorption than atmospheric oxygen (50–60 % vs 5 % absorption) resulting in 10-fold higher bio-stabilisation activity (Chauhan and Ahn, 2023). Chauhan and Ahn (2023) estimate that electrolysing 338 kg/d Advanced Treated Water would provide sufficient oxygen (300 kg/d) and twice as much power (1352 kwh generated by 37.5 kg/d hydrogen gas being applied to a fuel cell) required for aerobic digestion of wastewater (Figure 6).

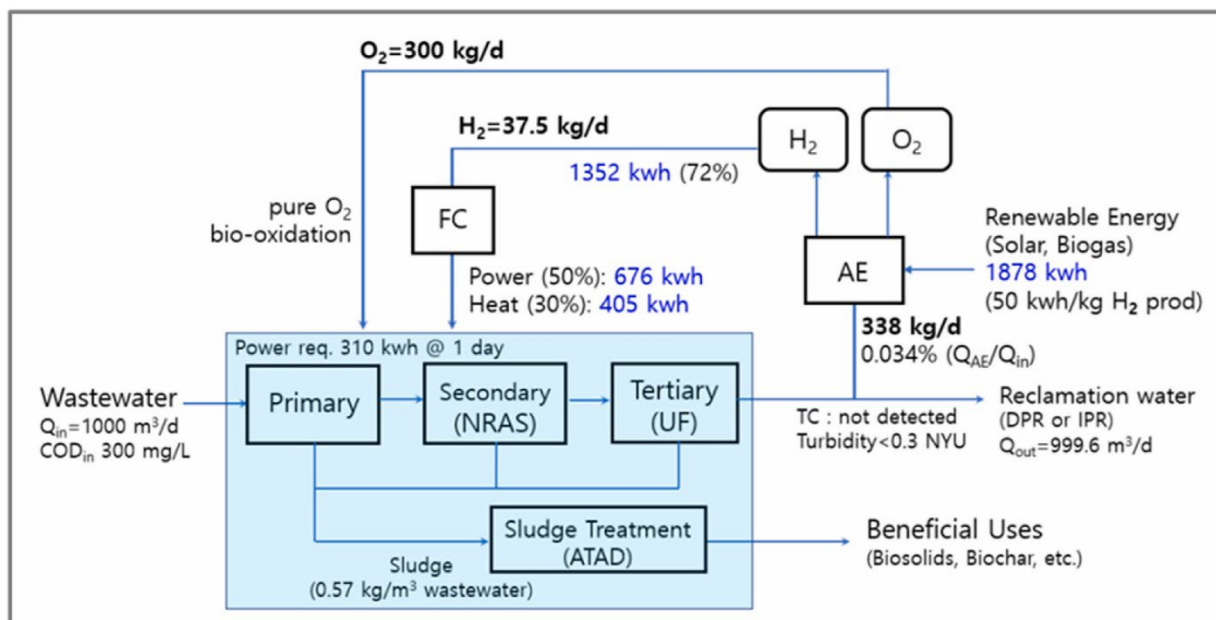
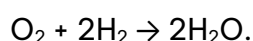


Figure 6. Proposed use of alkaline electrolysis in wastewater treatment plants. AE = Alkaline Electrolysis, FC = fuel cell. Figure obtained from Chauhan and Ahn (2023).

The most common contaminants of hydrogen produced via alkaline electrolysis of pure water are oxygen, nitrogen, and water (Ligen, Vrabel and Girault, 2020). Nitrogen, typically used to purge electrolyzers during maintenance, can have a diluting effect on hydrogen (Ligen, Vrabel and Girault, 2020). Whilst oxygen evolved at the anode can poison the hydrogen stream, in commercial alkaline electrolysis systems 0.2–0.6 % oxygen is found in hydrogen gas (Ligen, Vrabel and Girault, 2020). Oxygen is typically removed by catalytic condensation prior to a condensation drying step (Ligen, Vrabel and Girault, 2020):



Hydrogen gas has a tolerance to water contamination of up to 5 ppm – at such levels water remains gaseous preventing corrosion of metal components of the electrolysis system (Ligen, Vrabel and Girault, 2020). Hydrogen produced via Alkaline electrolysis is saturated with water which can be reduced by cooling the hydrogen followed by drying using temperature swing adsorption and pressure swing adsorption systems (Ligen, Vrabel and Girault, 2020). Impurities in hydrogen resulting from contaminants can be reduced by hydrogen purification steps (Becker *et al.*, 2023). Low concentrations of trace impurities in hydrogen, such as carbon dioxide and halogens, are tolerated in hydrogen fuel cells (Becker *et al.*, 2023).

In addition to hydrogen evolution, the electrolysis of wastewater can result in the generation of unwanted side-products due to the presence of contaminants within the water. Side-reactions can lower the quality of the hydrogen evolved during electrolysis (Becker *et al.*, 2023). Halogens such as Cl^- , Br^- and F^- are present in relevant concentrations in brackish water (Lindquist *et al.*, 2020). Halide reactions and chlorine reactivity are a particular concern for electrolysis of impure water (El-Shafle, 2023). Under acidic conditions the Chlorine Evolution Reaction outcompetes the Oxygen Evolution Reaction due to faster kinetics, resulting in the formation of Cl_2 (Lindquist *et al.*, 2020). Under neutral-basic conditions, the Oxygen Evolution Reaction is more favourable resulting in the formation of ClO^- which appears on the surface of the catalyst (El-Shafle, 2023; Lindquist *et al.*, 2020). Depending upon the pH, mass transport and current density of the wastewater, ClO_2^- , ClO_3^- and HClO may also be evolved (El-Shafle, 2023). The Bromine Evolution Reaction is also more thermodynamically and kinetically

favourable than the Oxygen Evolution Reaction, resulting in the formation of Br^{2+} . Similarly, BrO^- , BrO^{2-} , BrO^{3-} and HBrO may be evolved in the presence of bromine under neutral-basic conditions (Lindquist *et al.*, 2020). To date, published literature has focused on the effects of the Chlorine Evolution Reaction but it is thought that other anions may have similar mechanisms and effects (Becker *et al.*, 2023). Cl^- and products of the Chlorine Evolution Reaction can corrode the electrodes and other components of the electrolysis cell, reducing the stability and lifetime of the electrolyser (He *et al.*, 2023). The effect of halide ions on specific electrolyser components is discussed later in the review.

Current understanding of the products resulting from electrolysis of water contaminated with proteins and organic compounds is limited.

Fouling of electrolyser components during wastewater electrolysis

Microbes and small particulates present in wastewater may poison electrodes, catalysts and membranes limiting their long-term stability (Tong *et al.*, 2020). Ion exchange during redox may also be hampered by impurities present in the water accumulating on the electrode surface and membrane (Chauhan and Ahn, 2023). Cathode electrocatalysts are at risk of active site blockage and corrosion as a result of operating in impure water (Tong *et al.*, 2020). The effect of impurities on the electrodes, membrane and catalysts of electrolysis cells is discussed in more detail below.

Electrodes

OH^- , produced at the cathode during the Hydrogen Evolution Reaction, creates a locally basic environment which causes cations (such as Ca^{2+} and Mg^{2+}) to precipitate and form hydroxides (Lindquist *et al.*, 2020; Tong *et al.*, 2020). Ca^{2+} and Mg^{2+} deposition on the cathode as hydroxides can result in density losses of >50 % after 24 hours of operation (Tong *et al.*, 2020). The cathode surface may also be affected by reduction and electrodeposition of dissolved ions such as copper, cadmium, tin, and lead (Tong *et al.*, 2020).

Becker *et al.*, (2023) reported that transition metal cations such as Ni^{2+} and Fe^{3+} can improve the Hydrogen Evolution and Oxygen Evolution Reactions by adsorbing to both the cathode and anode thereby increasing the catalysts surface area. Li *et al.*, (2019a) found that at high temperatures and low current density, low concentrations of Fe^{3+} can improve the performance of the electrolysis cell. However, as the concentration of Fe^{3+} in the feed water increases, the performance of the cell is significantly degraded due to an increase in charge resistance on both electrodes (Li *et al.*, 2019a).

He *et al.*, (2023) investigated the effect of ion concentrations on direct alkaline seawater electrolysis and reported that increasing concentrations of Cl^- decreased the stability of both the cathode and anode. The Hydrogen Evolution Reaction overpotential was found to increase with increasing concentrations of Cl^- resulting in a negative effect on the activity of the reaction (He *et al.*, 2023). Nickel electrodes are easily corroded by Cl^- through the chloride-hydroxide formation mechanism (Ma *et al.*, 2021). Cl^- corrosion was found to convert the nickel skeleton of the anode to Ni^{2+} leading to the release of $\text{Ni}(\text{OH})_2$ in to the alkaline solution of the electrolysis cell (Ma *et al.*, 2021). Ma *et al.*, (2021) reported that addition of sodium sulphate (Na_2SO_4) to the electrolyte could limit the Cl^- corrosion of the anode as SO_4^{2-} anions are preferentially adsorbed to the electrode surface over Cl^- anions. Consequently, Cl^- anions are electrostatically repulsed from the surface of the electrode (Ma *et al.*, 2021). The amount of OH^- within 1 nm of the electrode surface did not change with addition of sodium sulphate, leading Ma *et al.*, (2021) to conclude that the Oxygen Evolution Reaction would not be affected by the presence of SO_4^{2-} .

To date, the published literature has not explored the effect of heavy metal contaminants on electrolysis of domestic wastewaters. To further our understanding, electrolysis of metal plating wastewater using aluminium electrodes has been reviewed (Cokay and Gurler, 2020). Hydrogen gas (51 %) and CO_2 were generated from nickel-plating wastewater after 5V voltage was applied (Cokay and Gurler, 2020). The high DC voltage decomposed organic matter in the wastewater to volatile fatty acids, CO_2 and H_2 , whilst hydroxyl radicals generated during the electrolysis process oxidised organic compounds – together these

resulted in a Total Organic Carbon removal efficiency of 40 % (Cokay and Gurler, 2020). However, the suspended solid concentration increased following electrolysis due to decomposition of the electrode (Cokay and Gurler, 2020). Similar results were observed for the electrolysis of copper-plating wastewater, with 50.5 % hydrogen gas generated, 41 % Total Organic Carbon removal and electrode decomposition at 5V (Cokay and Gurler, 2020). However, electrolysis of chrome-plating wastewater resulted in the generation of nearly pure (99 %) hydrogen gas and 60 % removal efficiency of Total Organic Carbon at 2V (Cokay and Gurler, 2020). An increase in the voltage from 2V to 5V increased the total hydrogen gas volume but did not further increase the hydrogen gas percentage (Cokay and Gurler, 2020). Whilst the work conducted by Cokay and Gurler (2020) demonstrated that hydrogen gas can be generated via electrolysis of heavy-metal wastewaters, the decomposition of electrodes brings into question the feasibility of using feedstock contaminated with heavy metals.

During the electrolysis of waste anaerobic sludge using aluminium electrodes, Al^{3+} ions were found to be released from the ionised anode and were subsequently deposited on the cathodic surface in the form of pure aluminium at 2V and 3V (Kargi, Catalkaya and Uzuncar, 2011). The highest amount of Al^{3+} ions were observed at 2V, correlating with the voltage at which the greatest amount of hydrogen gas was formed (Kargi, Catalkaya and Uzuncar, 2011). Kargi, Catalkaya and Uzuncar (2011) reported that Al^{3+} ions could be precipitated from the waste sludge by addition of lime ($\text{Ca}(\text{OH})_2$).

Further studies on the impact of inert impurities on electrodes is required, particularly given the increased interest in utilising impure water as feed for green hydrogen production via electrolysis. Whilst it is known that bacteria are oxidised at the anode to produce SO_4^{2-} and NO_3^- , the effect of microorganisms at the cathode also remains to be elucidated (Becker *et al.*, 2023).

Membranes

PFSA membranes used in Proton Exchange Membrane electrolysis cells can undergo reversible and irreversible degradation mechanisms (Fouda-Onana *et al.*, 2016).

Cationic impurities have the greatest impact on Proton Exchange Membrane cells by degrading the performance and lifetime of the catalyst, ion-conducting phase (or ionomer), and membrane (Becker *et al.*, 2023). Cations can affect membrane conductivity, compromise water transport properties of the membrane and overall membrane stability (Becker *et al.*, 2023). Cations have a higher affinity than protons for the end-group of the membrane (typically SO_3^-) resulting in proton displacement and reduced conductivity of the Proton Exchange Membrane (Becker *et al.*, 2023). Cations such as Na^+ , Mg^{2+} , K^+ and Ca^{2+} , which may be trace contaminants within wastewater treatment effluent, can be exchanged for H^+ in the membrane, resulting in an increase in the cell voltage (El-Shafie, 2023; Lindquist *et al.*, 2020). High-purity water can also degrade PFSA membranes due to the concentration of metallic cations (Fe^{3+} , Cr^{2+} and Ni^{2+}) in the water increasing as it is circulated in stainless steel circuitry (Millet *et al.*, 2010). Ionic contaminants can intercalate into the cation-exchange membrane increasing membrane resistivity (Lindquist *et al.*, 2020). Whilst calcium, sodium, and magnesium are the most significant elements to influence the cells performance, non-metallic cations such as ammonium (NH_4^+) can also substitute protons within the electrolysis membrane (Becker *et al.*, 2023; El-Shafie, 2023). Increasing concentrations of NH_4^+ has been associated with decreased membrane conductivity (Becker *et al.*, 2023). Cleaning of the membrane would recover performance, as discussed in more detail later in the review.

Ions of a higher valence are preferentially absorbed meaning that even when present at low aqueous mole fractions, higher concentrations may be present in the membrane (Becker *et al.*, 2023). However, in 1 M H_2SO_4 there was no loss in membrane conductivity when Fe^{3+} and Cr^{2+} were present at concentrations below 200–300 ppm, whilst in distilled water conductivity loss was observed at concentrations of 10 ppm (Becker *et al.*, 2023). Thus, the effects of cationic impurities can be mitigated at low pH (Becker *et al.*, 2023).

Uneven current distributions can result in irreversible membrane swelling (Fouda-Onana *et al.*, 2016). The PFSA membrane backbone may also be attacked by OH^- , generated by hydrogen peroxide formation, leading to the release of hydrogen

fluoride and subsequent membrane thinning (Fouda-Onana *et al.*, 2016). The effect of halogen ions on PFSA membrane is currently unknown.

Catalysts and ionomers

Organic contaminants may poison catalysts by adsorbing on the surface, reducing the electrochemically active surface and by increasing catalyst dissolution (Becker *et al.*, 2023). Oxidation of organic molecules can produce carbon monoxide and carbon dioxide, which introduces additional impurities into the system and can damage the electrolysis cell (Becker *et al.*, 2023). Hydroxyl and cyano functional groups of organic species can form stable complexes with dissolved metal ions, which can increase dissolution of the catalyst and, subsequently, loss of catalytic performance (Becker *et al.*, 2023; Martelli *et al.*, 1994).

Metal cations can also deposit on the surface of the catalyst. In the presence of 10^{-6} M CuSO_4 , copper was found to visibly deposit on a platinum catalyst (Kötz and Stucki, 1987).

The catalysts of Proton Exchange Membrane electrolyzers contain an ion-conducting phase, or ionomer, that increases the electrochemically active surface area (Becker *et al.*, 2023). Ionomers are typically thin layers of perfluorosulphonic acid and, as such, suffer the same cationic effects as electrolysis membranes described above (Becker *et al.*, 2023). Contamination of electrode water feeds with 0.05 M Na_2SO_4 resulted in a decrease in pH from pH 6 to pH 3 as protons were exchanged at the anode ionomer and sulphuric acid was produced in the water (Becker *et al.*, 2023; Zhang *et al.*, 2012). Following 3 hours of electrolysis, the pH increased to pH 11 as Na^+ migrated through the membrane and replaced protons in the cathode ionomer layer (Becker *et al.*, 2023; Zhang *et al.*, 2012). Electron Probe Microanalysis revealed that cations accumulated on the cathode when the anode water supply was poisoned with sodium and iron (Becker *et al.*, 2023; Kusoglu and Weber, 2017; Wang *et al.*, 2015). Cationic impurities at the ppm level within water can reduce performance of electrolysis catalysts by reducing the electrochemically active surface area (Becker *et al.*, 2023; Li *et al.*, 2019a; Li *et al.*, 2019b).

One of the most common problems associated with electrolysis of water containing anion contaminants is the initiation of side-reactions (Becker *et al.*, 2023). Halide ions can adsorb onto the surface of the catalyst – for I^- and Br^- this may be irreversible at sufficiently high concentrations (3M for HBr) – leading to a loss of >50 % of the electrochemically active surface area (Becker *et al.*, 2023). However, even in the presence of acid the Hydrogen Evolution Reaction on platinum continues to be a very fast reaction meaning that minor anion poisoning should not result in a great loss of performance (Becker *et al.*, 2023). Adsorption of Cl^- on the platinum on carbon cathode catalysts can enhance hydrogen peroxide production, which can promote breakdown of the perfluorosulphonic acid backbone (Becker *et al.*, 2023). SO_4^{2-} and HSO_4^- anions are by-products of the perfluorosulphonic acid membrane breakdown and may also specifically adsorb onto the surface of platinum catalysts (Becker *et al.*, 2023). Furthermore, Cl^- anions can also form chloroplatinic ligands which enhance platinum dissolution (Becker *et al.*, 2023).

Rejuvenation of electrolyser components

Whilst some contaminations of electrolyser components are self-reversing, others require cleaning to recover electrolytic performance. Light carbonates are an example of a self-reversible contamination – at high currents the generation of OH^- at the cathode purges carbonates from the cell as carbon dioxide (Becker *et al.*, 2023). Repeated changes of the electrolyte may eliminate soluble anionic impurities whilst ionic impurities may be removed by oxidation and/ or flushing of the system (Becker *et al.*, 2023). Furthermore, flushing of the system may help to remove metallic and insoluble salt impurities by adjusting the pH such that the contaminants are solubilised (Becker *et al.*, 2023). Adsorbed halide ions may be removed from the catalytic surface either by oxidising at very high potentials or by holding the catalyst at reducing potentials to evolve hydrogen (Becker *et al.*, 2023). High potentials may also remove organic contaminants, via oxidation (Becker *et al.*, 2023). Immersion of fouled perfluorosulphonated acid membranes in acid solutions (e.g. 0.5–1M H_2SO_4) can remove metallic cations and re-protonate ionomers (Becker *et al.*, 2023; Wang *et al.*, 2015).

Pre-treatment of wastewater prior to electrolysis

The sustainability and feasibility of hydrogen generation from industrial wastewater may be improved by incorporating pre-treatment processes. Wastewater substrates filtered through high-strength sulfonated PVDF ultrafiltration membrane was subsequently assessed for hydrogen generation via alkaline electrolysis (Chauhan and Ahn, 2023). The ultrafiltration membrane was found to be effective in removing coarse particulates and suspended solids from the wastewater, resulting in a reduction of sample turbidity (Chauhan and Ahn, 2023). Ultrafiltration improved the quality of water and, as a result, hydrogen generation was also improved, leading Chauhan and Ahn (2023) to conclude that to achieve the best Alkaline electrolysis of wastewater effluent turbidity should be removed. Ultra filtration of raw wastewater resulted in an additional 4.03 ± 1.53 % hydrogen being evolved vs. unfiltered raw wastewater (Chauhan and Ahn, 2023). An alternative to ultrafiltration of wastewater, would be electrochemical pre-treatment methods which remove organic and inorganic pollutants through the action of reactive oxygen species based on anodic oxidation (Cartaxo *et al.*, 2022). Physical pre-treatment methods include thermal and microwave treatment of wastewaters (Sharmila *et al.*, 2020). Biological treatment via microbial or enzymatic action is considered to be both a cost and energy efficient method for the degradation of complex organic matter within wastewater (Sharmila *et al.*, 2020). Following an extensive review of the published literature, Sharmila *et al.*, (2020) concluded that further research is required before successful commercialisation of wastewater pre-treatment methods for hydrogen production.

Effect of electrolysis on wastewater

Hydrogen generation via electrolysis of raw wastewater can result in the simultaneous removal of pollutants from water (Chauhan and Ahn, 2023). Chauhan and Ahn (2023) reported a 47.7 % reduction in the Chemical Oxygen Demand of raw wastewater following electrolysis. There was also a 38.7 % reduction in Total

Nitrogen, a 41 % reduction in Turbidity and Total Dissolved Solids were reduced by 2.9 % following 60 minutes of electrolysis at room temperature (Chauhan and Ahn, 2023). By differentially controlling the anode/ cathode potentials of an electrolysis cell, the Chemical Oxygen Demand and Total Nitrogen of pharmaceutical wastewaters were reduced (Aydin *et al.*, 2021; Yao *et al.*, 2019). Electrolysis of primary sludge from a wastewater treatment plant using a Microbial Electrolysis Cell was found to have a Chemical Oxygen Demand removal efficiency of 73 % (Aydin *et al.*, 2021; Zakaria *et al.*, 2019). The treatment of wastewater alongside hydrogen production makes electrolysis of wastewater an exciting application that could help to reduce greenhouse gas emissions from wastewater treatment facilities (Aydin *et al.*, 2021).

Electrolysis of wastewater from distilleries

SuperCritical have conducted a phase 1 feasibility study to investigate the generation of green hydrogen via electrolysis of distillery wastewater. SuperCritical have published an extensive report on the findings of phase 1 and an outline of plans for phase 2 of the project, as summarised below.

Wastewaters from the whisky distilling process have high levels of Chemical Oxygen Demand ($38,867 \pm 115 \text{ mg/L}$), Biological Oxygen Demand ($30,965 \pm 666 \text{ mg/L}$), sulphate ($190 \pm 31 \text{ mg/L}$), phosphate ($778 \pm 7 \text{ mg/L}$), ammonia ($45 \pm 7 \text{ mg/L}$), nitrate ($111 \pm 20 \text{ mg/L}$), nitrogen dioxide ($33 \pm \text{mg/L}$) and copper ($14.7 \pm 1 \text{ mg/L}$) (Gunes *et al.*, 2020). Despite this, SuperCritical (2020) believe that distillery wastewater requires minimal treatment prior to electrolysis.

In phase 1, a model was generated to assess the level of wind intermittency and how that would dictate the size of electrolyser and size of hydrogen storage required to fully decarbonise the distillery whilst maintaining its operation as a 24/7 facility (SuperCritical, 2020). The model, created using a full year's energy supply generated at an hourly level, showed a 45 % net capacity of a wind turbine located close to the distillery over the year (SuperCritical, 2020). The longest period of insufficient wind to meet the energy demands of the distillery was 230 hours – during this period hydrogen storage was required (SuperCritical, 2020). The

optimal hydrogen gas storage capacity, calculated based on the depreciated cost of hydrogen gas storage capex vs the benefits of storing the hydrogen, was 2.9 days of distillery demand (SuperCritical, 2020). For 1,289 hours in the year, backup grid electricity was used due to hydrogen stores being depleted (SuperCritical, 2020). SuperCritical (2020) concluded that a 52 % increase in the size of electrolyser used in the model would be required to meet the energy demands of the distillery whilst also topping-up stored hydrogen gas reserves after a period of low wind levels.

In phase 2 of the WhiskHy project, SuperCritical are deploying their proprietary membrane-less electrolyser technology at Ardmore distillery. They propose to perform electrolysis at $>375^{\circ}\text{C}$ and $>221\text{ bar}$ and view these conditions as major risks associated with the process (SuperCritical, 2020). The optimal method for increasing the size of the electrolyser to 50 kW, as shown to be required by the phase 1 model, was to be determined via enlargement of the existing cell in parallel with the design and testing of a multi-cell module (SuperCritical, 2020). Heat exchangers, pumps and vessels were to be externally sourced. In the pilot study, hydrogen was to be stored at the electrolyser's output pressure ($\sim 230\text{ bar}$) which would be reduced via a regulator enroute to the distillery's existing boiler (SuperCritical, 2020). Oxygen produced was to be vented during the pilot phase of the study, with oxygen use in the on-site wastewater treatment facility being explored (SuperCritical, 2020).

Development of the electrolysis technology was a priority for phase 2, with focus on maximising conductivity of the alkaline electrolyte whilst minimising corrosion of electrolyser components as well as evaluating alloys and/ or coatings for the catalyst and electrode housing (SuperCritical, 2020). A further goal was to develop catalyst production methods for ease and affordability of scale-up (SuperCritical, 2020). Electrolysis technology is planned to be modularly scaled-up, as per the prior commercialisation of Alkaline Water Electrolysis (SuperCritical, 2020).

SuperCritical (2020) estimated that the 50 kW electrolyser would allow for the production of 164,100 bottles (70 cL) of whisky per year without carbon emission. The electrolyser had a projected energy generation cost of £1.59/ kg of H_2 (equivalent to 4.8 p/ kWh) when produced, stored, and consumed at the distillery

from renewable energy sources (SuperCritical, 2020). The electrolysis of wastewater at Ardmore distillery is expected to be live in March 2024.

Conclusions

The review has shown that hydrogen generation via electrolysis of domestic wastewater is possible, with good hydrogen yield being obtained from raw wastewater. Contaminants present within wastewater can result in the reversible and irreversible fouling of electrolyser components. Methods to rejuvenate fouled components have been reported but feasibility studies are required to evaluate their effectiveness in an industrial setting. Ongoing research into the re-design of electrolysers to minimise fouling of cell components may have a great impact on the feasibility and efficiency of wastewater electrolysis. Rubbish Energy could develop a model to estimate the cost: benefit of wastewater electrolysis using different technologies. A model, similar to that used by SuperCritical in their phase 1 feasibility study, may allow for unsuitable technologies to be quickly ruled out. Knowledge gained as the technology solution is developed could be fed into the model as part of an iterative design process. The findings of the review support the initiation of feasibility studies to evaluate electrolysis of wastewater using off-the-shelf electrolysers for the production of green hydrogen.

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Considerations for next steps

Offshore Renewable Energy Catapult – £15k available to support SMEs scale-up and commercialise their technology.

<https://ore.catapult.org.uk/what-we-do/innovation/smes-agile-innovators/>

Energy Systems Catapult – technical, commercial and policy support

<https://es.catapult.org.uk/work-with-us/net-zero-innovators/>

Net Zero Hydrogen fund – UK Government funding to support commercial deployment of new low carbon hydrogen production projects.

Opportunities for collaboration with Newcastle University

Category	Duration	Cost/Contribution	Information/Contact
Student Internship	Flexible	Based on duration. • 50 hours – £625 bursary fully subsidised by the Careers Service • 100 hours – bursary £1250, employer contribution £625 plus VAT	Kate Chambers, Internships Manager kate.chambers@ncl.ac.uk www.ncl.ac.uk/employers/internships/
Student project: ▪ Undergraduate ▪ Masters	1-2 months 3-6 months	Project specific, possibly no cost	Academic(s) you wish to collaborate with – policies differ between academic schools
Student Placement	9-12 months	Variable, stipend required	cs.placementyear@ncl.ac.uk www.ncl.ac.uk/employers/placements/
Degree Apprenticeship (MSc/MBA/MEng)	Course-dependent	Apprenticeship levy: SMEs pay 5%, government pay 95% – funding band is degree specific	Operations or Departmental Manager, Digital and Technology Solutions, Coaching Professional, Senior Leader (Business) https://www.ncl.ac.uk/business-and-partnerships/expert-solutions/degree-apprenticeships/
PhD Student	3-4 years	Successful funding application	Academic(s) you wish to collaborate with (who are eligible to supervise a student)
KTP Associate	12-36 months	Typical cost for SME £28-33K per year, with total value of £90-100K per year	www.ncl.ac.uk/work-with-us/expert-solutions/ktp/
National Innovation Centres for Ageing (NICA), Data (NICD), and Rural Enterprise (NICRE)	Variable	Variable	<u>Ageing: NICA and VOICE</u> www.uknica.co.uk/contact-us/ www.voice-global.org/ <u>NICD:</u> nicd@newcastle.ac.uk www.ncl.ac.uk/nicd/work-with-us/ <u>NICRE:</u> Melanie Thompson-Glenn

			(Business Development Manager) Melanie.Thompson.Glen@ncl.ac.uk https://www.ncl.ac.uk/cre/nationalinnovationcentreforruralenterprise/
Collaborative Research	Variable	Successful funding application or company funded	Academic(s) you wish to collaborate with, who will liaise with Business Development & Enterprise Team. https://www.ncl.ac.uk/business-and-partnerships/expert-solutions/collaborative-research/
Contract Research	Variable	Variable	business@ncl.ac.uk
Consultancy	Variable	Variable rate, request quote	Complete enquiry form https://www.ncl.ac.uk/business-and-partnerships/expert-solutions/consultancy/
Facilities/ Equipment	Variable	Variable, e.g. pay per use or for contract research Via facility staff. Note: Post-Graduate students obtain discounts	All areas summary: https://www.ncl.ac.uk/research/facilities/ Science: www.ncl.ac.uk/medical-sciences/business/facilities/
Graduate Recruitment	N/A	No cost, simply register with Employer Portal	Recruitment fairs, and advertise free through careers service www.ncl.ac.uk/employers/vacancies/

An introduction to Business Support from our North East university partners	
Durham University	www.durham.ac.uk/research/helping-businesses/
Northumbria University	www.northumbria.ac.uk/business-services/
Sunderland University	www.sunderland.ac.uk/study/business-and-management/commercial-engagement