

Design and analysis of a membraneless divergent electrode flow through electrolyser for hydrogen production

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Thesis submitted in fulfilment of the requirements for the
degree *Doctor of Philosophy in Chemical Engineering* at the
North-West University

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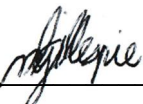
Graduation May 2018

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DECLARATION

I, Malcolm I. Gillespie, declare that the thesis entitled: "Design and analysis of a membraneless divergent electrode flow through electrolyser for hydrogen production", submitted in fulfilment of the requirements for the degree Philosophiae Doctor in Chemical Engineering, is my own work, except where acknowledged in the text, and has not been submitted in whole or in part to any other tertiary institution.

Signed at North-West University (Potchefstroom Campus)



Malcolm I. Gillespie

March 2018
Date

ACKNOWLEDGMENTS

To Corrie de Jager, CEO of Hydrox Holdings, for his continued support, sponsorship, and guidance in the development of the technology. He has provided me with a spectrum of opportunities that I'll be eternally grateful for. He has always challenged and motivated me to continually apply my mind in achieving success with my research.

To Prof. Cobus Kriek for the continued guidance and input into my research, and the development of the DEFT™ technology, to drive it to the success and level of precision that it possesses today.

To my lovely wife, Chelsea Gillespie, for supporting me through the long hours spent at work and on the development of this thesis.

To my wonderful parents who have always motivated me in aspiring to achieve greatness.

To the gentlemen at LANI service centre and Power Dynamics, for the use of their factory facilities and expertise in the fabrication, assembly, commissioning and testing of the various pilot plants used to perform this research.

To Hydrox Holdings Ltd., for the opportunity and sole funding for equipment and resources, to base my thesis on developmental work performed on their propriety patented technology.

ABSTRACT

Cost-effective renewable hydrogen production has been elusive to date, preventing the acceleration of water electrolysis technologies into the industrial market. The vast majority of hydrogen produced globally is derived from methods such as methane steam reforming, and hence renewable sources of hydrogen remain non-competitive with hydrogen derived from fossil fuel sources. A novel process whereby the manipulation of flowing electrolytic solution in opposing directions, through porous metallic electrodes, provides the means to create gaseous separation of constituent gases produced on the surface of the electrodes. The electrolyser configuration required to achieve this, is simplistic and cost-effective, providing reliable, efficient and, durable operation. Mass transfer limitations, and a reduced ionic resistance are characteristic of the Divergent Electrode-Flow-Through (DEFT™) membraneless alkaline water electrolysis system.

Current commercial water electrolysis technologies are connected by a number of issues, which drive up the cost to produce hydrogen and limit their long term reliability. Alkaline Water Electrolysis (AWE) represents the most mature and widely utilised electrolysis technology. It is nevertheless limited by an operating current density threshold, which, if superseded, will be plagued by enhanced bubble resistances and cross gas contamination. Their alkaline environment allows them to be constructed out of non-noble cost-effective materials, however, are large in scale due to their low power densities, leading to inflated capital expenditures. Proton Exchange Membrane (PEM) electrolysers attain greater current densities in reference to AWE systems, and are hence more compact in scale. Their membranes, however, lack reliability and are constructed from scarce and expensive materials. The costs associated with these systems make them non-competitive with large AWE systems. Research involved in this field is concerned with incremental improvements in performance and reliability while indirectly reducing the cost of components, however, restricted or limited improvements are not enough to drive accelerated renewable hydrogen production.

A number of membraneless electrolysis concepts exist, however, the fundamental difference between flow along and flow through operational principles provides unique advantages to the DEFT™ alkaline electrolysis solution. Initial investigations into proof of concept have revealed a system capable of efficient stack performance and generation of high purity product gases. This led to the development of a reliable, scalable DEFT™ stack design and practical plant configuration, to provide synchronisation of all essential components that will serve to provide the formula for the continued commercial development of the technology. The complete plastic design successfully demonstrated optimal performance of an enhanced PGM based catalyst comprising of aluminium, nickel, and platinum in mass ratio 0.36:0.55:0.09 respectively as the anode and pure platinum as the cathode. This catalyst demonstrated 0.477 A.cm^{-2} at 1.77 VDC and

2.62 A.cm⁻² at 2.5 VDC, at an operating temperature of 70°C, electrode gap of 2.5 mm, and flow velocity of 0.075 m.s⁻¹. The concept optimisation plant demonstrated optimal gas purities of 98.98 vol% H₂ and 97.6 vol% O₂ at a flow velocity of 0.075 m.s⁻¹, above the flammability limit of hydrogen gas.

After the initial successful demonstration of the technology, scalable designs were fabricated and tested. The Multiple Circular Electrode (MCE) electrolysis stack utilised a common pressurised chamber, housing a number of small circular electrodes, with each polarity discharging the bi-phase product into its own gas collection chamber. The MCE stack showed an improvement in performance reference to the concept optimisation stack due to the additional exposed surface area incorporated into the design, however, lacked severely in providing adequate product gas quality. The Horizontal Filter Press (HFP) concept utilised elongated electrodes that were fed from a slotted manifold, and exhibited an improvement in gas qualities. Gas qualities remained within the flammability limit and the stack ascertained a reduction in performance due to the lack of balanced flow and uniform current density distributions.

A culmination of the DEFT™ concept optimisation test plant, MCE stack, and HFP stack resulted in the optimised design of the technology utilising the compact benefits of a filter press configuration, along with the individual supply of power and fluid to circular electrodes, in order to provide superior balance in flow and current density. The design incorporated a number of flexibilities, one of which was an adjustable electrode gap. Results from the DEFT™ concept optimisation test rig and MCFPE (Mono circular filter press electrode) stack revealed an electrode gap of 2.5 mm to be optimal. An improvement in gas purity was yielded with this stack noting a hydrogen and oxygen gas purity of 99.81 vol% and 99.5 vol% respectively, at a temperature of 50°C, nominal current density of 3.5 A.cm⁻², electrode gap of 2.5 mm, and flow velocity of 0.075 m.s⁻¹. A large improvement in cell operating performance was yielded with the increase in available geometric surface area utilising a filtration mesh and metal foam. Compared to the DEFT™ concept optimisation, by doubling the 80 µm mesh yielded an improved performance across the cell potential range for the MCFPE stack. This does, however, have a significant reduction in the pore diameter, and hence restriction in gas and liquid flow. By utilising a larger mesh pore diameter of 200 µm incorporating two layers, enhanced performance greater than that of a single layer of 80 µm mesh along with hydrogen gas purities close to 100 vol%.

The MCFPE stack demonstrates ideal performance with overall plant efficiencies not yet comparable with commercial systems, however, with limited additional design optimisation and additional research and development, would enable the DEFT™ technology to compare favourably with existing systems. Development with regard to the balance of plant has yielded an effective solution to the unique problem of the rapid liberation of micro-bubbles from a flowing

solution. A working stack and gas/liquid separation solution therefore completes the basic building blocks for the DEFT™ technology.

A techno-economic study with current and future cost predictions, with the assumption of operating the technology from solar power, has shown that the current selling cost of hydrogen amounts to 9.85 US\$ / kg H₂ utilising an optimal nickel catalyst. With additional plant and stack optimisations, and the appropriate configuration allowing for lower parasitic loads, the current form of the technology would be capable of achieving a selling cost of 5.37 US\$ / kg H₂. Current forecourt electrolyzers operate in the region of 4.15 US\$ / kg H₂, with current indications pointing towards the DEFT™ operating principle surpassing this cost benchmark, close to that of methods associated with producing hydrogen from fossil fuel based sources.

The DEFT™ membraneless operating principle is therefore a unique means of performing water electrolysis, without the need of a membrane, to provide separation of product gases. This enhances the power density potential and yields a design with fewer components constructed out of inexpensive materials. The technology demonstrates significant potential to make cost-effective renewable hydrogen a possibility.

Keywords:

Alkaline water electrolysis, Membraneless, Divergent Electrode-Flow-Through technology, Hydrogen Production

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LIST OF SYMBOLS

Area (m ²)	A
Aluminium	Al
Laminar/Turbulent Correction Factor	α
Carbon Monoxide	CO
Carbon Dioxide	CO ₂
Electron	e ⁻
Stack electrical energy demand (kWh)	E
Cell Potential	E _{cell}
Standard equilibrium Potential (V)	E ⁰
Standard equilibrium potential for the cathodic electrode (V)	E ⁰ _{Cathode}
Standard equilibrium potential for the anodic electrode (V)	E ⁰ _{Anode}
Thermo-neutral Cell Potential (V)	E _{TN}
Faradays Constant (C.mol ⁻¹)	F
Acceleration due to Gravity (m.s ⁻²)	g
Standard Gibbs Free Energy (kJ.mol ⁻¹)	ΔG°
Standard Enthalpy (kJ.mol ⁻¹)	ΔH°
Hydrogen Ion	H ⁺
Hydrogen Gas	H ₂
Water	H ₂ O
Current (A)	I

Current Density (mA.cm ⁻²)	i
Iridium	Ir
Hydroxyl Ion	OH ⁻
Length (m)	l
Molecular mass (g.mol ⁻¹)	M
Mass (g)	m
Moles	n
Nickel	Ni
Faradic efficiency	η_{faradic}
Thermal efficiency	η_{thermal}
Overall efficiency	η_{overall}
Volumetric Flow Rate of Hydrogen (m ³ /s)	$\dot{n}_{H_2}$
Volumetric Flow Rate of Water (m ³ /s)	$\dot{n}_{H_2O}$
Volumetric Flow Rate of Oxygen (m ³ /s)	$\dot{n}_{O_2}$
Nickel Metal	Ni
Oxygen Ion	O ²⁻
Oxygen Gas	O ₂
Pressure (Bar)	P
Density (kg.m ⁻³)	ρ
Parts per million	ppm
Platinum	Pt
Friction Loss (N.m ⁻²)	ΔP_f

Pressure head (N.m^{-2})	ΔP_{lift}
Energy Absorbed/Released from the Environment (kWh)	Q_{cell}
Ruthenium	Ru
Thermo Neutral Voltage (VDC)	E_{tn}
Standard Entropy ($\text{J.mol}^{-1}.\text{K}^{-1}$)	ΔS°
Temperature (K)	T
Time (s)	t
Volume (m^3)	V
Work (kWh)	W
Displacement (m)	z

NOMENCLATURE

AWE	Alkaline Water Electrolysis
DEFT TM	Divergent Electrode Flow Through
CFD	Computational Fluid Dynamics
HER	Hydrogen Evolution Reaction
HFP	Horizontal Filter Press
HHV	Higher Heating Value of Hydrogen
MEA	Membrane Electrode Assembly
NREL	National Renewable Energy Laboratory
PEM	Proton Exchange Membrane
PEME	Proton Exchange Membrane Electrolysers
PGM	Platinum Group Metals
PP	Polypropylene
PTFE	Polytetraflouroethylene
SOE	Solid Oxide Electrolysis
LOP	Life of Plant
MCE	Multiple Circular Electrode
MCFPE	Mono Circular Filter Press Electrode
MEA	Membrane Electrode Assembly
MMO	Mixed Metal Oxide
OER	Oxygen Evolution Reaction

VFD

Variable Frequency Drive

1. INTRODUCTION

1.1 OVERVIEW

Water electrolysis will play a significant role in enabling hydrogen in becoming a key energy carrier in the industrial transport and energy generation sectors. It is the most efficient method of generating hydrogen from renewable energy sources, when compared to other methods, involving ultra-low carbon emissions [1]. The long term vision of driving an industry off renewable energy sources can be realised, through the use of hydrogen, to reduce industries' dependence on non-renewable fossil fuel sources of energy. Several technologies exist that can utilise the stored hydrogen in order to recapture the energy, such as hydrogen fuel cells, however, the generation, storage, and refuelling infrastructure, will need to be in place before these methods can be employed on a mass scale [2].

For years Alkaline Water Electrolysis (AWE) has remained the simplest and most developed means of deriving hydrogen from splitting water, and has been demonstrated numerous times on the mega-watt scale [3]. The state of AWE has not improved, as many existing systems still utilise asbestos as the membrane material of choice, however, focus has now turned to developing alternate environmentally safe materials with improved longevity and reduced resistance for use as a membrane separator [4].

Preferred methods of water electrolysis can be found in the form of Proton Exchange Membrane Electrolyser's (PEME's), which is considered an acidic based method. For this reason, PGM (Platinum Group Metal) materials, such as platinum, are used as effective electrode catalysts due to their corrosion resistance to the aggressive acidic environment in PEME's. This incurs additional costs, preventing the large scale adoption of water electrolysis technologies as an energy storage method [5]. AWE methods still largely prefer the use of nickel or other nickel based catalysts along with a number of non-noble metals, due to their corrosion resistant nature and superior catalytic qualities, making it suitable for low capital expenditure (CAPEX) hydrogen production.

Despite the deceiving simplicity of the AWE process, these systems still remain largely cost intensive to implement both on the small scale and on the large scale [5]. A thorough understanding is required of each performance influencing parameter, to optimise the efficiency of an alkaline system with cost reduction in mind. Current AWE systems operate with energy consumptions, per unit mass of hydrogen, of between 50 – 73 kWh/kg H₂ [1]. It is therefore preferred to optimise alkaline systems to operate within, or preferably below, this range to prove competitive to existing technologies.

Divergent Electrode-Flow-Through (DEFT™) alkaline water electrolysis technology serves to eliminate a number of challenges associated with modern day AWE systems. By utilising the flow of electrolyte within a stack, and directing the flow through porous electrodes in opposing directions, flow can be used to provide separation of the product gasses without the need for a membrane or diaphragm. The following illustration demonstrates the operating principle inherent to DEFT™ alkaline water electrolysis:

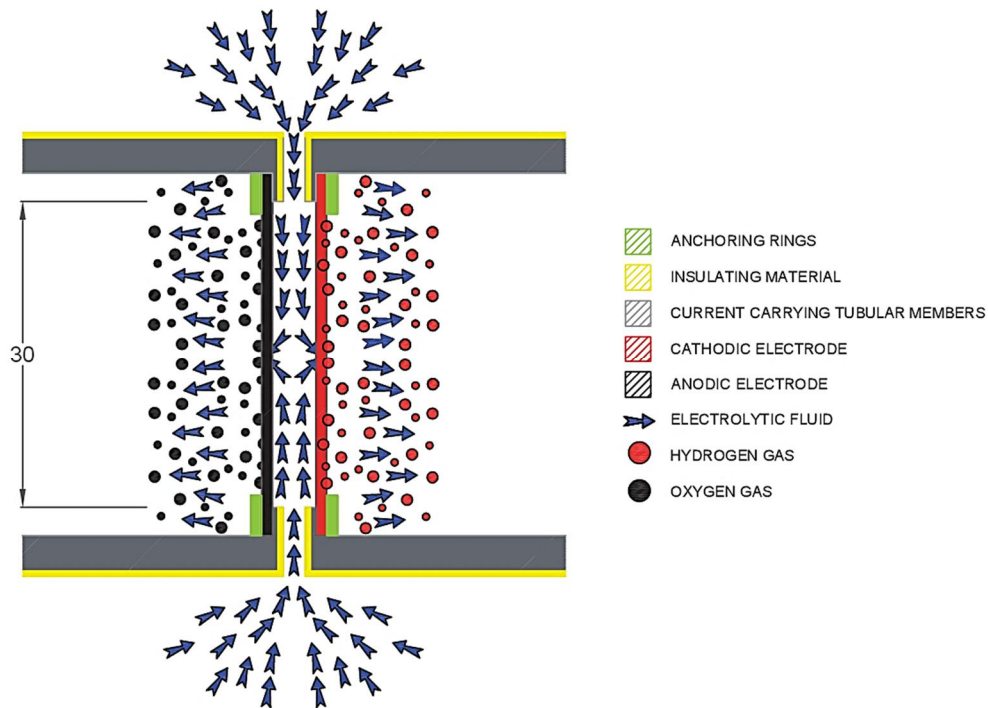


Figure 1-1: Operating principle of the Divergent Electrode-Flow-Through (DEFT™) alkaline water electrolysis redrawn from Gillespie *et al.* (2015) [6]

With reference to Figure 1-1, it is clear that the technology relies not only on the non-preferential split of fluid through each electrode, but additionally the fluid profile formed at the rear of the electrode, which must be as uniform as possible. Flow through a pipe generally assumes a 'bullet shaped' flow velocity profile, with the maximum flow velocity occurring in the centre of the pipe, and a no-slip flow velocity condition occurring near the pipe wall [7]. The electrolytic flow through a mesh leading into a tube type structure, however, does not follow this behaviour otherwise one would expect majority of the flow to occur at the centre of the electrode, and gas will remain non-separated nearer to the electrode supporting structure. This profile is therefore, highly dependent on the back-pressure that is created on the surface of the mesh in order to develop uniform flow velocity vectors across the surface of the electrode. There is, of course, a balance that occurs from the size of electrode, the porosity of the mesh, and the required electrolytic fluid flow that must be maintained to obtain near perfect separation of the gases, at a variation of current density

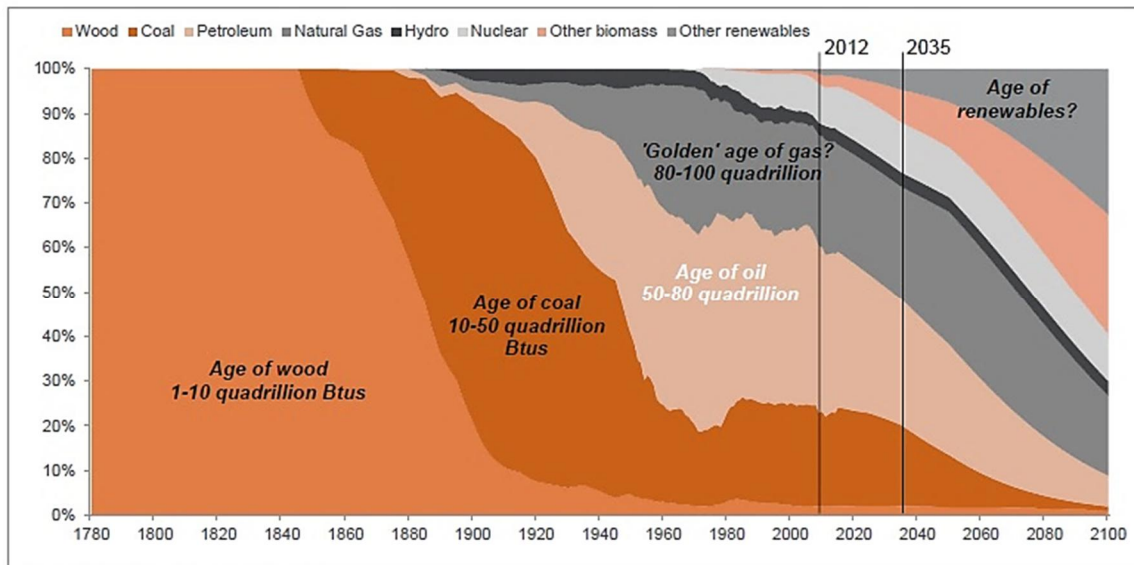
magnitudes [8]. These are the beneficial factors that are recognised in contrast to the difficulties in establishing a reliable and low resistance cell membrane/diaphragm.

The resistance of the electrolyte is lower compared to that of the membrane material [9]. Consequently, the stack would be capable of operating at higher efficiency levels, with the benefit of continuous enhanced bubble removal from the electrode surface, which positively benefits stack efficiency by reducing mass transfer resistances [10]. A type of flow dynamics should be present that minimises the pressure drop through system components, and maintains the required flow velocity for adequate separation of the products. This will ensure that parasitic loads, that would otherwise detrimentally affect overall plant efficiency, are minimised.

Initially DEFT™ performance parameters were investigated to identify the optimal range that maximises current density and minimises stack voltage on a DEFT™ concept optimisation test rig. This information was then used to investigate whether the technology can be scaled for commercial output volumes and further optimised on a larger scale. The primary objective for the three commercial DEFT™ pilot plants would be to investigate fundamental differences in design and methods for scaled hydrogen production, and will serve as a formula to produce an optimised commercial scale production plant. Additionally, factors such as the gas/liquid separation regime will be investigated to find the optimal mechanism that provides adequate separation at high liquid throughputs for a potential commercial scale system.

1.2 PROBLEM STATEMENT AND RESEARCH MOTIVATION

An article published by *Investing Daily* makes a prediction concerning the degree of use of current energy sources into the future [11]. The assumption is made that energy generation techniques are likely to follow a similar development trend to that of the modern smartphone, computer or the internet, where the device will be made available to the user in a decentralised format [11]. The following illustrates the prediction of how the degree of use of each energy source will change in the coming future based on past data and future trends:



Source: IEA, EIA, Citi Research

Figure 1-2: Energy density by unit mass and volumes for certain energy carriers in comparison to hydrogen [11]

From Figure 1-2, it is observed that the use of solid fuels such as coal and wood would effectively be negligible at the end range of the graph near to the year 2100. Likewise, the use of liquid fuels derived from oil would also be used in limited quantities near to the same timeline. As per the current date, the use of liquid fuels proves to be the primary energy source, however, by 2035 it is predicted that the majority of the global energy needs will be satisfied through the use of gas, alternate renewable, and sustainable energy sources such as biomass [11]. Reduction in the global availability of fossil fuels that drive current industries and economies, has raised concerns for the environment, while an increase in the global demand for energy has driven the need to provide cleaner, more abundant, energies [12]. Currently, hydrogen is revealing itself as a valuable energy storage medium, yet the majority of hydrogen is currently produced by methods such as steam reforming of natural gas due to the greater cost associated with producing hydrogen from water electrolysis methods [13].

Most industrial water electrolysis systems require a potential difference of at least 1.65 - 1.7 VDC to start operating, but to produce gas at appreciable quantities, a potential difference of 1.8 - 2.6 VDC is generally applied [3]. At these operating cell potentials, efficiencies of these systems normally range between 56 and 73 HHV%, however, when applying the efficiency of converting the gas back to electricity, this number is more realistically between 25 - 40 HHV% [13]. The low efficiency of water electrolysis technologies, coupled to the intensive capital and

operating costs, results in this method not having any contention with existing methods of producing hydrogen gas, and hence these systems need to be run in certain configurations in order for them to compete [1]. Currently large forecourt alkaline systems have the potential of producing hydrogen with the lowest end cost, where electricity has the greatest cost contribution to produce hydrogen [3]. Smaller decentralised methods do not have the required efficiency or low end capital cost to allow for the production of cost-effective hydrogen.

The motivation for this research project is therefore, to examine a simplistic approach to hydrogen production by means of a membraneless method with the end goal of reducing the cost to produce hydrogen for decentralised applications. Since electricity costs vary largely depending on the country of consideration, this new technology will be largely developed with the end goal of being used in conjunction with solar power [1]. Solar technology costs have reduced significantly due to the improvement in manufacturing techniques and materials, technological innovations, and the increase in mass scale production by 16 fold only in the period between 2005 -2012 [14]. Water electrolysis technology costs have decreased marginally, due to the lack of mass scale production adoption and production method optimisations, despite the potential for significant technology innovation [1]. Divergent Electrode-Flow-Through (DEFT™) alkaline electrolysis represents a notable deviation to the conventional water electrolysis technologies used in industry today. It has been designed to overcome a number of notable short-comings of alkaline water electrolyzers, such as the operating current density threshold, and the accumulation of bubbles on the electrode surface [15]. Previous bench scale tests have shown that the technology has the capability of operating at current densities more than 3 A.cm⁻², allowing it to operate at thresholds greater than the typical operating limits of PEME's [16]. This would imply that the size of the alkaline stack would be greatly reduced making the plant more compact and less capital intensive.

1.3 RESEARCH AIMS AND OBJECTIVES

The principle aims of this study are to quantify the performance and economics of the DEFT™ alkaline water electrolysis technology. This will be done initially by

- (i) proving the technology principle by means of a concept optimisation test rig, to provide a comparison of performance to existing technologies and highlight the key performance influencing parameters in retrospect to the DEFT™ technology,
- (ii) studying the implications and performance for operating the technology on a scalable design basis,
- (iii) studying the fundamental design criteria that will be listed and discussed as critical factors for which to design future DEFT™ production plants, and

- (iv) investigating the techno-economics as an important consideration into the market feasibility of the technology, which will be formulated upon conclusion of an optimal plant design and construction.

In order to achieve the above aims, the following objectives will need to be accomplished:

- i. Formulation of a basic design based on prior work done, and on current research for a DEFT™ test rig, with basic safety considerations and relevant process automations taken into account,
- ii. Evaluation of various typical performance influencing parameters, and observing their effect with respect to being in contradiction, replication or improvement on current operating performances of water electrolysis technologies, and in addition identifying the optimal operating regions for the DEFT™ technology,
- iii. Design and fabrication of various concepts of scaled production plants utilising DEFT™ technology, for examining the best route for scaled hydrogen production outputs,
- iv. Evaluation of scaled production plants performance based on generated polarisation data, gas purities, and energy balance efficiencies,
- v. Consideration of fundamental design criteria considering enhancements and limitations based on the optimal operating characteristics for scaled production plants for the formulation of the basic design formula for future DEFT™ plants, and
- vi. A techno-economic consideration on the optimal design of the scaled production plant, in order to deduce a market comparison and competitive feasibility analysis to existing technologies, to place the DEFT™ technology in the space of a renewable hydrogen generation market.

1.4 RESEARCH DESIGN AND METHODOLOGY

The research approach is based solely on the experimental analysis of designed and fabricated DEFT™ electrolysis pilot plants. The experimental method will serve to identify trends with respect to performance influencing parameters such as temperature, concentration, or flow rate, considered inter-parameter relationships, and the relevant parameter ranges to test, based on literary findings. There are a number of parameter outputs that will be used to quantify the magnitude of change of the input parameters, and these will be recorded for a minimum of three results to ensure repeatability and accuracy of an experimental condition.

The appropriate scientific equipment to simulate input parameters or record output parameters were either sourced or assembled in order to provide raw data. Each scientific instrument was either delivered with a certificate of calibration, or had been calibrated according to a standard

before extensive testing commenced. Data logging techniques will be employed to allow adequate time for experimental conditions to reach a steady state, and to record data for extended periods of time to reach an adequate conclusion on operating stabilities.

High level Computational Fluid Dynamics (CFD) modelling was performed on each of the scaled production electrolysis stacks in order to gain a theoretical flow model to better optimise the design of each DEFT™ reactor. Since the DEFT™ design principle relies on the flow of electrolytic fluid, CFD design provided an initial outlook into the probability of success for each reactor model.

1.5 THESIS OUTLINE

This thesis will take the form of a traditional thesis and will be presented in nine chapters including this introductory chapter. One chapter which will serve to introduce the start of the evaluation of the DEFT™ technology concept that will be based on a full-length article already published in the *Journal of Power Sources*, which can be read independently of this thesis [6]. The abstract of this article can be made reference to in Annexure D. An additional chapter has been accepted for publication and will be furthermore be published in the *Journal of Power Sources* [17]. A further chapter will be formulated into a full-length article, which will be submitted for publication at a later stage. Following this introductory chapter:

- **Chapter 2** – presents a literary review, which will serve to provide an introduction into the basic principles and thermodynamics of the water electrolysis technology. It will provide a comparison of the existing technologies currently in industry, and explain the potential advantages that membraneless electrolysis techniques would have over existing membrane techniques,
- **Chapter 3** – will serve as an introductory chapter based on a full-length article published in the *Journal of Power Sources* [6]. It has been performed on a rudimentary concept optimisation test rig for the purpose of exploring the optimal ranges of common performance influencing parameters in reference to alkaline water electrolysis,
- **Chapter 4** – will present the original attempt at enhancing the production rate utilising a multi-electrode design similar to the concept optimisation test rig, that will be discussed in Chapter 3. The purpose for this chapter is to explore the feasibility of producing hydrogen on a large scale using a rudimentary approach based on the DEFT™ operating principle,
- **Chapter 5** – based off a full-length article published in the *Journal of Power Sources* [17]. It will present results from a pilot plant originally designed to demonstrate the compact capability of the DEFT™ technology, and an alternate approach to gas/liquid separation, but was later reformulated to test the effectiveness of a number of catalyst combinations

and derived overall plant efficiencies. Findings of this chapter has been accepted for publication for a full-length article in the *Journal of Power Sources* [17],

- **Chapter 6** – will present results from a pilot plant that was assembled as a combination of the favorable attributes from the prior two test plants from Chapters 4 and 5. This plant will be fundamental in testing gas purity relationships, and deduction of optimal catalytic behaviors. Findings of this chapter will be incorporated into a journal paper for publishing,
- **Chapter 7** – will examine and discuss a number of design and operational criteria that are fundamental in the design of a DEFT™ alkaline water electrolysis system, all deduced from experimental work performed on the four pilot plants,
- **Chapter 8** – will consider the techno-economics of the plant fabricated in Chapter 6. This will outline the costing method of hydrogen produced from the DEFT™ technology for a number of scenarios, utilising similar assumptions made to costs calculated on industry examples, in order to obtain an accurate comparison to existing commercial products, and
- **Chapter 9** – will provide an overall conclusion of the thesis based on the study of DEFT™ alkaline water electrolysis.

2. LITERATURE REVIEW

2.1 HYDROGEN AS A POTENTIAL ENERGY CARRIER

Hydrogen in its elemental gaseous form exists as the lightest gas on the periodic table of elements, and is considered a primary energy source due to its ability to be directly converted into energy [12]. It is one of the most common elements, however, exists mainly within molecules found in nature [18]. It is a unique combustible gas in the fact that when hydrogen reacts with oxygen, the only product that is formed is water with the reaction giving off heat in addition, making it a clean and attractive process [19]. Hydrogen can be produced from fossil fuels or by renewable methods as detailed in the following processes [18]:

- Catalytic steam reforming of coal, oil or natural gas,
- Steam reforming of methanol,
- Coal or biomass gasification,
- Partial oxidation of carbonaceous fuels, and
- Alternative methods (water electrolysis, photo-electrochemical conversion, Kvaerner thermo-cracking).

Most methods involving hydrogen generation from fossil fuels, or carbonaceous sources, resolves in the generation of greenhouse gases such as carbon monoxide and carbon dioxide [18]. About 96% of hydrogen produced globally, amounting to approximately 65 million tonnes, is derived from non-renewable methods [1]. The balance is derived by cleaner methods such as large alkaline water electrolyzers.

Unless more efficient means are employed that would allow for an 80% or greater reduction in emissions, any reduction below this will not be robust enough to cope with an ever expanding global population, or the increasing intensity with which these technologies are utilised [20]. While the use of fossil-fuel derived sources of hydrogen allows for the integration of hydrogen to energy conversion technologies, the 50-year horizon associated with the limited fossil fuel global reserves, will not allow for these practices to be a sustainable solution in the long term [20]. Therefore, the conversion to sustainable hydrogen technologies is inevitable if global energy demands are to be met into the future.

By unit mass, hydrogen carries the greatest amount of energy compared to any other fuel source available [18]. The difficulty is in the storage of hydrogen due to its low gaseous density. High

pressures and low temperatures are required in order to ascertain a volumetric energy density competitive to that of existing fuel sources. The following data compares the relative mass and volumetric energy densities of hydrogen at different states to that of alternative energy carriers [18]:

Table 2-1: Energy density by unit mass and volumes for certain energy carriers in comparison to hydrogen at various temperature and pressure conditions [18]

Energy Carrier	Molecular State	Energy Density by Mass (kWh / kg)	Energy Density by Volume (kWh / Litre)
Hydrogen	Gas @ 200 Bar	33.3	0.53
	Gas @ 248 Bar	33.3	0.64
	Gas @ 300 Bar	33.3	0.75
	Liquid @ -253°C	33.3	2.36
	Metal Hydride Storage	0.58	3.18
Natural Gas	Gas @ 200 Bar	13.9	2.58
	Gas @ 248 Bar	13.9	3.01
	Gas @ 300 Bar	13.9	3.38
	Liquid @ -162°C	13.9	5.8
Liquid Petroleum Gas	Liquid	12.9	7.5
Methanol	Liquid	5.6	4.42
Petroleum	Liquid	12.7	8.76
Diesel	Liquid	11.6	9.7

The easiest and most cost-effective means of storing hydrogen is by compression, however, inspection of Table 2-1. reveals that the energy density of hydrogen gas on a volumetric basis is not comparable to any other energy carrier, and therefore would require more volume for chemical storage to obtain an equivalent stored energy quantity. Using the stored chemical energy, for example the conversion of hydrogen's chemical energy to electrical energy, using a fuel cell in contrast to an internal combustion engine is found to be twice as efficient. Therefore, more of the fuel is used for the intended purpose of creating electrical energy or kinetic energy [19].

Storing hydrogen in its liquid state would imply the requirement of significant effort, and therefore high energy losses to cool and maintain hydrogen at the required -253°C [18]. Storing hydrogen by absorbing it into solid molecular structures exhibits the advantage of high volumetric energy

storage densities and low storage pressures, however, additional cooling and heating is often required to absorb or release the stored hydrogen with the added impracticality of limited cyclability [18].

Production of hydrogen from renewable sources of energy by means of sustainable efforts is drawing increased attention, global leaders search for alternatives that prove significantly less environmentally pollutant [18]. The low efficiency of the solar energy to hydrogen gas water electrolysis process is the key contributor to the lack of adoption of these processes for the renewable production of hydrogen gas [19].

Electrical costs play a large role in determining the end cost of hydrogen produced, specifically for forecourt hydrogen generation systems where the capital cost is the smaller contributing factor. A decrease in the cost to make hydrogen from solar sources is being observed globally, which would make renewable hydrogen production by means of electrolysis economically viable. The idea will become increasingly attractive as hydrogen supplies from fossil fuel based processes diminish [19]. Solar sources are also becoming more efficient, with existing methods such as solar tracking, boosting solar efficiencies above the 40% mark. This would contribute to further positive cost reductions for hydrogen gas production by means of water electrolysis [19].

2.2 WATER ELECTROLYSIS THEORY OVERVIEW

Water electrolysis was first performed by the English scientists, William Nicholson (1753-1815) and Anthony Carlisle (1768-1842) in the year 1800 [16]. The product gases from water electrolysis, hydrogen and oxygen, were later separated by German scientist Johann Ritter, by arranging the electrodes in a manner that allowed the gases to be collected independently [16]. Additionally, Ritter also identified that the evolution rate of product gas increases, as proximity between electrodes was decreased. This provided the early beginnings of identifying and investigating several parameters that affect the performance of a water electrolyser.

Worldwide, the effects of greenhouse gas emissions are being considered, and clean renewable energy generation methods are being extensively researched. Renewable methods prove largely unreliable at providing a stable energy base load, and consequently methods of storing the excess energy in an environmentally friendly way are required. Hydrogen has emerged as a contender for storing renewable energy, with the fuel cell as a promising method of converting the gas to electricity. If one considers the amount of hydrogen society will need in order to drive major energy requirements, large hydrogen plants will be required to satisfy the demand. PEMECs show the best performance for hydrogen generation, however, there will be difficulty experienced with

satisfying the prevailing demand [21]. AWE's, on the other hand, are a simple and developed means of providing a proven solution for large scale hydrogen production [21].

A basic alkaline water electrolysis cell fundamentally consists of an anode, cathode, diaphragm/membrane, power supply, and alkaline electrolyte as illustrated in the following diagram [22]:

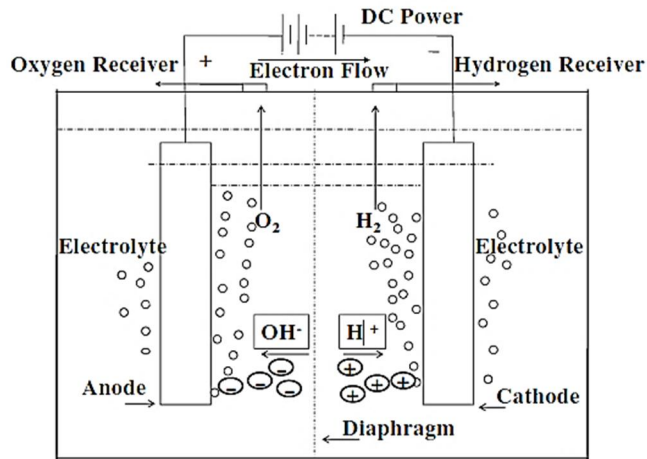
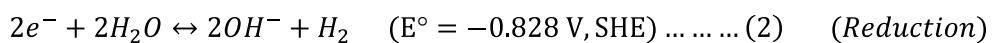
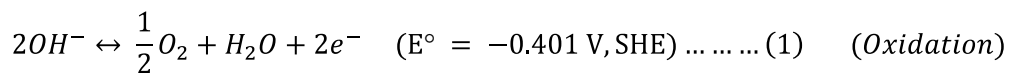


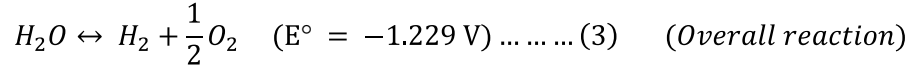
Figure 2-1: Schematic illustration of an alkaline water electrolysis cell [22]

Direct Current (DC) is applied across the anode and cathode providing a driving force for the reaction to occur. The cathodic electrode becomes negatively charged, reducing the protons to hydrogen gas. The anode is positively charged, attracting hydroxide ions within the electrolyte, and are responsible for conducting ions through the solution to the anode in order to keep the electrical charge balanced [22]. A diaphragm or membrane is used to create separation of the produced hydrogen and oxygen gases, but at the same time, permitting the movement of ions between the electrodes.

The process described above can be written in the form of two half reactions, where the net result of these would be the overall water electrolysis reaction [22]:



A combination of these reactions yields the desired overall reaction:



By observing the number of electrons transferred in the water electrolysis reaction above for the production of either 1 mole of diatomic hydrogen or oxygen gas, and by correlating this to Faradays constant which articulates that 96 485 Coulombs of charge is present in 1 mole of electrons, the outlet molar flows of product (or the consumption rate of reactant) can therefore be determined by the following expressions [23]:

$$\dot{n}_{H_2} = \frac{I}{2F} \dots \dots (4)$$

$$\dot{n}_{O_2} = \frac{I}{4F} \dots \dots (5)$$

$$\dot{n}_{H_2O_{consumed}} = \dot{n}_{H_2O_{in}} - \frac{I}{2F} \dots \dots (6)$$

Where, $\dot{n}$ (mol.s^{-1}) is the molar flow of product or reactant, F (C.mol^{-1}) is Faradays constant, and I (amperes) is DC current.

The conversion of molar flow rate into mass flow rate, and in turn into volumetric flow rate, can be achieved by re-arranging the molecular weight and density expressions:

$$n = \frac{m}{M} \dots \dots (7)$$

$$\rho = \frac{m}{V} \dots \dots (8)$$

Where, n is moles, m (g) is mass, M (g.mol^{-1}) is molecular mass, V (m^3) is volume, and ρ (kg.m^{-3}) is density.

2.3 BASIC THERMODYNAMIC CONSIDERATIONS

Zeng and Zhang (2010) describes the various resistances involved within a water electrolysis process by using the electrical circuit analogy [22]. Within every electrical circuit, a number of

resistances are present that inhibit the free movement of charge. In order to sustain or increase the movement of charge, a driving force is required in the form of a potential difference. The larger the combined resistance of a circuit, the greater the cell potential required in order to generate the same charge transfer rate. Therefore, the cell potential is a measure of the thermodynamic efficiency of a water electrolysis cell, and the charge transfer rate, or current, is a measure of the production rate. The typical resistances encountered within every electrolysis cell are as follows [22], and the sum of these resistances will equate to the total resistance for that particular electrolysis cell or water electrolyser:

Conductor/Circuit Resistance: The resistance generated by the external conductors responsible for supplying the electrolysis cell with charge.

Electrode/Catalytic Resistance: Resistance that originates dependent on the reaction kinetics of either the hydrogen or oxygen evolution reaction occurring on the surface of the electrode.

Bubble Resistance: Resistance generated due to the presence of bubbles adhered onto the electrode surface occupying parts of the electrode that would otherwise be active, and additionally, the presence of bubbles within solution between the electrodes or electrode gap possesses an additional resistance in inhibiting the flow of ions.

Electrolytic Resistance: Resistance characteristic of the electrolytic solution of choice dependent on the operating temperature and concentration of ions in solution.

Separator/Membrane Resistance: A physical conductive/non-conductive barrier that embodies a resistance to the free flow of ions between the cathode and anode electrodes.

The equilibrium cell potential can be calculated by the standard electrode potentials shown in Equations 1 and 2, and is easily determined by the following equation [22]:

$$E_{cell}^{\circ} = E_{Cathode}^{\circ} - E_{Anode}^{\circ} \dots \dots (9)$$

Where $E_{Cathode}^{\circ}$ is the standard reduction potential for the Hydrogen Evolution Reaction (HER), and E_{Anode}° is the standard reduction potential for the Oxygen Evolution Reaction (OER).

The Gibbs free energy of a REDOX reaction can be related to the equilibrium cell potential by the following equation [22]:

$$\Delta G = -nFE^0 \dots \dots (10)$$

Where ΔG is the standard Gibbs free energy, which equates to $237.2 \text{ kJ.mol}^{-1}$ for the water electrolysis reaction in the liquid state, n is the number of moles of electrons transferred in the reaction, and E^0 is the equilibrium potential for the water electrolysis reaction which equates to 1.23 VDC.

The significance of the equilibrium cell potential is that it defines the minimum required electrical energy in order for the water electrolysis reaction to take place under standard conditions quantified by the Gibbs free energy [16]. If an electrolysis cell is set to the equilibrium potential, no reaction will occur as the reaction at standard conditions is non-spontaneous, and therefore not enough energy is provided for the reaction [22]. Operating above the equilibrium potential makes water electrolysis feasible, however, the reaction will require heat for it to proceed favourably, or the temperature of the cell will drop with time until the production rate becomes negligible, should a constant heat source or adiabatic conditions be absent. The enthalpy of the reaction therefore describes the total energy requirement from an electrical and heat aspect in order for the reaction to proceed spontaneously, as represented by the following equation:

$$\Delta H = \Delta G + T\Delta S \dots \dots (11)$$

Where ΔH is the total enthalpy of the water electrolysis reaction in the liquid state equating to $285.8 \text{ kJ.mol}^{-1}$, $T(K)$ is temperature, and ΔS equates to $163.1 \text{ J.mol}^{-1}.\text{K}^{-1}$ for the water electrolysis reaction in the liquid state, and is the change in entropy, which is representative of the heat quantity consumed by the reaction.

A cell potential condition exists that defines the minimum amount of energy necessary for the water electrolysis reaction to take place if there was no exchange of energy to or from the surroundings, or otherwise described as a spontaneous reaction that is neither exothermic nor endothermic. This voltage is referred to as the thermo-neutral voltage, and can be related to the enthalpy of the reaction by the following equation [16]:

$$\Delta H(T) = nFE_{TN}(T) \dots \dots \dots (12)$$

Where, ΔH is the Enthalpy energy in kJ.mol^{-1} for the water electrolysis reaction at temperature $T(\text{K})$, n is the number of moles of electrons transferred in the reaction, and E_{TN} (VDC) is the thermal neutral voltage for the water electrolysis reaction at temperature $T(\text{K})$.

Both the enthalpy and thermo-neutral cell potential are functions of temperature, however, for electrolysis reactions below 100°C the thermo-neutral cell potential approximates to be 1.48 VDC [16]. If a cell is operated above the equilibrium potential, but below the thermo-neutral voltage, it will require additional heat in order for the reaction to remain spontaneous and hence be endothermic. At a cell potential above the thermal-neutral voltage, the reaction will give off heat being exothermic in nature, resulting in the temperature of the cell to rise.

At the Thermo-neutral voltage, the rate of water electrolysis occurs at a noticeably slower rate. A voltage greater than this is required, in order to overcome cell resistances described above, and allow the water electrolysis reaction to occur at an enhanced rate as to maximise hydrogen production, and minimise capital costs at the expense of efficiency [16].

The efficiency of the stack can be calculated based on the total electrical energy input. From the Equilibrium and Thermo-neutral voltages, two efficiency terms can be derived, termed the Faradic and Thermal Efficiencies [22]:

$$\eta_{faradic}(25^\circ\text{C}) = \frac{E^0}{E_{cell}} \dots \dots \dots (13)$$

$$\eta_{thermal}(25^\circ\text{C}) = \frac{E_{TN}}{E_{cell}} \dots \dots \dots (14)$$

Where, $\eta_{faradic}$ and $\eta_{thermal}$ are the Faradic and Thermal efficiencies respectively, E^0 and E_{TN} are the Equilibrium and Thermo-neutral voltages respectively, and E_{Cell} is the cell operating potential.

The difference between Equation 13 and Equation 14, is that the Faradic efficiency can never be more than 1, as electrolysis is not electrochemically feasible below 1.23 VDC. However, the thermal efficiency can be greater than 1 in cases where the reaction will require a net heat input in order for the reaction to remain spontaneous [23].

From Equation 11, the total enthalpy of the reaction is composed of the entropy term and the Gibbs free energy term. The entropy term typically describes the energy contribution provided in

the form of heat, and the balance of energy will be provided by the Gibbs free energy term in the form of electricity [23]. The Faradic and Thermal efficiencies, therefore, largely only depend on the electrical inputs, and their output can be largely affected, depending on the operating temperature of the cell [10].

2.4 OVERPOTENTIAL REDUCING FACTORS

As indicated, a number of resistances or overpotentials are present that adds to the minimum amount of energy required to make the water electrolysis reaction spontaneous. In order to reduce these 'barriers' to electrolysis, a number of standard parameters can be optimised [22]:

2.4.1. Electrolytic Concentration

One of the key advantages of membraneless systems is that, with the elimination of a membrane between the electrodes, a key resistance is disposed of as the membrane/diaphragm material has an order of magnitude resistance larger than the standard electrolytic solution [24]. The behaviour with respect to changing concentrations of the electrolyte is expected to be identical to that of membrane electrolyzers in terms of the optimal conductivity and change in temperature relationships. The most common alkaline electrolytes in use are sodium hydroxide and potassium hydroxide, where the optimal conductivity of each can be expected to change with regard to temperature. Potassium hydroxide is more conductive than sodium hydroxide as a liquid electrolyte. Its conductive behaviour at lower temperatures resolve to be at lower value concentrations, and at higher temperatures, higher concentrations will maximise conductivities [25].

In industry, the common concentration of a potassium hydroxide electrolyte will range between 25-30 mass% for electrolyzers operating between 40-90°C [22]. A critical concentration exists when the additional increase in the electrolytic concentration will resolve in zero net gain in conductivity, and the opposite applies. The condition occurs when the concentration of ions in solution become saturated to a point where the ions can no longer distribute charge in the shortest pathway possible [25].

It is not only the concentration of the electrolytic solution that determines its conductivity, but also the presence of product bubbles between the electrodes themselves, and it is this condition that provides a limitation to the maximum achievable current densities of water electrolysis systems [16]. The current density of a system has a direct proportionality with the bubble evolution rate

and void fraction that exists between the electrodes, which suggests that an optimal condition will exist, which will maximise the efficiency of a stack [26].



Figure 2-2: Expected bubble evolution profile from solid plate electrodes at a temperature of 40°C, 40% KOH, and 1 A.cm⁻² [26]

Figure 2-2 illustrates the expected gas bubble collections at a reasonably high current density with electrodes that are approximately 20 mm apart. It can therefore be envisaged that with electrodes gaps of 2 mm or smaller, the concentration or void fraction of these bubbles will be significantly more prominent, resulting in the increase in electrolytic resistance.

2.4.2. Electrolytic Temperature

Catalysts deposited on the surface of a substrate material have the potential of reducing the operating cell potential of an electrolytic cell. Equation 11 shows that the total enthalpy of the water electrolysis reaction is a combination of the Gibbs free energy and entropy. Heat contributes to the entropy term, which in turn contributes a larger portion to the required enthalpy of reaction [27]. For this reason, a number of high temperature electrolyzers such as SOE's (Solid Oxide Electrolyzers) can operate at extremely low voltages, and potentially operate at an efficiency greater than 100% on the basis of calculating it against the higher heating value [28]. There is a limit to the degree of temperature that can be applied to a water electrolysis plant due to material stability considerations, thus in all instances, strict temperature control is required for the stack, increasing the complexity of these systems [22]. All electrolyzers operate more efficiently at higher

temperatures as an improvement in the surface reaction kinetics and an increase in the electrolytic conductivity is observed [10]. Conducting electrolysis at higher temperatures is seen to reduce the equilibrium potential of the water electrolysis reaction, however, the drawback is that bubbles evolved into solution is seen to be generated with a smaller diameter, and can increase the void fraction of gas between the electrodes therefore hindering efficiency [26].

For most membrane systems, difficulty is experienced in operating at elevated temperatures, especially for modern AWE's and PEME's. The solid polymer electrolyte of PEM systems is particularly sensitive to elevated temperatures and enhanced proton conductors are required for these systems if they are to operate at temperatures in excess of 90°C [16]. An increase in both the operating temperature and operating current density would lead to a reduction in operating and capital costs respectively.

The DEFT™ technology is unique in that it contains no sensitive materials that are crucial to its operation, other than the electrode materials, which are found in general to be particularly temperature sensitive. A unique opportunity is available where this technology can still be tested at medium temperature over and above the current operating norm limit, for conventional alkaline water electrolysis systems, of 80°C [29]. Above 80°C, conventional alkaline membrane materials, such as asbestos, begin to experience stability issues, however, materials such as this have been phased out due to toxicity issues. Thermo-plastic materials such as Polytetrafluoroethylene (PTFE) and Polypropylene (PP) show good stability in a potassium hydroxide solution above normal alkaline operating conditions, however, for an ion conducting material to be effective, it must remain wetted. The hydrophobic nature of these materials create unnecessary resistances for alkaline systems [29]. Although the price of modern day perfluorinated sulfonated membranes have decreased, they remain cost intensive due to the scarcity of materials used for construction and their limited longevity within high temperature environments [30].

2.4.3. Electrode Gap

By reducing the electrode gap between the anodic and cathodic electrodes, it reduces the path length that ions need to travel in order to transfer charge. The optimum condition of the electrode gap can vary according to the operating parameters and the specific cell configuration [31]. For low current densities, ranging between 0.1 and 0.5 A.cm⁻², the cell potential is typically found to decrease as the electrode gap becomes smaller [31]. However, at slightly elevated current densities, greater than 0.6 A.cm⁻², with the smaller electrode gap range (1-2 mm), the cell potential is found to increase slightly. This slight increase in overpotential can be attributed to a condition referred to as void fracture, being a condition defined as the occupancy of the space between the

electrodes by gas, which increases the resistance for charge transfer between the electrodes. An additional knock-on effect of this is, the coverage of valuable effective reactive electrode surface area [31].

An example taken from Nagai *et al.* (2003) indicates the expected trend as a function of electrode gap:

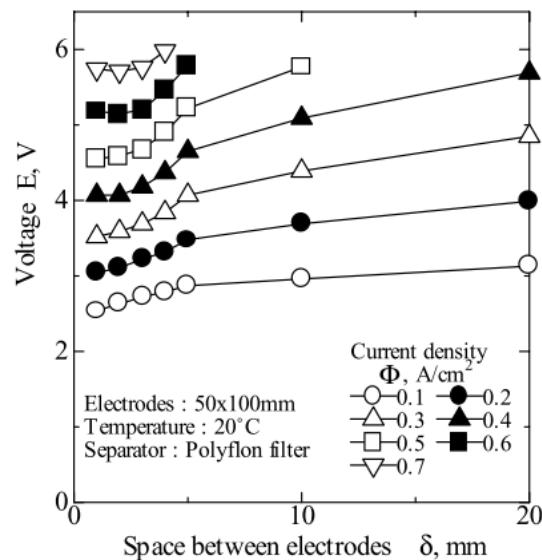


Figure 2-3: Electrode gap versus cell potential as a function of current density taken from Nagai *et al.* (2003) [31]

It was also found by Nagai *et al.* (2003) that, with the addition of a separator between the electrodes, efficiency worsened at smaller electrode gaps due to the separator obstructing the release and flow of gas bubbles that formed on the surface which results in void fracture [31].

The introduction of the zero-gap system for alkaline water electrolyzers has had a number of positive enhancements. In these systems, membrane surfaces make contact with gas diffusion electrodes, with the membrane being only a few microns thick, this substantially reduces the resistance between the electrodes, eliminating the formation of gas in this interstitial space. These electrolyzers are capable of overcoming any deficiencies with regard to the current density thresholds (in the region of 1 A.cm⁻²) that most modern alkaline electrolysis are limited by [15]. However, gas bubbles are still able to reside within the interspatial voids of the gas diffusion electrodes in the absence of a driving force to actively purge the forming gas. The DEFT™ solution utilises a unique approach to solving issues related to void fracture, as the continuous flow of electrolytic solution through the porous mesh electrodes reduces the presence of gas bubbles between the electrodes, and reduced the residence time that bubbles spend on the electrode surface before being released [6].

2.4.4. Electrolytic Flow, Bubble Resistance and Gas Purity

Solution flow, through or over the electrodes, can achieve additional gains in efficiency. As previously mentioned, product bubbles that form on the surface of electrodes tend to collect and propagate within the area between the electrodes, which creates unnecessary resistance. Various authors have commented on methods employing ultrasonic vibrations or the use of super gravitational fields, which would reduce the residence time of that bubbles spend on the surface of the electrode. These methods additionally increase their rise velocity so that the bubbles leave the area between the electrodes as quickly as possible, resulting in savings in running costs between 10% and 25% [32,33]. Yet another simple method employed by the DEFT™ technology, utilises the flow of electrolyte through or over the electrode surface, in order to reduce bubble residence times and reduce the incidence of occurrence of bubbles between or on the electrodes. With an increase in solution velocities, polarisation performance will exhibit higher current densities for the same applied cell potentials, and in the case of the DEFT™ technology, greater purities of product gases can be expected with larger flow-through velocities [6].

A build-up of gas can be expected on the surface of the electrode generating a gaseous meniscus, which would become unstable when insufficient solution velocity prevails, resulting in void fracture and impacting the product gas separation mechanism. It is vital to maintain a balance between current density and flow velocity as a function of the solution properties, in order to ensure adequate gas product qualities [6]. The following diagram represents this concept:

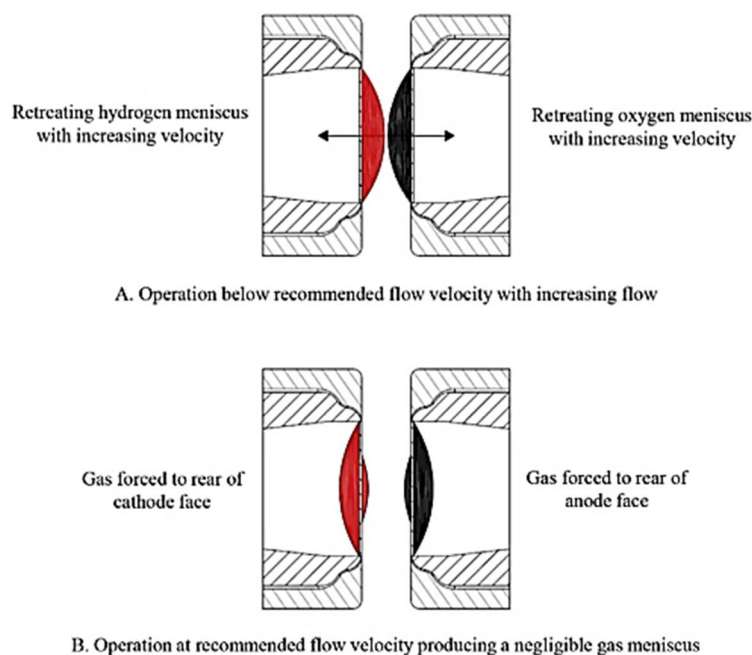


Figure 2-4: Influence of electrolytic flow velocity on the formation properties of the gaseous product meniscus [6]

The gas purity generated from the conventional water electrolyser is largely dependent on a number of factors. The most prominent of these factors is that of the gas impermeable, yet ion permeable, membrane. Previously, the majority of large alkaline systems made use of toxic asbestos as the 'ideal' membrane, due to its high degree of wettability. But, gradually research has focused to developing polymer based membranes as a less hazardous alternative [4]. It has been found that membranes that are proton conducting, in the case of PEM electrolysers, have a lower resistance compared to membranes that conduct hydroxide ions utilised in AWE's [15].

Currently, efforts have been focused on improving the properties of a hydroxide conducting membrane. For example, using polysulphone binders for higher temperatures of operation, and Wollastonite, Forsterite, and Barite based membranes for improved conductivity to overcome the limitations of the modern commercially accepted membrane, Zirfon, and that of the outdated asbestos membranes [34]. These materials still remain cost intensive and scarce, despite their improved resistance to the alkaline environment with their generated gas purities around ~99.83 vol% for hydrogen [34]. The DEFT™ technology has the key advantage of not having to consider the drawbacks and resistance limitations related to membranes as the stack assembly does not contain any membrane. The flow of electrolytic solution can be thought of as a reliable method of maintaining the gas quality and, being inherently a mechanical process, should not degrade over time in comparison to that of a membrane. Similar gas qualities, as that generated by membranes, can be generated effortlessly using this concept [6].

2.4.5. Electrode Catalytic Materials

Typical materials used for alkaline water electrolysers, for the anodic and cathodic electrodes, can be summarised as follows [35]:

Anodic catalysts: Nickel, Cobalt, Manganese Oxides, and Perovskites

Cathodic catalysts: Nickel, Cobalt, and Iron based catalysts

It is common with AWE's to use non-noble materials, such as the materials listed above, as the base materials of a catalyst lend themselves to low corrosion, with years of stable operation in large scale operations. Additionally, the cost of PGM materials is not economically efficient when applied to large alkaline plants operating at low current densities [36]. PEME's are not as flexible in terms of base materials for catalysts as that of AWE's. Due to the high acidic nature of the polymer membrane, materials in contact with the membrane need to demonstrate high corrosion tolerance at a low pH, and consequently substantiates the primary reason why PGM materials

are applied as the basis materials in PEME's [37]. The following list are common base materials for catalysts applied in PEME's [35]:

Anodic catalysts: Mixed oxides of ruthenium, iridium, and platinum in some cases doped with tantalum, cobalt, niobium, palladium, and tin.

Cathodic catalysts: Platinum based catalysts along with sulphide, phosphide, carbide, and nitride compounds.

Importantly, when choosing or developing an electrocatalyst, the following fundamental requirements need to be fulfilled in order to obtain a reliable and efficient electrolysis system [35]:

- (i) high selectivity for the desired reaction, whether it be for the hydrogen evolution reaction (HER) or the oxygen evolution reaction (OER),
- (ii) excellent surface characteristics that allow for the rapid removal of gas bubbles from the surface, but concurrently provide for a high surface area to increase active sites for gas formation,
- (iii) excellent current conducting characteristics and pathways,
- (iv) chemical and electro-chemical stability as the catalyst of choice should not be deactivated to an extent where it is deemed to be no longer effective in a short span of time, and
- (v) adequate mechanical characteristics when under the influence of handling, flow or temperature.

Since the DEFTTM technology is based on the alkaline reaction path, the focus will be placed on discussing the relevance of catalysts in an alkaline environment. It is typically accepted that noble metal oxides (IrO_2 , RuO_2 , PtO_2) are the most active when it comes to the OER in PEME's, however, in an alkaline solution, low cost transition metal oxides are used due to their high abundance and stability [38,39]. Nickel based materials play a key role, not only as common electrocatalysts for the OER, but in addition for the HER as well, due to its high stability and chemical resistance in an alkaline environment [36].

Normally nickel electrodes in the form of either a mesh or a high surface area coating are employed in industry to reduce the overpotential associated with the anodic and cathodic reactions. Raney nickel (composition of nickel and aluminium/zinc) and skeletal nickel-based catalysts have large surface areas with the potential of doping materials that exhibit high intrinsic activities such as platinum, phosphorus, and cobalt [36]. Generally, oxides of metals, such as iron, nickel, and cobalt are reported as effective catalysts having a selective affinity for the OER in an alkaline environment, however, it is generally found that the oxidised nickel is a superior catalyst when considering options for the OER reaction [40]. By combining nickel with a second

element, such as iron, additional improvements on the kinetics of the OER reaction are observed [35]. The OER reaction is known to be the limiting step in the water electrolysis reaction, and attention has been given to this reaction to improve the kinetics of this rate limiting step [40]. The cathodic reaction can also be catalysed by a number of materials all exhibiting their own unique affinity for the HER. Platinum is regarded as the best elemental catalyst for the HER, especially in the case of PEME's [30]. Platinum can positively assist the alkaline electrolysis reaction, however, limited additional performance gains are found if the rate limiting step is still governed by the OER [6]. Alternate pure metal catalysts and catalyst combinations have been found to work effectively in an alkaline environment, since PGM catalysts are considerably more sensitive to poisoning [37].

Noble metals and oxides are often not ideal for use in electrolyzers, and fuel cells, due to their high cost, low abundance and low stability in some cases. Therefore, non-noble transition metals and oxides are used predominantly as catalysts for the OER in AWE [35], with nickel oxide (NiO) being the most commonly used transition metal oxide. NiO demonstrates superior activity, and high resistance to corrosion, when placed in an aggressive environment [41]. A nickel hydroxide layer or film ($\text{Ni}(\text{OH})_2$) grows on the main substrate when exposed to an alkaline environment, and with increased exposure, would grow in thickness increasing the metals activity toward the OER [35]. Nickel demonstrates an improved stability reference to other transition metals such as iron and cobalt. However, the main concern with using this metal on its own is that it demonstrates insignificant activity levels at the more efficient lower current densities, thus in many instances, various alloys involving nickel or oxides of nickel are prepared to enhance the kinetics for both the HER and OER [35].

Alternatively, improving the activity of a pure nickel surface can be achieved by changing the surface morphology of the catalyst to employ a larger real active area and create a greater concentration of nucleation sites for the gas to form on. The following SEM photograph, taken from Manabe *et al.* (2013), portrays the surface morphology of Raney nickel, demonstrating the irregular highly active surface area:

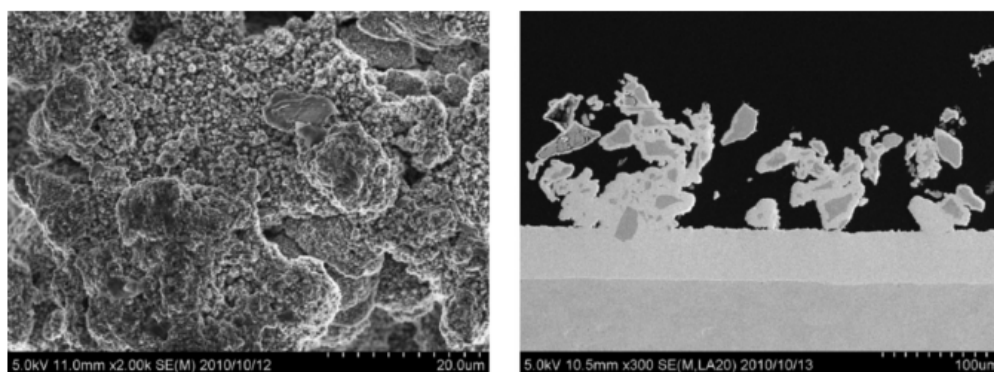


Figure 2-5: Surface morphology of Raney nickel electrodes [21]

Raney nickel is prepared by creating an alloy of 50% nickel and 50% aluminium or zinc. The aluminium or zinc represents the leachable components, that when leached, reveals high surface area morphology as shown in Figure 2-5 [5]. This material does, however, lose its activity with time due to the structure deteriorating under enhanced current densities [41]. The activity of this material is determined similarly to that of alternate porous materials. The smaller the pores within the structure and the more irregular they are, the more active the resulting material would be [41].

2.4.6. Basis of Current Density

Current density is dependent on a number of factors extending from the chosen structure of the electrodes to the nature of the electrocatalyst surface geometry. The DEFT™ electrode geometry can be considered as a three-dimensional structure, that is similar to gas diffusion electrodes employed in zero gap alkaline systems, or in PEM electrolyzers [6].

It is widely accepted that the term 'current density' is relative, and can be applied to a number of calculated area scenarios. The cross sectional current density can be regarded as the current applied to the total 'wetable' area of the electrode or, in other terms, the geometric area. Conventionally the actual current density would rather rely on the total area exposed under contribution to the electrolysis reaction. Current density is additionally dependant on the number of active sites present on the electrode surface involved in the reaction, which can be order of magnitude larger than the cross-sectional area [42].

The chosen standard for this research project will be adopted on the basis that the electrodes are gas diffusion electrodes, and current density is determined based on the apparent cross sectional area, as geometric current density for these electrodes would generally be low. However, when considering the total volume of the electrodes themselves, and the total volume that they occupy within reactor (which is small), the calculated current density would resolve to be greater [6,43].

By basing the calculation of current density on the grounds of cross sectional area would represent a realistic approach for the DEFT™ technology, as the technologies overall efficiency is dependent on the optimisation of the flow area to the total current capability of the particular experimental set-up. By dividing the total current of the electrode by the flow area, instead of the total wettable area or active area, provides a scenario of optimisation. The goal for DEFT™ therefore, is to maximise the current density for a certain flow area, as this will ultimately reduce the required parasitic load needed for circulating the fluid. It would be impractical to determine current density on the basis of geometric area or active area, as the result would not identify the optimal conditions for overall efficiency optimisation.

2.5 EXISTING WATER ELECTROLYSIS TECHNOLOGIES

There are two main parameters that largely affect the performance and pathway of the water electrolysis reaction. The first is temperature, which will have a large influence on determining the equilibrium and thermo-neutral cell potentials [16]. The E° and E_{TN} parameters mentioned previously have been stated with the assumption that the reaction is occurring at room temperature or 25°C. Large changes in temperature, however, will have the effect of significantly altering the reaction equilibrium and the thermo-neutral voltage. Figure 2-6 illustrates the effect of altering the temperature [16]:

The enthalpy change of the water electrolysis reaction remains largely unchanged, yet a reduction in the equilibrium potential is observed with increasing temperature, as a larger quantity of the required energy is provided through the means of heat as per Equation 11 [16]. The thermo-neutral cell potential only increases slightly over the temperature range, as the inclusion of the overpotential of the electrodes themselves have a small dependence on temperature, which increases the material resistances [22].

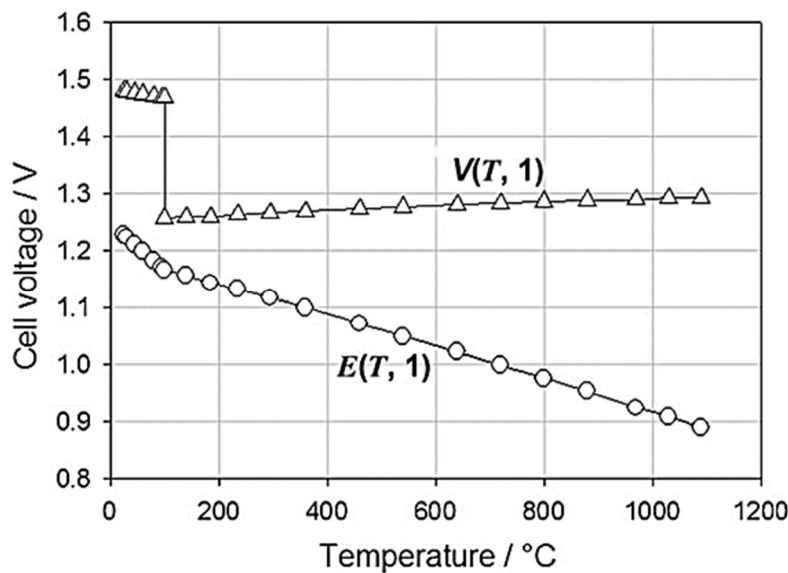


Figure 2-6: Equilibrium and thermo-neutral cell potentials as a function of cell operating temperature [16]

The second major parameter of water electrolysis is the pH of the electrolyte. The half-reactions occurring at the anode and cathode are different depending on whether the electrolyte is alkaline

or acidic. If the pH indicates that the electrolyte is acidic, the protons or hydrogen ions (H^+) will be responsible for the transfer of charge between the electrodes. If the pH is alkaline, the hydroxyl ion (OH^-) will be responsible for charge transfer [16]. A concentrated electrolyte is required in order to avoid additional overpotentials. Many metals used in the alkaline environment are passivated and severe corrosion is prevented. However, liquid acidic systems are rarely found due to the presence of aggressive conditions. As a result, the acidic medium is normally confined to a membrane electrolyte [16].

The common attribute that many modern-day electrolyzers share, is the presence of a membrane or diaphragm. The key responsibilities of the membrane or diaphragm is to separate the anodic and cathodic compartments to eliminate any undesired side reactions, and prevent the mixing of product species that could lead to contamination of the cell or electrodes [30]. The improvement of this 'barrier' represents a subject of constant research, as it contributes a significant overpotential due to the resistance that it creates to the flow of charge. As discussed previously, the indirect overpotential contribution of the membrane is a result of void fracture or bubble saturation that takes place when the current density threshold is superseded, for the particular cell design, resulting in a loss of performance efficiency due to the interruption of the flow of ions [30]. For this reason, current densities in existing technologies must be limited. An increase in capital costs is therefore observed as larger cells are now required to produce a set quantity of hydrogen gas in order to avoid this phenomenon.

The two most common types of electrolyzers mentioned are Alkaline Water Electrolyzers (AWE's) and Proton Exchange Membrane Electrolyzers (PEME's). AWE's make use of an alkaline liquid electrolyte, whereas PEME's make use of an acidic solid polymer membrane electrolyte [44]. The water electrolysis reaction from these two systems produce pure oxygen and hydrogen with no presence of carbon containing molecules, which is ideal for use in systems where gas product purity is of utmost importance [39]. The third method of water electrolysis, which has yet to find its grounding in the commercial market sector, is that of high temperature solid oxide electrolyzers (SOE's). This method of electrolysis is generally conducted with steam or vapour feed at a temperature of between $550^{\circ}C$ - $800^{\circ}C$ [22]. At these temperatures, the water electrolysis reaction is favoured thermodynamically, and it is the transfer of the oxide ion (O^{2-}) to the anode that represents the transfer of charge [22]. The following is a brief explanation and comparison of each of the technologies.

2.5.1. Alkaline Water Electrolysers

The following diagram illustrates the basic principle behind alkaline water electrolysis:

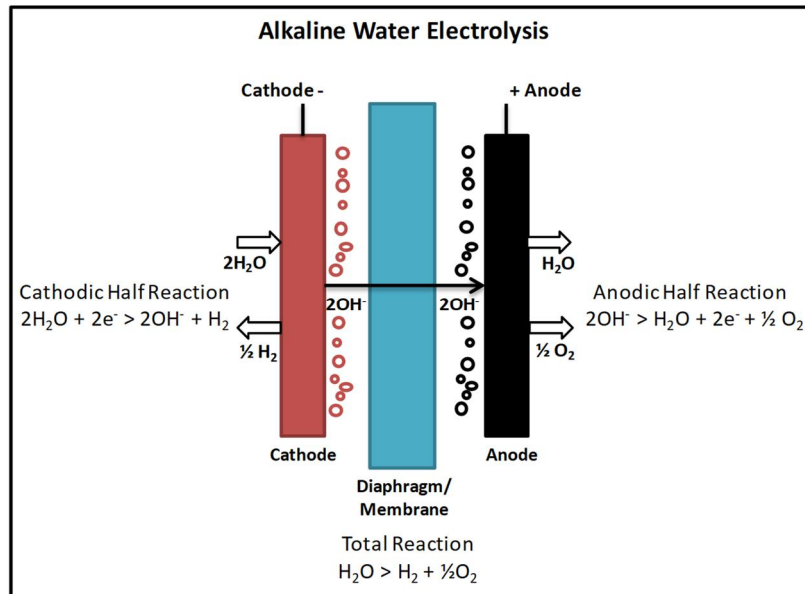


Figure 2-7: Schematic diagram of an alkaline water electrolysis cell [16]

The liquid electrolyte illustrated above is commonly an aqueous solution of potassium hydroxide (KOH) with a concentration range of 25-30 % [10]. Sodium hydroxide solutions (NaOH) are used to a lesser extent with a concentration range of 20-30 % [45]. Two conductive electrodes are immersed in the aqueous solution with the separating membrane or diaphragm dividing the anodic and cathodic compartments [16]. The only reactant being consumed in this reaction is water, therefore a constant feed of water must be provided to the electrochemical cell in order to maintain the desired concentration of electrolyte. The cell temperatures are normally maintained between 60-120°C. Consequently, the process is referred to as a low temperature process with dry gas purities generated in the order of ~99.9 vol% [16].

Alkaline systems have the advantage of a less aggressive environment, enabling the use of non-noble metal catalysts without the risk of severe corrosion [38]. Electrodes are typically based on stainless steel (cathode) or nickel (anode), which are activated by the appropriate non-noble catalysts comprised of nickel, cobalt or iron based spinels and perovskites [30]. A drawback of the alkaline technology is when current densities increase, a larger void fraction of gas forms between the electrodes, a resistive film will resultantly occupy the space between the electrodes ensuing in a drop in the cell efficiency with the build-up of resistance. Therefore, the current densities of large alkaline systems are usually limited to a maximum of 0.5 A.cm², which creates

difficulties for the technology in comparing favourably with regard to efficiency to the more advanced PEME systems [16].

Recent improvements to AWE's have yielded the zero-gap configuration whereby gas diffusion electrodes are placed back-to-back with the ion conducting membrane, which can be up to a few microns in thickness [15]. These systems have the advantage of allowing a large effective reaction surface area to improve the efficiency of the systems, and enable current densities as high as 1 A.cm^{-2} , along with the absence of void fracture between the electrodes as they are seamlessly in contact with the separating membrane [15]. Additional research is still being conducted on improving the conductivity and activity of the membrane and electrode materials. These systems still represent the larger portion of the water electrolysis market due to their flexibility and cost-effectiveness in materials of construction. However, due to their enhanced operating performance thresholds, PEME's are receiving increasing amounts of attention [16].

2.5.2. Proton Exchange Membrane Electrolysers

The following diagram illustrates the basic principle behind proton exchange membrane electrolysis:

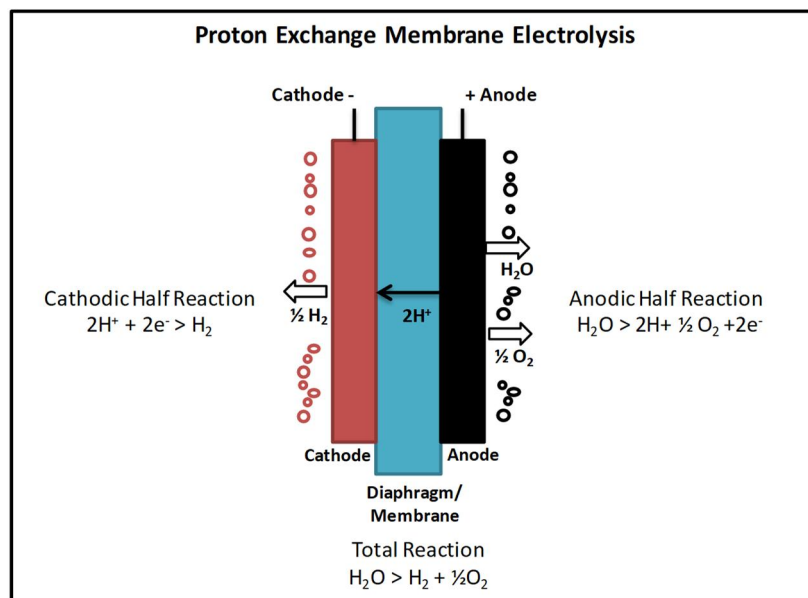


Figure 2-8: Schematic diagram of a proton exchange membrane electrolysis cell [16]

Illustrated above, two electrodes are pressed together, and are in contact with a proton conducting solid polymer membrane. The assembly for PEME's is referred to as the 'membrane electrode assembly' or MEA [16]. The MEA is immersed in the reactant that comprises of pure water whilst the mobile acidic species is confined to that of the membrane structure. These systems are ideal from a safety aspect, in contrast to alkaline systems, as there is no corrosive liquid medium present. To provide the membrane with significant conductivity, the acidity of the membrane must be high, however, the drawback is that any elements in contact or exposed to the membrane is presented with harsh aggressive conditions [37]. Consequently, the use of highly active PGM's is considered for PEME's to avoid extensive deterioration of the electrode.

These systems have yet to be extensively demonstrated on a mega-watt scale, but current research has shown that their ability to rapidly respond to inputted fluctuating power sources, may make them ideal for decentralised hydrogen generators using renewable sources of power [37]. In contrast to AWE's, PEME's have the capability of producing hydrogen gas at elevated pressures (up to 200 Bar on the hydrogen side only), and superior gas product purities (~99.99 vol%), which can be attributed to the effectiveness of the membrane to maintain almost complete compartment seclusion [46].

PEME's are largely considered an improvement over the older alkaline water electrolyser technology due to their ability to operate at elevated current densities ($> 2 \text{ A.cm}^{-2}$) [37]. With the PEME's specialised designs and materials, they remain largely capital intensive with uses primarily for niche applications [16]. As a result of the aggressive conditions, a complete overhaul of the MEA is often required, which incurs higher operational costs in comparison to alkaline systems [16]. They are known to be restricted in terms of their temperature operating limits of 60 - 90°C, due to the aggressive acidic environment, hence restricting their operating efficiency threshold [16].

Alkaline systems are known for their leniency toward feed water purity, but due to the sensitivity to poisoning of the membrane and electrode materials, the use of ultra-pure distilled water for PEME's systems is essential [28]. The majority of research concerning PEME's are concerned with the improvement of the 'robustness' of the membrane along with the reduction of PGM catalyst loading, so as to reduce capital costs associated with these systems [30].

2.5.3. Solid Oxide Water Electrolysers

The following diagram illustrates the basic principle behind solid oxide water electrolyzers:

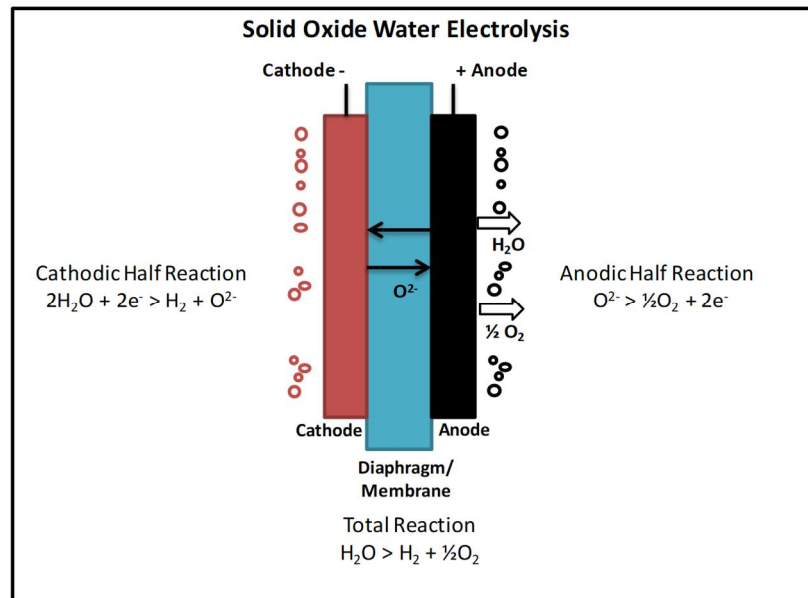


Figure 2-9: Schematic diagram of a solid oxide electrolysis cell [16]

Solid oxide water electrolyzers make use of an oxide conducting ceramic or non-porous metal oxide (ZrO₂) as a solid membrane and electrolyte. The process occurs at high temperatures, between 800°C and 1000°C, with the charge transfer occurring when the oxide ion moves through the crystalline solid by means of diffusion toward the anode [16]. The resistance of the solid ceramic, or metal oxide material, is higher than that of a hydroxide of proton conducting system, and therefore the separating barrier needs to be made as thin as possible [16]. These systems are capable of much higher electrical efficiencies compared to AWE's and PEME's with current densities nominally being within the region of 2 A.cm⁻². There are primarily two main drawbacks associated with this technology: (a) the high cost of the solid electrolyte, and (b) the large amount of thermal energy required to get the system up to, and maintained at operating temperature [28].

These systems exhibit encouraging longevity with high electrical efficiencies, in some cases greater than 100%, however, motivation for these systems are low due to the extensive capital costs involved, and lack of commercial applications [16]. Safety is also a key consideration when dealing with SOE's especially when the generation of hydrogen is handled at such high temperatures [45].

2.6 WATER ELECTROLYSIS TECHNOLOGY INDICATORS

A number of performance indicators are available for water electrolysis technologies. These indicators (listed below) are fundamental in determining a technology's position in the market relative to existing technologies, and are key in considering whether a type of technology can be successfully commercialised [1].

- (i) Efficiency and lifetime,
- (ii) Capital cost,
- (iii) Pressurisation,
- (iv) Equipment size,
- (v) Operating cost,
- (vi) Dynamic and flexible operation.

The efficiency of an electrolyser system can be difficult to define, so as to compare it against existing systems. In short, efficiency is generally defined as the energy input into the system per unit mass hydrogen produced [1]. Currently, the benchmark for 'state-of-the-art' systems are in the order of 50 kWh/kg H₂, however, this benchmark typically applies to a system operating at low current density, and for large forecourt systems [1]. A number of smaller commercial electrolysers can effectively compete with systems that are of higher capital cost, even when their efficiency range is within 75-90 kWh/ kg H₂, as they are specifically designed for low capital cost [1]. The following table expresses the range of electrical energy inputs for alkaline and PEM electrolysers:

Table 2-2: Electrical energy input per kg H₂ produced for alkaline and PEM systems [1]

Electricity input ⁽¹⁾			Today	2015	2020	2025	2030
kWh _{el} /kg _{H₂}	Alkaline	Central	54	53	52	51	50
		Range ⁽²⁾	50 - 78	50 - 73	49 - 67	48 - 65	48 - 63
	PEM	Central	57	52	48	48	47
		Range ⁽²⁾	50 - 83	47 - 73	44 - 61	44 - 57	44 - 53

⁽¹⁾ at system level, incl. power supply, system control, gas drying (purity at least 99.4%). Excl. external compression, external purification and hydrogen storage

⁽²⁾ some outliers excluded from range

Other means of expressing efficiency can be in the form of calculating the Higher Heating Value (HHV) efficiency. This has proven to be a common way of reporting stack and system efficiencies.

Efficiency here is the ratio of the total calorific energy contained within the hydrogen product, and the amount of work required to initially produce the specific quantity of hydrogen [23]:

$$\eta = \frac{m_{H_2,out} HHV}{W} \dots \dots (15)$$

Where, $m_{H_2,out}$ is the mass flow rate of hydrogen exiting the system boundary (kg/hr), HHV is the Higher Heating Value of hydrogen equating to 39.4 kWh/kg H_2 [1], and W is the work required by the system in kWh.

The higher heating value of hydrogen is used as it can be assumed that the hydrogen gas by-product originates from the liquid state of water [22]. It is found that in efficient processes, systems typically operate just above the thermo-neutral voltage.

Operating too far above the thermal-neutral voltage will place additional wear on electrolyser components such as the electrodes and catalyst coatings. Current electrolysers have demonstrated lifetimes of >60 000 hours [1]. At this point it is assumed that the commercial viability has been proven with regard to the longevity of components. Implications are, however, on the capital cost as enhanced materials have to be used in order to extend the life of plant (LOP).

2.7 EXISTING MEMBRANELESS TECHNOLOGIES

The DEFT™ technology described will strive to provide a solution to mitigate the current density threshold of current AWE technologies, by inhibiting the performance reducing effects of the product gas bubbles in the solution. Additionally, stability and performance issues with regard to separation membranes will no longer be of concern [22]. The majority of membraneless water electrolysis methods are in the study of microbial electrolysis cells, which seems to provide reduced resistance between the anodic and cathodic electrodes [9]. Other areas making use of membraneless methods appear in fuel cells, making use of liquid reactants on primarily small scale operations, due to their membrane counterparts suffering mainly from electrode and membrane stability issues [47].

Membraneless water electrolysers are considered to be the latest advancement in technology, and are being explored by a number of individuals and research institutions. A simple scalable solution for membraneless electrolysis that can be performed across the pH-scale is illustrated in Figure 2-10 [48]. This solution relies on the flow of electrolytic fluid through angular porous electrodes in order to achieve separation of the constituent gases to an extent that allows only

2.8 vol% of the hydrogen to cross over to the oxygen stream at a current density of $0.1 \text{ mA}\cdot\text{cm}^{-2}$ [48].

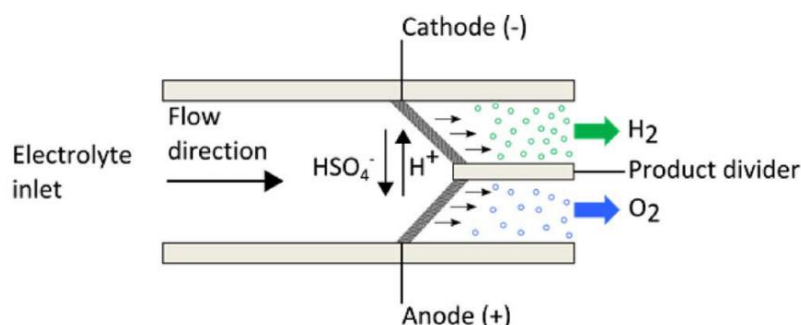


Figure 2-10: Membraneless electrolyser design principle based on angled flow-through mesh electrodes [48]

It is, however, observed in literature that electrodes that are not parallel to one another would have non-uniform current lines, and would represent a non-ideal electrode configuration. Localised current density configurations will form on the electrode surface resulting in certain parts of the electrode being under-utilised [49]. Less current lines will be found to intercept areas of the electrodes that are further from the oppositely charged electrode [27]. This design therefore may result in increased inefficient performance at greater current densities as areas closer to one another will become saturated with current.

Similar to the DEFT™ alkaline electrolysis concept is US patent 8940151 B1 by Hartvigsen *et al.* 2015. This design makes use of porous electrodes, however, it is not a true flow-through system as the DEFT™ concept. The flow, instead, takes a perpendicular path along solid electrodes to discharge bi-phase product streams at the top and bottom of the electrode assemblies [50]. Figure 2-11 illustrates the structure of this membraneless electrolyser.

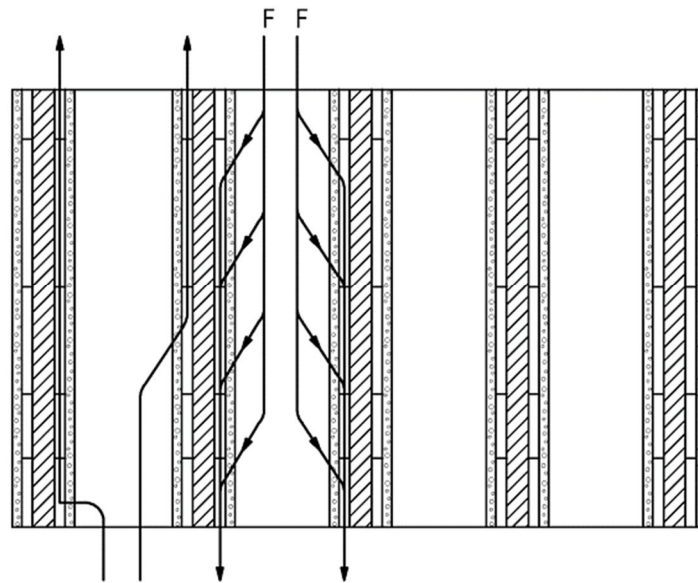


Figure 2-11: Membraneless electrolyser design principle based on electrolyte flow-through of porous electrodes against solid electrodes [50]

The operating principle of this concept is different in the manner that the bi-phase solution does not divert directly into a collection chamber, but instead transverses against a solid plate electrode situated behind the porous electrode structure of the same polarity. It is predicted, however, that this design does not solve the issue of a limited current density threshold associated with conventional AWE's. High solution flows are required in order to maintain separation of the product gas menisci that build up on the parallel electrode frontal surfaces. Solution flow paths in addition, should remain limited in length, in order avoid the occurrence of areas of no solution flow through the electrodes. Any inconsistencies in the flow gradient would result in product gasses collecting between the electrodes, with instances of excessive void fracture and cross gas contamination occurring [6].

A membraneless electrolyser making use of flow along electrodes has been developed by the Swiss Federal Institute of Technology. This technology utilises the natural laminar flow velocity profile developed between two parallel electrodes in order to force the product gas bubbles to

remain close to the surface of the respective electrode, also known as the Segre-Silberberg effect, as illustrated in Figure 2-12 [51].

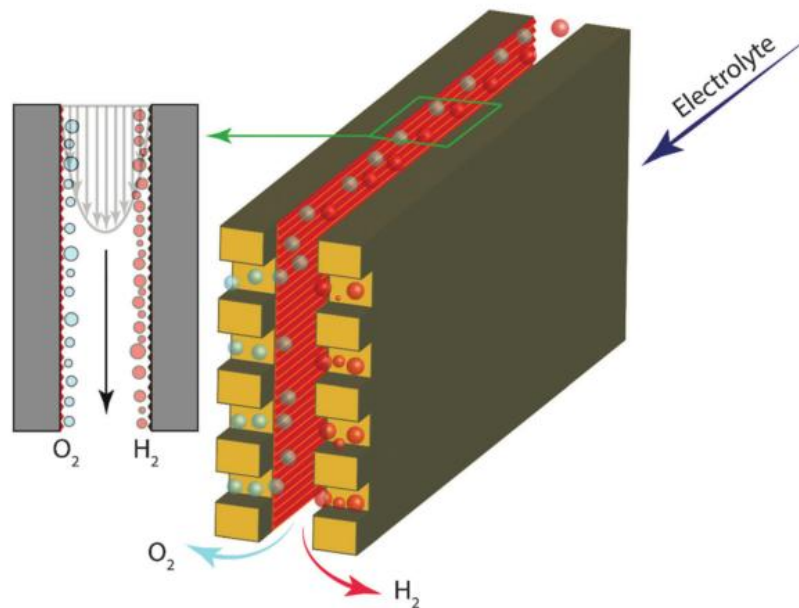


Figure 2-12: Membraneless electrolyser design principle based on laminar flow along parallel electrodes which causes the evolved gas bubbles to move along the surface of the electrodes [51]

This concept was tested on a small scale basis, and it is predicted that difficulties would be encountered during the scale up of this design, or if the design had to be used in conjunction with greater current densities. Enhanced current densities would enhance the negative effect of void fracture along with cross contamination of the product gases [10]. This would be a direct result from the breakdown of laminar flow between the electrodes. This design will therefore only be applicable for a cost-effective micro-electrolyser application.

The DEFT™ technology is not only an improvement over conventional alkaline water electrolysis systems, but also on alternative membraneless electrolysis applications.

2.8 ADVANTAGES OF DEFT™ OVER EXISTING ALKALINE WATER ELECTROLYSIS TECHNOLOGIES

The following schematic diagram indicates the operating principle behind the DEFT™ alkaline technology:

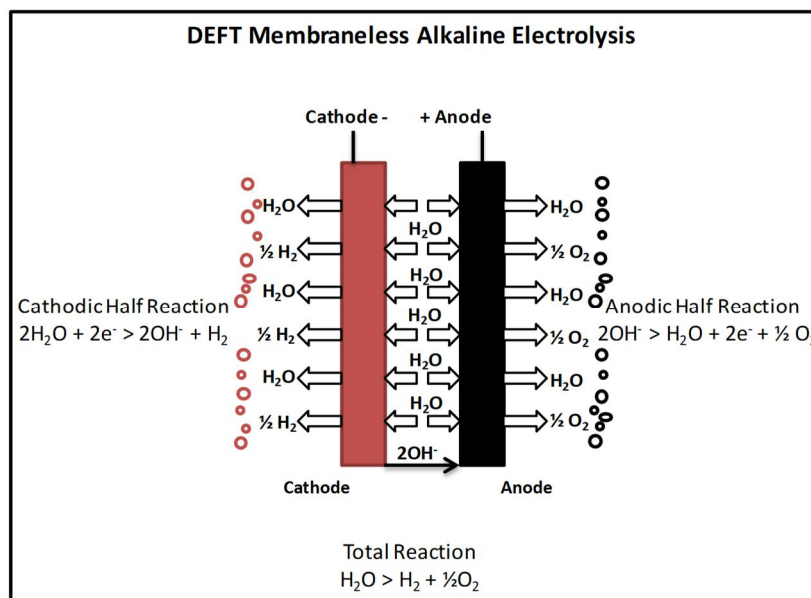


Figure 2-13: Schematic diagram of a DEFT™ Membraneless alkaline electrolysis cell

As observed, modern alkaline systems have a number of shortcomings that are causing the transition of newly developed systems towards PEME technology. It is the goal of the DEFT™ technology to overcome some of the shortcomings of existing alkaline water electrolyzers, with specific reference to the fact that current density thresholds exist due to the presence of concentrated product gasses between the electrodes [30]. Because the DEFT™ technology relies on the flow of an alkaline electrolyte through porous electrodes, gas bubbles are continuously removed from the space between the electrodes removing the additional resistances caused by their presence. Additionally, more of the electrode area is exposed for reaction due to the physical removal of formed bubbles [26]. Higher current densities can therefore be achieved similar and greater to that of PEME's.

It has been stated that the electrolytic resistance of an alkaline solution is of lower magnitude than that of a membrane separator, allowing for a decrease in resistance for the flow of charge between the electrodes of a DEFT™ system [9]. Therefore, the need for an ineffective, unstable hydroxide ion conduction polymeric membrane is not required, whilst benefiting from the use of non-noble metals as the electrode materials [30]. The temperature restrictions are once again not subject to the maximum temperature of a membrane material, but rather to the materials of construction of

the electrodes and balance of plant. Current density distributions have the benefit of being more homogeneous due to the absence of concentration gradients of bubbles within the solution, which enables the effective use of the available electrode area [30]. Most systems will take some time to achieve a steady state condition, however due to the nature of the DEFT™ technology, steady state is achieved relatively quickly [52].

2.8.1. Gas carry-over in electrolysis

One of the major issues with modern electrolysis methods is the movement of gas from the cathodic compartment to the anodic compartment or vice versa. The three main purposes of the separator are to provide ionic conduction from one electrode to another, along with preventing short circuits, together with providing separation of the product gases. The separator therefore needs to be stable within the highly alkaline environment. Additionally, conductivity needs to be sufficient by providing excellent 'wettability' characteristics generally achieved by a substantial presence of small pores present in the separator. The problem faced by many large alkaline electrolyzers is the crossover of dissolved gases within the electrolyte through this separator [53]. Haug *et al.* 2017, describes an experimental setup making use of a zero-gap experimental arrangement employing a Zirfon™ Perl UTP 500 separator operating at various experimental conditions. The crossover of the gas is subsequently measured as a function of current density with electrolytic flow present [53].

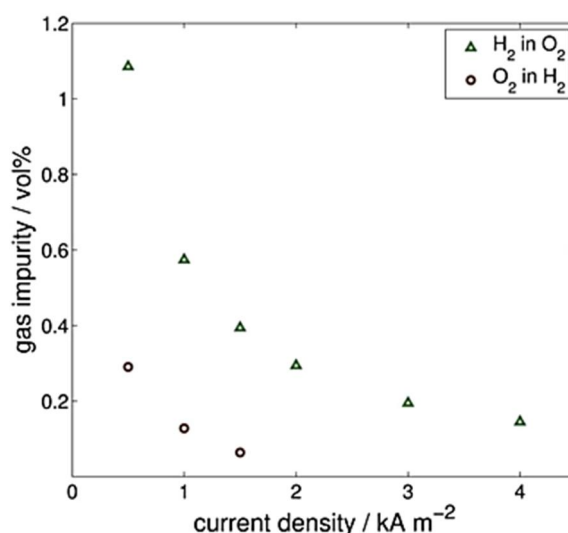


Figure 2-14: Gas crossover as a function of current density at 31.2 % KOH, 80°C, and 0.33 L/min [53]

From Figure 2-14, it can be seen that a greater percentage by volume, hydrogen gas is present in the oxygen stream, in converse to oxygen gas present in the hydrogen stream. For both streams, the extent of contamination is increased with the increasing current density. It is reported that with the presence of flow moving through the stack, the extent of gas crossover is lessened with an improvement in gas production rates [53].

With a membraneless system, gas crossover is more prominent as there is no physical barrier separating the anodic and cathodic compartments, however, a number of alterations in experimental parameters can be made to reduce the extent of this crossover. It was found by O'Neil et al. 2016 that around 2.6% of the hydrogen produced had crossed into the oxygen stream. This was easily mitigated by increasing the flow of solution, or enhancing the current density [48].

2.8.2. Concepts for scaling membraneless water electrolysis technologies

AWE systems are usually arranged in either a bi-polar or mono-polar/uni-polar configuration. The following diagrams illustrate the differences between the two configurations:

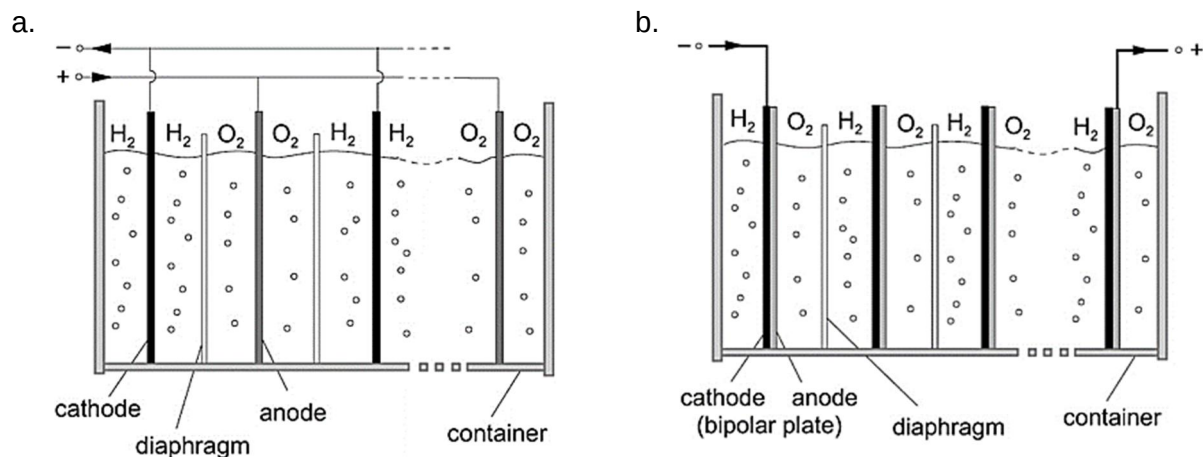


Figure 2-15: Principle of operation of (a.) a mono-polar system, and (b.) a bi-polar system [54]

The mono-polar cell makes use of individual parallel connections from a common polarity to each electrode, whereas the bi-polar design makes use of a series electrical connection whereby the charge is able to polarise the opposing faces of the electrodes [54]. Advantages of the bi-polar configuration is the shorter current lengths involved in the electrodes and conductors therefore reducing the internal resistance. These designs are plagued particularly by parasitic currents that would otherwise by-pass their intended destination. Mono-polar designs make for a simple and reliable configuration along with being less cost intensive to construct, yet despite this, a majority

of large alkaline water electrolyzers are bi-polar in nature [54]. Due to the operating principle employed by the membraneless DEFT™ principle, a mono-polar principle of operation must be employed as fluid flows through the porous electrodes, and each electrode pair is effectively isolated from the next, to prevent parasitic currents or gas mixing. This does have the disadvantage of requiring a parallel connection, which entails a low operating voltage. Therefore, step-down transformers and larger diameter cables need to be employed in order to increase the rate of production which results in increased costs.

A number of methods can be employed to scale the hydrogen production output from water electrolysis technologies. Electrolyzers have a limitation to electrode size that they can employ, and if they are reliant on flow, such as membraneless technologies, they can be stacked in series or parallel to achieve the desired production rate of hydrogen [48]. For the case of many alternate membraneless electrolyzers, tests have only been performed on the micro scale, and thus it is difficult to envisage how the principle would work with larger electrodes, since many variables will alter [51]. The concept described by Hashemi *et al.* (2015) illustrated the use of two parallel flow friendly electrodes, that are in close proximity to each other. The flow is manipulated by the Segre–Silberberg effect, whereby evolved gases are pushed against the electrode surface by the nature of the velocity profile developed [51].

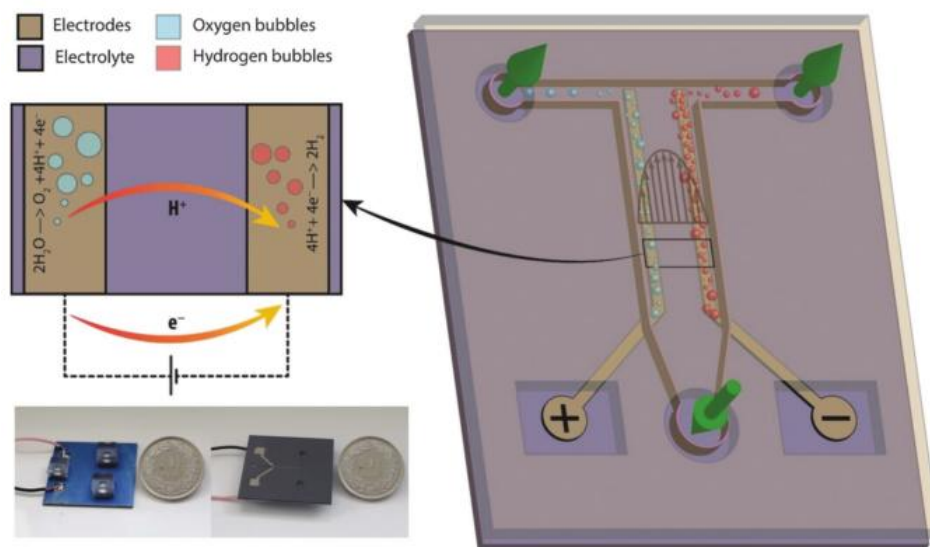


Figure 2-16: Schematic of operating principle of scale illustration of a membraneless electrolyser for the production of gas across the pH scale [51]

From Figure 2-16, it is clear that the concept depicted is on the micro scale with the electrode gap being only a few microns thick. While this design would be efficient, the current density and flow length would be severely inhibited by the allowable production rate, before unwanted cross gas

contamination takes place. Therefore, the above design would only prove scalable for production by means of a number of modules in series or parallel with one another.

Other membraneless concepts appear to be perfectly scalable in electrode size by means of standard modules. O' Neil *et al.* (2016) making use of inclined porous electrodes with a centre separator to divide the terminating cathodic and anodic flows [48]. While this method produces high purity gas, and can be scaled with regards to the area of the electrode, the efficiencies obtained from this unit are inadequate when compared to conventional alkaline water electrolyzers, and the DEFT™ system. Therefore, a large reactor would be required in order to produce the desired hydrogen production rate.

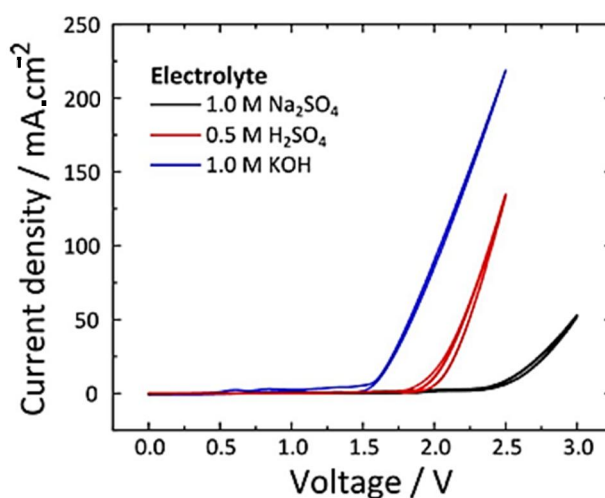


Figure 2-17: Polarisation curve of a membraneless inclined porous electrode concept making use of a platinum plated anode and cathode as a function of electrolyte concentration and type [48]

In reference to Figure 3-6 (page 52), it is evident that the attained current density of the DEFT™, utilising a platinum plated anode and cathode, resolves to be 0.729 A.cm⁻² at 2.5VDC. Figure 2-17 indicates that the resolving performance utilising potassium hydroxide as the electrolyte at 2.5VDC is approximately just short of 0.225 A.cm⁻², and therefore an order of magnitude reduction factor of three in performance between the two technologies [48]. It is well known in electrolysis that parallel electrodes make for conditions that utilise the entire surface area of the electrode uniformly, otherwise a noticeable reduction in current density would be observed, as indicated in the example above [10].

2.8.3. Gas/Liquid separation of a high-throughput bi-phase stream

An aspect rarely discussed with regard to water electrolysis systems, with AWE being a case in point, is the gas/liquid separation systems used to extract the gaseous product from the aqueous electrolyte. These systems need to be designed to obtain the highest degree of separation efficiency in order to circumvent a number of issues that can occur. Challenges that can arise are:

- (i) The re-entrainment of the gas (for example, the catholyte) through the system, which may expel a small quantity of dissolved gas when recycled to the anodic compartment. This may be significant if a high purity product gas is to be obtained. The correct size separator would need to be employed, however, this is especially a case for a system where the aqueous media is under pressure [53].
- (ii) The flow rate of the electrolyte in the recycle may accelerate the phenomena described above. All alkaline systems need to maintain circulation of the aqueous media in order to preserve a constant concentration of electrolyte. As described previously, flow is a useful means of removing product gas bubbles from the electrode surface, and from between the electrodes in order to improve efficiency [45]. If the flow is too large for the separation system to handle, it may be found that dissolved gas will find its way around the system in greater volumes. A viable way of reducing the cross-over rate of contaminant gas would be to increase the bubble growth size by means of greater operating current densities [53].
- (iii) Greater concentrations of solutes within solvents also typically reduce the amount of dissolved gas that can remain within the solution as the solution is already saturated with salts. Increased temperatures have a similar effect as the solubility of dissolved gases reduces [53].

Typical AWE systems make use of a small volumetric recycle, where a plant within the megawatt range only requires circulatory pumps of a few kilowatts in order to recycle electrolyte continuously, for the purpose of purging the stack of produced gases [55]. The matched conventional gravitational separators, smaller than the stack themselves, are therefore adequate to yield high purity gas at substantially high pressures [16].



Figure 2-18: Typical gas/liquid separator scale located above a 500 Nm³/hr alkaline water electrolysis plant [16]

The difficulty arises when trying to remove the majority of the dissolved micro-bubbles from the liquid electrolyte, which is the characteristic product of the DEFT™ technology. A number of existing simple technologies are available that utilise a variety of mechanical principles in order to remove gases from a flowing liquid. For any gas/liquid process to be successful, sufficient contact area needs to be provided to allow adequate transfer of the gas phase out of the liquid phase or vice versa [56]. A relatively new industrial product on the market deals with using membranes for gas/liquid separation whereby a bi-phase liquid is passed through a contactor, and the gas is extracted through a membrane, which allows solely for the gas phase to pass into a dry volume by means of a pressure gradient generated by a vacuum pump. These systems are particularly flexible in handling a number of different gases and liquids even in cases where particulates are present [56]. These systems have a number of advantages in contrast to packed, spray or gravitational settling solutions [56], which include:

- (i) compact, modular and scalable with a low pressure drop,
- (ii) large turn-down ratio (variation of liquid flows), and
- (iii) any orientation and configuration.

These systems are particularly difficult to source in terms of compatibility with extracting gas from a potassium hydroxide solution or alternate aggressive liquid mediums. For this reason, the simple gravitational methods of separation were incorporated into the pilot plants for the DEFT™ technology.

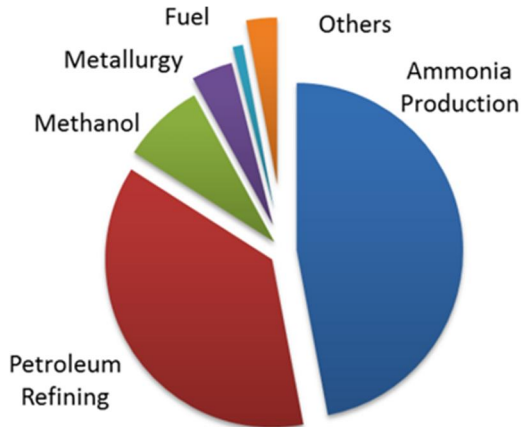
2.8.4. Early alkaline water electrolysis plant limitations

Modern alkaline water electrolysis plants are monolithic in scale (measuring a few tonnes in mass), due to their low operating current thresholds limiting them to a range of between $0.4 - 0.5 \text{ A.cm}^{-2}$, in order to keep operational costs reasonable [16]. More modern systems, such as the zero-gap system, are capable of overcoming this limitation by allowing operations up to 1 A.cm^{-2} [15]. The electrodes are generally constructed out of steel grids, or made out of solid nickel or stainless steel. Common electrode materials are comprised of an alloy of nickel and zinc, whereby the zinc is leached out of the structure in order to obtain a high surface area for hydrogen formation [16].

As previously mentioned, asbestos was used as the material of choice for separating the anodic and cathodic compartments, due to its wettability and impermeable nature to gases. However, this separator is deemed an environmental risk, and was limited to a maximum temperature of 90°C . As a result, this separator was replaced by alternative materials such as Teflon bonded potassium titanate, which are more stable at higher temperatures. [57]. The use of this porous type of separator creates a few issues with regard to gas crossover, specifically at higher temperatures. With the system at temperature, chemical vapours often move with the product gas requiring condensation and extraction at a later stage. Therefore, additional gas conditioning equipment is required to get the product gas to the adequate standard [16].

The largest alkaline electrolyzers manufactured today are capable of producing hydrogen up to 60 kg/hr , for various applications such as ammonia production. They are capable of several tenths of thousands of hours of operation, and are deemed to be profitable over the long term [16]. Major uses for these plants tend to be restricted to the chemical sector. Smaller volumetric consumers of hydrogen are restricted to the jewellery-, laboratory-, and medical industries, while the largest volumetric consumers are in the metals processing- and food industries [58].

a.



b.

Industrial application	Typical size electrolyser
Jewellery, laboratory and medical engineering	5 - 500 NI/h
Generator cooling in power plants	5 - 20 Nm ³ /h
Feed Water Inertisation (BWR water chemistry)	10 - 50 Nm ³ /h
Float glas production (protective atmosphere)	50 - 150 Nm ³ /h
Electronics industry	100 - 400 Nm ³ /h
Metallurgy	200 - 750 Nm ³ /h
Food industry (fat hardening)	100 - 900 Nm ³ /h
Military und aerospace	< 15 Nm ³ /h

Figure 2-19: (a) Subdivision of globally produced hydrogen in reference to industry categories, and (b) typical required electrolyser sizes according to volumetric production rates [58]

The major drawbacks of the modern alkaline water electrolysis technology are the replacement of outdated membrane/diaphragm materials, along with finding improved electro-catalysts capable of long term operation [36]. The performance of alkaline electrolysis plants is slowly being out-classed by more modern technologies such as PEME's and SOE systems [58]. The following diagram indicates the threshold limitations, and various performance regions for commercially available electrolysis technologies:

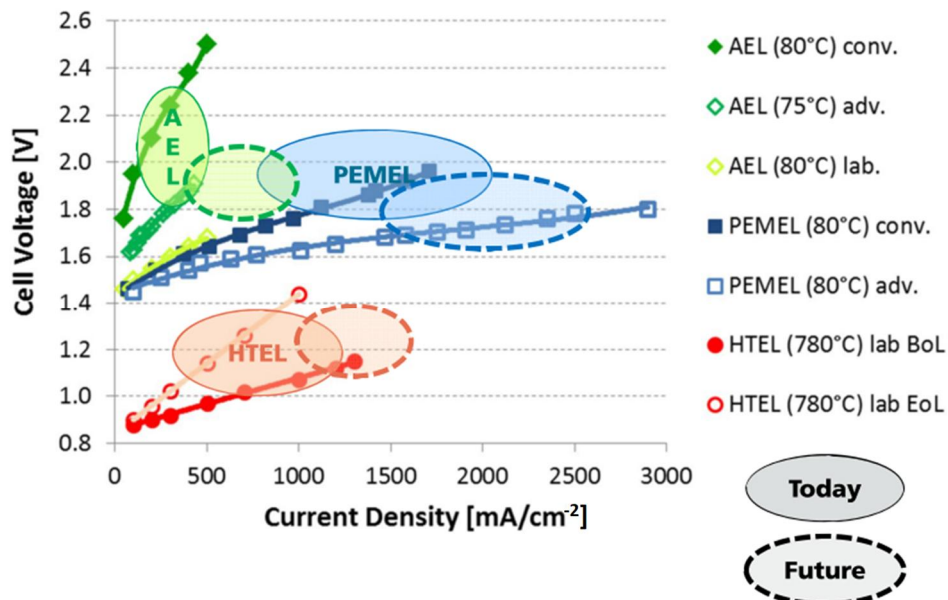


Figure 2-20: Performance regions of operation for modern available electrolysis technologies (AEL – Alkaline Electrolysers, PEMEL – Proton Exchange Membrane Electrolysers, HTEL – High Temperature Electrolysers) [58]

The diagram above, shows that AWE systems are almost not comparable to the performance of PEM and SOE systems, however, the latter named systems have a number of alternate drawbacks relating to the longevity and capital cost of components, making AWE systems more economically proven and viable [58].

3. INITIAL OPTIMISATION OF THE DIVERGENT ELECTRODE- FLOW-THROUGH MEMBRANELESS ELECTROLYSIS CONCEPT

3.1 OVERVIEW

The following chapter serves to provide an initial introduction and summary for the optimisation steps taken, to confirm whether the DEFT™ technology has the potential for commercialisation, to compete in the spectrum of already well-developed technologies. This chapter is based on a full-length article that was published in Journal of Power Sources [6] (see the first page in Annexure D). It describes all intrinsic parameters of water electrolysis, and serves to compare the DEFT™ technology in order to establish whether similar trends are followed, and whether these trends show any significant improvements over existing technologies.

Initial optimisation of the DEFT™ technology entailed the use of a large polypropylene plant that was constructed specifically with the intention to eliminate as many unknown variables that could otherwise create bias at a later stage of testing. The technology utilised 30 mm diameter circular filtration mesh electrodes with an adjustable electrode gap of between 0.8 – 5.5 mm. A number of parameter ranges were tested in order to compare the findings with literary findings. These parameters are as follows:

- (i) relationship of electrolytic concentration to cell performance (20 - 50 wt% KOH),
- (ii) relationship of electrolytic temperature to cell performance (40 - 70°C),
- (iii) relationship of the electrode gap to cell performance (0.8 mm – 5.5 mm),
- (iv) relationship of electrolytic flow velocity to cell performance (0.075 – 0.125 m.s⁻¹),
- (v) kinetic performance of four catalysts with the aim of maximising cell performance, and
- (vi) gas purity determination as a function of the electrolytic flow velocity.

The intention of investigating the above parameters, in stated variable ranges, was to identify a more defined region for future experimental tests. At the conclusion of this investigation it was found that, when employing an electrode gap of 2.5 mm, at a current density of 3.5 A.cm⁻², and a flow velocity of 0.2 m.s⁻², a hydrogen and oxygen gas quality of 99.83 vol% and 98.84 vol% was obtained respectively [6]. This signifies that less than 1 vol% of the hydrogen is carried over to the oxygen stream indicating that low losses are associated with the technology, and that gas purities are within the norm of 99.9 vol% associated with modern AWE's [16]. A common and

effective catalyst employed in the Chlor-alkali industry utilises a mixed-metal oxide (MMO) combination catalyst i.e. $\text{RuO}_2/\text{IrO}_2/\text{TiO}_2$, for the anode and a platinum catalyst for the cathode [21]. When employing this catalyst combination, it was found that current densities of $0.126 - 0.270 \text{ A.cm}^{-2}$ (at 1.80 VDC) and $0.268 - 0.575 \text{ A.cm}^{-2}$ (at 2.00 VDC) are achievable, which matches well with the current expected performance of alkaline water electrolysis technologies within the experimental ranges previously mentioned [6]. By allowing for additional reactive surface area in the form of employing additional mesh layers, an enhancement in current densities at set cell potentials can be obtained. A specialised catalyst, that comprised platinum (9%), nickel (56%), and aluminium (35%) by mass (obtained through co-deposited physical vapour deposition) on the anode with pure platinum on the cathode, yielded increased performance of 0.477 A.cm^{-2} at 1.8VDC and 1.198 A.cm^{-2} at 2 VDC (at an electrode gap of 2.5 mm, and an electrolytic flow velocity of 0.075 m.s^{-1}). The stability testing of this catalyst will be of great importance when coupled to a scalable pilot plant reactor.

3.2 METHODOLOGY AND APPARATUS

3.2.1. Overview

The full plastic concept optimisation test rig was designed with the intention of eliminating all possible unknowns for testing purposes, and for demonstration of the technology. The caustic solution is known to oxidise various materials, however, the sole use of plastics would eliminate the introduction of metallic ions which could have the feasibility of creating unknowns in experimental tests. All auxiliary components were designed to be oversized in order to maintain constant parameters, and to ensure complete separation of the product gases from the liquid electrolyte.



Figure 3-1: (a) DEFT™ concept optimisation test rig, (b) internals of the DEFT™ concept optimisation reactor, and (c) balance of DEFT™ concept optimisation test rig [6]

The following flow diagram illustrates the process flow principle of the concept optimisation test rig [6]:

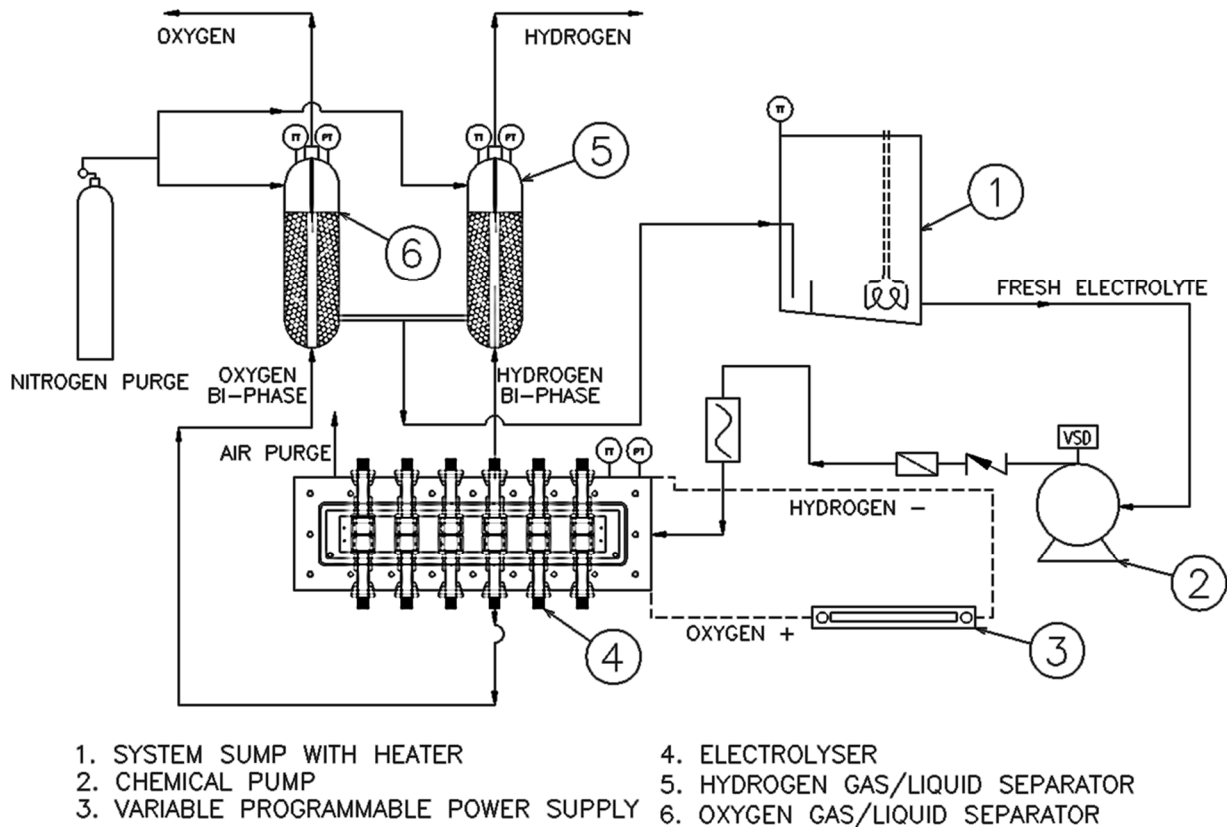


Figure 3-2: Process flow diagram for concept optimisation test rig for demonstrating the DEFT™ concept [6]

With reference to Figure 3-2, fresh electrolyte is introduced into the sump where various parameters are monitored and recorded including the control of the electrolytic temperature. A

chemical pump linked to a 2.2 kW Delta VFD (Variable Frequency Drive) is responsible for the control of electrolytic flow rate. A read out of the electrolytic flow rate is provided by an electromagnetic flow meter. The fresh electrolyte then enters the DEFT™ reactor, which splits the flow into the anodic and cathodic bi-phase streams. These two streams, containing the oxygen and hydrogen gases respectively, then reports to gravitational packed media separators that separates the gases from the liquid electrolyte. The electrolyte is then re-circulated to the sump under gravity. Variable DC power is supplied to the DEFT™ reactor by means of a 2.4 kW TDK programmable switch mode power supply that is monitored and controlled by Labview™ software. Temperature and pressure is monitored by gauges for all gaseous and liquid streams, while gas flow-rate is indicatively measured by means of Aalborg gas flow rotameters. Temperature control of the system was achieved through the use of a PID temperature controller, PT-100 temperature probe and chemically resistant heating elements inserted into the system sump. For safety and gas quality measurements, nitrogen gas was used to purge the system of air / contaminant gases, before testing was initiated. Gas quality measurements was conducted by an external quality lab (AirSep Labs) who performed gas analysis using Agilent 6890 gas chromatograph. At the specified experimental conditions at which gas samples were extracted by means of a sampling bag, sufficient time (6 hours) was provided for the system to attain steady state.

3.2.2. DEFT™ reactor details and employed electrode materials

The DEFT™ reactor, employed with the plastic concept optimisation rig, utilises four 30 mm diameter circular electrodes. The reactor is designed to create non-preferential flow to each electrode to ensure equal current density distributions, and flow-rates between electrodes in a pressurised chamber (Figure 3-3 and Figure 3-4). This was achieved by placing a flow distribution plate at the base of the reactor.

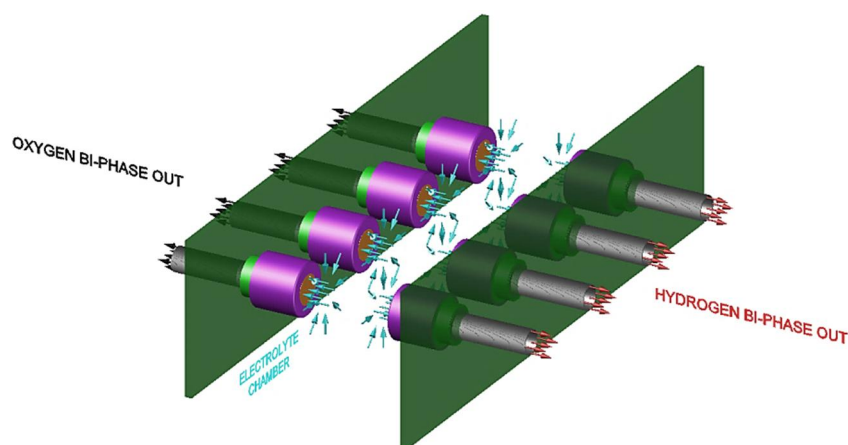


Figure 3-3: Configuration and flow principle for the DEFT™ concept optimisation reactor

The electrodes themselves were designed to have a self-tensioning design that when screwed in, ensures that the electrode surface has a tort and perfectly flat surface with the absence of edges (Figure 3-5). The electrode has a conductive extrusion extending from the flat circular surface, which makes a contact surface with the conductive electrode head. The tensioning covers (Figure 3-5 No's. 3 & 4.) are designed to insulate the assembly from the surrounding electrolytic fluid. The conductive head (Figure 3-5 No. 1.) allows for an adjustable electrode gap by screwing onto a threaded industrially pure nickel pipe (Figure 3-5 No. 5.). This pipe was contacted on the exterior of the electrolyser by means of a threaded conductor ring (Figure 3-5 No. 6.). The following schematic provides the design for the electrolyser itself, and the electrode head with tensioning cover:

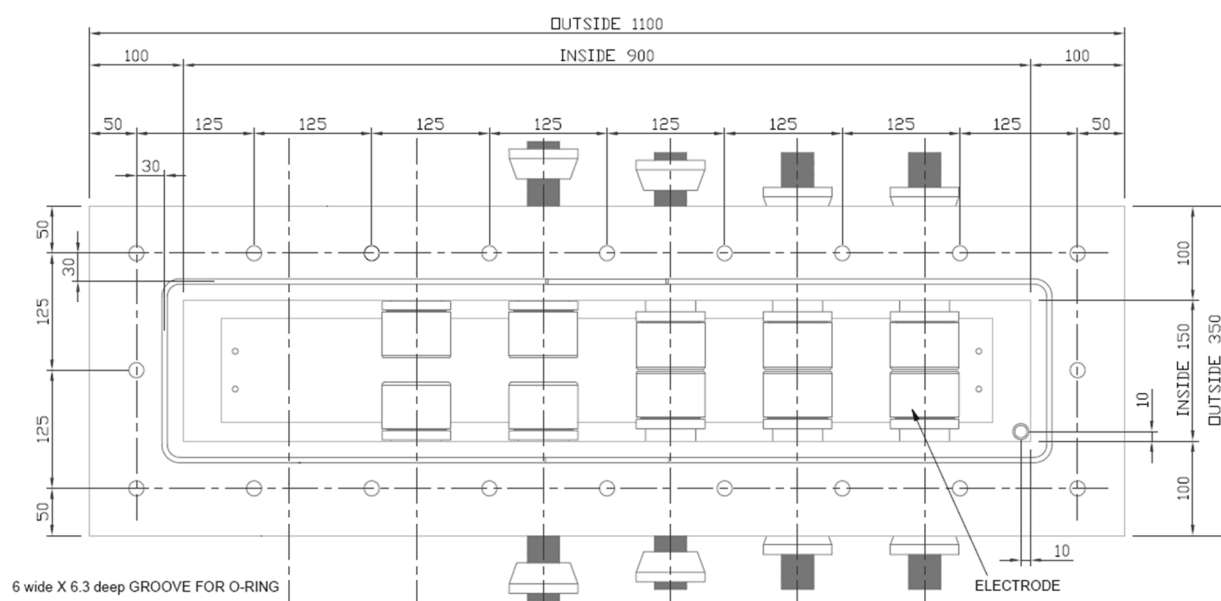


Figure 3-4: DEFT™ concept optimisation reactor top view illustrating the assembly of a pole pair of electrodes

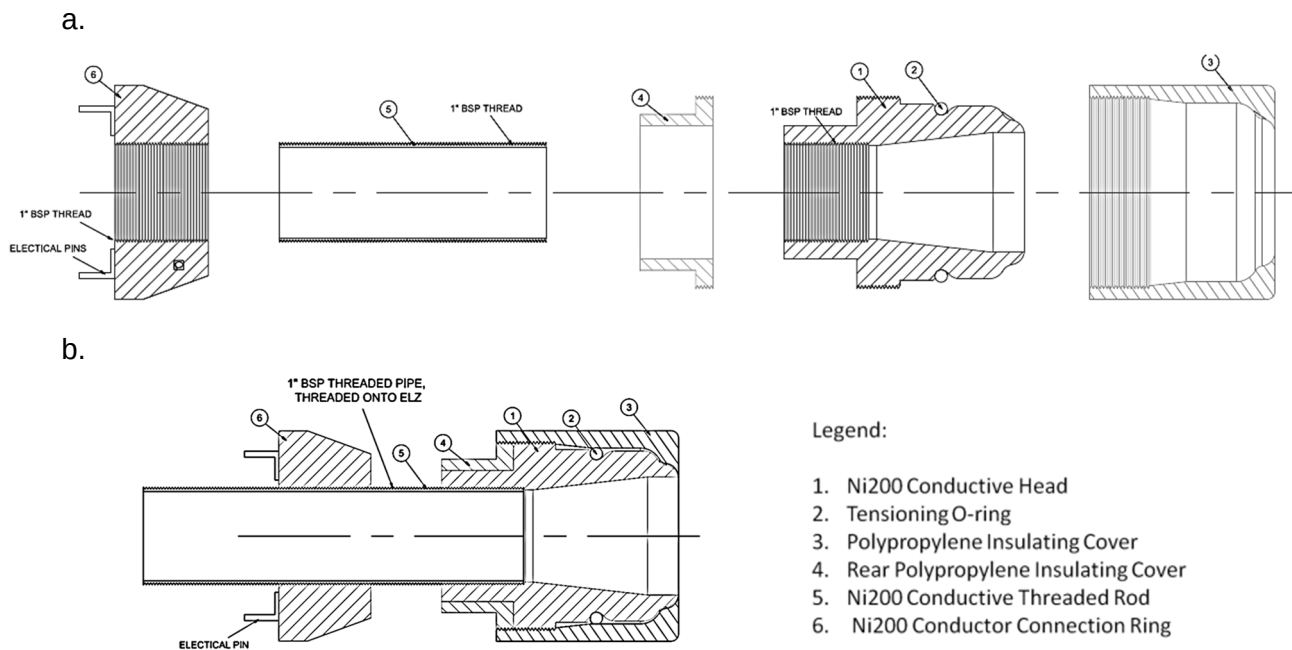


Figure 3-5: (a) Exploded view of the 30 mm electrode assembly, and (b) assembled view of the 30 mm electrode assembly for the concept optimisation test-rig

The electrodes are manufactured out of 80 μm nominal retention dutch weave filtration mesh (sourced from: Merco Industries, Hebei Nanrui Wire Mesh Company & Ofolan Wire Mesh Company) that comprised of stainless steel 316, industrially pure nickel mesh (Ni200 alloy), or titanium grade 1, depending on the catalytic coatings of choice. It was chosen to test the stainless steel 316 and industrially pure nickel mesh in contrast to two other catalytic combinations of choice. The first combination utilises a Mixed-Metal Oxide (MMO) on the anode comprising of TiO_2 , RuO_2 , and IrO_2 in a mass ratio of 55:35:10 respectively, coated onto a titanium substrate [6]. The cathodic electrode comprised of pure platinum, with a loading between 35 - 65 g.m^{-2} plated onto a titanium substrate, as it is well-known in the fuel cell industry that platinum is an effective electrocatalyst for the hydrogen evolution reaction [59]. The second combination catalyst is the $\text{Pt}_9\text{Ni}_{56}\text{Al}_{35}$ catalyst, sputtered onto a nickel substrate by the North-West University, and represents the anodic catalyst with pure platinum electro-plated onto a titanium substrate representing the cathode. The motivation for the anodic catalyst is the substantial reduction in platinum loading, which currently represents a sever drawback in CAPEX and OPEX for modern PEM commercialised systems [60].

3.2.3. Separation concept for DEFT™ concept optimisation test rig

Typical gas/liquid separation systems for AWE and PEM systems involve the use of gravitational separators, where electrolytic mixtures are left to settle evolving gases under the effect of the evolved bubbles' natural buoyancy [53]. The DEFT™ technology, as previously mentioned, relies on the flow of electrolyte in order to create separation of the produced gases at the electrodes. This does, however, imply a significant throughput of solution containing a bi-phase mixture of aqueous potassium hydroxide 30%, and product gas being either hydrogen or oxygen. Attempts have been made to separate gas from a liquid by allowing the liquid to flow in thin films, as to allow for maximum surface area of contact, of the surrounding gas and liquid [56]. A similar concept has been employed for this gas/liquid separation system illustrated as follows:

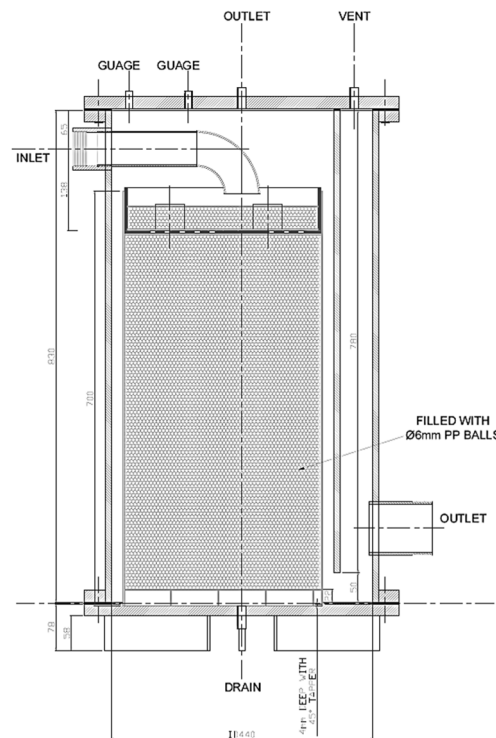


Figure 3-6: Gas/Liquid separator for concept optimisation test rig

The bi-phase aqueous solution enters the gas/liquid separator in a tangential manner in the upper hemisphere of the separator (Figure 3-6). The mixture falls onto a distribution plate to ensure that the liquid is distributed equally through the entire volume of the separator. The packing is a medium of 6 mm polypropylene balls, which ensures that a thin liquid film of electrolyte will propagate through the entire length of the separator. In this manner, entrained gas bubbles will be able to escape out of the electrolytic solution effectively, provided that the liquid throughput is not excessive. The 'liberated' solution is then able to flow under the influence of gravity back to the system sump, where if any bubbles had remained within the solution, it would have an opportunity to leave the system as a purge gas via the system sump exit.

3.2.4. Variables to be tested

The key objective of the concept optimisation rig is to establish a proof of concept for the DEFT™ technology on which further research and development work will be based upon. Therefore, tests were designed to evaluate the performance of the technology under a variation of process parameters, some intended to confirm literary findings of conventional alkaline water electrolyzers, and others to establish rig-specific experimental trends in order to define, or compare performance to existing technologies. A specific experimental test run with set experimental conditions was allowed to run for at least 10 minutes to reach a steady state value before proceeding to the next condition. Each test run was repeated three times in order to ensure accuracy and repeatability of results. Uncertainty was then determined by determining the standard deviation of the mean, and multiplying it by the 95% confidence interval factor, representative for two degrees of freedom.

Standard Parameter Confirmation Experiments

The optimal concentration of a potassium hydroxide solution used for AWE systems would be in the order of 30% [16]. A comparison was drawn using standard external parameters while employing a variation of electrolytic concentrations from 20% to 50%. Simultaneously, performance was recorded for the gradual increase in temperature to understand the degree of benefit with respect to increasing temperatures.

It is well-known that the smaller the electrode gap between electrodes, the higher the efficiency of an electrolyser setup, and therefore electrode gaps of between 1 – 5.5 mm were tested to perceive the drop in efficiency with an increasing electrode gap [31]. Expected trends are well known for the above parameters, and these tests aid in quantifying the specific performance implications for the DEFT™ technology.

Technology Specific Parameter Experiments

Flow is a unique method of creating separation of produced gases, and for increasing the efficiency of an AWE electrolyser. It is, however, dependant on a number of parameters such as the temperature and concentration of the electrolyte. In turn, together with the current intensity applied to the electrodes, the purity of the gas can either be positively or negatively influenced. Therefore, a small investigation into the purity capability of the DEFT™ technology was performed using an Agilent 6890 gas chromatograph to establish accurate readings on gas purity [6].

It is expected that tests using the DEFT™ technology, for many common and new catalysts employed in alkaline electrolysis, will produce greater current densities for set cell potentials in comparison to many membrane-based electrolysis operations. Therefore, polarisation curves

were generated over cell potential ranges, in order to quantify the performance comparison, and efficiency of various catalyst combinations.

3.3 RESULTS AND DISCUSSION

3.3.1. Effect of concentration, flow velocity, and temperature

A range of temperature and flow velocity conditions were tested that should have an impact on the peak performance of the reactor at a variety of concentrations. It is demonstrated in literature that the optimal concentration of an immobilised alkaline solution peaks at 35% with a maximum temperature of 100°C [25]. From generated results, a 30% aqueous solution of potassium hydroxide demonstrated peak performance employing stainless steel electrodes, for both the anode and cathode.

It can be expected that with the increase in temperature to the fluid, an increase in conductivity can be expected. It is therefore expected that with higher concentrations, an improvement in the transfer kinetics can also be expected. An opposing effect is shown regarding concentration in Figure 3-7A and Figure 3-7B, where 30% shows superior performance across the entire tested cell potential range, Figure 3-7C illustrates that a concentration of 50% is superior at cell potentials 3 VDC and 3.5 VDC. The optimal concentration utilised in industry is between 20-30% due to elevated corrosion rates to plant components at any concentration exceeding this [45], therefore it can be observed that the optimal concentration found in this investigation is at 30% across most tested cell potentials, temperatures, and flow ranges. Due to the high concentration of ions in the solution, at the temperature of 60°C for concentrations exceeding 30%, it is found that charge transfer is congested, and not enhanced as one might expect [25]. Greater solution temperatures provide the formulae for allowing enhanced performance at greater concentrations of electrolyte, as the enhanced kinetics allows for accelerated movement of ions.

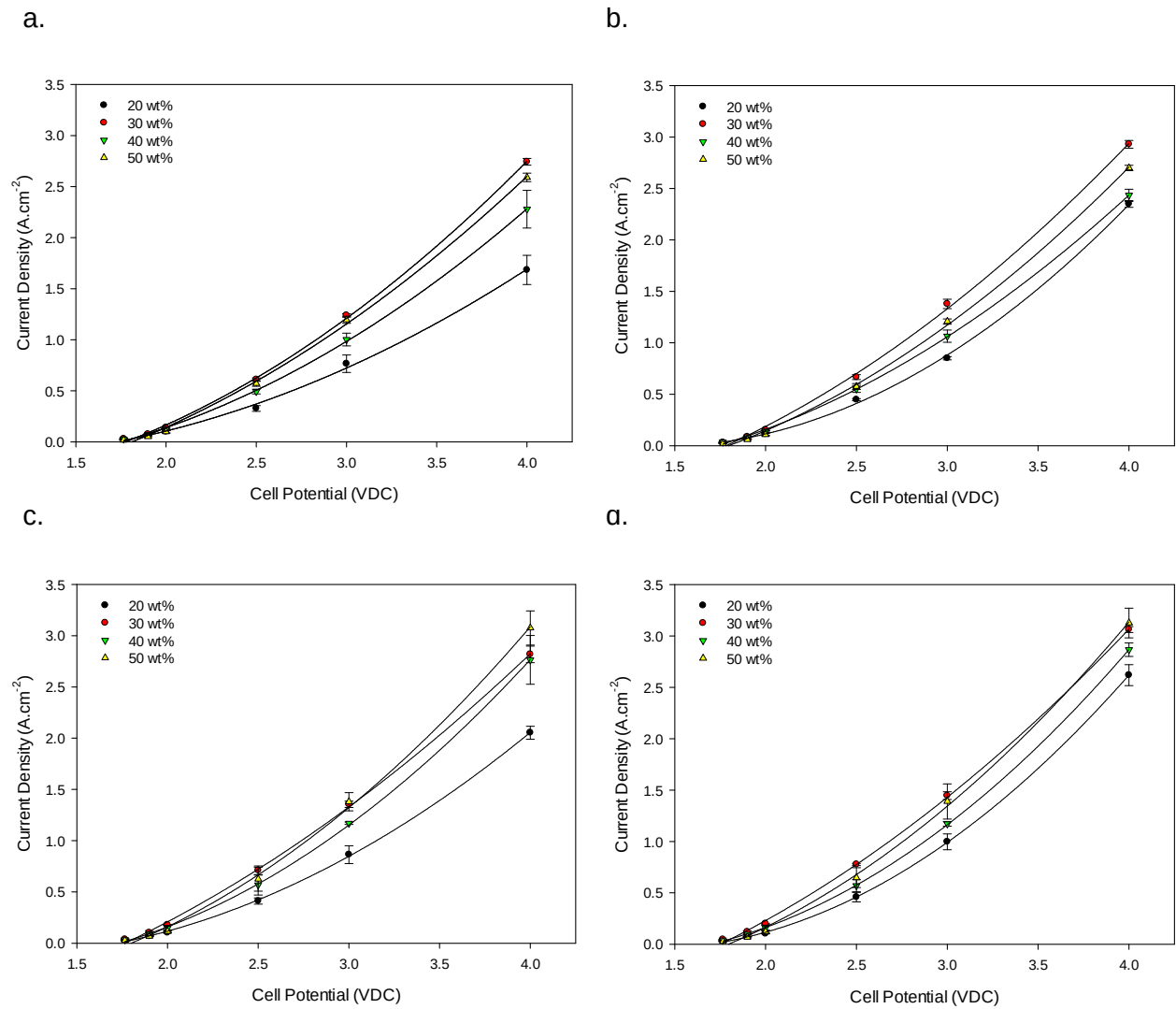


Figure 3-7: Polarisation curves of the concept optimisation stack as a function of potassium hydroxide (KOH) concentration at (a) a temperature of 60 °C, and a flow velocity of 0.075 m.s⁻¹, (b) a temperature of 60 °C, and a flow velocity of 0.15 m.s⁻¹, (c) a temperature of 70 °C, and a flow velocity of 0.075 m.s⁻¹, and (d) a temperature of 70 °C, and a flow velocity of 0.15 m.s⁻¹ at an electrode gap of 2.5 mm for stainless steel 316 electrodes

From the above figures, it is clear that temperature presides over determination of the optimal concentration, and not the flow velocity. The flow velocity of the solution simply provides the means of reducing the resistance between electrodes by continually ‘washing’ or increasing the disengagement rate of bubbles from the electrodes, and by reducing the void fraction of bubbles between the electrodes [51]. The additional advantage of increasing the flow velocity and temperature of the electrolytic solution, is that the increase in the solution viscosity reduces the gaseous meniscus formed on the electrode surface, thereby improving the gas product quality of the hydrogen and oxygen gases [10].

3.3.2. Cathodic and anodic catalyst comparison

Common catalytic materials were sourced and prepared for testing in the DEFT™ concept optimisation test rig in an attempt to find a combination that would optimise the kinetic performance. The performance was recorded at the maximum attainable temperature of 80 °C.

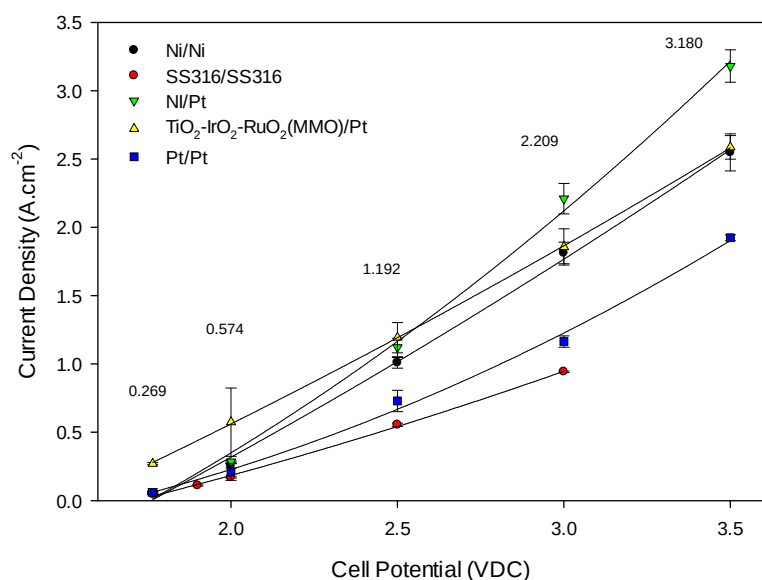


Figure 3-8: Polarisation curves for the DEFT™ concept optimisation test rig as a function of anodic and cathodic materials for a temperature of 80 °C, a flow velocity of 0.1 m.s⁻¹, an electrode gap of 2.5 mm, and 30 wt% KOH

Figure 3-8 illustrates that the use of a pure nickel anode and a platinum plated nickel cathode maximises the performance at cell potentials greater than 2.5 VDC, under prevailing conditions. By carefully selecting materials for the HER and for the OER, the kinetics would be collectively increased for the overall water electrolysis reaction [59]. Based on volcano plots published in literature, platinum maximises the performance of the HER to a greater extent in contrast to alternate noble and non-noble pure metal combination catalysts [61]. The OER, on the other hand, is known to be the limiting reaction within the overall water electrolysis reaction. Nickel, and its oxides, are commonly used as the general catalyst for anodic reactions in industry, and has been reported to have a higher catalytic activity for the OER compared to that of platinum, and any other pure noble metal catalysts. Therefore, using platinum for the anode will not yield results superior to pure nickel or oxides of nickel [62]. Metal oxides are suggested to dramatically improve the catalytic response of the oxygen evolution reaction [40], specifically that of the noble metal oxide combinations readily used in PEM systems [59]. Based on theoretical calculations, the optimal suggested catalysts exhibiting the highest degree of catalytic activity are RuO₂ and Co₃O₄.

It should, however, be observed that catalysts that are suggested to be theoretically optimal may not always perform as well when subjected to real experimental conditions in terms of durability and stability [40].

The TiO_2 , RuO_2 , and IrO_2 combinatory catalyst representing the anode is normally paired with a platinum plated cathode which can be seen represented on Figure 3-8. This catalyst exhibited the highest performance for the potential range of 1.765 VDC – 2.5VDC, generating a current density of 0.269 A.cm^{-2} at an operating cell potential of 1.765 VDC. Stainless steel 316 generated the worst performance result across the potential range of 1.765 VDC to 3 VDC. It was found in experimental observations that the metal, specifically on the anodic side, demonstrated severe instability. Consequently, under a short duration of testing at elevated potentials, it resulted in a sudden reduction in operating performance. Industry employs stainless steel electrodes mainly as the cathode, however, plated stainless steel or alternative stable materials are utilised as the anode [33].

The advantage of using an oxide catalyst paired with a platinum plated cathode is clear when considering the instances where a platinum plated cathode has been paired with a pure nickel anode or platinum plated anode. This specifically has relevance at the more efficient lower cell potentials smaller than 2.5 VDC. Optimal performance is attained by the platinum plated cathode and pure nickel anode, when considering cell potentials greater than 2.5 VDC. Beyond this cell potential, a nickel anode paired with a nickel cathode is capable of matching performance to that of the MMO and platinum plated combination. It is fundamental for the membraneless DEFT™ technology to remain as cost-effective as possible, by minimising the capital cost, as well as the operating cost to produce hydrogen. To this regard lower platinum loadings, and non-noble catalysts will be considered.

Currently, the current density threshold of modern alkaline water electrolyzers is at 0.5 A.cm^{-2} at 2 VDC, and it is hoped that by 2030, the threshold would have been improved to 1 A.cm^{-2} at 2 VDC [16,15]. DEFT™ technology has the capability of operating well above 3.5 A.cm^{-2} at below 2.75 VDC, with stable performance already superseding this limitation, due to the elimination of past restrictions brought on by the need for a membrane between the electrodes. An efficiency target set by Yde *et al.* (2013) for alkaline water electrolyzers at 88 HHV% or 1.7 VDC is in the region of 0.2 A.cm^{-2} [61]. It can be seen that the MMO/Pt catalytic combinations supersede this value implying that the stack efficiency attained is already greater than with what can be expected with modern alkaline water electrolyser technologies.

3.3.3. Superior catalyst tests, and increases in surface area

Raney nickel has been accepted as an effective electrocatalyst for AWE systems due to its high surface area morphology. Platinum has been found to be effective for both PEM and AWE systems due to its high activity [10,63]. It is reported that if Raney nickel has excessive nickel content, the structure would not be porous enough to promote enhanced reaction kinetics, and hence an optimal alloy composition will exist [63]. Paidar *et al.* (2016), reports that a high surface area nickel-based electrode, doped with platinum, provides enhanced performance over and above what can be expected by the pure non-metal material alone [30]. Hence the use of Raney nickel, containing highly active platinum species, is benchmarked as follows at 70°C. The temperature of 70°C represents the only test temperature for which the $\text{Pt}_9\text{Ni}_{56}\text{Al}_{35}/\text{Pt}$ catalyst combination was tested:

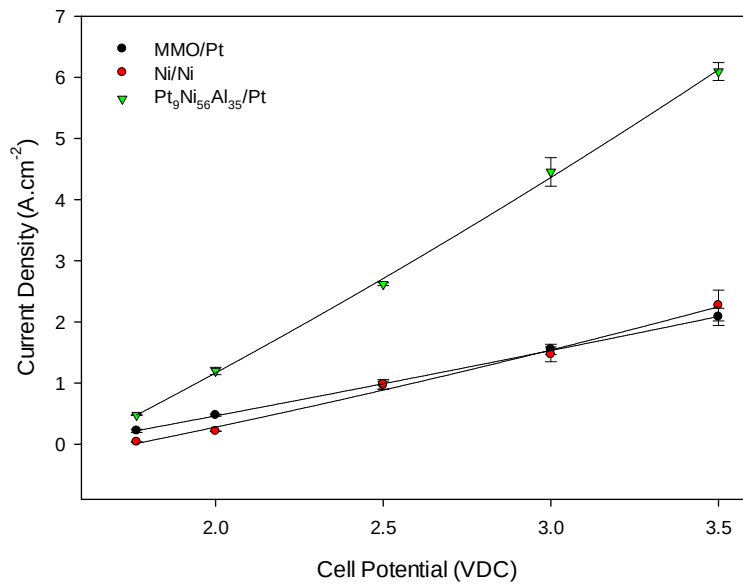


Figure 3-9: Polarisation curves of the concept optimisation test rig stack as a function of electrode material at an electrode gap of 2.5 mm, a flow velocity of 0.075 m.s⁻¹, temperature of 70 °C, and 30% KOH

The $\text{Pt}_9\text{Ni}_{56}\text{Al}_{35}/\text{Pt}$ catalytic combination developed a stern improvement over the benchmark Ni/Ni catalyst, and industry standard MMO/Pt catalyst, in some instances more than two-fold improvements are observed at the elevated cell potentials. High surface area and active component doping are therefore vital to enhancing the electro-kinetics of the DEFT™ technology [22]. By using an alloy composition whereby one element is leachable, as to create a high surface area structure (such as the aluminium component in the $\text{Pt}_9\text{Ni}_{56}\text{Al}_{35}$ catalyst), along with doping the alloy with active components, an improvement in kinetics on a micro scale can be seen in Figure 3-9.

An effective and simple means of enhancing catalytic behaviour is by increasing the effective electrode area available for reaction, such as the case of gas diffusion electrodes [15]. This can be accomplished by simply doubling the mesh on each electrode. From Figure 3-10 it is clear that the use of a double layer of 80 μm nominal retention dutch weave mesh accounts for an improvement of between 27-49% in the upper potential range (>2.5 VDC). Effectively, the exposed geometric area of the mesh electrode is doubled when stacking mesh layers, however, pore sizes diminish, and gaseous bubbles require more force to effectively pass through the mesh. Gas bubbles trapped within the mesh structure additionally reduce the effective reactive area enhancing bubble resistance [45]. By utilising flow-friendly structures and configurations, that would allow for gas bubbles to be liberated / purged easily from the electrode surface, would prove effective for producing maximised quantities of gas from a stream of electrolyte. The key to enhancing the overall efficiency of the DEFT™ technology, is by either reducing the flow demand of the reactor, or by increasing the amount of gas produced as a ratio of the cross-sectional electrode area by using high activity catalysts and three-dimensional electrodes.

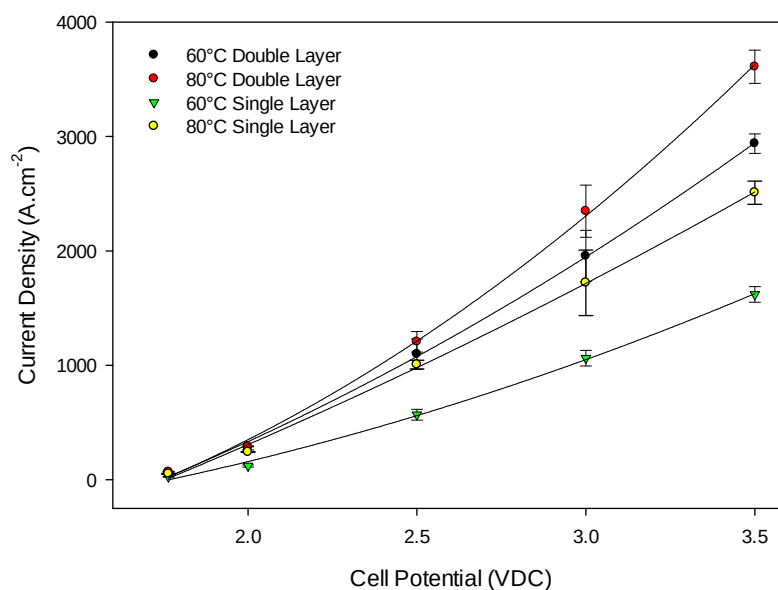


Figure 3-10: Polarisation curves of the concept optimisation test rig stack as a function of multi-layered nickel mesh anode and cathode electrodes and temperature, at an electrode gap of 2.5 mm, a flow velocity of 0.075 m.s^{-1} , and 30% KOH

3.3.4. Effect of electrode gap

With the absence of a membrane, the DEFT™ technology would be capable of operating with relatively small electrode gaps. An optimal relationship would exist, whereby the gaseous meniscus formed on the electrode surface at the correct flow velocity, would be of a thickness

enabling an acceptable degree of cross contamination of product gases, at various current densities, which preserves the purity of the produced hydrogen gas at low ionic resistance levels. A breakdown of performance is expected if gaseous product is present at elevated levels between the electrodes in the event of menisci making contact with one another. This would result in a deterioration of the operating performance, and a condition making use of larger electrode gaps, will be established as the optimal electrode gap. The following graphs depict the optimal electrode gap determination for various flow velocities [6].

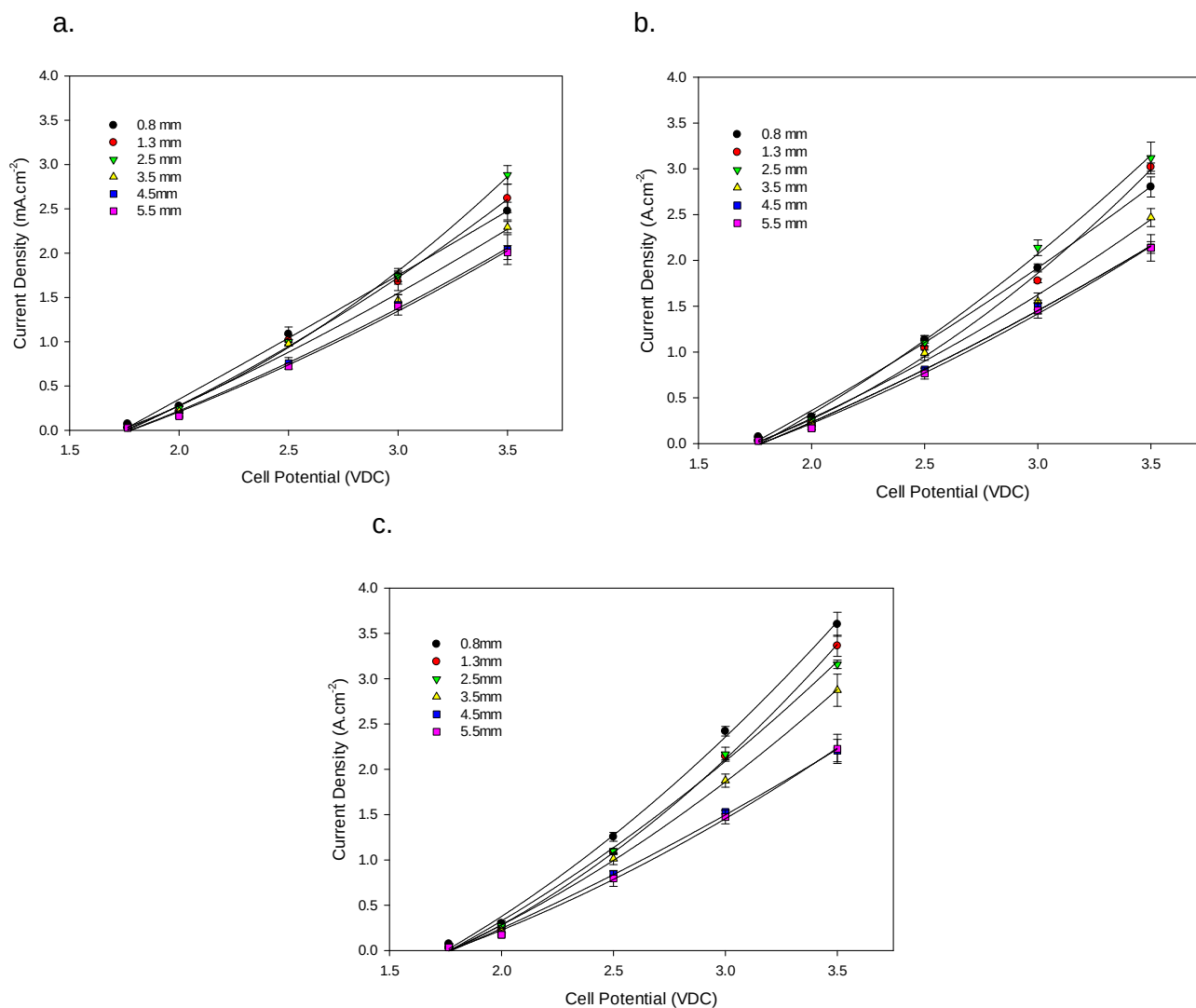


Figure 3-11: Polarisation curves of the concept optimisation stack utilising pure nickel anode and cathode electrodes, as a function of electrode gap at flow velocities (a) 0.075 m.s⁻¹, (b) 0.1 m.s⁻¹, and (c) 0.15 m.s⁻¹ for pure nickel electrodes, at 70 °C, and 30 wt% KOH

The optimal electrode gap is dependent on the current density (or applied cell potential), temperature, and electrolytic flow velocity at a constant concentration. Current density has the greatest bearing on determining the optimal electrode gap, as greater current densities result in greater gas evolution rates, and is likely to create a thicker gaseous meniscus on the electrode

surface. Greater fluid velocities are required in order to push the produced gas in the desired direction. If the electrode gap is too narrow, a breakdown of performance and gas quality is observed due to void fracture [26].

It is observed from Figure 3-11, that the flow velocity at a set concentration and temperature condition has precedence on deciding optimal electrode gap. At lower fluid velocities, larger electrode gaps are preferred, within reason, in order to optimise stack performance, as smaller electrode gaps experience greater resistance between the electrodes due to the enhanced incidence of void fracture. Higher flow velocities enable smaller electrode gaps to be used. Crossover between optimal electrode gaps are evident, specifically in reference to Figure 3-11b where, with an increase in current density, the smaller electrode gap 0.8 mm is replaced with the electrode gap of 1.3 mm, due to the elevated gas production rates at current densities generated above 3 VDC.

It has been observed that providing an external agitation on the gaseous bubbles formed on the electrode surface, would have positive repercussions for the operating performance [45]. The motion of fluid over the electrode can be seen to improve operating performance to a significant extent.

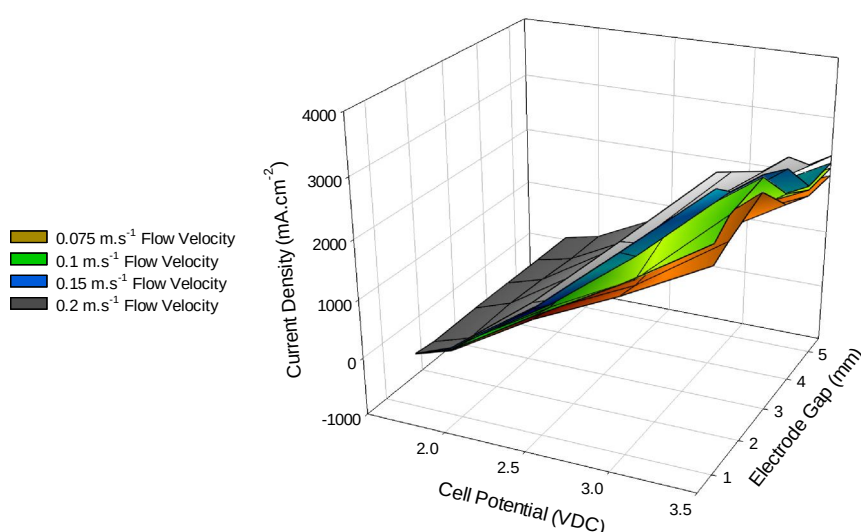


Figure 3-12: Polarisation curves of the DEFT™ concept optimisation stack utilising pure nickel anode and cathode electrodes, as a function of electrode gap and flow velocities, for pure nickel electrodes, at 70 °C, and 30 wt% KOH [6]

Figure 3-12 illustrates that small increases in flow velocities for small electrode gaps make a large difference in improving the operating current density. Beyond a flow velocity of 0.15 m.s⁻¹, it is difficult to notice any substantial improvement in current density, and therefore on an energy

basis, it would not make any additional benefit to the overall efficiency of a membraneless plant to operate at a flow velocity exceeding this [6]. As the electrode gap increases, larger flow velocities make very little difference to the operating performance of the stack. It can again be seen that high current density values are promoted at smaller electrode gaps and greater fluid velocities, where lower flow velocities would have an optimal current density value at smaller electrode gaps.

3.3.5. Resulting gas purity measurements from the DEFT™ concept optimisation test rig

Several operating conditions were identified during testing that resulted in stable performance without a significant degree of fluctuation. It was decided to set the plant up at these stable conditions, and record the gas purities of both the hydrogen and oxygen streams. These tests were conducted at a temperature of 30 °C, an electrode gap of 2.5 mm, a current density of 3.5 A.cm⁻² and flow velocities of 0.075 m.s⁻¹, 0.1 m.s⁻¹, and 0.15 m.s⁻¹. Operating at a low temperature would have repercussions for the viscosity of the solution, making it potentially more difficult for product gas to pass through the mesh. Therefore, operating at a lower temperature would be considered a worst-case scenario within the conditions. The following results were obtained with the full report presented in Annexure A.

Table 3-1: Gas purity analysis of DEFT™ concept optimisation test rig at 3.5 A.cm⁻², utilising pure nickel anode and cathode electrodes at an electrode gap of 2.5 mm, temperature of 30°C, as a function of flow velocity [6]

<i>Test Item</i>	<i>Velocity 0.15 m.s⁻¹</i>	<i>Velocity 0.10 m.s⁻¹</i>	<i>Velocity 0.075 m.s⁻¹</i>	<i>Uncertainty of result</i>
<i>H₂ Outlet</i>	99.83	99.78	98.98	±0.1%
<i>O₂ Outlet</i>	98.84	96.69	97.6	±0.1%

It can therefore be concluded that the DEFT™ concept optimisation stack is capable of producing high purity hydrogen and oxygen gas, which is not within the flammability range of a hydrogen and oxygen gas mixture. The Society of Automotive Engineers (SAE) Standard J2719 states that the required gas purity for fuel cell operations needs to be 99.97 vol% allowing for some additional impurities such as 0.2 ppm CO, with the general industrial grade of hydrogen being specified with

a purity of 99.95 vol% [44]. Current alkaline water electrolyzers produce hydrogen gas within the range of 99.3 to 99.9 vol% hydrogen [1].

In regard to the results above, it is clear that the DEFT™ membraneless technology will require, to some extent, gas conditioning equipment, if the grade of hydrogen is to be maintained at a reasonable gas quality. Improved gas qualities are achieved at elevated electrolytic flow velocities, and a similar trend can be observed for the oxygen product line, except for the flow velocity of 0.1 m.s^{-1} , where a drop in quality was recorded due to an unintended change in the separator level during a collection of the oxygen sample. This resulted in a slight contamination by atmospheric air entering the system, as the system did not have check valves on the gas lines to ensure that the compartments are completely separate from air contaminants.

3.4 CONCLUSION

The DEFT™ concept optimisation test rig performed its function in providing an irrefutable proof of concept of a new membraneless water electrolysis operating principle. A number of strategic performance influencing parameters, well known to existing water electrolysis technologies, were investigated in order to identify optimal points of operation such as electrolytic concentration, operating temperature, fluid flow velocity, various material catalyst combinations, and their effects on maximising current density and gas purity for a given cell potential value. The presence of a gaseous meniscus on the electrode surface demonstrates the need to obtain an optimisation between all parameters listed above in order to maintain stable performances and gas purities, which will be investigated further in test plants to follow.

It was ascertained that the membraneless technology is capable of operating at performance levels that supersedes that of current alkaline water electrolysis technology operating thresholds (current densities $> 0.5 \text{ A.cm}^{-2}$ at 2 VDC), and stack efficiencies with gaseous purities similar to the current AWE standard. Using a $\text{Pt}_9\text{Ni}_{56}\text{Al}_{35}$ anode paired with a platinum cathode, a current density of 1.19 A.cm^{-2} at a cell potential of 2 VDC, 2.5 mm electrode gap, 70°C , 0.075 m.s^{-1} , and 30% KOH was obtained. This operating performance surpasses performance benchmarks for advanced zero-gap alkaline water electrolyzers.

By reducing the electrode gap ($< 2.5 \text{ mm}$), in order to promote a lower resistance for the flow of ions between the electrodes at greater current densities ($> 3 \text{ A.cm}^{-2}$), an elevated flow velocity

(0.15 m.s⁻¹) is required in order to maintain stable performance. This required flow velocity, results in a significant parasitic load that needs to be maintained, to retain high purity separation of produced product gases. This is not always ideal, and it was found that an electrode gap of 2.5 mm maximises current density, but at a significantly lower flow velocity, that translates into a more practical solution for a commercial application of the DEFT™ technology.

Take-home observation(s):

- (i) Performance is maximised when a catalyst making use of active components, or a high morphology surface area is utilised for the anodic reaction, as the OER represents the rate limiting step in the overall water electrolysis equation,
- (ii) Using industrially pure nickel reveals to be highly effective for use as the cathodic electrode,
- (iii) By doubling the layers of mesh electrodes, employed in a single electrode housing, yields performances up to 50% greater,
- (iv) Beyond a flow velocity of 0.15 m.s⁻¹, stack performance is no longer maximised to a significant extent, and
- (v) Gas qualities generated from the DEFT™ technology resolves to be in line with qualities provided by commercialised alkaline electrolysis systems.

4. MULTIPLE CIRCULAR ELECTRODE (MCE) DEFT™ COMMERCIAL SCALE REACTOR

4.1 OVERVIEW

Upon completion of the initial proof of concept on the DEFT™ concept optimisation test rig, scale up of the technology was attempted in the form of a Multiple Circular Electrode (MCE) DEFT™ reactor, that incorporates forty-nine 30 mm circular electrode housings sharing the same fluid injection chamber, and common bi-phase product collection chambers. This is similar to the DEFT™ concept optimisation test rig, that also utilised a common injection chamber, as well as a common bi-phase collection manifold for both product gases produced. The design of the MCE reactor is an attempt at a scalable reactor, that will help formulate all the preliminary issues with regards to scaling the technology for mass production. The design of the plant was based on design criteria formulated from prior experimental studies.

Since this plant is intended to provide an indication of potential issues involved in scale up, the focus will not be on continued optimisation of the technology, hence stainless steel 316 electrodes were chosen as the electrodes of choice for both the anodic and cathodic electrodes. Visual observations of the plant dynamics will also create an understanding for general plant design going forward. Basic gas purity analysis would reveal the electrolyser's separation efficiency along with the gas/liquid separation efficiency.

A comprehensive electrical panel was designed and constructed for the purpose of providing power to the stack, controlling all systems by means of a manual circuit logic, or PLC input. Experimental conditions remained fixed for the stack with the only variable parameters being flow velocity, cell potential, and temperature. Hydrogen purity was measured for the plant in order to identify any trends that had impacted on the purity of hydrogen being generated.

At the conclusion of the investigation it was found that the performance of this plant was superior to the DEFT™ concept optimisation test rig, due to the presence of additional conductive surface area in the internal regions of the electrode housings. In terms of gas purity, it could not match that of the concept optimisation test rig, and hence improvements would need to be made to both the reactor and separation system.

4.2 METHODOLOGY AND APPARATUS

4.2.1. Overview

This introductory test plant was designed with the intention to establish the difficulties of scaled hydrogen production employing the DEFT™ technology. Auxiliary plant components and systems were designed, as a trial step to establish the effectiveness of using a horizontal gravitational 'knock-out' drum to separate out the produced gases from a liquid electrolyte. The separation effectiveness was unknown before testing. The following flow diagram illustrates the process flow associated with the MCE DEFT™ reactor system:

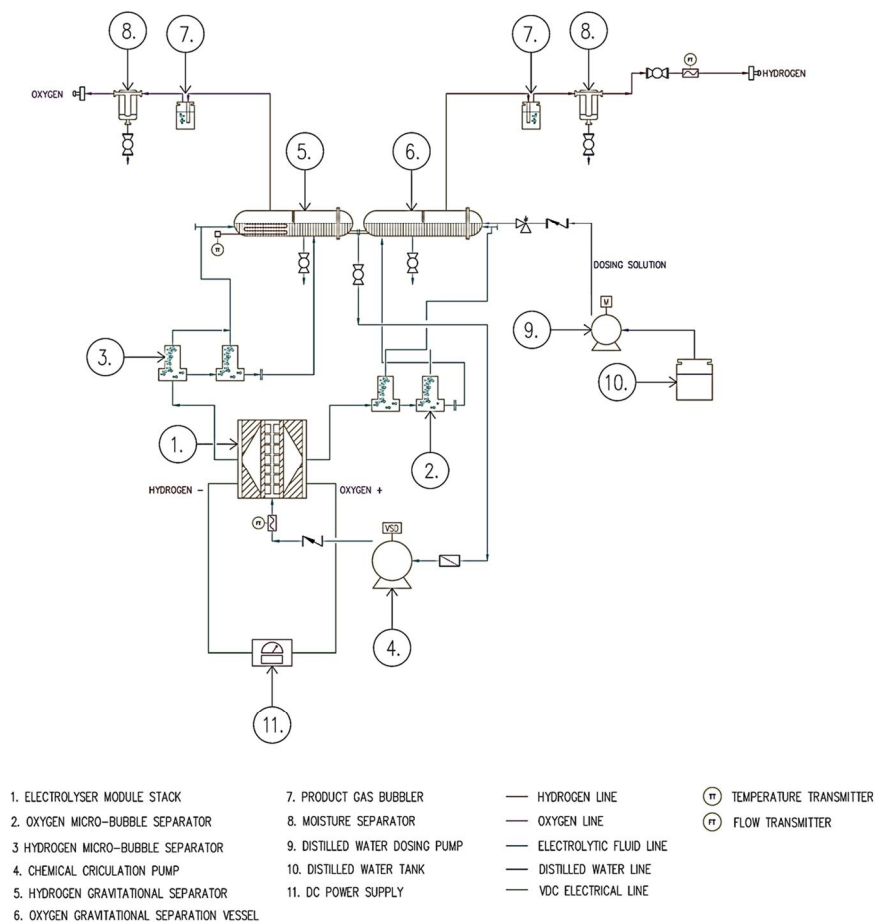


Figure 4-1: Process flow diagram for the MCE DEFT™ electrolyser pilot plant

Two horizontal separators double as both the sump and gas/liquid separators, with a transparent lid serving as a view port to observe electrolytic levels and clarity while the plant was operational. A chemical pump linked to an Emerson 2.2 kW VFD (Variable Frequency Drive), serves the purpose of controlling the set point flow rate from a PLC input using a PID controller, or from a variable resistance pot. The PLC and test panel, additionally, have the capability of recording and

controlling multiple process inputs and outputs including liquid and gas temperatures, pressures, and flow rates along with stack amperages, and cell potentials with both constant current and cell potential modes.

For this specific plant, the flow and temperature of the electrolyte was controlled and measured, along with the hydrogen gas flow, temperature, and pressure. Temperature was linked to a PID controller with a selectable set-point. Stack amperage was controlled and generated by means of a variable rectifier power supply capable of 1350 amperes, and a maximum cell potential of 10 VDC. The PLC responsible for all variable data logging and control was a Siemens S7 1200 controller making use of TIA Scada software. The software front panel is represented in Annexure I. Additionally, electrical circuit designs concerning the control panel can be referred to in Annexure F. These circuit diagrams represent plant logic control circuits, safety interlocks, and PLC interfaces for the various process parameters. The panel is designed for versatile control of any commercial scale DEFT™ for current and successive test plants.

a.



b.



Figure 4-2: (a) Exterior of the universal test panel for use of testing pilot plants with a maximum output amperage of 1150 Amperes, and (b) control circuitry within the universal test panel

4.2.2. MCE DEFT™ reactor details, and electrode materials

The MCE DEFT™ reactor makes use of forty-nine 30 mm circular electrodes yielding a total cross-sectional area of 346.36 cm². The plant is designed to operate at a nominal design current density of 3.5 A.cm⁻², therefore producing a total amperage of 1212 Amperes. This corresponds to a total

hydrogen production rate of 1.1 kg H₂ over a period of 24 hours, using faradays law as a means of a theoretical production rate calculation [64]. The initial production target for the scalable reactor pilot plants for the DEFT™ technology is aimed at achieving 1 kg H₂ over a period of 24 hours, which is near to the maximum of the production capability of the AC-DC power supply. The following diagram is a sectional view of a three-dimensional illustration of the stack:

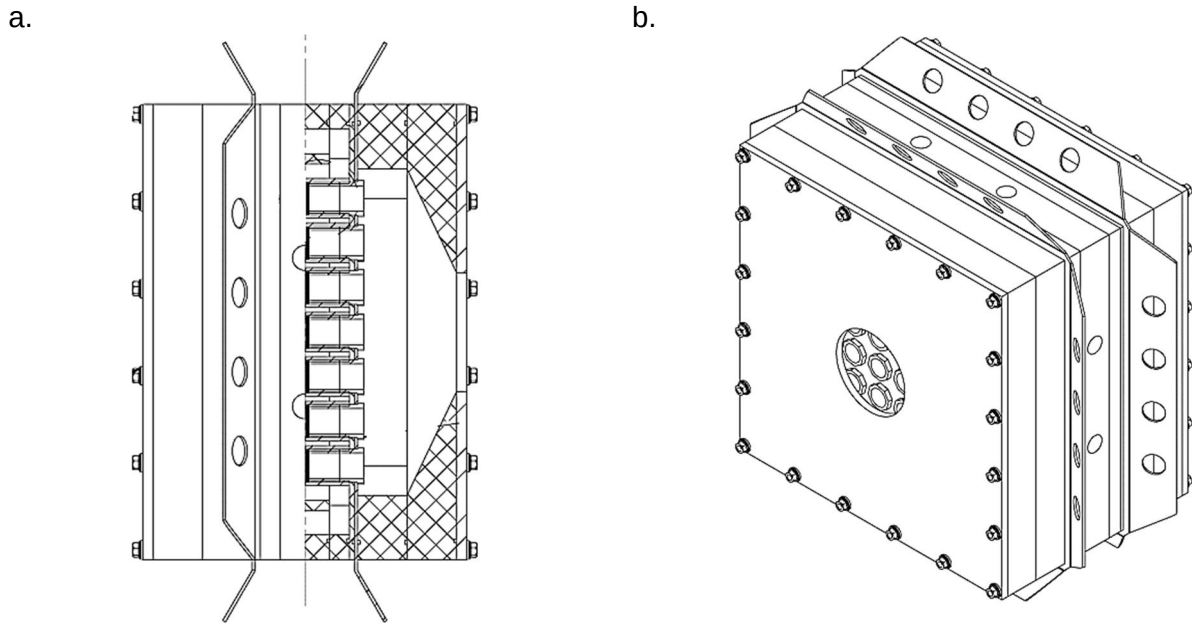


Figure 4-3: (a) Partial sectional, and (b) isometric view of the MCE stack

The stack receives electrolytic fluid from a distribution manifold, which leads into 8 inlets, of which 2 inlets are located adjacent to each other per side. The inlets open into a distribution channel designed to ensure the fluid is distributed evenly along the entire injection edge, yet in a manner that does not allow for direct injection toward the electrode gaps. Fluid has to flow around the electrode structures before entering the electrode gap. This ensures that non-uniform injection of the fluid does not occur. The following represents the configuration and fluid path within the MCE reactor:

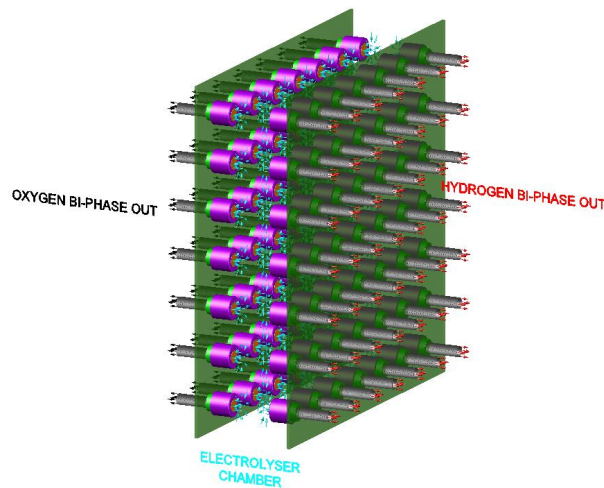


Figure 4-4: Configuration and flow of electrolyte within the MCE DEFT™ reactor

Each electrode nozzle is constructed out of a 1" BSP standard tube threaded on the inside for a partial length. It is secured to a common current plate by means of a threaded connection. The copper current distribution plate is plated with electroless nickel (A&A Plating), that provides it with corrosion protection, and has electrical connections located on the exterior of the reactor. The product bi-phase electrolyte flows from all of the cathodic and anodic electrodes, and enter a common collection chamber separately on either side of the reactor. A purge port located on the top of each of these chambers ensures that the collected gas bubbles have a means of escaping the reactor.

The electrodes themselves are made of stainless steel 316 dutch weave filtration mesh with a nominal retention rating of 80 μm (Merco Industries). The mesh is secured within each electrode housing by means of a securing ring. The outside of each electrode housing has been coated by an epoxy resin to ensure that the reaction only takes place on the desired areas.

4.2.3. Computation Fluid Dynamics for the MCE DEFT™ reactor

The nature of the arrangement for each of the circular electrode housings required an intuitive look into the Computational Fluid Dynamics (CFD) of the reactor, to ensure that all parameters are optimised, so that each electrode obtains a uniform and distributed flow quantity of electrolytic solution. A number of detailed simulations were run to determine the optimal attributes for the reactor. It was found that a number of flow issues occurred relating to the presence of eddy

currents (turbulence) and pressure concentrations. The following topics were investigated to ascertain the most optimal design, at the lowest flow velocity possible, to ensure balanced flow:

- (i) electrolytic inlet locations and number of inlets,
- (ii) flow manipulation within the inlet chamber,
- (iii) injection chamber geometry,
- (iv) bi-phase collection chamber dimensions and shape, and
- (v) bi-phase outlet diameter sizes.

For each of the simulations, inlet velocities for the model were calculated on the total volumetric flow required for a minimum flow velocity of 0.05 m.s^{-1} in order to generate a scenario with worst case conditions. A K-epsilon turbulence model was inputted to model the effects of turbulence within the reactor. Newtonian fluid characteristics were selected for a 30% potassium hydroxide solution at 60°C . Modelling was performed on Ansys Fluent.

The following aspects were tested by altering the boundary conditions and model geometry of the MCE DEFT™ stack:

Inlet chamber:

This refers to the geometry responsible for distributing the electrolytic flow in a manner so that all electrodes receive a non-preferential flow distribution. Two aspects were examined here, namely, parallel entry and side entry:

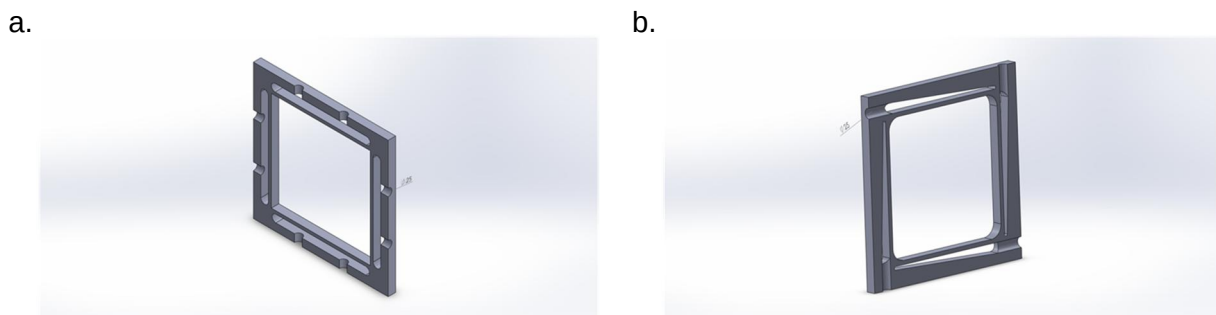


Figure 4-5: (a) Parallel entry, and (b) side entry sectional representations of the fluid introduction plate zone

The benefit of using a side entry into a tapered distribution channel, is the possibility of having less inlets. Various radii were tested for the termination of the side entry channel to maintain an equal pressure along the flow path. It was found that the parallel entry of fluid, by means of eight injection points (two on each side), yielded improved fluid distribution behaviour.

Fluid chamber spacer:

The fluid chamber is the internal boundary wall creating the void around all electrode housing structures. One aspect was examined here, by noting whether the fluid turbulence would be benefitted, by adding a significant radius to the internal corners of the spacer plate. It was found by eliminating sharp corners within the model, a reduction in the occurrence of turbulent behaviour. The fluid chamber spacer was subsequently modified to facilitate the observed behaviour.

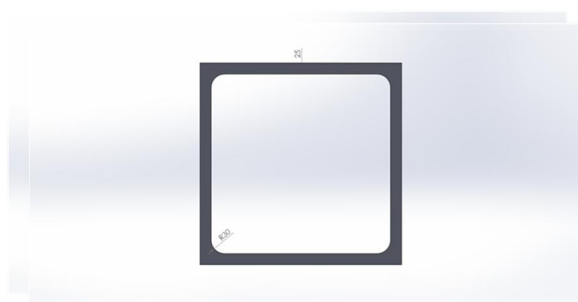
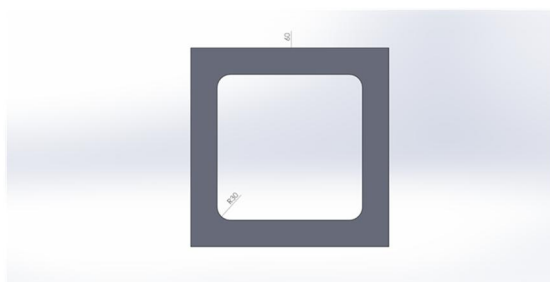


Figure 4-6: Fluid chamber spacer plate with significant radii for all previously sharp corners

Bi-phase collection chamber:

Once the electrolytic solution has passed through the electrode housing structure, it passes into a common fluid collection region, referred to as the bi-phase collection chamber. This region was previously modelled as an orthogonal structure for the ease of construction. During simulation it was observed that circulating eddy currents within the chamber was affecting the equal distribution of solution flow through each of the electrode housings. The chamber was therefore re-modelled to represent a gradual decreasing volume void free of sharp edges to draw fluid from all housing outlets uniformly.

a.



b.

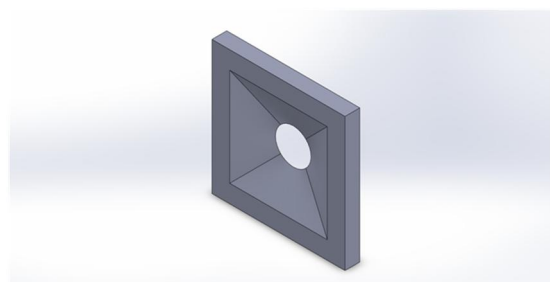


Figure 4-7: (a) Initial electrode collection void, and (b) gradual reducing area gas collection chamber for the MCE stack

Outer collection plate outlet diameter:

A stainless steel plate located on the outside of the bi-phase collection plate is responsible for taking the combined flow to the gas/liquid separators. It was investigated whether or not a reducer should be used to gradually constrict the flow area beyond that of the bi-phase collection chamber, or if a direct restricted outlet would be sufficient. A larger outlet was found to improve the collection distribution from all electrode housing outlets, and it was therefore decided to incorporate a gradually reducing flanged outlet before the terminating stainless steel plate, that is used for tensioning the assembly.

The following illustrations present the differences in the flow velocity contours that compare the originally proposed design (Figure 4-8a & b), and the improved design (Figure 4-8c & d), as concluded by CFD simulations performed:

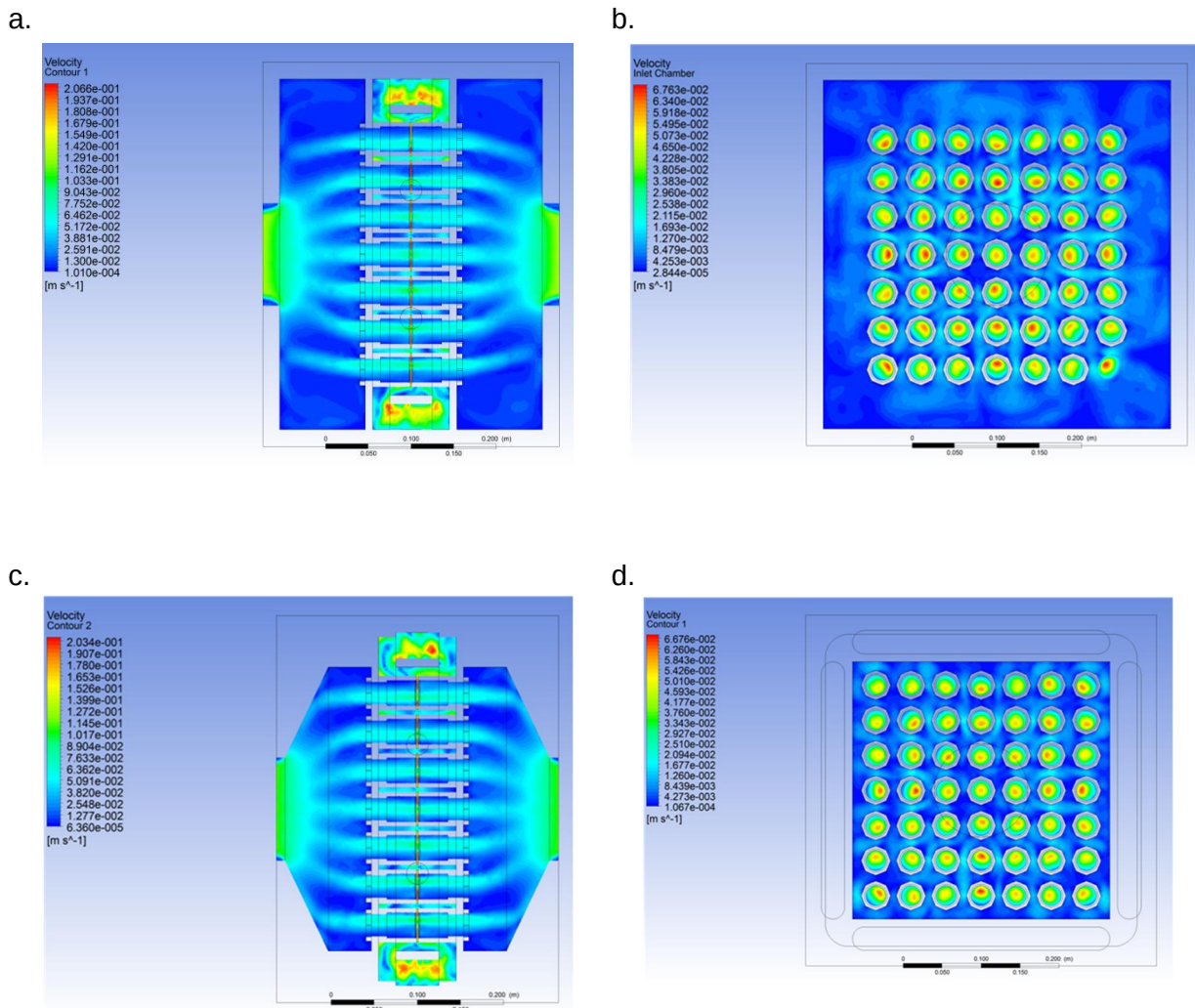


Figure 4-8: (a) Central sectional velocity contour view of the original design, (b) frontal electrode velocity contour view of the original design, (c) central sectional velocity contour view of the CFD optimised design, and (d) frontal electrode velocity contour view of the CFD optimised design

Previously, with the original design, it was observed that the outer electrodes experienced the lowest flow velocity output, with the flow localised to the internal facing regions of the electrolyser (Figure 4-8a & b). By implementing a gradual decreasing area for the bi-phase collection void, the collection of fluid from the outer most electrodes were greatly improved for the stack (Figure 4-8c & d). It is, however, observed that the flow velocity contours are still favoured toward the centre of the stack, which suggests an uneven velocity distribution for the outer electrodes.

4.2.4. Gas/liquid separation system for the MCE stack pilot plant

A horizontal gas/liquid separator was designed for the purpose of extracting micro-bubbles from the oxygen and hydrogen flow circuits. These separators were orientated in the horizontal position to maximise contact area with the gas above the liquid. Baffles and filters were inserted in the design for the purpose of trapping or coalescing gas bubbles as they passed through the medium. The baffles additionally aided in creating a circulation that prolonged the residence time of fluid within the separator, and maximised the use of the available volume within the separator. The following objectives were needed to be met by a successful gas/liquid separation system:

- (i) a compact system able to achieve a high degree of separation efficiency,
- (ii) no re-entrainment of product gas back into the solution brought about by turbulent eddy currents,
- (iii) high separation efficiencies at high solution throughputs with a large turn-down ratio, and
- (iv) no-incidence of atmospheric contaminants introduced into the separation system.

The conventional alkaline systems make use of a horizontal gravitation gas/liquid separation system positioned above the stacks, so that gasses always move up with natural buoyancy under the influence of gravity. The flow of solution through the system is relatively small, and therefore these systems are quite compact for the quantities of gasses that they extract [16,32].

The vessel sizing basis is different for the removal of a gas from a liquid in the manner that the vessel size depends on the bubble rise velocity [65]. Slettebø (2009) examined the separation of gases from liquids in viscous systems, and therefore a number of methods were presented for determining the rise velocity of a gaseous bubble through a solution [65].

Although the practical application of bubbles in motion within a solution is related to bubble swarms, it is important to understand the motion of a single bubble through a stagnant solution. A bubble will rise through a solution due to density differences as illustrated in the following diagram:

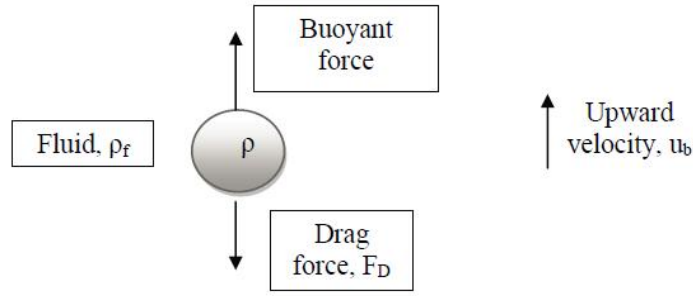


Figure 4-9: Single bubble bubble force balance theory [65]

The rise velocity is generally dictated by the net difference between the buoyant force and the drag force. The drag force will be the main function of the relative bubble size and the solution properties, for example, a bubble is considered to have a larger rise velocity in a solution that is less viscous in nature. Generally, this drag consideration is closely linked with the developed rise velocity, and from Stettebø (2009) it was chosen to consider two correlations that take into account the entire Reynolds number range for bubbles of any shape [65].

Terminal rise velocity is approximated using the following equation:

$$u_t = \sqrt{\frac{4gd_e}{3C_D} \frac{\rho_f - \rho_b}{\rho_f}} \dots \dots \dots (16)$$

Where, u_t (m.s^{-1}) is the terminal rise velocity, g (m.s^{-2}) is the gravitational acceleration constant, d_e (mm) is the equivalent bubble diameter, C_D is the drag co-efficient, ρ_f (kg.m^{-3}) is the density of the fluid, and ρ_b (kg.m^{-3}) is the density of the bubble. The drag co-efficient (C_D) can be determined accurately by taking into account real behavioural aspects of bubbles in a viscous solution by reference of two methods, namely the Karamanev method and the Bozzano and Dente method [65]. The breakdown explanation of these methods is found in Annexure H.

By injecting a volumetric quantity of gas, with bubble size classification as represented in Figure 4-10, and applying the described equation methods, theoretical separator efficiencies can be determined from a range of pre-selected separator sizes. This is determined by identifying whether or not the rise velocity would allow for a bubble to be liberated, during the allocated residence time that the bubble is entrained within the separator fluid, before being recycled to the reactor.

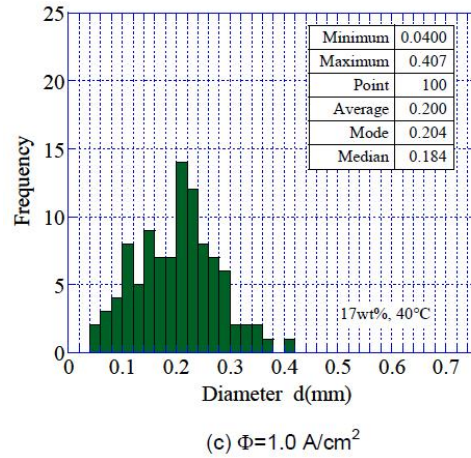


Figure 4-10: Expected bubble size distribution that can be expected from a stationary alkaline electrolysis system operating at a current density of 1 A/cm^2 [26]

From the results it was found that a separator, having dimensions of 1000 mm x 255 mm, would provide a separation efficiency of 95%. Therefore, with the addition of a pre-separation step, a greater efficiency should be achieved.

Based on this theoretically determined separator capacity, CFD simulations were performed to create a design that would utilise the maximum available flow volume with limited turbulence. The CFD examined the following parameters in order to determine the ideal design:

- (i) inlet/outlet positions and tapered designs,
- (ii) inclined baffle plates, baffle plate heights and curvatures for internal flow distribution, and
- (iii) packing media for gas coalescence and flow distribution.

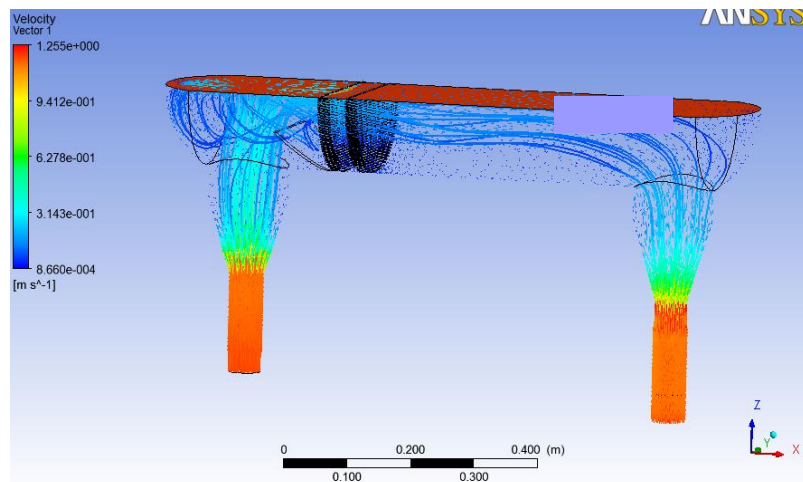


Figure 4-11: Optimal computational fluid dynamics design for the horizontal gas/liquid separator

By introducing an inclined baffled plate, it was found that initial turbulence was reduced substantially, with packing media increasing the back pressure for the fluid, which improved fluid distribution. Tapered inlets and outlets additionally improved the fluid introduction and collection flows to maximise the use of the separation volumes.

4.2.5. Variables to be tested

The major objective of this test plant is to establish the scalability of the DEFT™ electrolysis technology by introducing numerous circular electrode housings into a common pressure chamber. This serves to provide a more intuitive feel for the basic design criteria that will allow for scalable hydrogen production. Yet again, tests were run for set experimental conditions and were repeated three times in order to determine the error within experimental values in order to assess accuracy and repeatability. A total time duration of at least 10 minutes was provided for the system to reach steady state at set conditions. A similar method was employed throughout the research.

Standard Parameter Comparison Experiments

Utilising optimal parameters deduced from earlier investigations, stainless steel will be used as the ideal material to produce comparison results to stainless steel results achieved with the optimised concept stack. Results will yet again be recorded as a function of increasing temperature. A maximum temperature of 60°C is attainable by this test rig, due to the nature of materials of construction, and maximum heating capacity by the heating system. In terms of the flow velocity, the maximum value was previously intended to be 0.075 m.s⁻¹, however, the effectiveness of the gas/liquid separation system will be ascertained when testing commences. Basic gas purity analysis will be performed together with observations, to ascertain the effectiveness of the gas/liquid separation system with a handheld Oxycheq electrochemical cell.

It is well known that the smaller the electrode gap between electrodes, the higher the efficiency of an electrolyser set-up, and therefore the optimally deduced electrode gap of 2.5 mm will be tested [31]. The expected trends are all well known for the above parameters, therefore these tests will aid in quantifying the specific performance implications for the DEFT™ technology.

4.3 RESULTS AND DISCUSSION

4.3.1. Comparison of the MCE stack to the DEFT™ concept optimisation test rig

Prior tests utilising the DEFT™ concept optimisation test rig was conducted in a manner so as to obtain performance data pertaining to the filter mesh electrodes in isolation. The MCE DEFT™ test plant's electrodes only make use of an insulating layer on the exterior surface, and to that regard all interior surfaces are exposed to the electrolytic solution. It has been shown that the water electrolysis reaction is capable of reacting past catalyst surfaces within close proximity to each other, although to a lesser extent [49]. This does have an impact on the calculation method of current density, since current density is calculated based on the exposed cross-sectional area of the electrode. As a result, it is expected that current densities obtained for the MCE stack will be greater than results achieved by the DEFT™ concept optimisation test rig, due to the interior metallic surfaces of the MCE stack electrodes being exposed to electrolyte, as is not the case for the DEFT™ concept optimisation test rig.

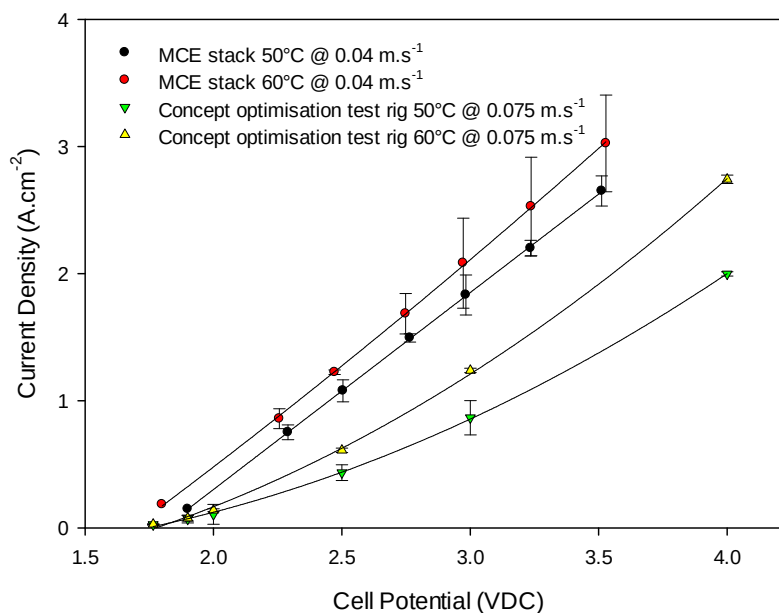


Figure 4-12: Polarisation curves for the polypropylene DEFT™ concept optimisation test rig as a function of temperature, at a flow velocity of 0.075 m.s⁻¹, versus the MCE DEFT™ stack, as a function of temperature, at a flow velocity of 0.04 m.s⁻¹, and 30% KOH

Figure 4-12 portrays the relationship between current density and cell potential for the MCE stack, compared to the DEFT™ concept optimisation test rig. The improvement in current density

observed for the MCE stack was, as already mentioned, due to the additional surface area provided by the three-dimensional electrode housing's conductive internals, which were not coated by a non-conductive material as in the case of the DEFT™ concept optimisation test rig. This was obtained with a maximum flow velocity of 0.04 m.s^{-1} , and improvements would be more significant if greater flow velocities were possible. The plant used to test the MCE stack was not capable of processing fluid flows greater than 0.04 m.s^{-1} , due to the high incidence of gas re-entrainment back into the reactor as a result of the gas/liquid separators not operating effectively (Figure 4-13). Theoretical calculations therefore did not accurately determine the settling velocity of bubbles as turbulence and solution properties cannot be accurately taken into account. Produced product bubbles may well be significantly smaller than the experimentally deduced bubble diameters illustrated in Figure 4-10. Separator levels are also dependant on the pressure drops in each of the product gas collection circuits, and therefore a number of factors can cause this to change resulting in an imbalance of flows from each separation circuit.

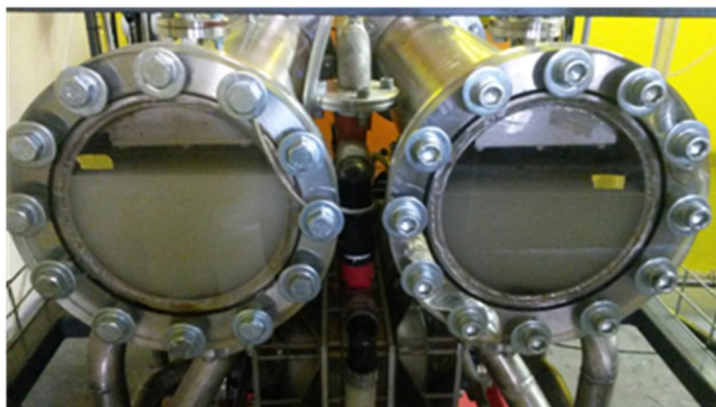


Figure 4-13: 'Milky' appearance of the liquid electrolyte at 40°C , and a flow velocity exceeding 0.04 m.s^{-1} attributing to re-entrainment of product gases

Horizontal gas/liquid separators are superior, for this application over submerged vertical gas liquid separators in theory, as there is more contact area between the gas and liquid phases along with the settling path for gas bubbles which is shorter, and in the opposite direction to gravity, allowing gas bubbles to settle easily out of solution. The gas/liquid separators are similarly proportioned in comparison to the reactor, as found in existing commercial alkaline electrolysis plants (Figure 4-14), however, they have been found to be ineffective at the high flows required for gas liberation from the solution, and therefore an optimised solution for the gas/liquid separation is therefore required [16].

a.



b.



Figure 4-14: (a) Horizontal gas/liquid separator scale for the MCE plant in relation to the balance of plant, and (b) MCE plant gas/liquid separation system

4.3.2. Comparison of temperature and flow velocity on stack performance for the MCE reactor

The polarisation curves generated for this initial commercially scaled stack are based on stainless steel electrodes, and are all linear in profile (Figure 4-15). In the case of the concept optimisation test rig, deactivation of the stainless steel electrodes was observed. However, for the MCE plant no significant reduction in performance was observed. This is likely due to the significant internal area available for reaction with regard to the MCE stack. Any reduction in reaction intensity in certain areas of the electrode is compensated for by the additional available area for reaction. The increase in performance with temperature can be seen clearly with equal percentage increases across the cell performance range.

At the optimal maximum temperature of 60 °C, flow velocity of 0.04 m.s⁻¹, and cell potential of 1.8 VDC, a current density of 0.184 A.cm⁻² was recorded. This is significantly larger compared to the previous result achieved by the concept optimisation test rig at 1.8 VDC, flow velocity of 0.075 m.s⁻¹, and 60°C, with the current density amounting to only 0.0348 A.cm⁻² (Figure 4-15). The benefit of additional reactive area, aside from the mesh electrodes themselves, demonstrates the additional performance that can be achieved by the same volumetric flow of electrolyte. By maximising the conversion of water to gas per unit volume flow, is key to maximising the DEFT™ technologies performance as this will serve to reduce parasitic loads in future plant and stack designs.

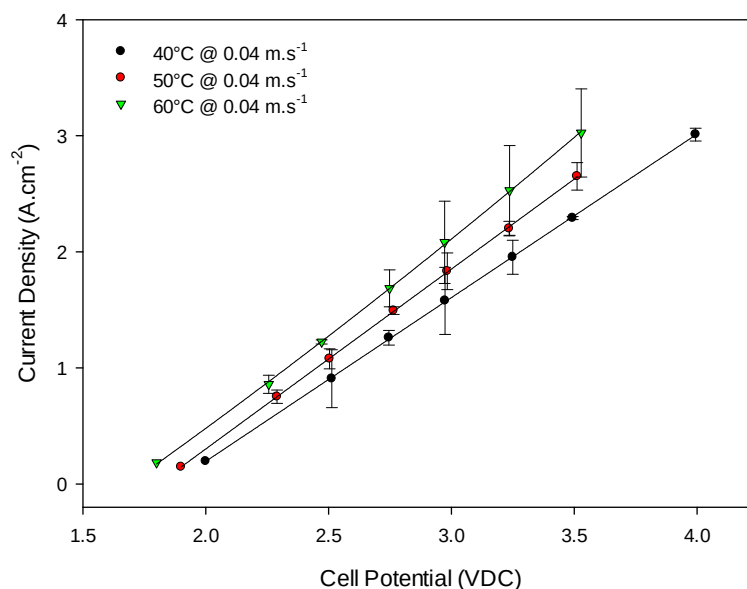


Figure 4-15: Polarisation curve for the MCE stack as a function of temperature, at a constant flow velocity of 0.04 m.s^{-1} , and 30% KOH

With reference to Figure 4-15 and Figure 4-16, the benefit of increasing the temperature by 10°C , or the electrolytic flow velocity by 0.005 m.s^{-1} seems to be limited, and only accounts for a maximum improvement in performance by $\sim 15\%$. The energy saved by this increase in performance would not account for the energy spent in pumping, or in additional heating when utilising stainless steel as the electrode material of choice. Stainless steel primarily is used on large AWE systems operating at low current densities ($0.3 - 0.4 \text{ A.cm}^{-2}$) as a cost-effective solution to reduce the cost of producing these large stacks [22]. It has been found that stainless steel lacks longevity of performance, and integrity at high temperatures and high alkaline solution concentrations, especially if it is used as current collectors [30]. Modern alkaline electrolyzers utilise electrodes composed of nickel, cobalt, and various non-noble metal oxides, with some noble metal species used in cases to boost operating current densities and efficiencies [21]. For this reason, catalyst choices for the DEFT™ electrolyzers will no longer employ the use of stainless steel 316 going forward.

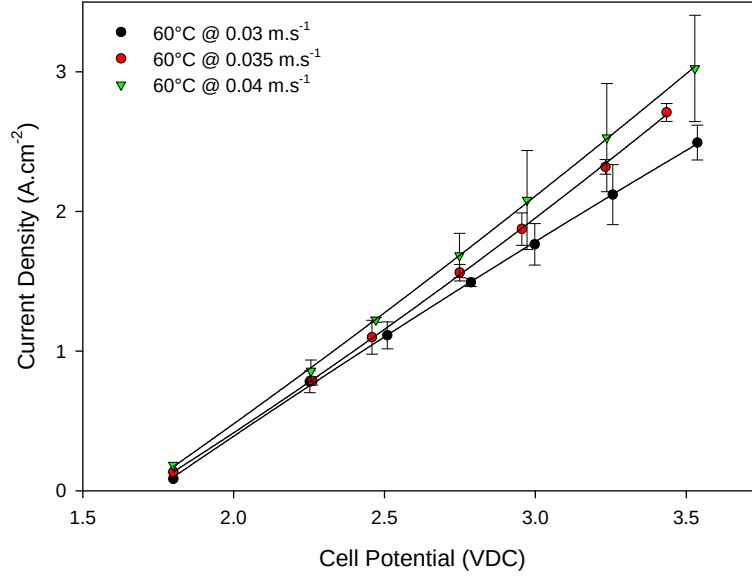


Figure 4-16: Polarisation curve for the MCE stack as a function of flow velocity, at a constant temperature of 60°C, and 30% KOH

4.3.3. HHV% efficiency for the MCE stack utilising stainless steel 316 electrodes

The HHV% efficiency has been determined by measuring the voltage and amperage outputs to various plant components from the main control panel. A modification of Equation 15 (page 33), provides a real indication into the higher heating value (HHV) efficiency for the plant at various operating conditions, referenced to the theoretically determined hydrogen production rate determined by Equation 4 (page 13) [66]. The higher heating value of efficiency is represented as follows [22]:

$$\eta_{overall} = \frac{\dot{N}_{H_2HHV}}{E + Q_{cell} + W} \dots \dots \dots (17)$$

Where, $\dot{N}_{H_2HHV}$ (kWh) is the theoretical energy contained in the produced hydrogen flow rate reference to the higher heating value of hydrogen, E (kWh) is the electrical energy consumed by the stack, Q_{cell} (kWh) is the nett heat consumed by the system, and W (kWh) is the energy demand of the circulation pump.

In the determination of the HHV% efficiency using equation 17, the total work contribution is taken as the combination of energy used by the pump and by the stack, which accounts for the majority

of the energy consumption. Energy used by the heating elements is never constant, and would create bias in recorded results with the assumption that a properly designed plant would only require heating upon start up, and would self-sustain its own temperature, based on the heat energy output operating above the thermo-neutral voltage [22]. Figure 4-17 illustrates that optimal HHV% efficiency obtained for the stainless steel electrodes was 28.94% at an operating cell potential of 3 VDC. This is achieved at the lowest flow velocity (0.03 m.s^{-1}) as the energy consumption by the pump, must be minimised to achieve greater efficiencies that are comparable to commercialised small scale AWE's. The shape of the efficiency curve explains why it would be redundant operating beyond a certain cell potential, as efficiencies would become severely hampered by degradation of the electrodes over time, which would affect long term performance specifically at elevated current densities [35].

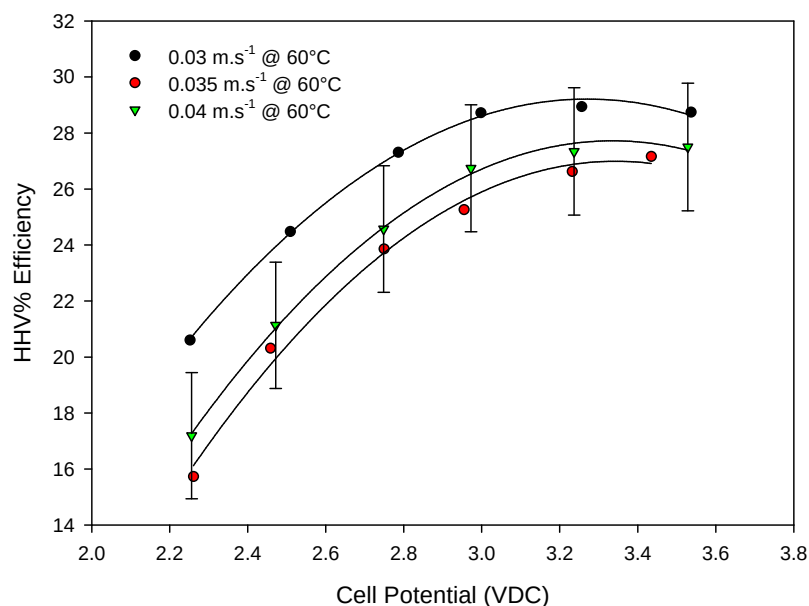


Figure 4-17: HHV% efficiency versus the operating cell potential for the MCE stack, as a function of flow velocity, at 60°C, and 30% KOH

4.3.4. Measure hydrogen gas purities

Hydrogen gas purities were measured as a function of flow velocity at the maximum electrolytic temperature of 60°C.

Table 4-1: Hydrogen gas purities measured at 60°C as a function of flow velocity

0.03 m.s^{-1}			0.035 m.s^{-1}		
Stack Voltage (VDC)	Current Density (A/cm^2)	Hydrogen Purity (vol%)	Stack Voltage (VDC)	Current Density (A/cm^2)	Hydrogen Purity (vol%)
2.249	0.765	84.533	2.265	0.892	86.067
2.518	1.190	85.067	2.507	1.268	85.433
2.771	1.533	84.567	2.756	1.619	84.333
3.031	1.882	84.500	3.021	2.023	84.533
3.253	2.207	85.033	3.249	2.351	85.433
3.509	2.594	85.067	3.503	2.729	86.067

0.04 m.s^{-1}		
Stack Voltage (VDC)	Current Density (A/cm^2)	Hydrogen Purity (vol%)
2.282	0.923	83.100
2.506	1.331	82.233
2.768	1.790	81.033
3.002	2.234	79.633
3.258	2.645	79.767
3.497	3.144	80.467

Table 4-1 refers to an increase in gas purity moving from $0.03 - 0.035 \text{ m.s}^{-1}$, however, degradation is observed at 0.04 m.s^{-1} , indicating a failure of the gas/liquid separation mechanism as the liquid throughput is too high to be processed efficiently. No specific trends are demonstrated between current density and gas purity, as gas purities tend to be around a constant level. The maximum gas purity amounts to 86 vol% at a flow velocity of 0.035 m.s^{-1} . It is evident that the stack itself is responsible for cross gas mixing, and therefore a multi-electrode approach sharing a common injection chamber, does not allow for an adequate separation mechanism at all electrode pairs as suggested by the CFD modelling.

4.4 CONCLUSION

The MCE DEFT™ stack was designed as an initial attempt to scale the DEFT™ technology to achieve enhanced gas production outputs. A number of significant issues were identified regarding the operation of the MCE DEFT™ electrolysis stack, and associated horizontal gas/liquid separation systems. In future plant designs, it will be attempted to address these issues with a multitude of solutions. A number of parameters were tested with the use of stainless steel 316 electrodes. It was shown that the performance of stainless steel used in these experiments produced greater current densities across the board in contrast to prior tests performed with stainless steel.

The uniqueness of the DEFT™ principle implies that a unique separation solution needs to be developed / sourced to ensure the successful removal of micro-bubbles from the electrolytic solution. Residence times were shown to be insufficient due to calculated separator sizes not taking into account variables such as turbulent solution flow and inaccurate bubble size classifications. This resulted in substantial re-entrainment of gases into the flowing electrolytic solution, creating cross gas contamination within the electrolyser.

The electrolyser design in addition was found to have a number of inconsistencies, as not all of the electrode pairs were observed to receive an equal amount of fluid. Though it was indicated by the CFD simulation output that the design would allow for relative equal solution distribution amongst electrodes, this was not emulated in practice. Subsequently, significant off-gas was observed in the central injection chamber. A more practical method is required to provide all electrodes with an equal volumetric quantity of solution.

The maximum efficiency obtained, with the current set-up of plant, was 28.94 HHV%, which is significantly lower than the efficiency goal for small commercial electrolysers, that is listed between 43 – 52 HHV% [1]. Hydrogen product gas qualities are in addition not equating to typical gas qualities expected from small alkaline systems, with the maximum purity recorded at only 86.07 vol%. Alternate stack designs and catalysts will be investigated to achieve the desired targets for both efficiency and gas quality.

The DEFT™ concept optimisation test rig differed in design to the MCE stack, since substantially more electrodes were installed into a common pressure chamber in the case of the MCE stack. It is more practical to have a single module capable of enhanced gas production in contrast to numerous lower production modules coupled in series or parallel. Liquid distribution was, however, more balanced and uniform for a lower number of electrodes in a pressurised chamber. Inconsistencies in flow increase caused by the addition of more electrodes, makes the MCE stack approach not viable for scaled hydrogen production.

Take-home observation(s):

- (i) Horizontal separation systems have been shown to be ineffective due to the lack of contact area, between gas and liquid, and sufficient filtration media to coalesce micro bubbles,
- (ii) Additional conductive surfaces, aside from the electrodes themselves, have shown promise in maximising cell performances,
- (iii) The incorporation of multiple electrodes fed from a single pressurised solution chamber is impractical at achieving balanced flow amongst all electrodes,

- (iv) Computation fluid dynamics modelling and theoretical calculations does not always show a direct correlation to what is observed in practice.

5. HORIZONTAL FILTER PRESS (HFP) DEFT™ COMPACT REACTOR

5.1 OVERVIEW

This chapter is based on a full-length article that has been published in *Journal of Power Sources* [17] (article abstract can be made reference to in Annexure K). During the investigation of the MCE stack it was observed that there was not an equal distribution of electrolytic solution amongst all electrodes. Rectifying this, would create uniform solution distribution along the electrode surface, which would enable a compact design. To that regard a filter press stack configuration was designed and constructed, that utilised elongated mesh electrodes with a limited flow path terminating in a flow barrier. This design would serve to feed each electrode pair independently, in contrast to the MCE design, where a multitude of electrodes obtained their flow from a common pressurised chamber. It is understood that the flow is only capable of entering the electrode gap from a single injection slot. The intention of this new design is to test the concept of employing a filter press design, as a means of providing a compact reactor for elevated hydrogen production.

The design housed 4 electrode pairs that was tested in a plant that initially made use of two cyclonic vacuum separators (sourced from DynaFLOW Inc.). However, these had to be altered to incorporate two smaller post-separation gravity separators. The basis of the design was, again, based on previous findings related to optimal parameters, however, a great deviation in the stack configuration was attempted as circular electrodes, and circumferential flow were not implemented.

Basic gas purity analysis was conducted together with the performance and long term stability evaluations of a number of popular catalysts employed in the electrolysis industry, for both AWE and PEM electrolyzers. A third stage of gas/liquid separation was employed in the form of a sump that formed part of the post separation system, to ensure that the recycled electrolyte was fully liberated from entrained product gas bubbles. An adequate indication of product gas quality could therefore be obtained for the separation mechanism at the reactor.

The same comprehensive control panel was used to control and log data variables. This Horizontal Filter Press (HFP) stack did not allow for variable geometric variables, similar to the MCE configuration, however, all performance variables could be altered to generate the necessary evaluation data.

Initial results revealed that the performance obtained from the DEFT™ concept optimisation test rig, provided superior results in contrast to that of the HFP stack, when comparing results

generated with the Ni/Ni catalytic combination. Overall, the HFP plant was capable of improving the overall HHV% efficiencies, in contrast to the MCE plant, with a NiO/Ni catalytic combination generating $\sim 0.5 \text{ A.cm}^{-2}$ at a cell potential for 2 VDC. Stability of the Ni/Ni and NiO/Ni catalytic combinations provided adequate results over a testing duration of 250 hours, however, deactivation was prevalent with regard to the MMO/Pt catalytic combination. Once again, the configuration of the HFP plant exhibited an improvement in terms of generated gas purities in contrast to the MCE plant, however, gas purities of hydrogen were in the order of $\sim 90 \text{ vol\%}$, and therefore requires additional attention.

5.2 METHODOLOGY AND APPARATUS

5.2.1. Overview

In the previous chapter it was established that the incorporation of a number of circular electrodes in a common injection chamber (the MCE plant), and using horizontal knock-out type separators, was ineffective at providing stable operating performance, and reasonable qualities of hydrogen. A deviation from the original methodology was subsequently attempted in the form of a compact stack set-up, that made use of a horizontal filter press (HFP) design incorporating elongated electrodes, to maximise the production capacity per unit volume of the stack. In addition, a mechanical method of separating the produced gas bubbles from the liquid electrolyte was attempted in the form of cyclonic vacuum separators. Figure 5-1 illustrates the process flow associated with the HFP reactor, and incorporates both the use of a separate sump and a separation system. Originally the system only had cyclonic separators installed, represented by 5 and 6 on Figure 5-1, without the need for an additional gravitational separation system represented by 7 and 8. The cyclonic separators were sourced from DynaFLOW Inc., and operated on the difference in densities of a viscous fluid and gas. A stable vortex core is formed in the centre by means of tangential injection of the bi-phase mixture. Due to the strong centrifugal forces involved, the gas tends to migrate to the centre of the cyclone liberating itself from the fluid medium, while the heavier fluid tends to form thin liquid films near the upper periphery of the cyclone [67].

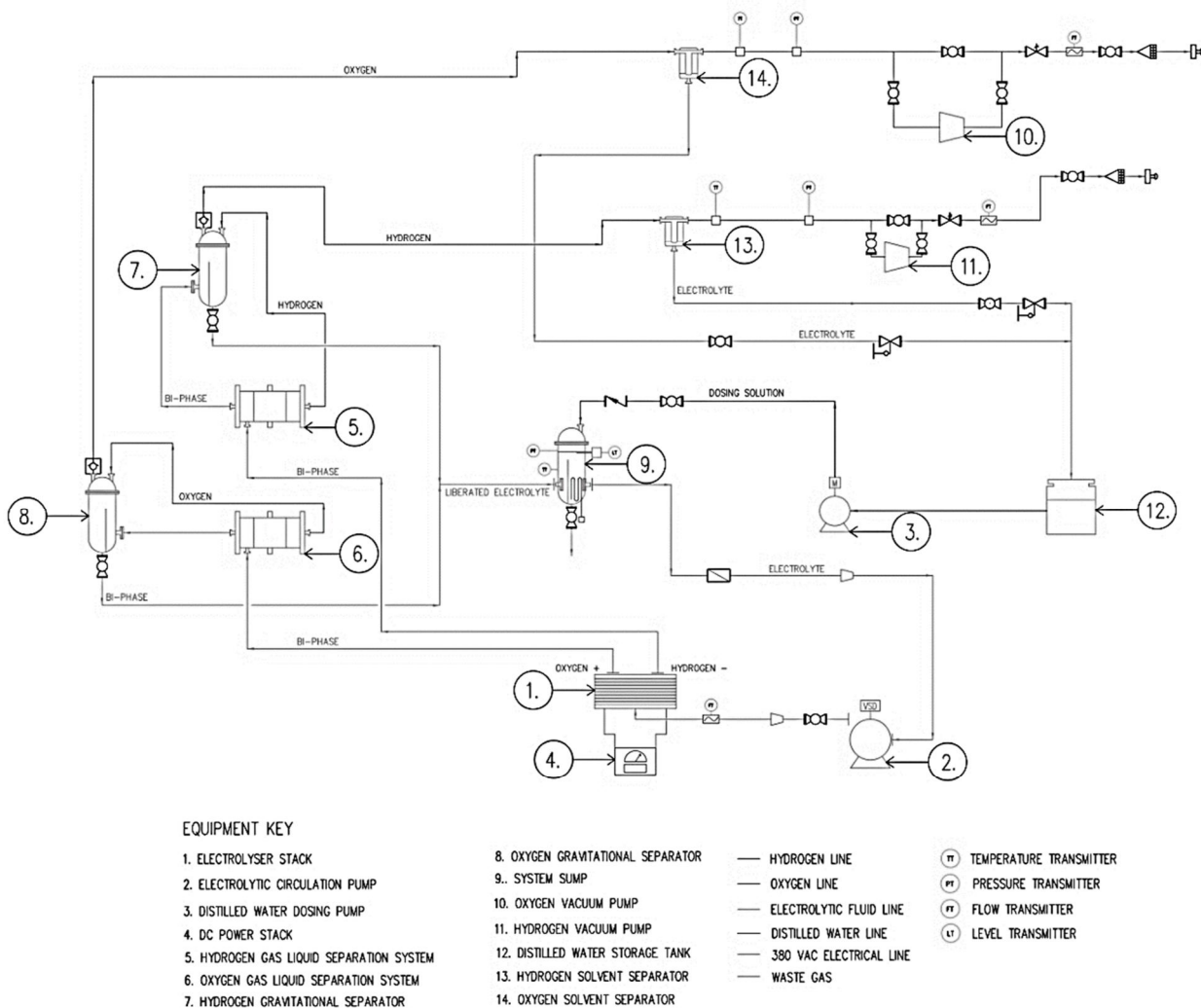


Figure 5-1: Process flow diagram for horizontal filter press (HFP) DEFT™ stack and plant

Figure 5-2 illustrates the formation of the stable gas core around a ‘gas only’ permeable membrane tube [68]. A vacuum is formed within this tube, represented by vacuum pumps (10 and 11 in Figure 5-1), thereby created a pressure difference to extract the accumulated gas into the gas extraction tubes. This set-up was altered to omit the vacuum pumps and a gravitational separation system (7 and 8 in Figure 5-1) was added. The membrane material used within these separators remains naturally hydrophobic to water, but when salt is added to the fluid medium, the membrane becomes wettable, resulting in undesirable hazardous solution moving into the gas collection tubes. A modification of the process was implemented, that initially allowed the cyclonic separators to coalesce the bubbles in the bi-phase stream, before the solution entered the gravitation separation system. Upon entering the gravitation separation system, large bubbles are able to collect in the upper hemisphere of the separator, while smaller entrained micro-bubbles are filtered and coalesced before exiting the separator. The collected gases are able to

escape the separators by means of gas purge valves, which ensures that the separators remain filled with solution at all times.



Figure 5-2: DynaFLOW Inc. separator vortex formation around the membrane tube [68]

The liberated solution combines from the separation systems, and enters the system sump (9 in Figure 5-1), which contains heating apparatus and level detection equipment. This is an additional post separation system that allows any entrained gas to collect, and be purged from the system sump. System pressure is regulated here by means of a back-pressure valve. This ensures that the system remains under pressure, and provides a driving force for the collected gases to be pushed out of the gravitational separators. The system sump is then able to automatically regulate its fluid level by means of two level probes. The low level probe initiates the dosing pump and the high level probe shuts the dosing pump off.

The solution is passed into the Horizontal Filter Press (HFP) stack by a magnetically coupled chemical circulation pump linked to a variable speed drive in the same control panel used for the MCE stack pilot plant. It is once again acknowledged that all pressures, flows, temperatures, voltages, and currents were monitored and controlled by the control panel and PLC system. Gas purity detection was once again measured by means of the handheld Oxycheq electrochemical

cell. Figure 5-3 portrays the HFP plant connected to the universal test panel (Figure 5-3a), the HFP plant itself (Figure 5-3b), and the assembled HFP reactor stack (Figure 5-3c).

a.



b.



c.



Figure 5-3: (a) HFP plant connected to the universal test panel, (b) HFP plant, and (c) assembled HFP reactor stack

5.2.2. Horizontal Filter Press (HFP) DEFT™ reactor details and electrode materials

The HFP DEFT™ reactor houses 4 pairs of 20 x 400 mm rectangular electrodes inclined in the horizontal position. When the plant operates at the intended design current density of 3.5 A.cm⁻², the stack should deliver 1120 Amperes, that relates to a total production of 1.01 kg H₂ over a period of 24 hours. Figure 5-4 illustrates the geometry and internal flow regime for a single pole pair of the horizontal filter press stack.

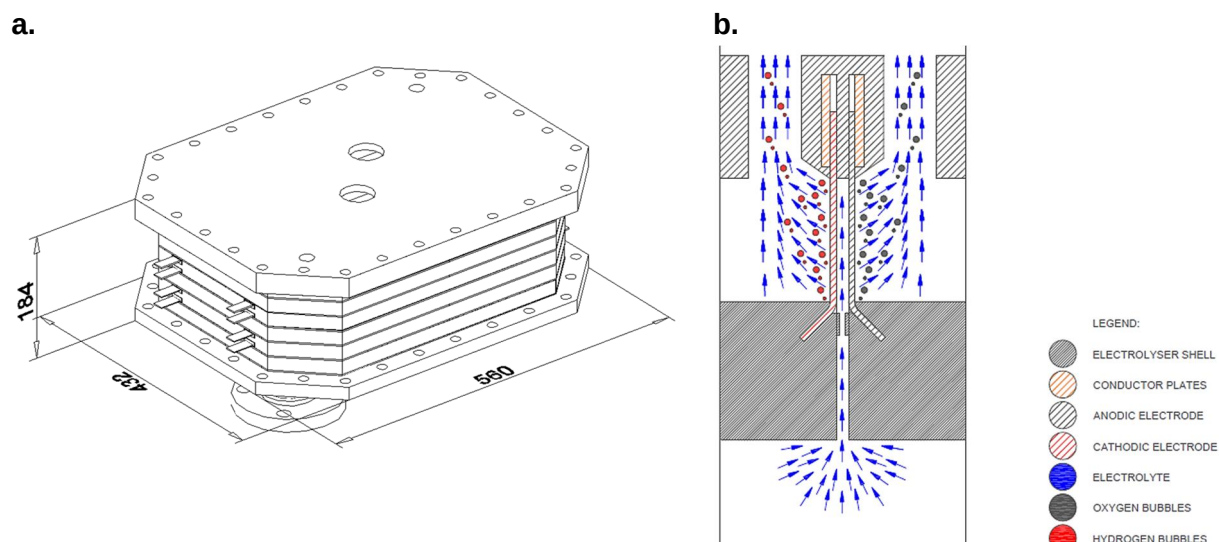


Figure 5-4: (a) Isometric view, and (b) operating principle of the HFP DEFT™ stack

With reference to Figure 5-4b, fluid moves into an injection channel that is 2 mm wide, and spans the total length of the elongated electrode. A terminating barrier is present at the end of the flow channel to build a back pressure within the electrode gap. Fluid is able to move through the porous electrodes into the bi-phase collection chamber. All common channels are re-directed to one outlet that reports to each respective cyclone separator. The electrodes themselves make a pressure contact with a bus bar that spans the entire electrode length as indicated in Figure 5-4. The deviation in operating principle can be easily distinguished from Figure 5-5.

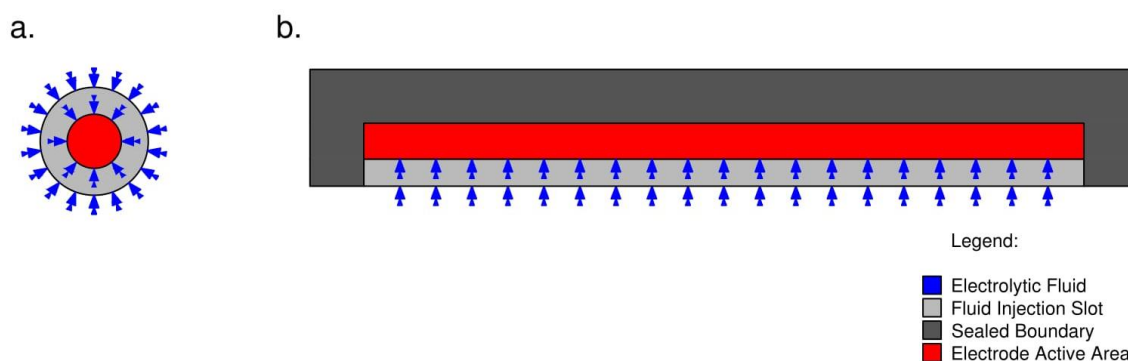


Figure 5-5: (a) Circumferential flow injection from a pressurised chamber, and (b) deviation in operating principle utilising point injection along the length of the electrode for a rectangular electrode

The electrodes tested in this reactor were industrially pure nickel (99.5% nickel) electrodes for both the anode and cathode (Hebei Nanrui Wire Mesh Company) with a nominal micron rating of 80 μm . Additionally, a second catalytic combination that comprised of geometrically similar

electrodes of stoichiometric nickel oxide (NiO) deposited onto a pure nickel substrate for the anode, paired with a pure nickel electrode as the cathode (Titanium International Fabricators (Pty) Ltd). A third test combination, that was tested in previous test plants, comprised of pure platinum plated onto nickel mesh for the cathode with the same MMO catalyst employed for the anode, which comprised of $\text{RuO}_2/\text{IrO}_2/\text{TiO}_2$ in the ratio 35:10:55 (NMT Electrodes). These three catalytic combinations were benchmarked, relative to one another to deduce, which combinations maximise plant efficiency over a variation of conditions.

5.2.3. Computational Fluid Dynamics for the HFP reactor

As the HFP stack was a deviation from the tried and tested designs investigated thus far, CFD modelling was conducted to optimise the geometry of the stack before testing commenced. As fluid would only be moving in a single direction over the electrodes, the main investigation would be to ensure that the velocity and pressures are as uniform as possible across the surface of the mesh. This should ensure that all gases are effectively removed from the electrode surface, which would imply that the reaction takes place as uniformly as possible. The following geometric parameters were investigated to obtain an optimised geometric design by investigating both the pressure drop in specific regions and the flow velocity contours:

- (i) research into the optimised mesh pore rating,
- (ii) flow path length, and
- (iii) collector chamber depth.

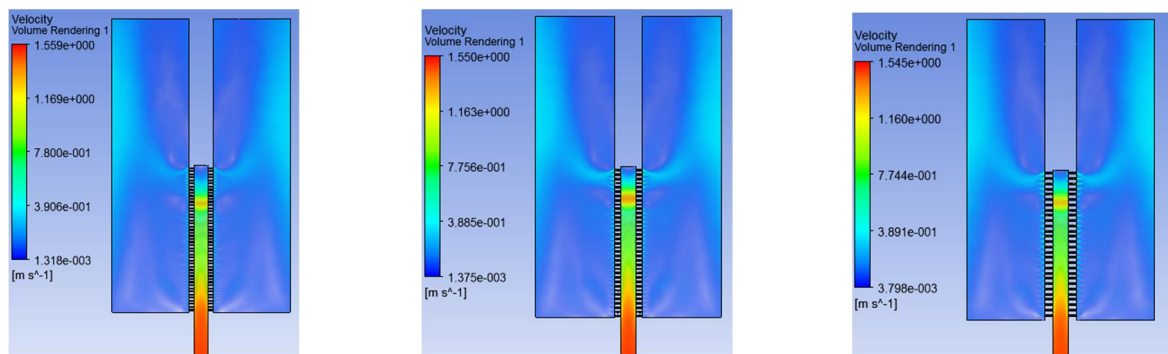
Once again, inlet velocities for the model were calculated on the total volumetric flow required for an optimal flow velocity of 0.075 m.s^{-1} . A K-epsilon turbulence model was inputted to model the effects of turbulence within the reactor. Newtonian fluid characteristics were selected for a 30% potassium hydroxide solution at 60°C , with modelling performed on Ansys Fluent.

Optimal pore rating as a function of flow velocity across a 20 mm flow path

The initial non-optimised stack geometry was utilised to deduce what the optimal mesh micron rating would be for the HFP DEFT™ stack. The requirement was to examine the average flow velocity moving through the mesh material in three divisions of the flow path, namely the lower third, the middle third, and the upper third sections. A flow path of 20 mm was chosen since the flow path of a 30 mm circular electrode would effectively be in the region of 15 mm. This value

was rounded to 20 mm, as the exposed effective electrode area would be further maximised, which would result in a more competitive ratio of gas production per unit volume of stack. The goal would be to ensure that flow exiting the mesh would be as uniform as possible, and that the terminating pressure would be as large as possible to ensure adequate back pressure towards the injection slot, in order to create the uniform flow. The illustrations (Figure 5-6) show the flow velocity profiles and pressure profiles of the mesh options in order of increasing mesh size, from 125 μm absolute micron rating, which represents the base case mesh, and moving to larger available standard mesh sizes:

a.

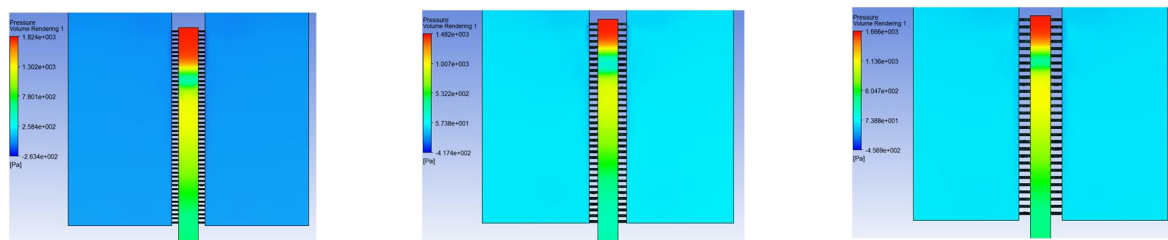


125 μm (Base Case)

200 μm

250 μm

b.



125 μm (Base Case)

200 μm

250 μm

Figure 5-6: (a) Flow velocity profiles, and (b) pressure profiles emanating from a mesh as a function of pore size, for a 2 mm electrode gap, and 30 mm flow path

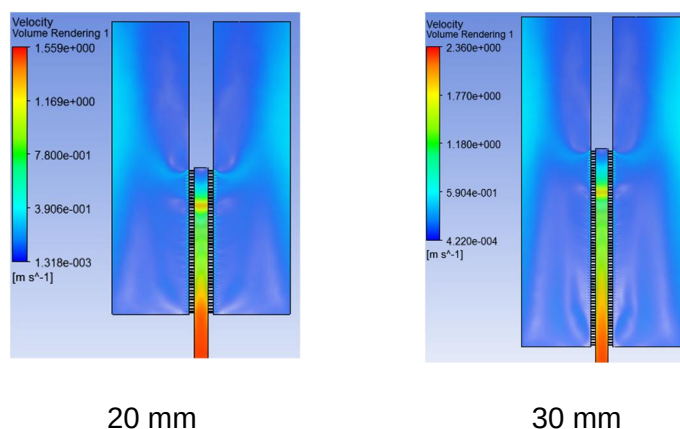
Figure 5-6b illustrates the development of a high pressure region at the terminating region of the flow path. A larger pressure region is developed for the 125 μm mesh in contrast to the larger pore mesh sizes with a moderate pressure region extending back from the high pressure region

toward the inlet. The back pressure is therefore expected to be of greater magnitude, and as a result the flow of electrolyte through the pores should be more uniform for the base case mesh. From Figure 5-6a, all velocity profiles seem to be similar, however, it is observed that only the base case mesh has the minimum amount of fluid emanating from the terminating point of the electrode gap. Conversely, the larger mesh sizes show that the majority of the fluid escapes near the termination where the pressure is largest. A finer mesh, therefore, allows for improved fluid distribution, however, it is important not to use a mesh that is too fine as the bubbles will not be able to penetrate, and will remain within the electrode gap region.

Flow path optimisation

As the CFD revealed, the base case mesh is a better option to ensure equal solution flow occurs across the entire electrode surface, and not isolated in the upper regions of the electrodes. It was investigated whether the solution path, greater than 20 mm, was feasible to maximise the effective area for reaction. A dimension of 30 mm was chosen, as an additional 5 mm increase would constitute too small an increase to show an observable difference between CFD models. Again, flow velocities were inputted into the model to achieve an average cross-sectional flow velocity of 0.075 m.s^{-1} through the electrode face.

a.



b.

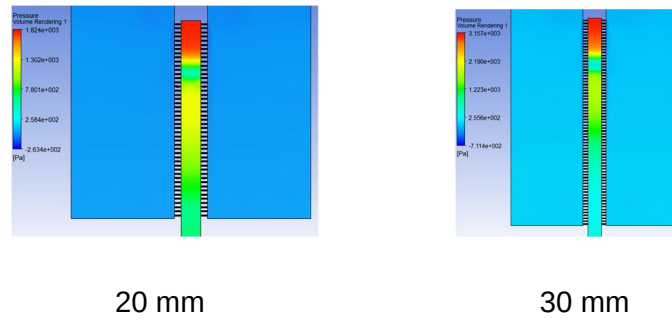


Figure 5-7: (a) velocity flow profile, and (b) pressure profile comparison for a 125 μm mesh and 2 mm electrode gap as a function of flow path length

Figure 5-7 illustrates the issues behind extending the fluid flow path past the set limit of 20 mm. The pressure profile does not extend uniformly along the flow path from the high pressure region. There are consequently areas on the mesh surface that are not under constant back pressure. Those areas, not under pressure, would likely have a lack of flow as illustrated in the velocity profile for the 30 mm flow path. It can be seen the contours emanating from the surface have areas that appear to be ‘dead’ with flow due to the observable inconsistencies of the contours moving away from the rear of the mesh.

Bi-phase collection chamber depth optimisation

Parameters pertaining to the flow path length (maximum length that the fluid can transverse across the electrode surface), and the optimal type of mesh have been determined. The remaining factor that may have an influence on how the fluid moves through the mesh being the depth of the collection chamber extending outward from the rear of the mesh. If this is too narrow, fluid build-up starting at the base of the injection slot, could result in lower flow velocities being prevalent in this region. Employing dimensions that are too large could furthermore add unnecessary additional capital expenditure to the plate design. The model was set up to incorporate all of the optimal parameters as listed above, while altering the bi-phase collection chamber depth from 2.5 mm to 10 mm. Pressure drop would be the determining factor, as a low pressure drop is preferred to reduce pumping demand. The pressure profiles in Figure 5-8, related to the bi-phase collection chamber depth, serve as a comparison.

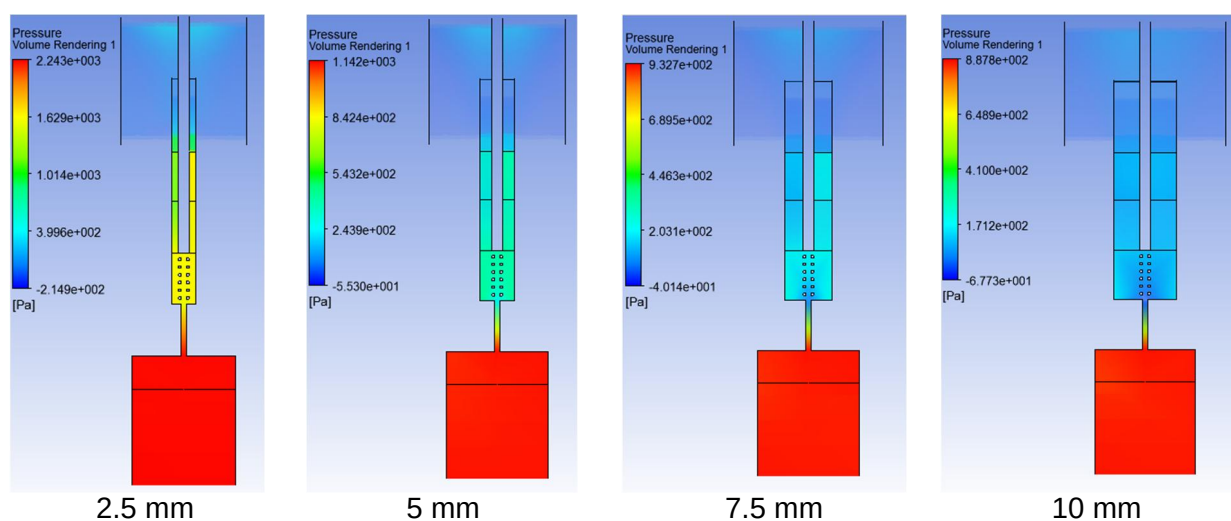


Figure 5-8: Pressure profiles as a function of collection chamber depth

From Figure 5-8, it is clear that for the same solution flow-rate through the stack, the pressure drop is relatively high for solution chamber collection depths of 2.5 mm and 5 mm respectively. The larger collection dimensions of 7.5 mm and 10 mm exhibit drastically smaller pressure drops. From the CFD observations made, a collection chamber depth of 10 mm was chosen as the pressure drop is negligible, which results from the depth being large enough not to interfere with the fluid dynamics occurring on the mesh surface. From Figure 5-9 it can be seen that a collection chamber depth of 10 mm results in solution flow velocities remaining balanced, throughout the reactor flow structure, with no regions showing distinguishable concentrated flows.

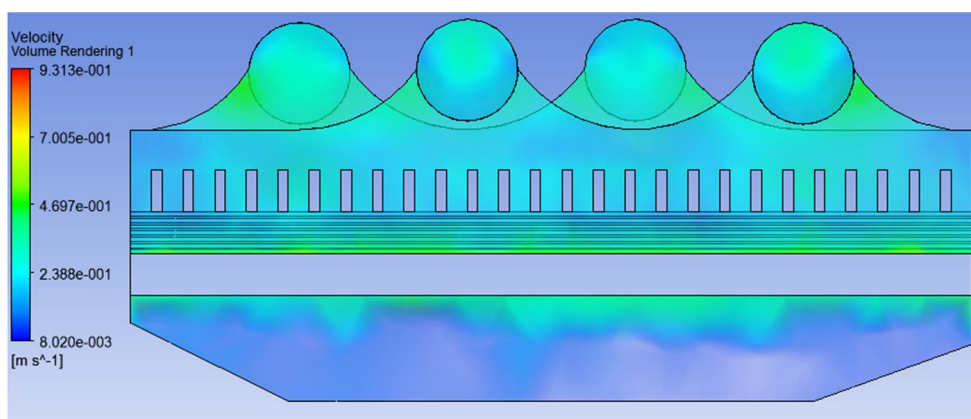


Figure 5-9: Optimal velocity profile for plate solution volume with a solution collection chamber depth of 10 mm

5.2.4. Vertical gravitational separator sizing

The dimensions and inlet/outlet positions of the vertical knock out drums were restricted due to the fact that they were retro-fitted for the plant. The space available beneath the cyclones, along with the cyclone outlet and the sump inlet positions, dictates the geometry of these separators. To that regard it was decided to conduct a high level CFD analysis on these separators, to design the internals, so as to maximise the time spent by a gas bubble within the separator. The inlet of the separator was positioned near the bottom of the separator with a baffle plate in close proximity. The baffle plate extends over the length of the separator up to the domed lid flange. This space would be used for gas accumulation. Once the flow has entered the domed upper hemisphere of the separator the solution will move down, against gravity, through a series of filters in order to trap and coalesce the remaining gas bubbles within the solution. A number of factors were investigated during the CFD analysis to determine which geometry maximises the residence time of the fluid, before it has passed through the filtration media. These factors include:

- (i) the baffle plate inclination,
- (ii) the position of filter media, and
- (iii) the number of filter media layers.

Modelling was performed on SolidWork FloExpress, in order to obtain the basic particle trajectories of water at ambient conditions within the vessels to note the effect of the factors above. Flow rates to each separator was determined based on the flow split from the reactor utilising 4 electrode pairs.

Number of media layers

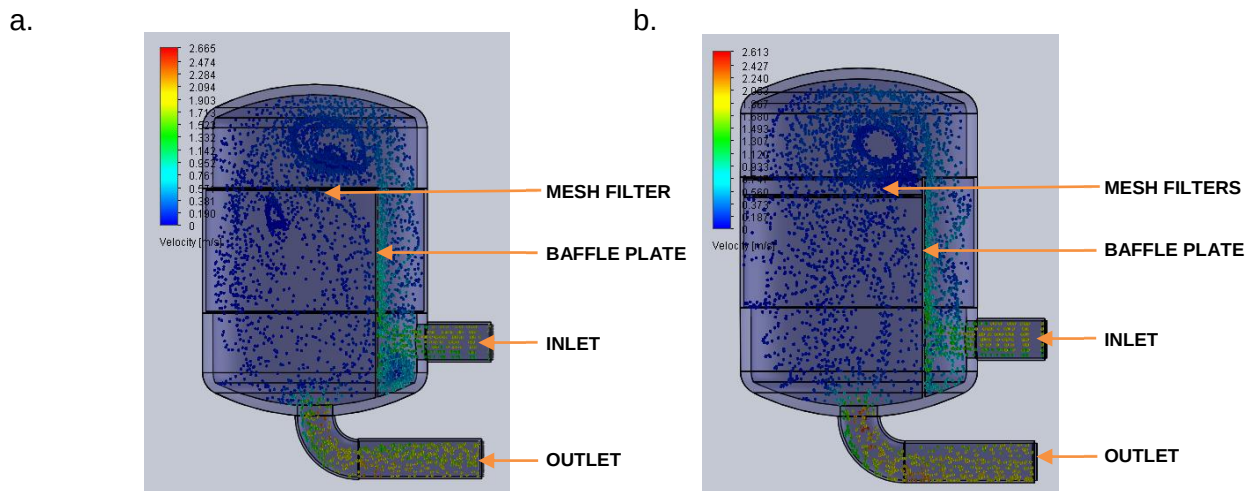


Figure 5-10: Particle velocities within vertical gravitation separator for (a) a single layer of media, and (b) a dual layer of media

By introducing an additional layer of media, more of the volume below the level of the mesh separators is used (Figure 5-10), which includes an improved use of area for the solution moving through the mesh separator in contrast to the flow only focused in discrete areas. It is apparent that a great deal of turbulence is present in the upper hemisphere of the separator. This would generate extended periods of residence time within the separator, that could potentially re-entrain bubbles that have already been collected for extraction.

Inclination of baffle plate

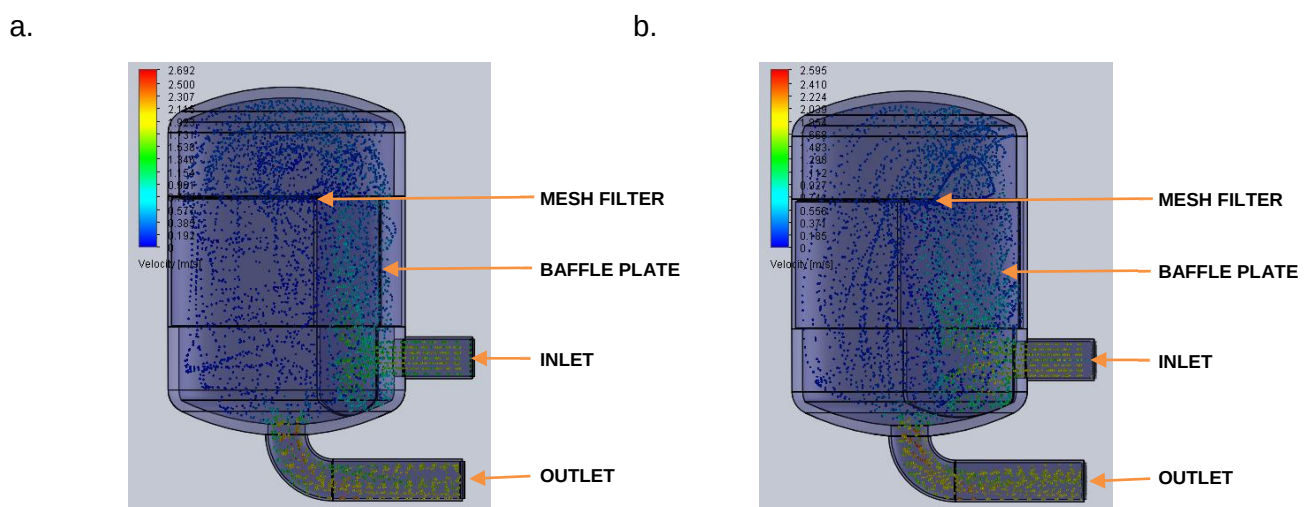


Figure 5-11: Particle velocities within a vertical gravitational separator for (a) a 20°, and (b) a 40° baffle inclination to the solution inlet

By inclining the baffle plate relative to the solution path, a perpendicular impact of solution is not observed, and consequently turbulence is less. When the baffle plate is inclined in excess, as in the case of Figure 5-11b, most of the solution would be displaced toward the farthest side of the baffle plate, resulting in an imbalance of flow with most of the flow moving along a common path. A shallow inclination therefore reduces turbulence without allowing majority of the flow to move along one common trajectory.

Position of filter media

As multiple filtration layers facilitate improved distribution of solution flow, and an inclined baffle plate reduces turbulence within the separator, the fluid in the upper hemisphere will be distributed to a lesser degree. This will contribute in reducing the risk of gas re-entrainment. From Figure 5-12, it is clear that the turbulent movement of solution extends below the top of the baffle plate, and allows for more laminar movement of the fluid in the upper hemisphere. This design allows the gaseous particles to spend a greater length of time within the upper hemisphere before moving through the filtration media. This will serve to reduce the risk of having collecting gases re-entrained into the exiting electrolyte.

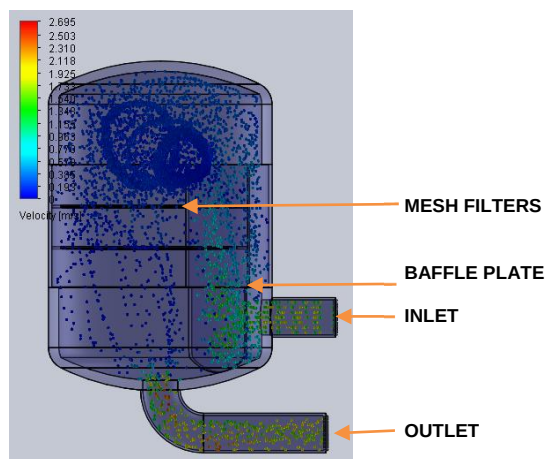


Figure 5-12: Optimal design of separator internals with filtration media located 50 mm below the baffle plate termination

5.2.5. Variables to be tested

The objective of this test rig is similar to that of the MCE reactor, however, it differs with regard to the reactor geometry varying greatly as a filter press design is utilised, and an alternate gas/liquid separation system is employed. This pilot plant would additionally be instrumental in benchmarking catalytic combinations and the medium term performance of those catalysts respectively.

Standard Parameter Comparison Experiments

Catalyst combinations that were tested for this investigation include (i) an industrially pure nickel anode and cathode combination, (ii) nickel oxide on the anode and pure nickel on the cathode, and (iii) a $\text{RuO}_2/\text{IrO}_2/\text{TiO}_2$ (MMO) anode and Pt cathode combination. Performance variations with regard to temperature and flow velocity were investigated with comparisons in performance made to prior test plants. A basic gas purity investigation was also undertaken with medium term performance stability investigated for the listed catalytic combinations. Testing near the optimal flow velocity of 0.075 m.s^{-1} will again be dependent on the effectiveness of the modified gas/liquid separation system.

5.3 RESULTS AND DISCUSSION

5.3.1. Performance comparison between the HFP stack pilot plant, and the concept optimisation test rig

The concept optimisation test rig made use of a discreet number of circular electrodes, and circumferential flow to achieve separation. It is apparent that the computational fluid dynamics with respect to circular electrodes results in a well-balanced flow velocity profile, with the lowest flow velocities occurring near the edges of the electrode. In Chapter 4, the CFD modelling of a circular electrode was performed, and the generalised flow velocity profile of an electrode can be conceptualised as depicted in Figure 5-13:

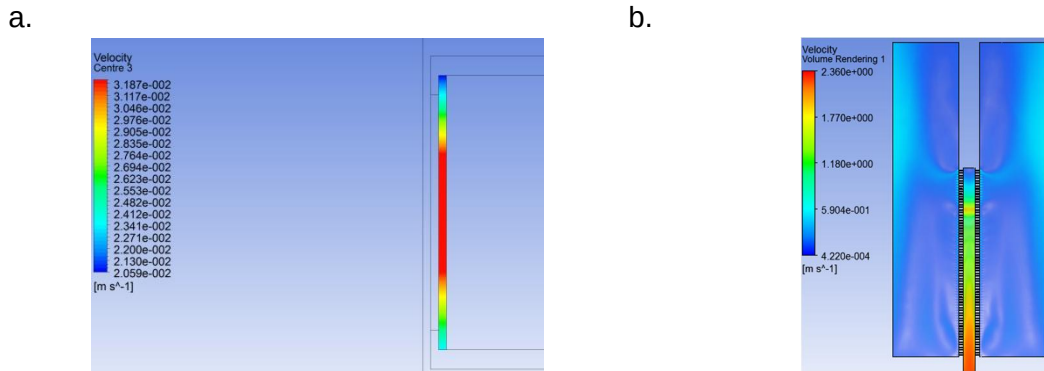


Figure 5-13: (a) Sectional flow velocity profile view of a 30 mm circular electrode mesh, and (b) sectional view of flow velocity profile of a rectangular electrode with a 30 mm flow path at a flow velocity of 0.03 m.s^{-1}

Reference to Figure 5-13a, the circular electrode flow profile shows a reduction in flow from the centre, to the outer edge of the electrode by around 25 - 35%. This can be taken as uniform flow velocity distributions, and the gas separation mechanism should be sufficient even at this low flow velocity. In contrast the rectangular electrode shows a reduction in flow velocity from the beginning to the termination of the flow path, however, it is evident that the volumetric flow of the solution exiting the electrodes near the termination barrier is greatest. Minimal flow is seen to exit the electrodes near the entrance to the electrode gap, and it can be expected that the current density distribution, and by direct influence, the gas separation of oxygen and hydrogen will be limited in this design of electrode, specifically when circumferential flow is absent.

As a result of the imbalance of current density distributions, a deviation between the performance obtained by the HFP stack, and the original concept optimisation rig making use of circular electrodes was observed. In addition, any deviations in the parallel nature of the electrodes would hinder the current density distribution, as charge is selective to the closest points relative to one another. From Figure 5-14 the electrodes were secured within the electrolyser supporting structure by means of a grip wedge to secure the lower edge. The electrodes were pressure pressed between the gasket and bus bar when the assembly was tensioned. The electrode itself, however, was not directly tensioned, and therefore relied on the pressure connection to even out its surface. Inconsistencies would be present irrespective of this configuration, and will have influence on how current would distribute itself across the electrode surface.



Figure 5-14: Uneven displacement of the rectangular electrodes due to the absence of a self-tensioning design

As hypothesised, a difference in performance between the two stacks can be clearly observed, as the HFP stack exhibits a maximum reduction in performance of 25.6%, in contrast to the concept optimisation rig at the highest cell potential (Figure 5-15). A reduction in performance is observed throughout the cell potential range, but is less notable at lower cell potentials. At lower current densities ($< 1 \text{ A.cm}^{-2}$) magnetic fields are less prominent between close proximity points, and are therefore less likely to affect cell performance [38], which is evident in the smaller performance difference at lower cell voltages. It is clear that circular electrodes, making use of circumferential flow, result in a superior design in creating balanced current densities and flow velocity distributions. Together with the above-mentioned influencing factors, the difference in the flow velocities for these measured points could also be attributed to the difference in performances, but is unlikely that it could account for the entire difference observed.

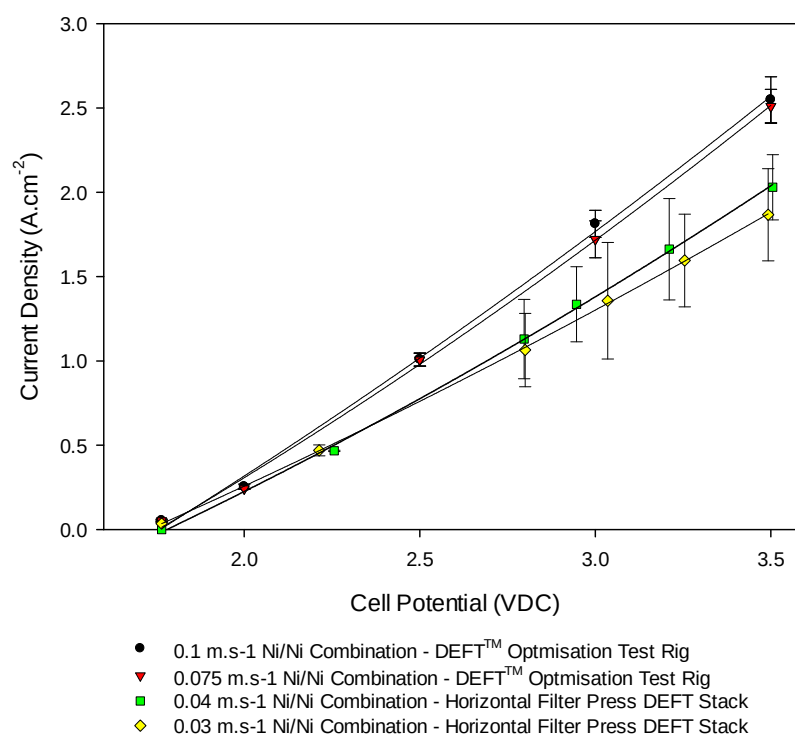


Figure 5-15: Polarisation curves for Ni anode and cathode catalytic combination for the concept optimisation test rig and the HFP stack, as a function of flow velocity, at a temperature of 80°C, and 30% KOH

5.3.2. Catalyst comparison on the basis of temperature and HHV% efficiency

Iridium is regarded as an effective electrocatalyst for the oxygen evolution reaction in an alkaline environment, yet it has been shown that the use of pure smooth nickel as an electrocatalyst, represents a more effective surface for the OER. Furthermore, recent published data shows that RuO₂/TiO₂ electrodes exhibit similar activities in contrast to using anodised nickel (NiO) for the OER. PGM based catalysts in an alkaline environment, for the OER, is therefore deemed unnecessary when alternate non-noble catalysts can be used instead, such as nickel oxide [57]. In reference to the RuO₂/IrO₂/TiO₂ (MMO) as an anode and plated Pt as the cathode, the Ru and Ir species are particular useful in enhancing the kinetics of the OER reaction, while the Ti species is used to stabilise the aforementioned [39]. Noble elements do possess high catalytic activity, however, these elements do pose a dilemma due to their high cost and limitation in future supply demands, if readily used [1]. As a benchmark of performance, RuO₂-IrO₂-TiO₂/Pt catalytic combination would be compared to the alternate catalytic combinations tested in the HFP stack.

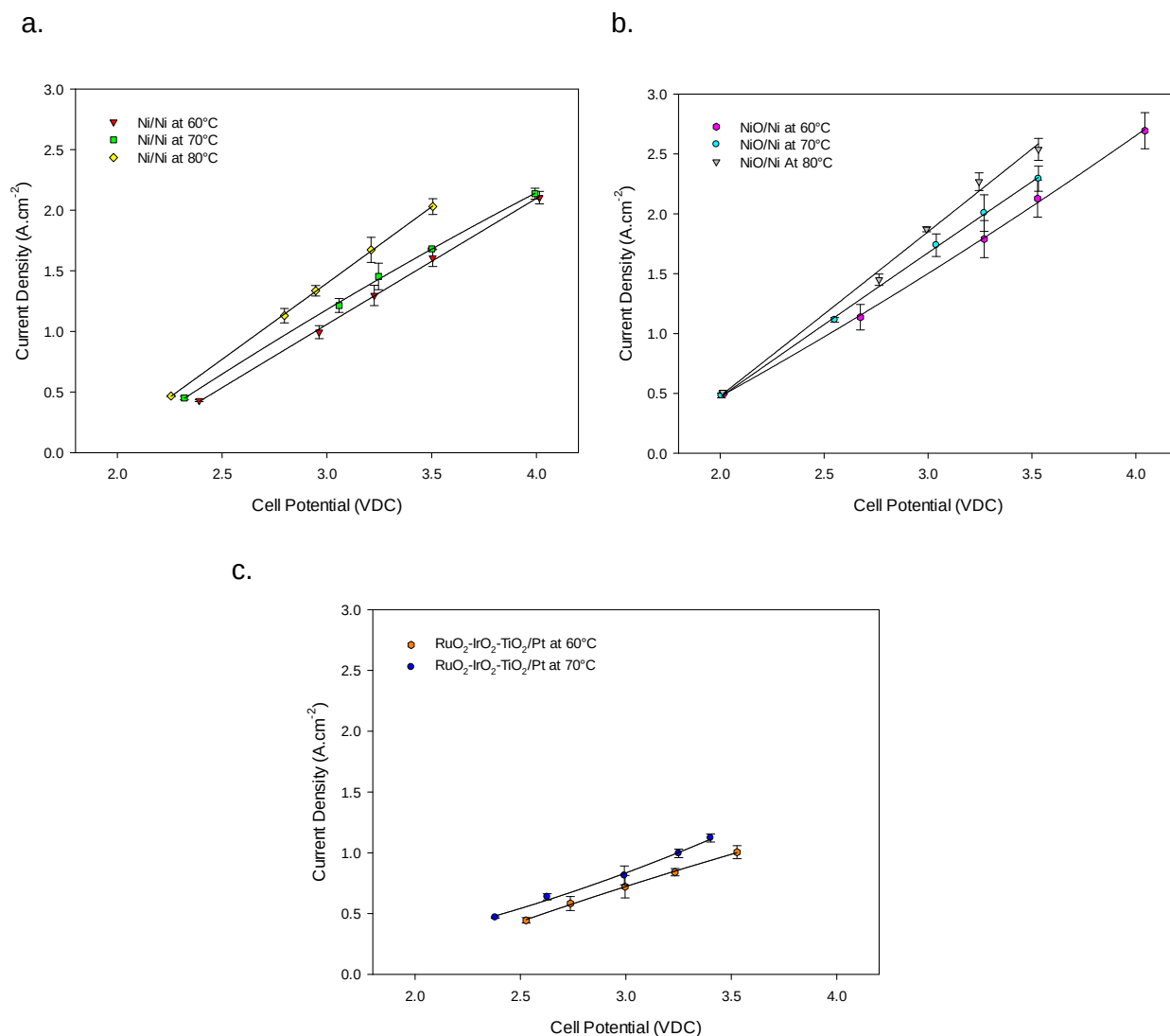


Figure 5-16: Polarisation curves for the HFP stack employing (a) pure Ni/Ni, (b) NiO/Ni and, (c) RuO₂-IrO₂-TiO₂ (MMO)/Pt catalytic combinations, as a function of temperature, at a flow velocity 0.04 m.s⁻¹, and 30% KOH

The temperature condition of 80°C for the MMO/Pt catalytic combination could not be tested due to the pilot plant's inability to attain this operating temperature. This was due to the cooler ambient temperature, and the installation of new heating elements, that replaced older damaged electrodes that had been more powerful in comparison. In contrast to results obtained employing the MMO/Pt catalytic combination in the concept optimisation test rig (Figure 3-8 (page 57)), generated trends in Figure 5-16 exhibit similar trends. Previously a current density of 0.474 A.cm⁻² was attained at an operating cell potential of 2VDC, a temperature of 70°C, and a flow velocity of 0.075 m.s⁻¹. The MMO/Pt catalytic combination appears to have lost activity, despite operating at lower flow velocities, as a similar current density was only attained at 2.4 VDC. The performance is lower than that of the Ni/Ni and NiO/Ni catalytic combinations across

the tested cell potential range. From prior difficulties with stainless steel (Chapter 3), the only source of poisoning experienced on the cathode, was a thin metal oxide layer, which could have been the result from the degradation of the stainless steel. Stainless steel tends to release contaminants such as chromium into solution when charged, or when the surface of the metal is no longer passivated, which can occur during extensive heating such as the welding process.

PGM based electrocatalysts are particularly susceptible to catalytic poisoning at elevated current densities [35]. Alkaline systems, in contrast to acidic systems, demonstrate significant tolerance in reference to the degree of contaminants present within the liquid electrolyte. Non-noble metals used as electrocatalyst constituents or as base materials demonstrate superior corrosion resistances, and resistance to catalytic poisoning when operating within an alkaline environment. As revealed in literature, using NiO on the anode coupled to using pure nickel as the cathode, to target the limiting OER, has a presiding effect on maximising current densities across the tested cell potential range [39].

Figure 5-17 confirms the overall plant efficiency of the HFP stack with changing stack cell potentials. It is important to cognisance that the configuration of the pilot plant does not make for optimised overall efficiencies, and therefore only assists in identify the optimal catalytic combination tested. The maximum overall plant efficiency achieved by the HFP stack is 32.01 HHV% (121.84 kWh/kg H₂) using a NiO/Ni catalytic combination. Efficiency is seen to increase with temperature as expected, as enhancements in the kinetics of the stack allows the stack to generate more product gas at a set cell potential [37]. The MMO/Pt combination demonstrated the lowest efficiencies, with the peak of the curve seeming to be generated for the tested cell potential range. The optimal efficiency would lie at higher cell potentials, due to the balance in loads that need to be achieved between stack load and pumping load. The more efficient catalysts such as the NiO/Ni and Ni/Ni combinations have their optimal peaks generated at lower cell potentials. The desired end result would be to generate as high an overall plant efficiency for as low a cell potential as possible. This can be achieved by employing catalysts with greater activities, and creating a pilot plant design that is optimised for as low a pressure drop as possible.

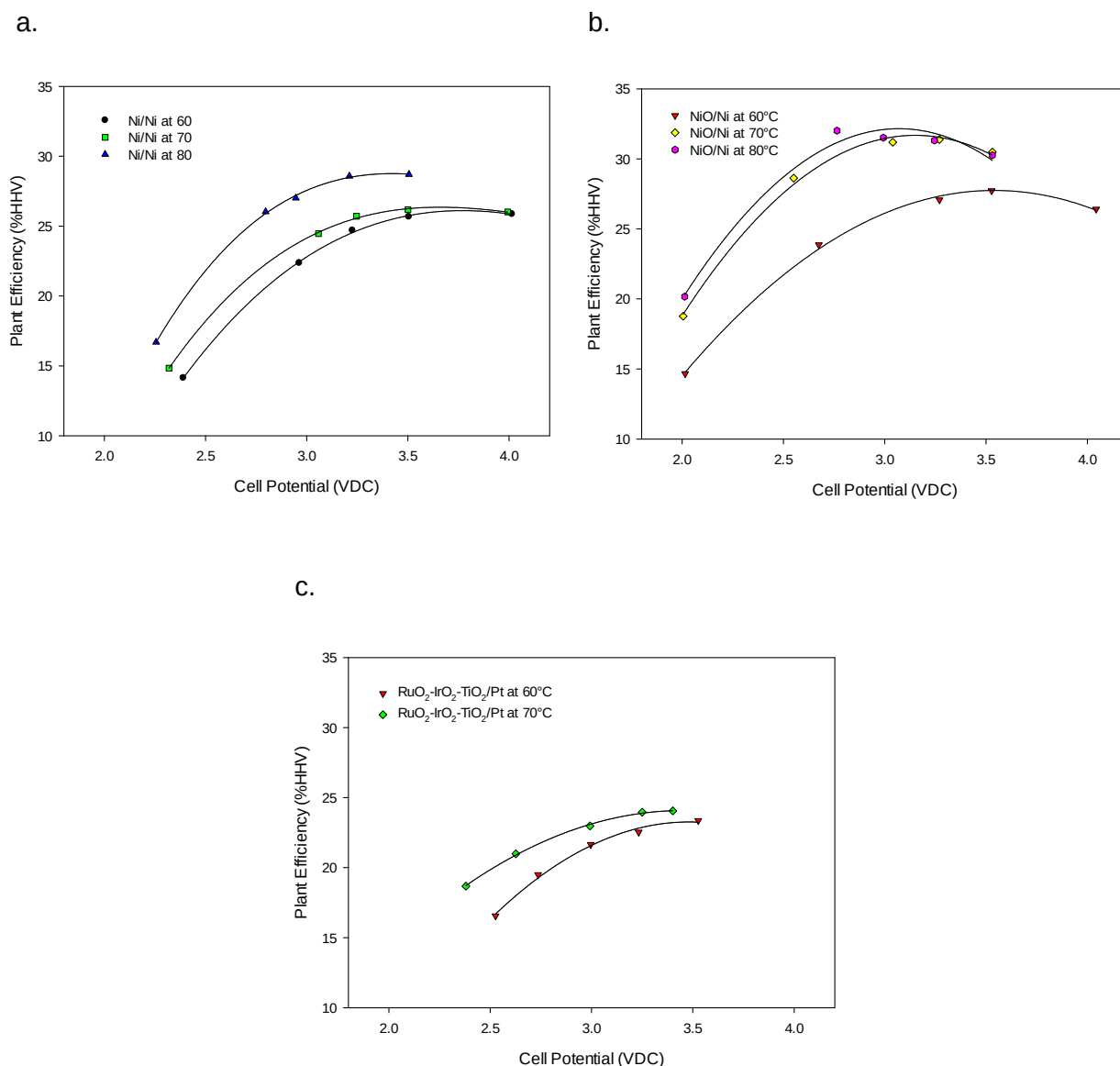


Figure 5-17: Plant efficiency (HHV%) versus cell potential for the HFP stack employing (a) pure Ni/Ni, (b) NiO/Ni, and (c) RuO₂-IrO₂-TiO₂/Pt electrocatalytic combinations, as a function of temperature, for a flow velocity of 0.04 m.s⁻¹, and 30% KOH

5.3.3. Catalyst comparison on the basis of flow velocity and HHV% efficiency

Divergent flow through the porous electrodes is the driving mechanism for achieving high purity gaseous separation, and enhanced stack efficiencies by continually removing gaseous products from the electrode surface itself, and from the inter-electrode space. This has the desired end result of reducing the ionic resistance between the electrodes [22]. Upon inspection of Figure 5-18, it is apparent that greater flow velocities maximise the stack performance, due to the positive influences of flow through the porous electrode. Conventional electrolyzers in contrast make use of flow along the electrode surface, and are limited by mass transfer resistances, and

extensive bubble coverage of the active area. This flow is predominantly for the removal of product gases from the stack itself, and for the small benefit of assisting bubble detachment, which is not quite as intensively utilised to the extent as in the case of DEFT™ technology [52]. As mentioned earlier, a flow velocity condition will be met whereby any additional benefit in enhancing the stack efficiency would become limited, and will no longer maximise the overall plant efficiency due to excessive parasitic load demands [1]. Depending on the electrocatalyst employed, stack geometry, and the plant pressure drop, this operating point will be different, and will need to be re-determined. Stack efficiency is considered a major determining factor of the overall plant efficiency. An optimised scenario exists, that represents a trade-off between power consumed by the stack, and the balance of plant that will resultantly maximise the overall plant efficiency.

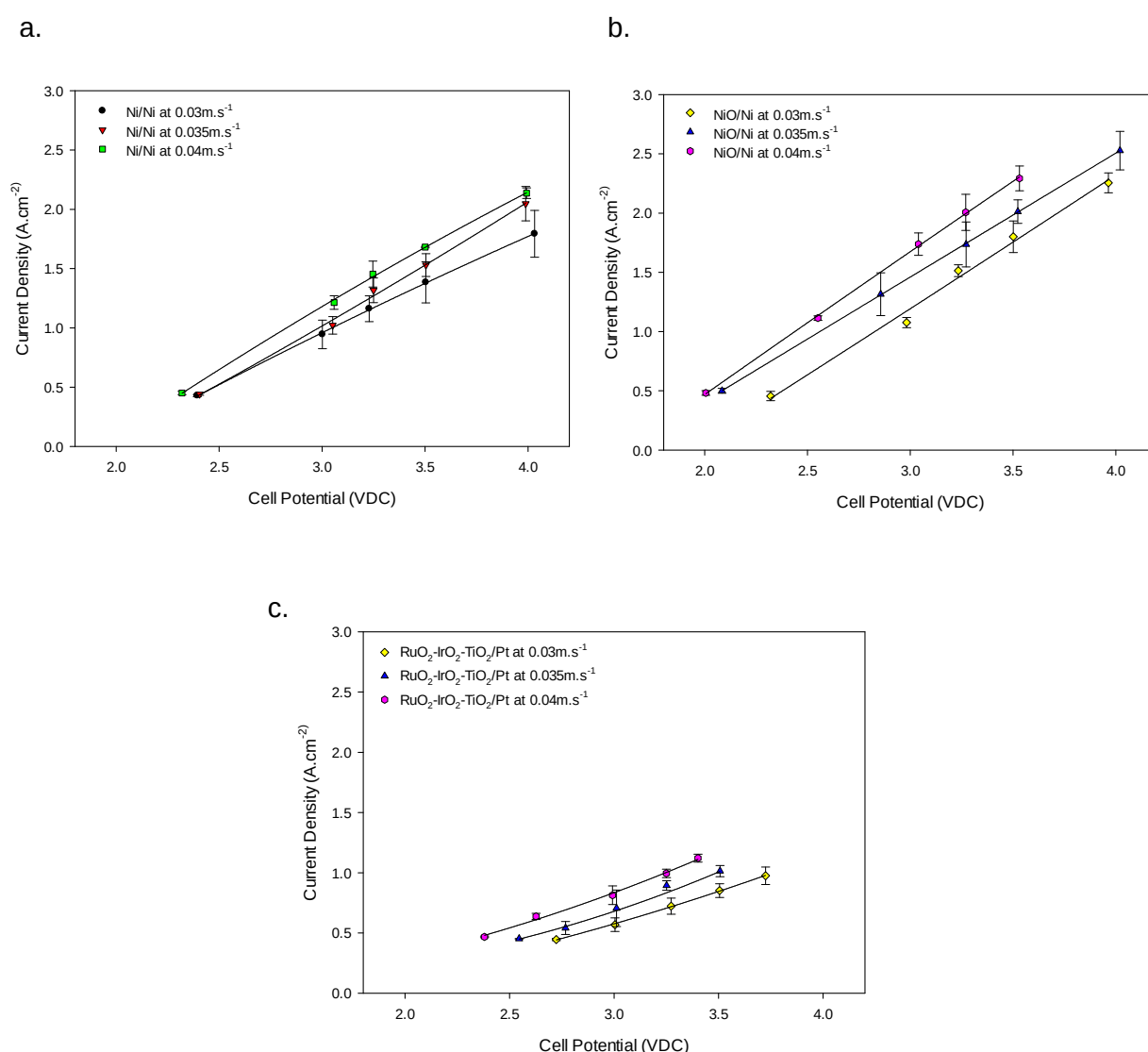


Figure 5-18: Polarisation curves for the horizontal filter press stack using (a) pure Ni/Ni, (b) NiO/Ni, and (c) RuO₂-IrO₂-TiO₂ (MMO)/Pt catalytic combinations, as a function of flow velocity, at 70°C, and 30% KOH

From Figure 5-19 (a and b) it is clear that the highest flow velocity resulted in the greatest overall HHV% efficiency for the HFP pilot plant. Curves are closer for NiO/Ni electrocatalytic combination, in contrast to the Ni/Ni combination, due to the lower activity of the Ni/Ni combination. Electrolytic flow has a larger contribution to performance enhancement for the Ni/Ni combination, as flow contributes minimally to elevating performance for the NiO/Ni electrocatalytic combination. The greatest efficiency achieved was once again by the NiO/Ni catalytic combination amounting to 31.38 HHV% (124.28 kWh / kg H₂).

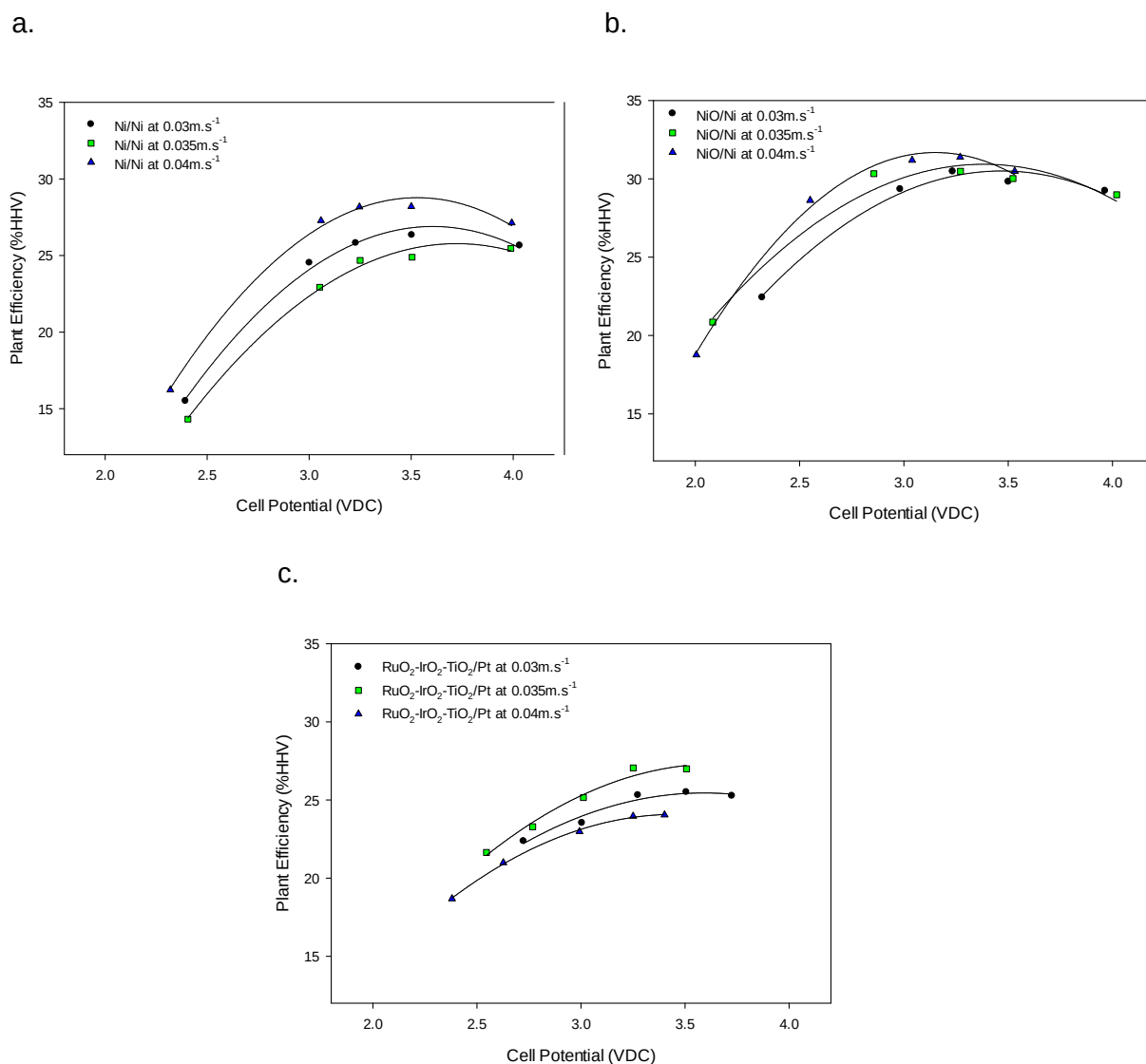


Figure 5-19: Plant HHV% efficiency versus cell potential for the horizontal filter press stack using (a) pure Ni / Ni, (b) NiO/Ni, and (c) RuO₂-IrO₂-TiO₂ (MMO)/Pt catalytic combinations, as a function of electrolytic flow velocity, at 70°C, and 30% KOH

The MMO/Pt catalytic combination contributed the lowest HHV% efficiency as PGM catalysts are primarily designed to operate within the lower operating cell potential. Deactivation of these material catalysts occurs more readily at elevated current densities, as RuO₂ components are said to suffer deactivation both in the acidic and alkaline environments [35]. Degradation of stainless steel components is furthermore to blame for the breakdown of PGM materials. PGM and other rare earth metals used in electrolysis technologies are among the least abundant on earth, and enhanced demand for these materials for electrolysis and fuel cell applications will not improve their CAPEX and OPEX for these components [35]. In contrast, non-noble metals, alloys, and oxides comprising nickel, are ideal for application in electrolysis systems as they are cost-effective and stable in an alkaline environment.

5.3.4. Catalyst comparison on the basis the basis of medium term stability

To investigate the medium term stability of the afore-mentioned electrocatalyst combinations, each combination was tested at constant current density, temperature, and flow velocity for 250 hours, to ascertain whether or not deactivation of the electrode is evident with time. Testing was conducted on an intermittent basis to enhance de-activation of electrodes.

From Figure 5-20b it is clear that the NiO/Ni electrocatalytic combination demonstrated the most stable behaviour between all tested catalytic combinations, altering very little with regard to cell potential, and eventually settling to a lower cell potential in comparison to the starting potential after 250 hours. For the Ni/Ni (Figure 5-20a) electrocatalytic combination, cell potential is seen to initially increase, but after 100 hours of testing, the cell potential stabilised to values similar to that of the starting value. The Ni/Ni electrocatalyst can therefore be said to exhibit adequate stability [10]. All nickel containing catalysts are generally observed to have superior catalytic stability in an alkaline solution when compared to alternate catalysts [32]. Oxides or alloys of these materials, is said to change the intrinsic electro-catalytic activity, altering the morphology of the surface, and enhancing corrosion resistance in aggressive alkaline environments [41]. The MMO/Pt electrocatalytic combination (Figure 5-20c) does, however, not indicate any establishment of stability, as a gradual increase in cell potential is observed over time. The same argument can be employed here as per the lack in performance experienced for the same electrocatalytic combination used in the concept optimisation test rig (Chapter 3) [6]. Due to the elevated presence of contaminants in the electrolyte of the HFP plant, compared to the concept optimisation test rig, which made liberal use of plastic only components, these electrodes experienced rapid degradation in performance due to the enhanced levels of contaminants [35].

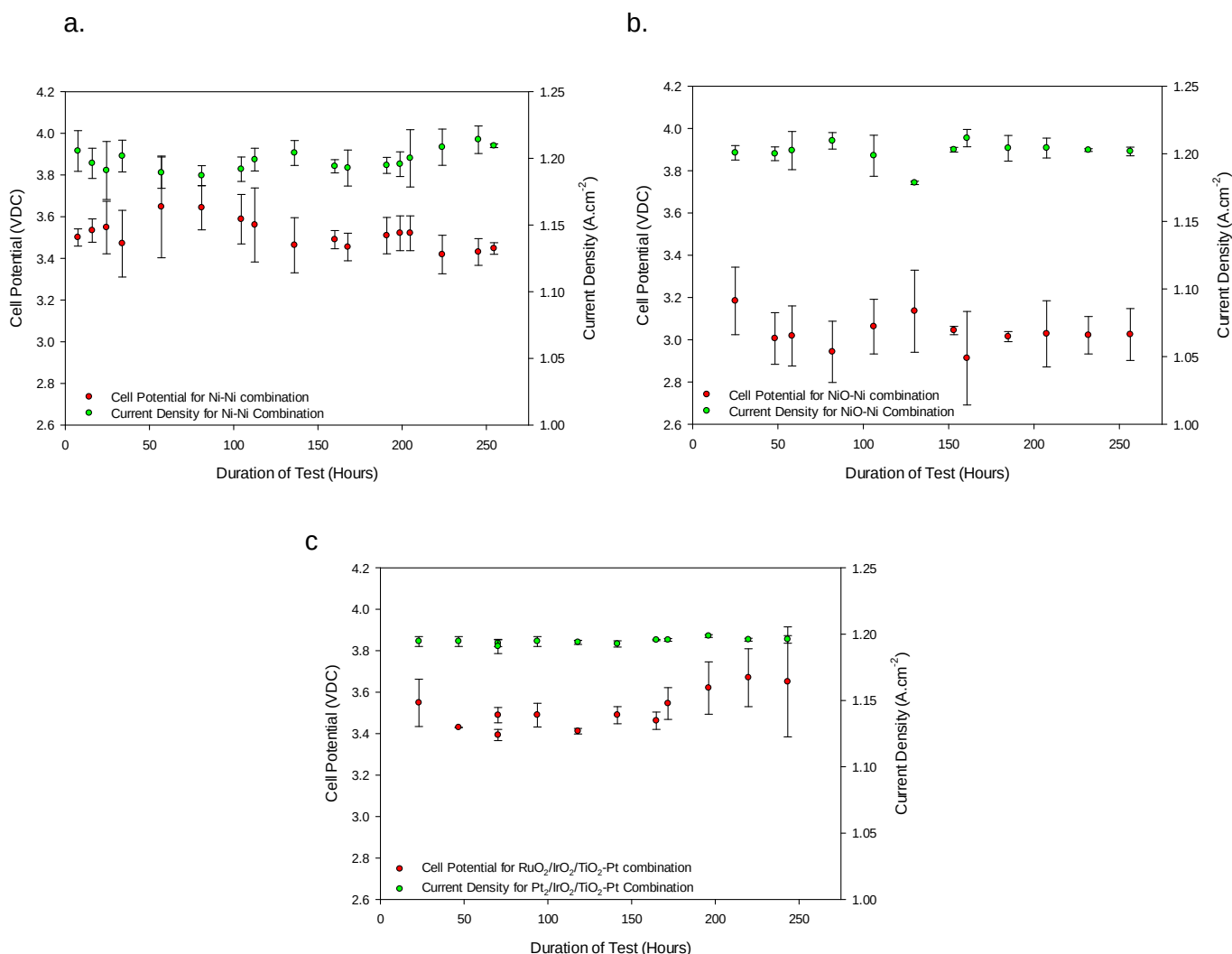


Figure 5-20: Medium term stability for the HFP pilot plant for (a) pure Ni/Ni, (b) NiO/Ni, and (c) RuO₂-IrO₂-TiO₂ (MMO)/Pt electrocatalyst combinations, as a function of cell potential and current density, at 60°, 0.04 m.s⁻¹, and 30% KOH

5.3.5. Gas purities generated from the HFP reactor

Basic gas purity analysis was conducted for both the hydrogen and oxygen gas product streams in order to ascertain the effectiveness of: (i) creation of an adequate separation mechanism of the product gases from one another in the stack by employing divergent flow, and (ii) the removal of the product gases from the electrolyte within the gas/liquid separation system. It is important to recognise that if the gas/liquid separation system is ineffective, then it is impossible to determine the effectiveness of the divergent flow separation mechanism within the stack. Initial observations of the effectiveness of the gas/liquid separation system were observed at flow velocities

0.03 – 0.04 m.s⁻¹. This was brought about due to the failure of the original gas/liquid separation system, and subsequent modifications which limited the system volume, and effectiveness due to spatial restrictions. A large discrepancy exists in gas purities obtained in contrast to gas qualities required, which should be in the region of > 99.3 vol% for H₂ gas alone for conventional alkaline membrane systems [29].

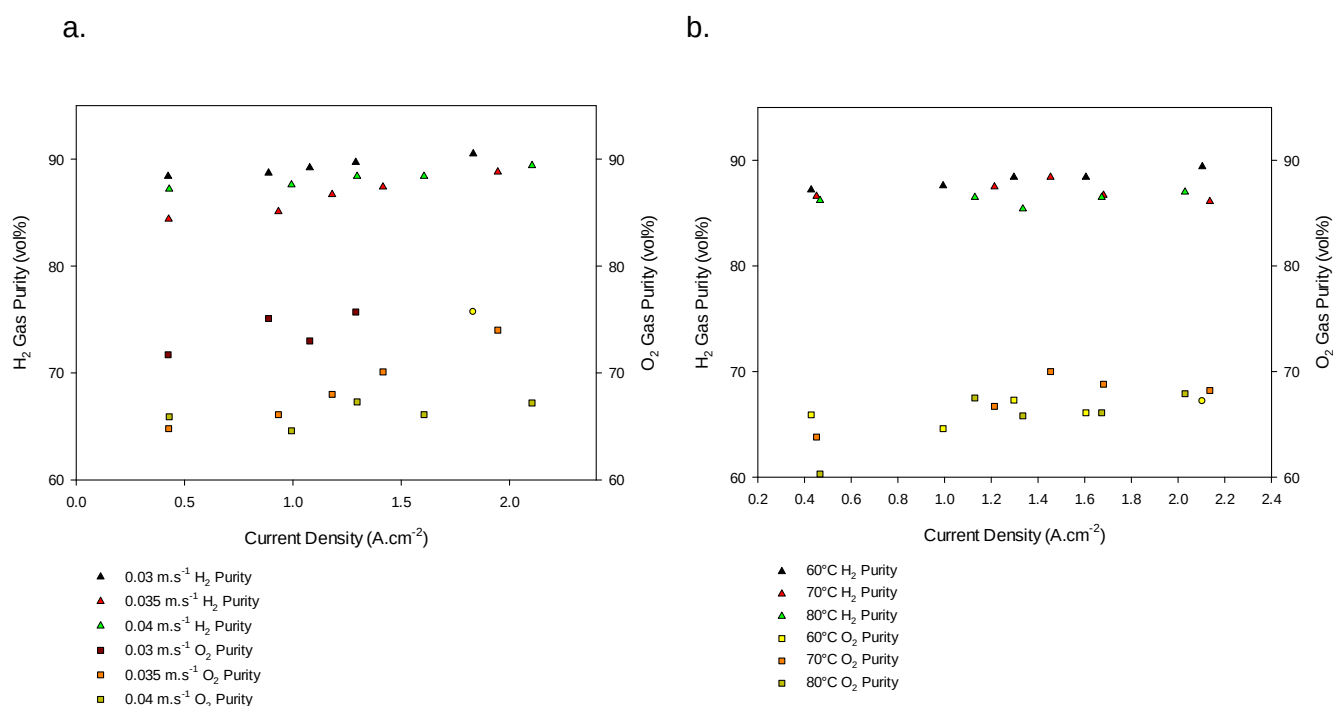


Figure 5-21: Product gas purities for both hydrogen and oxygen gas streams versus current density of the HFP stack as a function of (a) electrolytic flow velocity at a constant temperature of 60°C and, (b) temperature at a constant flow velocity of 0.04 m.s⁻¹

From Figure 5-21, it is evident that hydrogen gas purities are maximised at a lower temperature with no real correlation for oxygen gas. The maximum hydrogen and oxygen gas qualities was 90.5 vol% H₂ and 75.7 vol% O₂ measured at 60°C, and a flow velocity of 0.03 m.s⁻¹. Figure 5-21a clearly illustrates that gas quality decays with increasing flow velocity, which points towards the separation system being inefficient in its gas/liquid separation mechanism. Re-entrainment of gas to the stack is lower at lower flow velocities, however, the separation mechanism of the stack is ineffective, and results in inadequate gas qualities. The DEFT™ technology does make for fairly constant gas purities across the operating current density range for both oxygen and hydrogen product streams. The quality of the evolved gases from the HFP pilot plant are not comparable to results previously obtained by the concept optimisation test rig (Chapter 3), and a radical improvement in the gas/liquid separation system needs to be implemented to properly benchmark the technologies' performance to existing technologies.

5.4 CONCLUSION

A horizontal filter press (HFP) concept was designed and tested, utilising the DEFT™ technology, as an alternative in the pursuit of scaling the technology, with the inherent aim of it being more compact (with fewer components of construction) in contrast to the MCE DEFT™ stack. This should result in a reduced CAPEX and OPEX as fewer components would have to be fabricated, assembled and disassembled. The major investigation for this pilot plant was to test the performance of three electrocatalytic combinations namely, (i) a Ni/Ni, (ii) NiO/Ni, and (iii) IrO₂-RuO₂-TiO₂/Pt anodic and cathodic electrodes respectively. This investigation revealed that the NiO/Ni electrocatalytic combination was superior both in performance and durability, with the Ni/Ni electrocatalytic combination performing incrementally lower with regard to both performance and durability.

Considering the Ni/Ni electrocatalytic combination, as a means of comparing the performance of the HFP pilot plant to that of the concept optimisation test rig, it is evident that a current density of 0.052 A.cm⁻² (1.75 VDC) at 0.075 m.s⁻¹ was achieved for the HFP pilot plant, compared to 0.038 A.cm⁻² (1.75 VDC) at 0.04 m.s⁻¹ for the concept optimisation test rig, with the balance of operating conditions being the same. Little deviation in performance in the lower cell potential range is observed, with differences occurring only at greater cell potentials, which are clearly confirmed at a cell potential of 3.5 VDC where a current density of 2.51 A.cm⁻² at a flow velocity of 0.075 m.s⁻¹ was obtained for the concept optimisation test rig, in contrast to 2.47 A.cm⁻² at 0.04 m.s⁻¹ for the HFP stack at the same operating cell potential (3.5VDC).

The best efficiency obtained by the pilot plant amounted to 32.01 HHV% with optimal gas purities recorded to be 90.5 vol% H₂ and 75.7 vol% O₂. This demonstrates an improvement in the results achieved by the MCE DEFT™ stack. It is evident that further improvements need to be performed to both the stack and pilot plant, to balance current densities and flows more uniformly, and to provide for a more effective gas/liquid separation.

Take-home observation(s):

- (i) Circumferential injection utilising a circular electrode is superior in contrast to mono-injection utilising a rectangular/elongated electrode,
- (ii) A self-tensioning design is essential in ensuring the electrode surface remains consistent and uniform,
- (iii) Ni200 is a favourable catalyst for both the HER and OER, in addition to NiO demonstrating enhanced performance for the OER,

- (iv) Due to the observed poisoning of electrode, the use of PGM based catalysts prove ineffective for use with the DEFT™ principle, specifically if utilised for the HER,
- (v) For different electrode catalyst combinations, the overall plant efficiency will resolve to be a balance between stack efficiency and parasitic load operating within optimally deduced operational parameters,
- (vi) The incorporation of a system sump is not necessary as this adds to the complexity and scale of the plant, and
- (vii) A separation system capable of enhanced contact surface areas and extended residence times would aid in boosting gas/liquid separation effectiveness.

6. MONO CIRCULAR FILTER PRESS ELECTRODE (MCFPE) DEFT™ REACTOR

6.1 OVERVIEW

All positive (and negative) design and operational criteria of the previous pilot plants, i.e. the concept optimisation test rig, the MCE plant, and the HFP plant, were incorporated to design a new pilot. This would be an amalgamation of the circular electrode concepts, employing circumferential flow, and the filtered press concept, to create a compact reactor setup. A pressurised chamber would once again be used, however, it would only feed a single electrode pair fed by means of injection slots. The chamber would also incorporate a purge channel to remove any gas that does not adequately separate out of the reactor. Scalability was achieved by adding additional electrode pairs onto the reactor stack, by means of common module plates which house the electrodes themselves. A total of 20 electrode pairs was feasible for integration into the pilot plant, however, an optimal number would exist for a fixed volume of the improved gas/liquid separation system. If this is not effectively balanced by the volume of solution flowing through the system, the gas/liquid separation system would be affected negatively. The gas/liquid separation system was configured such that modifications could be easily made to demonstrate whether a fully submerged or a contact type separation system would be more effective.

The principle aim of this pilot plant was to identify all intrinsic relationships to factors that affect gas purity, with the goal of identifying constraints related to conditions that disallows gas production of adequate purity (for both hydrogen and oxygen). Additional and existing electrocatalyst combinations, along with different electrode structures/configurations, was investigated, to compare the performance to previous test plants in an attempt to establish an optimal electrode performance. The flexibility of this stack lies in the fact that it allows for the testing of a variable electrode gap, which was briefly examined, along with the addition of additional/multiple electrode layers in an attempt to improve the available area for reaction.

Yet again, the same comprehensive test panel was used in the evaluation of the performance parameters and control thereof. Initial test results revealed that the mono-circular filter press electrode (MCFPE) reactor optimised both current density at set cell potentials and gas purities for similar test conditions performance on all past test rigs. Achieving > 99.3 vol% purity for both hydrogen and oxygen, validates the MCFPE reactor stack to be the most optimised, and successful demonstration of the DEFT™ technology to date.

6.2 METHODOLOGY AND APPARATUS

6.2.1. Overview

By incorporating numerous circular electrodes in a common injection chamber that made use of circumferential injection (MCE stack), or by creating individual rectangular electrode pairs fed from a single leading edge (HFP stack), has revealed a number of difficulties with balancing flow velocities and current densities across the electrode surface. The MCFPE stack will serve to take advantage of the positive design factors from all of the prior test stacks and pilot plants. Two concepts of gravitational gas/liquid separation were tested for this pilot plant in order to develop an effective system for the rapid removal of micro-bubbles from a high liquid throughput system, which has remained elusive in the development of the technology so far. The flow diagram depicted in Figure 6.1 illustrates the process flow associated with the MCFPE stack.

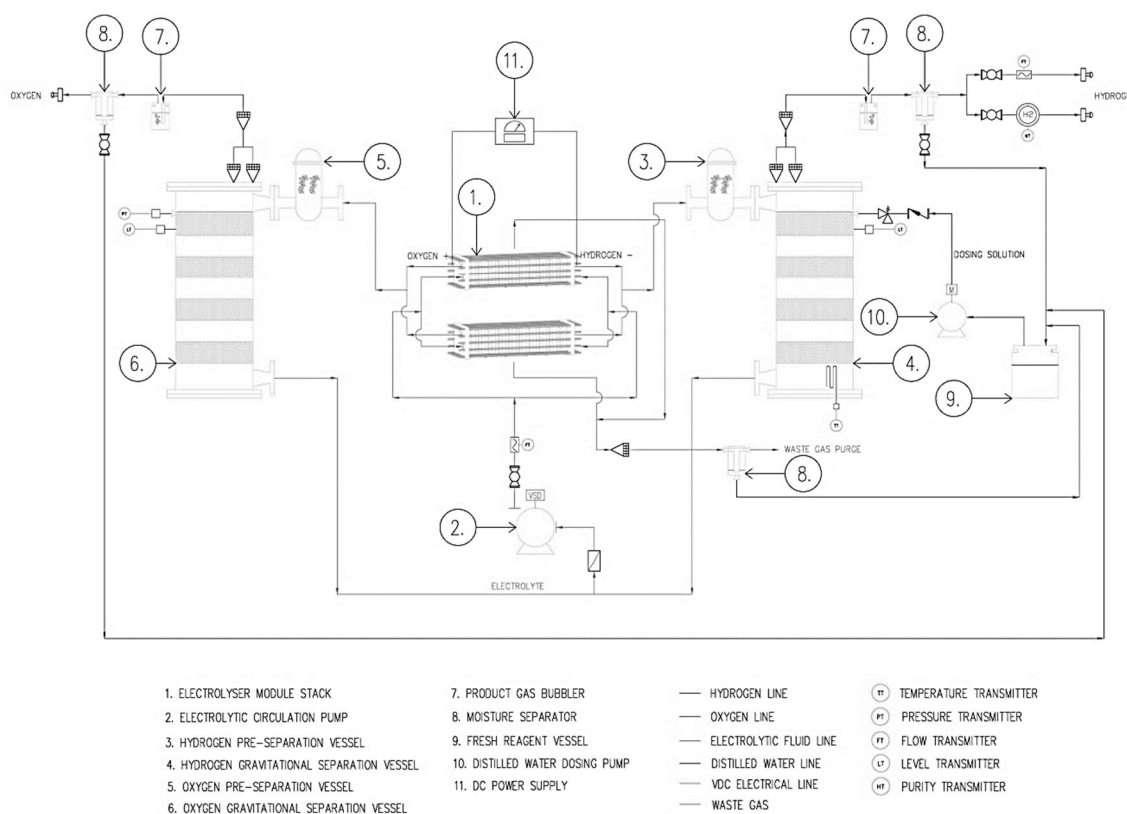


Figure 6-1: Process flow diagram of pilot plant incorporating MCFPE reactor

The design and operation of this pilot plant had been greatly simplified in comparison to previously tested pilot plants. This had been done with the intention of the system utilising a modular design, and thereby not making use of any intermediate sumps. Fresh electrolyte enters the twin parallel

reactors (Figure 6-1 no.1) by splitting the flow equally through a geometrically symmetrical manifold system employing the circulatory pump (Figure 6-1 no.2). Initially the system is setup to incorporate a pre-separation system (Figure 6-1 nos. 3 & 5) to assist in extracting all large gas bubbles, and to reduce the extent of problematic foam entering the separation system. However, the benefit gained was limited, and it was removed after the first few experimental test runs.

The flow from the pre-separation systems enters the vertical gravitational separators (Figure 6-1 nos.4 & 6) near the top, whereby a series of packed media and wire mesh filters are used to coalesce and remove product gas from the liquid. Purge tubes are utilised to move gas from high pressure regions, to low pressure regions that are located in the form of a gas void at the top of the main separators. The liberated flow is re-circulated to the reactor system once filtered of any solid particles, while liberated gas is continually purged from the system by means of gas purge valves located at the top of the separators (for safety purposes). The gas is then subsequently passed through a bubbler system (Figure 6-1 no.7), which cools and cleans the gas, and additionally accomplished the additional role of a flash back arrestor. Once the gas passed through the bubblers, it moves through a moisture separator (Figure 6-1 no.8) to remove any additional vapours present in the gas.

Once again, variable DC power, control of process hardware and data logging of variables was performed by the same comprehensive test panel previously designed and utilised for pilot plants discussed in Chapters 4 & 5. Figure 6-2 depicts the MCFPE pilot plant in its completed form after numerous experimental tests.

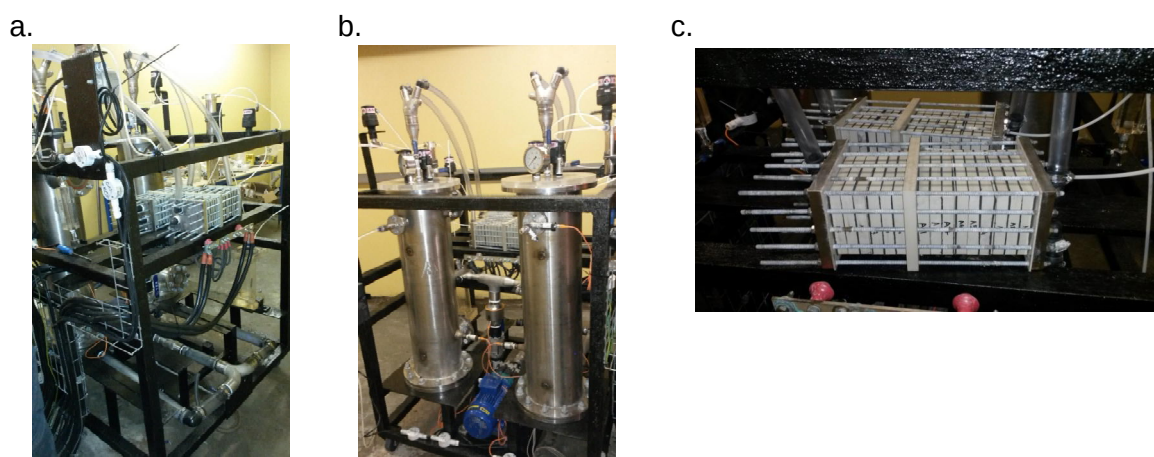


Figure 6-2: MCFPE plant with view of (a) the plant from the reactor side, (b) the separator side, and (c) the MCFPE reactors only

6.2.2. MCFPE reactor details and electrode material

The MCFPE reactor can house a total of 10 circular electrode pairs (30 mm in diameter) with two reactors being incorporated in parallel into the described pilot plant. The number of electrode pairs can, however, be altered depending on the operating limits of the incorporated gas/liquid separation system. The maximum cross-sectional area available for the cathodic and anodic electrode pairs is 141.37 cm². At the intended nominal design current density of 3.5 A.cm⁻² the combined stack amperage will total 494.8 Amperes, which is significantly lower than previously designed pilot plants. This will improve the balance between gas production, and gas/liquid separation capacity. The pilot plant, when operated with all electrode pairs, should be capable of delivering 0.45 kg H₂ over a period of 24 hours. The following illustrations (Figure 6-3) denote the stack geometry and internal flow regime for the MCFPE reactor.

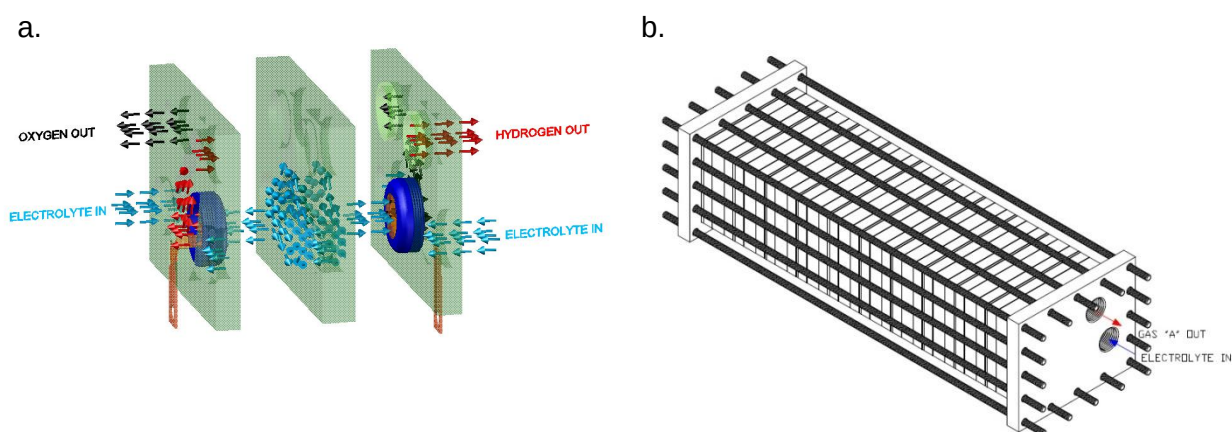


Figure 6-3: (a) The flow philosophy for the MCFPE reactor for a single electrode pair, and (b) the assembled view of the MCFPE reactor comprising of 10 electrode pairs in a filter press assembly

Fluid enters the fresh electrolytic injection tubes flowing counter current for the entire length of the reactor. Tapered injection channels insert flow into the central pressure chamber in a uniform manner behind the electrode housing. It is important to observe that flow was not directed at the electrode gap itself, but rather follows an indirect path, which promotes laminar flow, and eliminates turbulence. All flow geometries within the reactor eliminated the use of sharp edges or irregular geometries to avoid the occurrence of excessive eddy currents. The design facilitates a self-purging mechanism, which disallows any contaminated gas entering the inlets from exiting out of the electrode housings by the nature of the inlet flow philosophy. These gas bubbles are forced into a flow-free tapered area above the electrode pair whereby a purge channel eliminates the gas from the reactor, and ensures that the reactor was fully submerged at all times.

The bi-phase product from each electrode pair is directed into a collection chamber which ensures that the flow is immediately directed upward to a collection tube that spans the length of the reactor. Additionally, the product streams, for both the hydrogen and oxygen, travels in a counter current direction to ensure that a balanced flow was maintained for the entire length of the reactor. Removable separation plates had been introduced between each pole pair to avoid mixing of product bi-phase streams. The reactor had been configured, however, to remove the separation plates as to allow these common bi-phase streams to enter into common collection chambers as to reduce reactor components. It was feared that the movement of two streams into the same collection chamber may have cause unwanted turbulence that could have altered the way in which the fluid distributed itself across the surface. This was, however, investigated.

The electrodes tested within the MCFPE reactor were manufactured from industrially pure nickel mesh, of dutch weave type (Hebei Nanrui Wire Mesh Company), with a nominal retention of 80 μm . The same catalyst (tested in Chapters 3 & 5) comprising of a coating of $\text{RuO}_2/\text{IrO}_2/\text{TiO}_2$ (MMO) in the ratio 35:10:55 on pure nickel representing the anodic electrode, and Pt (with a loading of between 35 – 65 g.m^{-2}) plated onto pure nickel, representing the cathodic electrode (NMT Electrodes), was tested to ascertain any performance similarities to results achieved in Chapter 3. The advanced electrocatalyst developed at the North-West University's Potchefstroom campus (tested in Chapter 3), was tested in the MCFPE reactor. This electrocatalyst comprised of a vapour deposited coating of $\text{Pt}_{90}\text{Ni}_{10}\text{Al}_{35}$, co-sputtered onto a pure nickel substrate that represented the anodic electrode, with a pure nickel electrode that represented the cathode. Its performance had not been tested for extended durations of time, and this aspect will be examined in more detail for the future. An alternate means of enhancing current densities is by altering the configuration of the electrodes, and hence multi-layered electrodes and metal foam electrodes (fabricated out of industrially pure nickel) was examined in addition.

6.2.3. Brief examination of the computational fluid dynamics of the MCFPE reactor

Modelling the geometry described in section 6.2.2, fluid dynamics modelling was performed on the basis of examining solution particle trajectories and flow velocities. Two important aspects needed to be accomplished for the computational fluid dynamics modelling, (a) ensuring that circumferential flow is achieved for the electrode housing, and (b) ensure that all electrode pairs in the stack receive similar amounts of volumetric flow.

The following simulations were conducted to understand the necessary design/operational alterations required for balanced flow using Solidworks FloExpress:

- (i) a singular electrode pair model, to observe if flow was entering the electrode housing equally from the periphery of the electrode at both the minimum flow (0.05 m.s^{-1}) and the maximum flow (0.1 m.s^{-1}), and
- (ii) a full stack of electrode pairs comprising of 10 pairs of 30 mm diameter electrodes. This analysis was conducted both at maximum (0.1 m.s^{-1}) and minimum (0.05 m.s^{-1}) flows. The following flow regimes were tested
 - co-current flow from one side only of the reactor for both inlets and outlets,
 - co-current flow whereby the inlets will flow from the same side, and the outlets will exit from the same opposing side, and
 - counter-current flow whereby the inlets will enter in opposite positions relative to each other and the outlets will exit at opposite sides to one another.

Figure 6-4 depicts the fluid region for a single pole pair used to examine the fluid distribution around the periphery of the electrode housing.

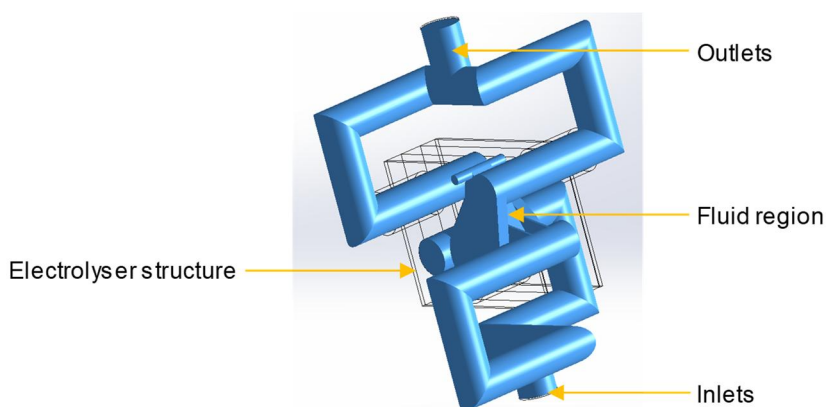


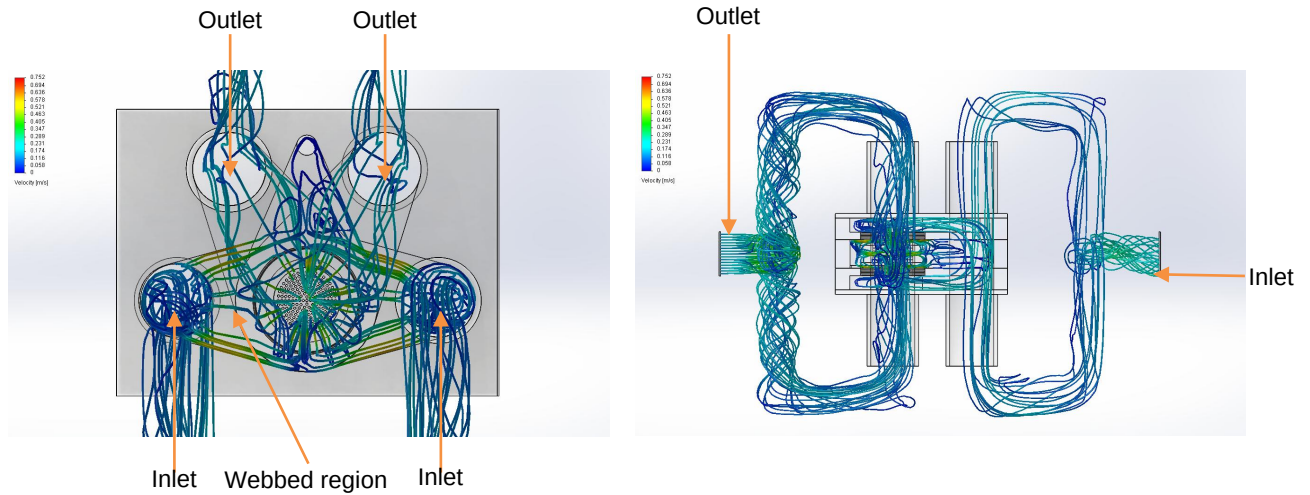
Figure 6-4: Representation of the fluidic region of a single electrode pair of the MCFPE reactor

Single electrode pair design simulation

The flows exiting the inlet tubes distribute themselves evenly within the webbed injection zone (Figure 6-5). An increase in flow velocity, within this restricted region, up to $\sim 0.55 \text{ m.s}^{-1}$ results in a build-up of pressure within the inlet pipe, which is ideal when pairs are added in parallel as each pair will likely receive the same volumetric quantity of electrolytic fluid. For both the minimum and maximum flow conditions, flow distributes itself evenly around the circumference of the electrode housing. It is evident that the higher flow condition (0.1 m.s^{-1}) does allow for penetration of flow all the way to the centre of the electrode in comparison to that of the lower flow condition (0.05 m.s^{-1}). Low flow velocity could perhaps be described as being close to the limit of flow required for uniform flow across the electrode surface, however, this condition would be more

dependent on the generated gas purity linked to the applied current density. Dead flow regions are present in the upper region of the electrolytic injection chamber, which is an ideal location for the turbulence free collection of purge and trapped gas within the system. An equal balance of flow can be seen leaving each bi-phase collection chamber thanks to the geometrically identical design incorporated into the stack for balancing flows (Figure 6-5).

a.



b.

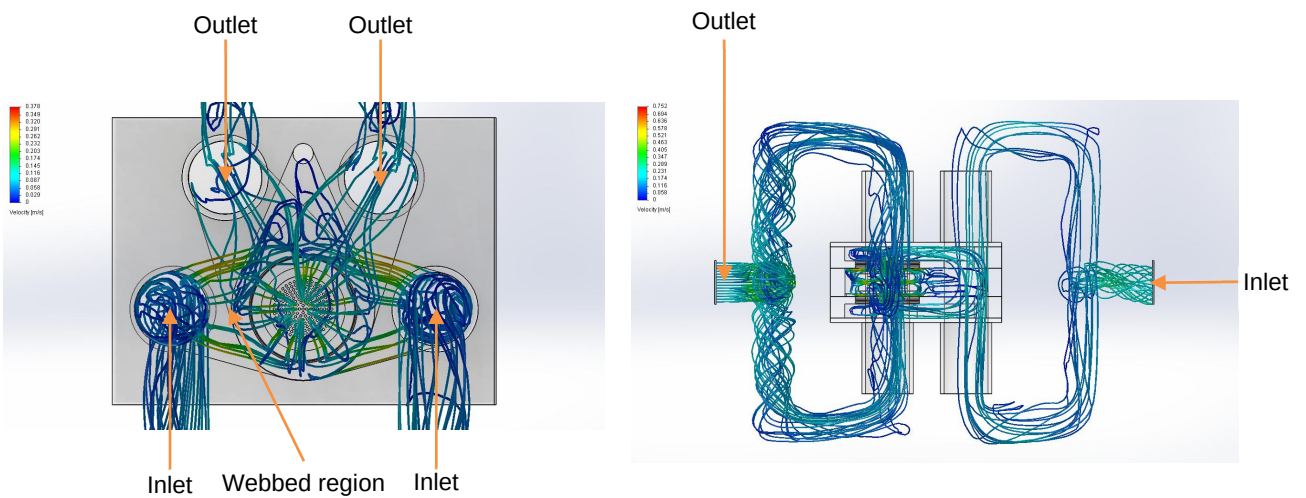


Figure 6-5: Streamline velocity profiles for a single electrode pair for (a) 0.1 m.s^{-1} , and (b) 0.05 m.s^{-1} for the MCFPE reactor

Multiple electrode pair simulation: Co-current for inlet and outlet from the same side

It was initially hypothesised that if flow had to enter and exit from the same side, not enough back pressure would be created by the design, to ensure that all stack pairs receive the same amount of electrolytic fluid. The design can be altered to generate additional back pressure, however, this would be undesirable as it would contribute unnecessarily to the parasitic load on the system. Figure 6-6 illustrates the unsuitability of this flow regime due to the flow being incapable of penetrating to the end of the stack, which suggests that flow should be introduced in a manner that distributes it evenly amongst all electrode pairs.

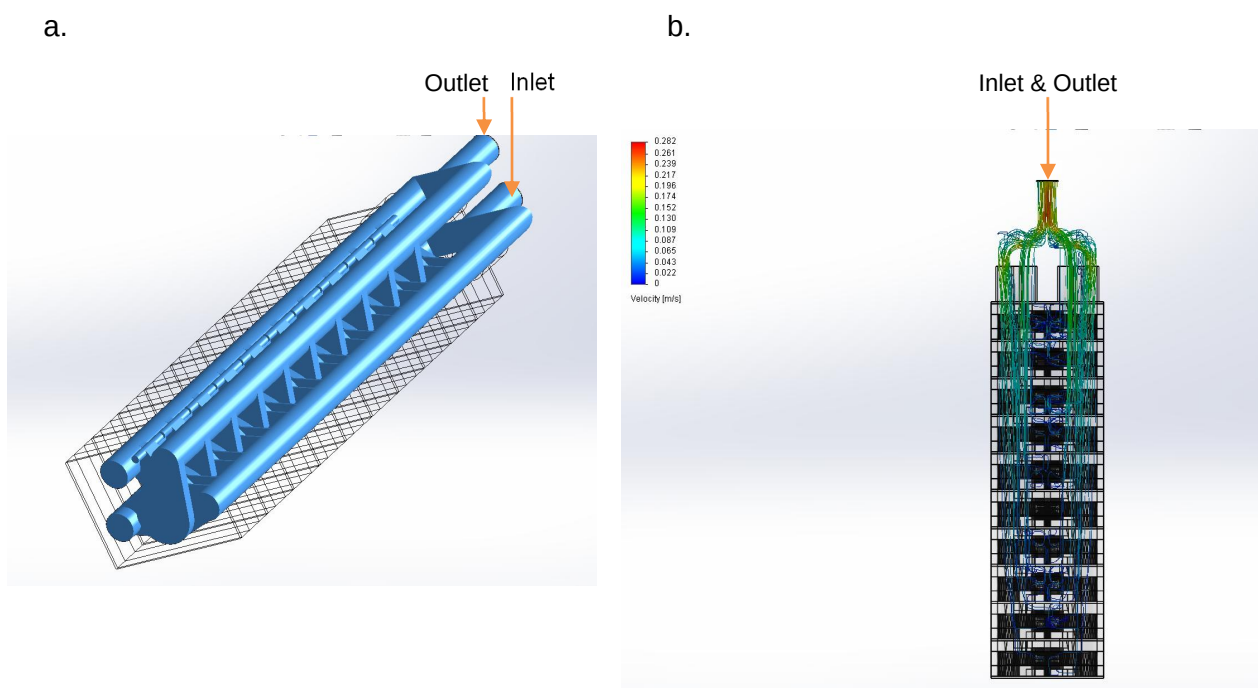


Figure 6-6: MCFPE reactor stack (10 Pairs) depicting (a) the fluid volumetric region of co-current flow, and (b) the streamline flow velocity distribution for the inlet and outlet from one side only at a flow velocity of 0.1 m.s^{-1}

Multiple electrode pair simulation: Co-current for inlet and outlet from opposite sides

By introducing the flow of liquid electrolyte from one side, and allowing it to exit from the opposite side, the flow should allow for improved balancing relative to each of the electrode pole pairs. The fluid region is represented in Figure 6-7. As fluid travels down a pipe with a termination, it will be found that near the termination pressure will build up where the highest flow velocity is experienced, as observed with the CFD design of the HFP electrode stack. Back pressure built

up along the pipe manifold will dictate the quantity of flow that would exit out of the initial electrode pairs [69].

Figure 6-8 shows behaviour indicative of lower flow velocities to the different electrode pairs. At a flow velocity of 0.1 m.s^{-1} (Figure 6-8a), flow is present for all electrode pairs for the whole length of the reactor. However, at a flow velocity of 0.05 m.s^{-1} (Figure 6-8b) flow is omitted for the last two pairs of the stack, indicating that not enough back pressure is present in the design to provide sufficient flow to the termination of the flow path. Considering both flow scenarios above, flow is not balanced for both the maximum and minimum flow velocity conditions.

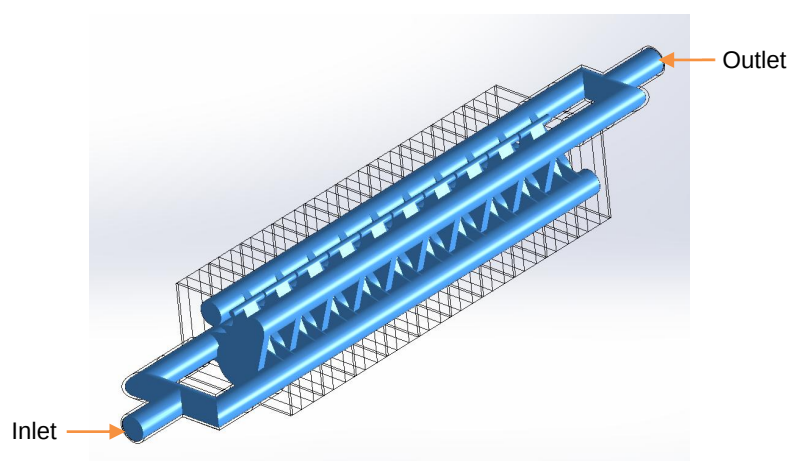


Figure 6-7: Representation of the fluid region of the MCFPE reactor stack utilising co-current flow with inlets and outlets on opposite common sides

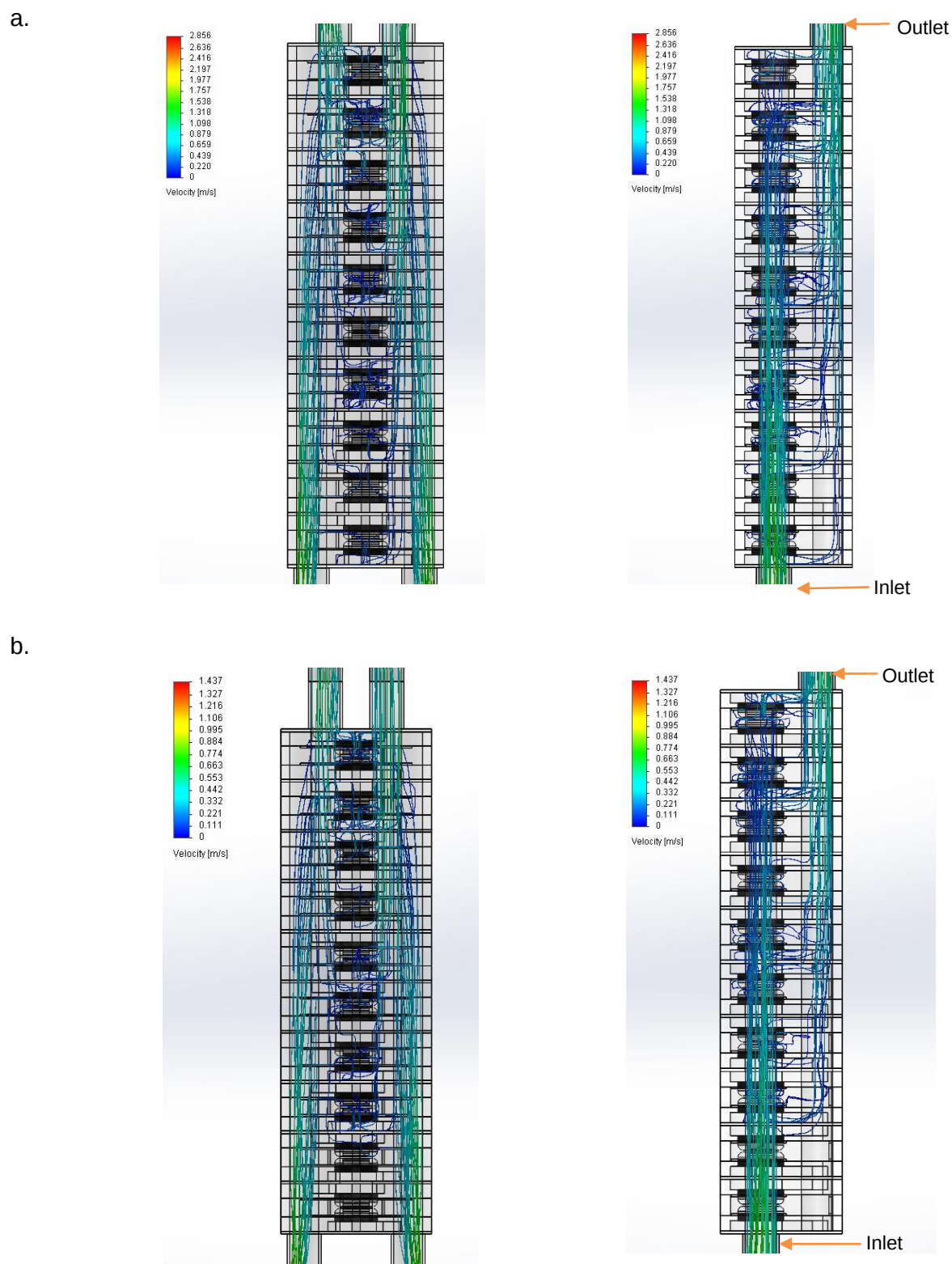


Figure 6-8: Streamline velocity profiles for a multiple electrode stack using co-current flow for the inlets and outlets from the same side for (a) 0.1 m.s^{-1} , and (b) 0.05 m.s^{-1} for the MCFPE reactor concept

Multiple electrode pair simulation: Counter current flow

All flow scenarios simulated above suggests that a flow regime needs to be adopted that allows for even flow distribution to each electrode pair. A counter current flow regime would serve to balance the flows by letting both inlets enter from opposite sides with the same flow philosophy adopted for the outlets. The finalised fluid region, that allows for a counter current flow, is represented in Figure 6-9. In theory, pressure should build up at opposite ends of the reactor creating a balancing effect for flow, and since flow is drawn from each electrode pair in opposite directions, fluid flow to each of the electrode pairs should be balanced. This analysis was performed at the maximum flow velocity to demonstrate the balancing effect (Figure 6-10), and it shows that flow moving from each electrode is similar, if not enhanced, towards the ends of the reactor stack. This indicates that the stack would have a limitation to the number of electrode pairs that it can house before electrodes located in the centre are limited to the amount of flow that they could receive. This is directly related to: (i) the back pressure created by the electrodes themselves, (ii) the electrode injection chamber slots, and (iii) the size of the inlet and outlet tubes respectively. A counter current flow regime has therefore been adopted for the MCFPE reactor stack, and will form the standard for future stack design.

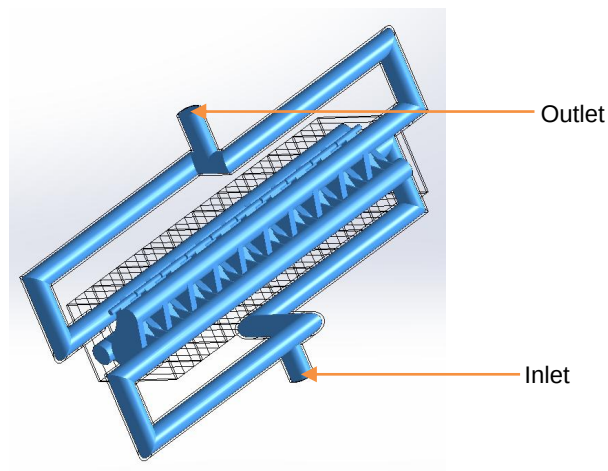


Figure 6-9: The fluid region representation of a MCFPE reactor stack utilising counter-current flow with inlets entering from opposite sides and outlets exiting from opposite sides

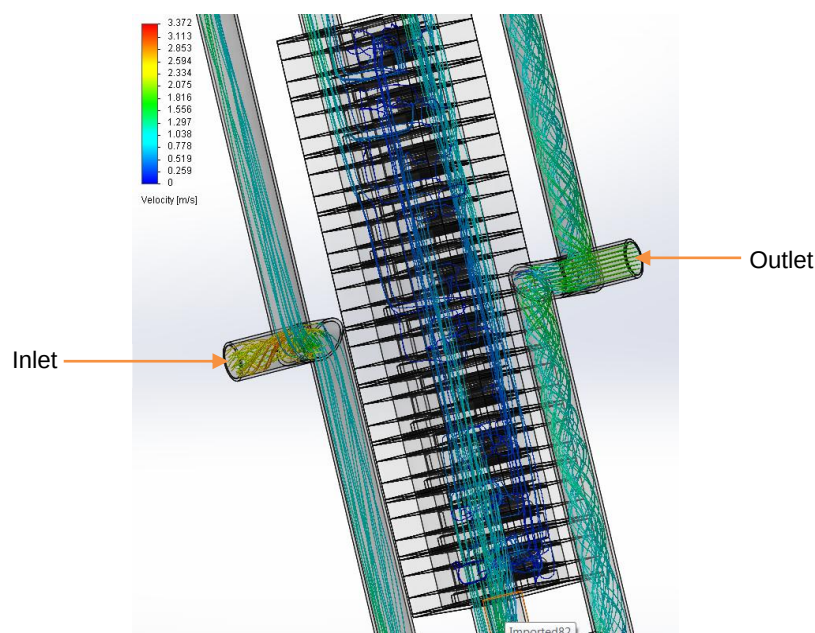


Figure 6-10: Streamline velocity profiles for a multiple electrode stack using counter current flow for inlets and outlets entering and exiting from opposite sides at 0.1 m.s^{-1} for the MCFPE reactor

6.2.4. Gas/liquid separation system modifications for MCFPE reactor stack

The medium to be separated, i.e. a product solution from the DEFT™ stack technology, is a heterogeneous mixture composed of a gas and liquid of which the void fraction of liquid is considerably larger compared to the gas phase [70]. The gas phase is inherently present in the form of micro-bubbles in the solution. This type of separation is complex and unique, as the extraction of these micro-bubbles is from a rapid throughput liquid medium, which is largely not dealt with in any available commercial system. A number of existing systems are available that deal with the scenario of removing small liquid amounts from a gaseous stream [70]. By relying on conventional mature gravitational methods, employed by conventional membrane based electrolysis technologies, would prove to be impractical for the DEFT™ technology as the outcome would not be compact, and would drive up initial capital expenditure and operating costs, due to excessive electrolytic volumes that need to be handled [71]. The separation of heterogeneous mixtures is normally achieved by physical/mechanical means by utilising gravitational and centrifugal forces [70].

From prior pilot plants, centrifugal action and submerged gravitational separation methods have been attempted to create the desired separation effect. One of the key drawbacks of centrifugal separators, such as cyclones, is that significant pressure drops they incur and additional pumping head, which would suggest larger parasitic loads for the pump [67]. This method would be ideal if applied as a pre-separation or post-separation step, but it would not suffice to be a feasible standalone system, due the requirement of extracting the balance of bubbles leaving the

underflow of the cyclone separator. It is ideal to have a single separation step linked to the DEFT™ system in order to keep the process as simple and as modular as possible. Previously, the use of membrane contactors has been deemed a viable and a compact solution to achieving high efficiency gas liberation from a flowing liquid volume, however, incompatibility of the membrane with the electrolytic medium itself discounts this solution, as it makes the membrane significantly more wettable, which reduces its ability to be hydrophobic surrounding liquid medium [56]. Two separation derivatives will therefore be considered for testing in the MCFPE pilot plant illustrated by Figure 6-11.

A single stage separation system will be used for both the oxygen and hydrogen circuits, with a comparison drawn between using a submerged separation system, in contrast to a packed bed system whereby the liquid is allowed to contact the surrounding gases. The liquid moves against the buoyancy of the product gas, and a balance of forces will apply [65]. If the gas bubbles possess enough buoyancy, so that the drag force created by the fluid can be overcome, it will be successfully separated. If the bubble is not of a sufficient size, it will continue to move down the separation column until the filtration media increases its size by means of coalescing the bubble with other smaller or larger bubbles trapped within the media. This gas can then find its way to the top of the separator by means of exhaust tubes.

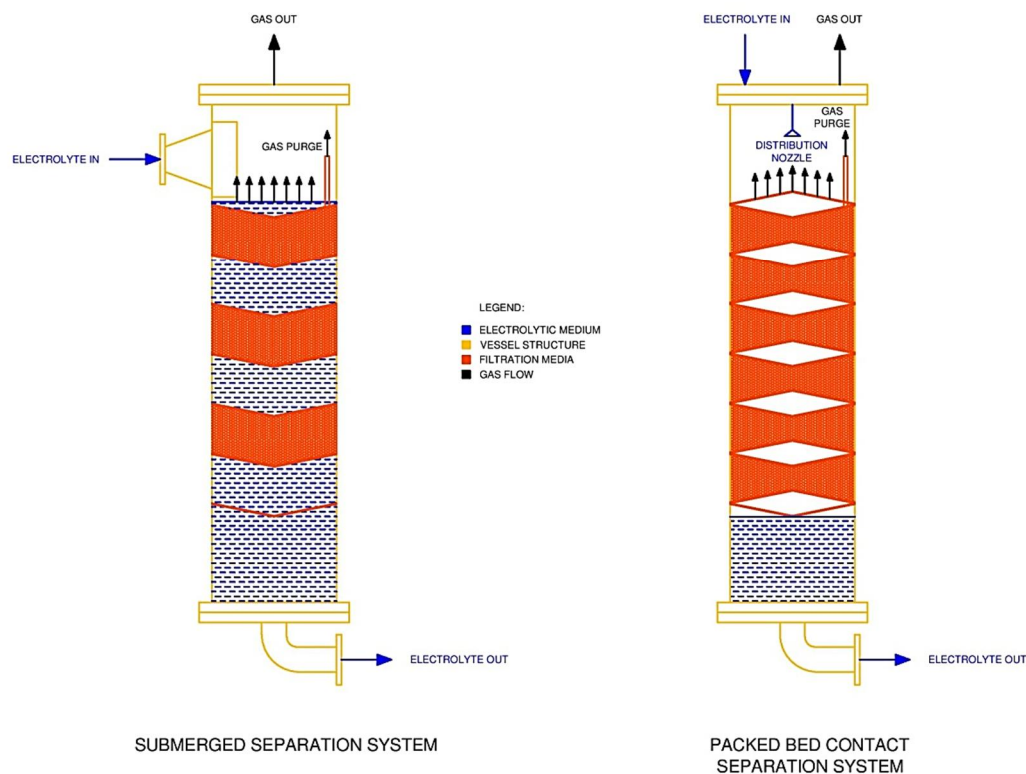


Figure 6-11: MCFPE gas/liquid separation plant derivatives

For a packed bed system, liquid is allowed to flow with thin films over media. Gas that is entrained in the liquid is allowed to escape from the liquid easily, whereby the gas can effortlessly make it towards the separator's upper hemisphere by means of exhaust tubes or through the copious voids formed in the packed media. Through contacting the liquid with surrounding gases, this allows for effective stripping of the liquid of gas, especially when a concentration gradient is developed, in the case of forming a vacuum which would result in effective removal of gases from the liquid [56]. Foaming commonly occurs, which is related to the liquid properties, and can cause introduction of unwanted solvents into the gas lines. Introduction of a nozzle or a liquid distribution plate would effectively spread the liquid evenly over the medium to utilise all available media area, along with effectively breaking down the foam by mechanical action [70].

6.2.5. Variables to be tested

The MCFPE pilot plant has been designed and constructed taking into consideration all positive attributes that resulted from the technology development thus far. Its main objective is to comprehensively take into account all optimal parameters, and determine all trends, associated to the quality of gaseous products evolved, which has been a continued challenge in this research. Additional electrocatalytic combinations will also be tested to benchmark performance to the previous test plants.

Gas purity, as already mentioned, is dependent on the operating temperature, as it would have an effect on the viscosity of the electrolytic medium. This will in turn determine the extent of turbulence experienced on or near the electrode surface, that would lead to benefits to the performance of the electrolyser in that mass transfer effects are eliminated. However, this could have cross gas contamination implications [22]. Gas purity is also dependent on the current density, as increased current density would result in an increase of the bubbles evolution diameters. This would consequently result in an enhanced separation force leading to improved gas purities, however, enhanced solution flow velocities would serve to decrease bubble diameters, which yields an optimisation problem between the two parameters [27].

Previously the optimal electrode gap, which was concluded as a balance between performance and gas quality, was observed to be in the region of 2.5 mm (as investigated in Chapter 3) [6]. The design of the MCFPE reactor allows for a variation of electrode gaps between 2.5 – 4.5 mm, so as to confirm the optimal electrode gap.

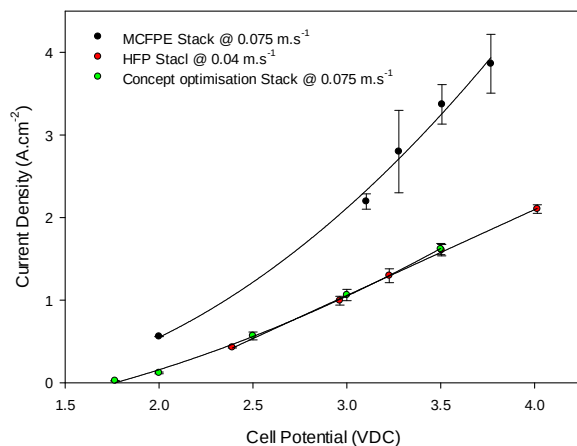
6.3 RESULTS AND DISCUSSION

6.3.1. Performance comparison of the MCFPE, HFP, and concept optimisation pilot plants

Similar electrocatalysts have been applied for the various test plants, which takes precedence in comparing any additional performance enhancement to be obtained, by employing favourable geometries that would make for balanced flows, and uniform current density distributions. Two electrocatalysts have been selected for this comparison, i.e. (i) industrial pure nickel filtration mesh, for both the anodic and cathode electrodes, and (ii) the $\text{IrO}_2\text{-RuO}_2\text{-TiO}_2$ (MMO) coated anodic electrode and platinum plated cathodic electrode both on a pure nickel mesh substrate.

A temperature of 60°C has been selected for the comparison, as this represents a test temperature common to all test rigs, due to the material limitations related to some. The MCFPE system is limited in regards to the maximum operating temperature due to its materials of construction. PVC materials can only operate at 60°C in aggressive alkaline environments despite the capability of materials such as stainless steel and polypropylene, to operate at temperatures of up to 90°C [72,74]. From Figure 6-12 it is clear that the MCFPE stack exhibits superior performance in contrast to the other experimental test rigs when operated with the Ni/Ni electrode pair. Even though the data represented for the HFP test stack is recorded at a lower flow velocity, it would not have the capability of matching the performance obtained for the MCFPE stack. The fact that the MCFPE stack provides individual power source connections, with current distribution rings, and fluid injection chambers, allows this stack to eliminate inconsistencies which hampers the performance of alternate tested stacks. In this manner, non-homogeneous distributions of current lines reduce the occurrence of 'hot spots' on the electrode surface, which is the preventable goal of many electrolyser systems [46]. The positive effect that an optimised geometry has on cell performance is reiterated, and discussed for an alternate membraneless technology by O'neil et al. (2016) [48].

a.



b.

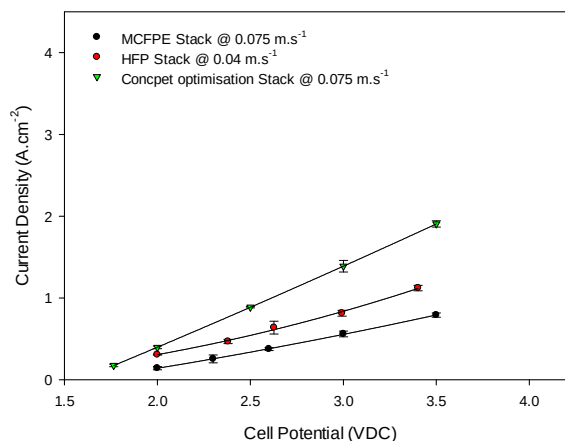


Figure 6-12: Polarisation curves employing (a) pure Ni/Ni, and (b) RuO₂-IrO₂-TiO₂ (MMO)/Pt electrocatalytic combinations, as a function of stack type and flow velocity, at 60°C and, 30% KOH

With regard to the MMO/Pt electrocatalytic combination, the concept optimisation test stack exhibited the best performance, with both the MCFPE and HFP stacks demonstrating significantly lower performances. These two plants have one aspect in common as they both have stainless steel incorporated into structural elements. As discussed, stainless steel, whether charged or not, is a source of contamination that results in the de-activation of catalytic surfaces [35]. Figure 6-12b is, however, not a fair comparison of the performance enhancement obtained from the different stacks, and since stable performance has been obtained from a pure nickel combination, it can be concluded that the MCFPE design, in terms of performance, is the superior stack design tested to date for the DEFT™ technology.

6.3.2. Performance comparison of full, 4/5, and half scale MCFPE stacks

As described, the MCFPE system makes use of individual 30 mm electrodes in a single injection chamber, i.e. each with its own injection chamber. A full stack comprises of all manufactured electrode pairs, which amounts to ten pairs per stack. The 4/5 scale stack makes use of eight electrode pairs, and the half stack makes use of five electrode pairs. In theory, performance differences should be present for the different stack sizes, as variations will occur in relation to how the fluid distributes itself along the length of the reactor. With fewer pairs present in a stack, it would be found that the solution would distribute itself more equally amongst the electrode pairs as shown by CFD results. This effect would boost performance; as current densities would be better balanced between the electrode pairs. Comparisons have been presented at the maximum

operating temperature of 60°C, since performance and stack efficiency are always maximised with increasing temperature [10].

Even at a low flow velocity of 0.05 m.s⁻¹, a difference in performance is observed for the different stack sizes (Figure 6-13). This flow velocity was chosen as it is one of the greatest flow velocities feasible for the full stack that enables the separation system to deal with the solution throughput. Flow velocities greater than this, result in the accumulation of fluid within filtration layers, which deteriorates the gas/liquid separation efficiency of the separators. From Figure 6-13 it is clear that the full stack exhibited the best performance with the 4/5 scale stack representing the lowest performance. The differences are within a ~20% deviation, which does not represent a significant difference in performance. These differences may be a result of conductivity differences of the external circuit and internal circuit, due to the presence of inconsistencies in the experimental set-ups. By comparing various flow velocities, for both the full and half stack, it would be clear whether significant differences are evident.

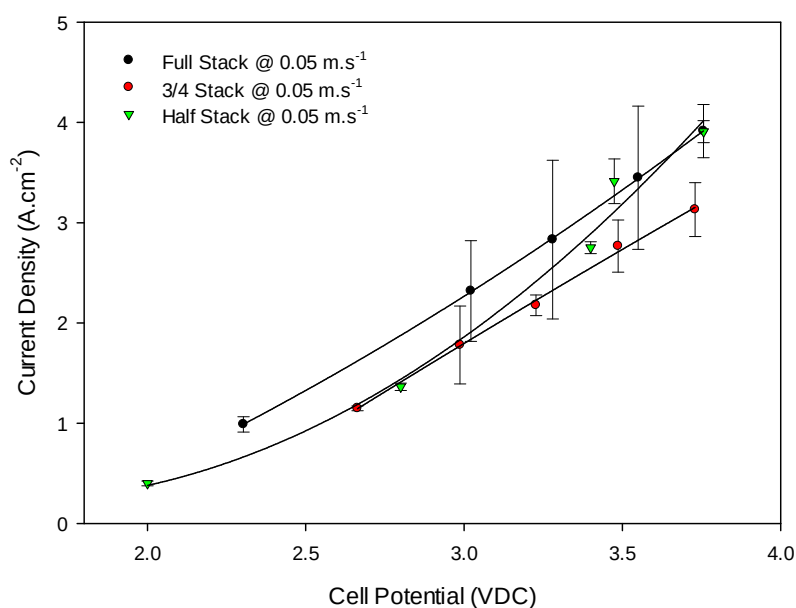


Figure 6-13: Polarisation curves for a variation in MCFPE stack size utilising pure nickel electrodes, at 60°C, a flow velocity of 0.05 m.s⁻¹, and 30% KOH

From Figure 6-14a it is evident that the performance of the half stack is optimised for the highest flow velocity tested. For the lower flow velocities, the full stack demonstrates the best performance. The full stack as a result also demonstrated superior overall plant efficiencies, with a maximum efficiency of 34.1 HHV% obtained utilising pure nickel anodic and cathodic electrode combinations at the lowest flow velocity (Figure 6-14b). For all stack sizes, the greater flow

velocities inhibit the overall efficiency of the MCFPE pilot plant. These results suggest that larger flow velocities are more selective to smaller stacks in contrast to lower flow velocities. Solution flows distribute themselves more evenly between electrode pairs in a longer stack at lower flow rates when a sufficient back pressure is present to enable this. Larger flows tend to create point pressures, which tend to favour enhanced flows in certain regions. By examining the gas purities of these alternate length reactor set-ups, it can be deduced whether stack length has any prominent effect on gas purity, which takes preference over stack performance. Gas purities have again been compared at the lowest flow velocity, due to the breakdown of gas/liquid separator performance, at enhanced flow rates associated with the larger stacks.

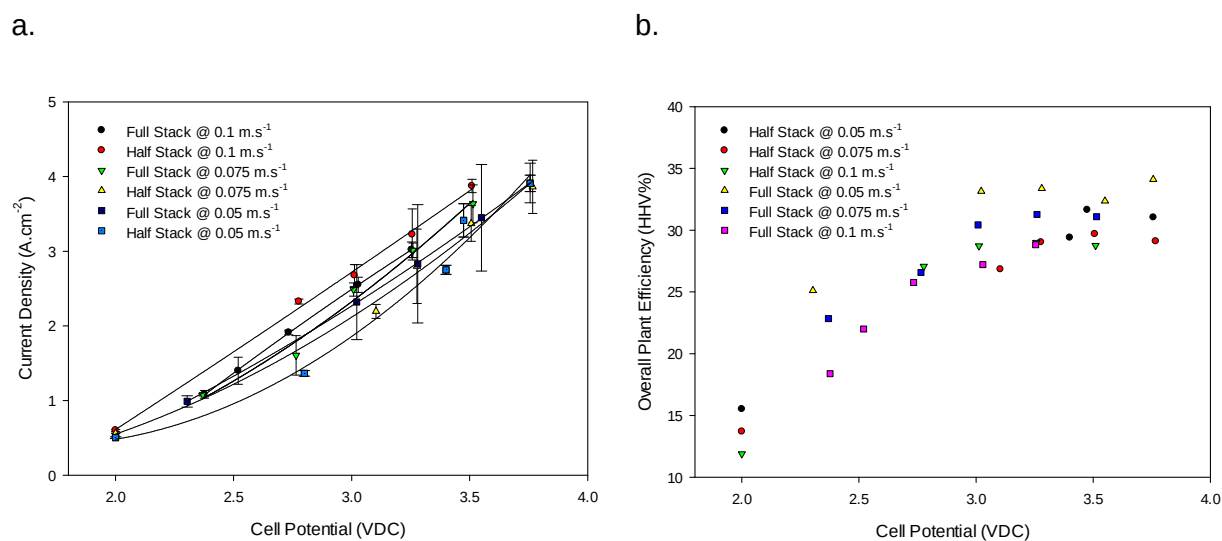


Figure 6-14: (a) Polarisation curves, and (b) HHV% efficiency versus cell potential for the full and half MCFPE stacks utilising pure nickel electrodes, as a function of flow velocity, at 60°C and, 30% KOH

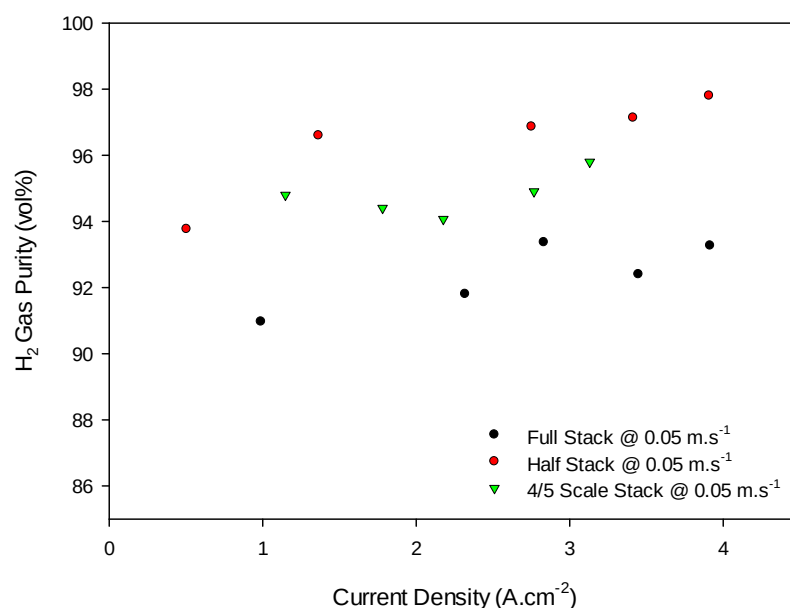


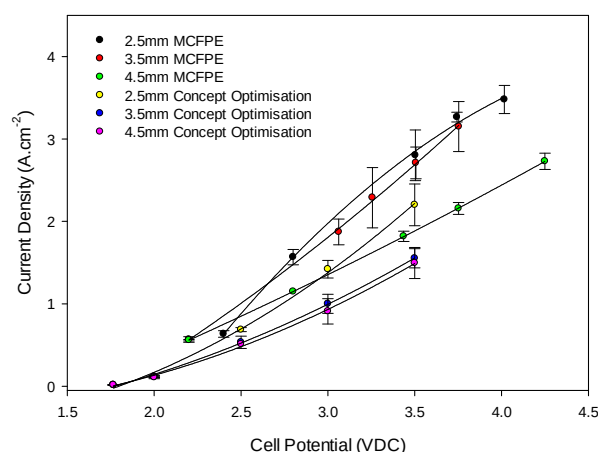
Figure 6-15: Hydrogen gas purity versus current density for a variation in MCFPE stack scales utilising pure nickel electrodes for a flow velocity of 0.05 m.s⁻¹, 60°C, and 30% KOH

Gas purity is a clear indication of what is occurring with reference to the flow dynamics within the MCFPE stack. It is evident that the half stack developed the best gas purities in contrast to lesser qualities obtained with the full stack. The shorter stack therefore remains the best option for enhanced gas qualities. Although the above values do not represent long term steady state values, it is clear that the values are significantly superior in contrast to the HFP stack (Figure 5-21 (page 109)), and are shown to hold a relatively constant value for a broad current density range.

6.3.3. Electrode gap performance comparison

Performance with respect to the electrode gap has already been discussed in previous chapters, however, the MCFPE stack allows for this flexibility to ascertain whether the result is repeatable for different geometries of the DEFT™ technology.

a.



b.

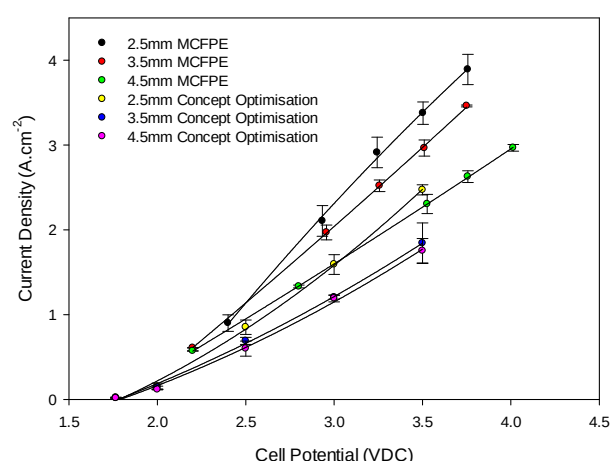


Figure 6-16: Polarisation curve comparison between the MCFPE stack, and the concept optimisation stack utilising pure nickel electrodes for (a) a flow velocity of 0.075 m.s⁻¹ and, (b) a flow velocity of 0.1 m.s⁻¹, at 50°C and, 30% KOH

Figure 6-16 illustrates the differences in performance with respect to similar electrode gaps for the MCFPE and concept optimisation systems. It is shown that the smaller electrode gaps enhance cell performance, however, a compromise must be met between the performance and the generated gas purities [6,31]. The MCFPE stack however generated superior performance in contrast to the original DEFT™ concept optimisation test rig. The concept optimisation stack made use of a common injection chamber to feed 4 electrode pairs. Through feeding each electrode pair independently and indirectly, has shown to improve the performance of the said pair, which is again observed in the comparison. The smallest electrode gap tested here is 2.5 mm, as deduced as the optimal electrode gap from prior investigations [6]. Smaller electrode gaps further improve cell performances, however, the incidence of gas cross contamination would be more prevalent.

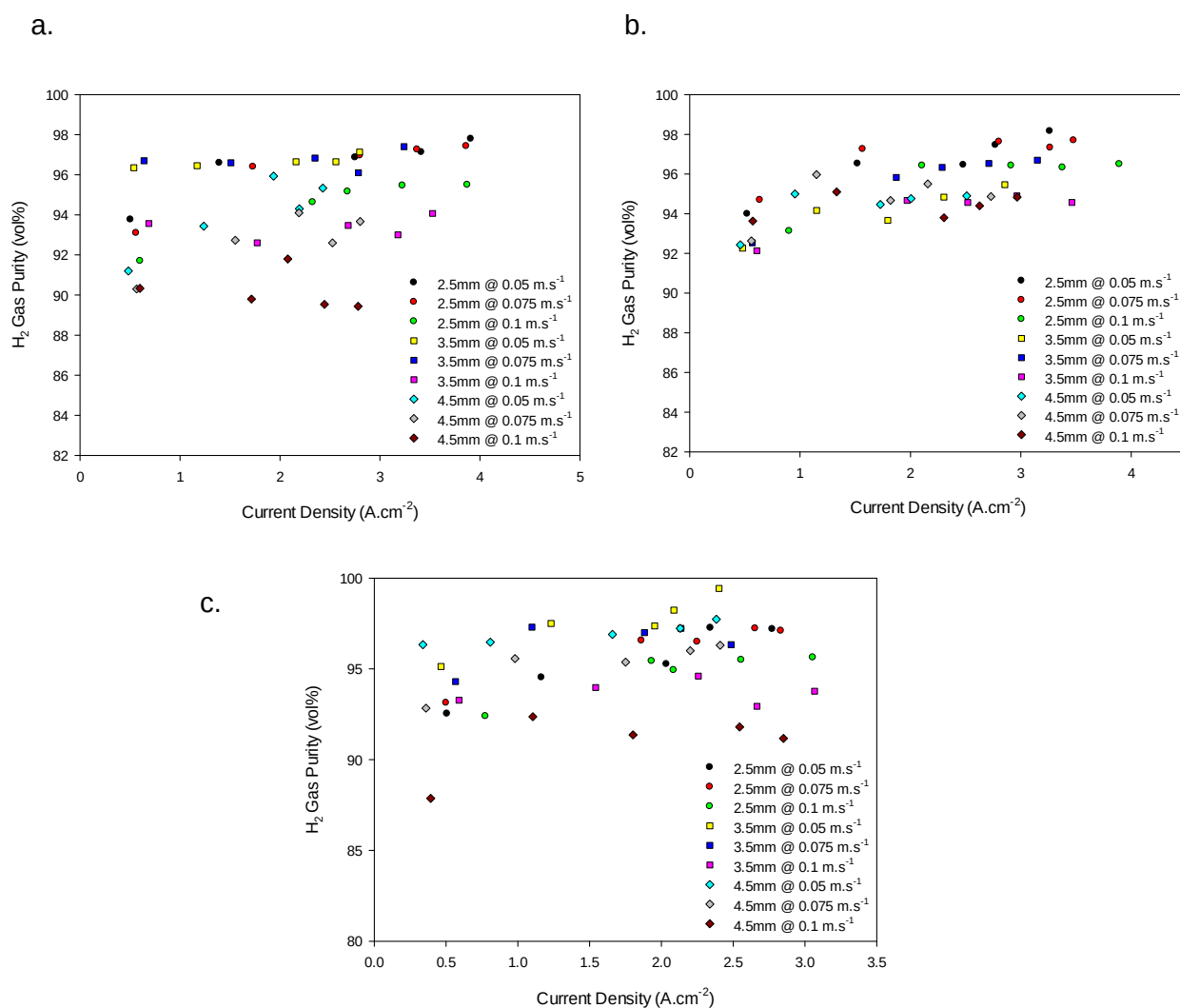


Figure 6-17: H₂ gas purity versus current density utilising pure nickel electrodes as a function of the electrode gap, and flow velocity for (a) 60°C, (b) 50°C, and (c) 40°C for 30% KOH

Analysis of the relationships formed between the hydrogen gas purity, current density, and electrode gap reveals the true optimal electrode gap for the system (Figure 6-17). For all test temperatures it is apparent that the highest flow velocity of 0.1 m.s⁻¹, generates gas purities lower than that of 0.075 and 0.05 m.s⁻¹. This is once again a deficiency on the part of the gas/liquid separation system, being incapable of handling the additional liquid throughput due to its submerged operating philosophy. For 60°C, both 2.5 mm and 3.5 mm electrode gaps generated similar purities at 0.05 and 0.075 m.s⁻¹, and the operating ideal would be toward the 2.5 mm electrode gap, due to the additional performance gained. The same trend is observed for 50°C, however, for 40°C it is evident that improved gas purities are seen at 3.5 mm in contrast to 2.5 mm. At the lower temperatures, the ease with which the gas bubbles escape from the surface is reduced, resulting in an enhanced, thicker gas meniscus on the surface of the electrode. A larger electrode gap is therefore required to compensate for the thicker gas meniscus formed [6].

Taking a conservative approach, the electrode gap of 3.5 mm caters for most operating conditions, yet, 2.5 mm would enhance performance when the system is operating above 50°C.

6.3.4. Long term gas purity analysis

It has been shown that the Oliver IGD Tocsin 903 hydrogen gas sensor, used to determine the vol% quality of the hydrogen gas both in the hydrogen product stream and oxygen stream, has in a few instances not recorded a hydrogen purity greater than 99 vol%. It has often been found, that if the system is left unattended for extended periods of time, the purity of gas increases to be within a desirable range of purity of >99 vol%. Due to the extensive nature of tests performed, and due to time constraints, it is not possible to allow the plant to reach a steady state, in order to rapidly analyse the produced trends. The plant, however, is allowed the same set time between recorded readings, until a stable reading is recorded. An analysis was performed using an independent laboratory (AirSep Labs) to analyse samples extracted from the MCFPE pilot plant at defined experimental parameters, to determine what the actual gas purities are emanating from the pilot plant.

Since favourable gas qualities were recorded at flow velocities of 0.05 and 0.075 m.s⁻¹ compared to 0.1 m.s⁻¹, these flows were chosen as the benchmark for the analysis. The following experimental conditions and test results were generated for the first batch of experimental runs. For each batch, the plant was operated continuously for more than 6 hours, to ensure that a steady state was attained, and that the separators were clear of most atmospheric contaminants.

Table 6-1: Batch 1 external laboratory gas purity confirmation at elevated flow velocities utilising pure nickel electrodes

Stream Sampled	Flow Velocity (m.s⁻¹)	Operating Temperature (°C)	Current Density (A.cm⁻²)	Gas Purity on IGD 903 (vol%)	H₂ Result (vol%)	O₂ Result (vol%)	N₂ Result (vol%)	Uncertainty (Vol%)
A-Hydrogen	0.076	51.1	3.44	100.6-OL	99.2	0.12	0.68	0.2
D-Hydrogen	0.079	51.27	3.85	100-OL	99.81	0.06	0.13	0.2
B-Oxygen	0.076	51.4	3.45	87.4	<0.2	99.5	0.47	0.2
C-Oxygen	0.064	50.78	2.73	88.1	<0.2	98.8	1.16	0.2

For the above test results, the clarity of the outlet streams from both separators along with the clarity of the solution from the view ports located at the base of the separators were observed for

each experimental condition (Figure 6-18). For all recorded results, it was found that these lines and viewports remained void of any evidence of gas passage.

The IGD 903 sensor in hydrogen rich conditions provides readings past the maximum reading of 100%, due to enrichment conditions. The tolerance is reported to be in the region of ± 1 vol%, and the results obtained from the Agilent 6890 gas chromatograph reports gas purities well above 99 vol% for the optimal flow velocity and at high current densities. The IGD 903 sensor is designed to operate in a hydrogen rich atmosphere, and hence in conditions where the hydrogen concentration is low, it provides an inaccurate value for oxygen purity. The oxygen purity, however, has been revealed to be well above the flammability limit of 96 vol%, which is ideal for the DEFT™ technology [48]. It was observed that some atmospheric contaminants were present in the gas samples, which suggests that the purities are in fact greater than what was recorded. At a lower flow velocity and current density, the purity of the oxygen gas is still preserved, which initially provides intuition into still obtaining reliable gas purities at lower flow velocities of 0.05 m.s^{-1} . An additional batch of results therefore was run to credibly establish whether adequate gas separation would be feasible at lower flow velocities. The independent gas analysis report can be found in Annexure B.

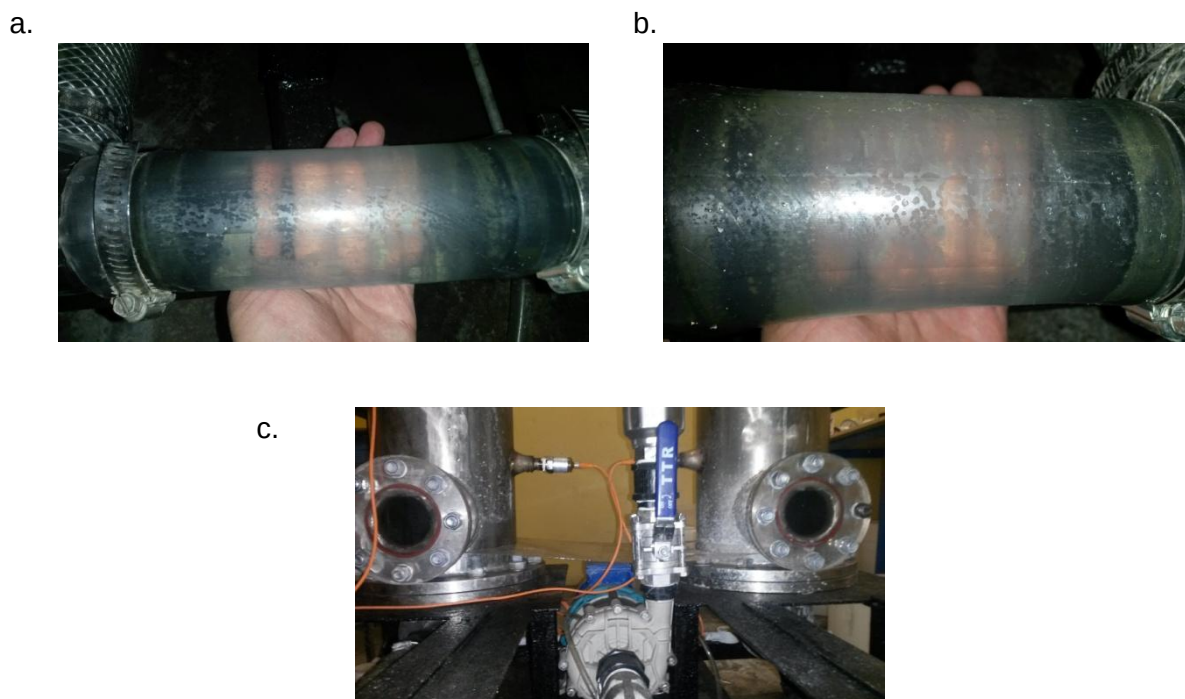


Figure 6-18: Observable clarity examination of (a) the left separator outlet, (b) the right separator outlet and, (c) view ports at the base of each separator for purity batch 1

Table 6-2: Batch 2 external laboratory gas purity confirmation at low flow velocities utilising pure nickel electrodes

Stream Sampled	Flow Velocity ($m.s^{-1}$)	Operating Temperature ($^{\circ}C$)	Current Density ($A.cm^{-2}$)	Gas Purity on IGD 903 (vol%)	H₂ Result (vol%)	O₂ Result (vol%)	N₂ Result (vol%)	Uncertainty (Vol%)
A-Hydrogen	0.05	46.2	1.49	99.1	94.94	4.51	0.55	0.2
C-Hydrogen	0.05	50.4	3.57	101-OL	96.02	3.65	0.33	0.2
B-Oxygen	0.05	46.2	1.49	82.4	<0.2	99.4	0.6	0.2
D-Oxygen	0.05	50.4	3.57	83.6	<0.2	99.14	0.86	0.2

Examination of the outflow view areas yet again confirms that no entrained gas was visible in the solution, indicating that product gas purity results are a direct consequence of processes happening within the reactor.

According to the stoichiometry of the water electrolysis reaction, the volumetric quantity of hydrogen produced, is twice that of oxygen [35]. It is then to be expected that, in the event of cross gas contamination, it would lead to hydrogen gas contaminating the oxygen gas product stream due to the larger quantity of hydrogen evolved. However, results tabulated in Table 6-2 point towards the opposite effect, i.e. hydrogen gas being contaminated by oxygen. The oxygen gas purity is above 99 vol%, at both high and low current density operating conditions, whereas the hydrogen gas purity is hindered by the presence of oxygen gas, which is enhanced at lower current densities. Without the production of gases on the mesh surface, and with identical electrode geometries, it is expected that the balance of flow to the anodic and cathodic collection compartments should be the same.

The formation of gases on the electrode surface can, however, alter the pressure drop characteristics of the structure, which can alter how the solution distributes itself between the anodic and cathodic electrodes. This is especially the case at critical low flow velocities of $0.05 m.s^{-1}$, and less so at enhanced flow velocities of $0.075 m.s^{-1}$. Increased gas formation on a surface increases the pressure drop for fluid to pass through the mesh. The hydrogen gas meniscus is not adequately reduced, and hence forced to the rear of the electrode, and consequently is subject to contamination by other gases such as oxygen present within the electrode gap. As oxygen is produced to a lesser extent, the flow of solution favours the oxygen side due to the lower pressure drop, and an appreciable separating force exists to ensure that the oxygen gas is pushed through the electrode, which preserves oxygen gas quality. At greater flow

velocities, oxygen is instead subject to cross contamination due to the enhanced incidence of turbulence present in the electrode gap region whereby contaminant gases, to a lesser extent, most likely to be hydrogen, are extracted to the oxygen side due to the enhanced separation mechanism to the oxygen side. This behaviour is diagrammatically explained in Figure 6-19.

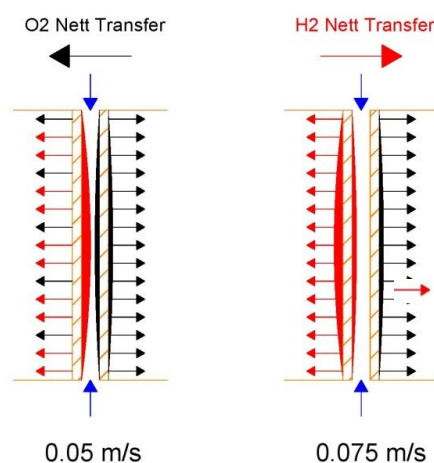


Figure 6-19: Cross gas contamination phenomena as a function of electrolytic flow velocity

Therefore, from the results collected, the flow velocity of 0.075 m.s^{-1} maintains an appreciable separation effect, keeping the majority of the formed gases extracted to the rear of the electrode, and preventing an appreciable build-up of a gas meniscus on the surface of the porous electrode. This holds true for a broad range of current densities and operating temperatures.

6.3.5. Submerged separation versus contact separation

Poor performance has been attributed to the submerged gravitational gas/liquid system. Although this system is ideal for linking multiple electrolysis systems in parallel with one another, as fluid pressure allows the same flow rate to transverse multiple systems, it is attributed with multiple operational difficulties, and requires a significantly larger volume in order to attain similar separation efficiencies in contrast to contact type systems [56]. Contact type systems allow for a high surface area contact of the liquid with surrounding gases, which allows for easier liberation of entrained gases from liquids [65]. It is clear from experimental results that the efficiency of the contact type systems is significantly improved over the submerged system for the same volume of the gas/liquid separation system.

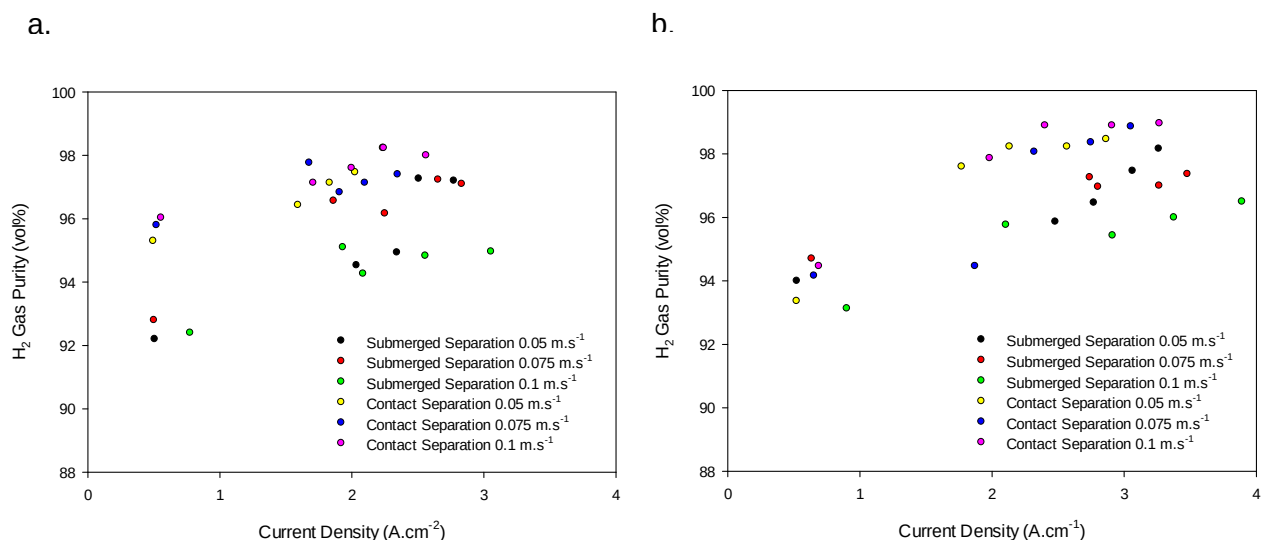


Figure 6-20: Hydrogen gas purity versus current density for the submerged and contact gas/liquid separation system utilising pure nickel electrodes for (a) $40^\circ C$ and, (b) $50^\circ C$, as a function of flow velocity, at an electrode gap of 2.5 mm, and 30% KOH

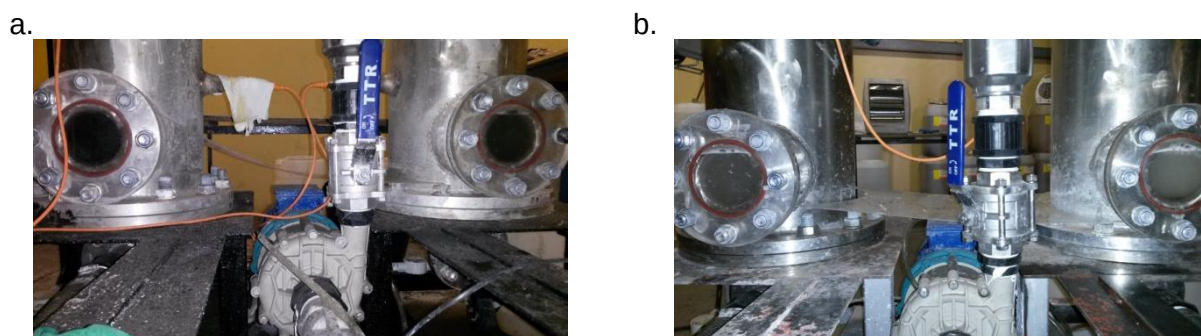


Figure 6-21: Electrolytic clarity of separator viewports for (a) contact and, (b) submerged gravitation separation systems at, $0.075 m.s^{-1}$, $50^\circ C$ and, 30% KOH

Figure 6-21 illustrates a clear distinction between the two separation system alternatives for the same experimental parameters. The submerged separation system draws substantially more entrained gas down the length of the column, which would certainly hinder developed gas purities. This is apparent in the results collected for both $40^\circ C$ and $50^\circ C$, as for both temperatures, the gas purities are superior for the contact separation system in contrast to the submerged gravitation system. For the contact separation system, purities increase with increasing separation flow, which indicates that purities are instead subjected to the integral workings of the MCFPE stack, rather than the operational efficiency of the gas/liquid separation system. As observed in previous results, a drawback of a separation system was, when a decline in product gas purities is observed with increased flow velocities, as the separation system is incapable of providing liberation of gases from the liquid medium at enhanced throughputs. A contact type

separation system is therefore ideal for the DEFT™ technology, as it provides a smaller efficient solution to achieve liberation of entrained gases.

6.3.6. Removal of MCFPE barrier plates

Barrier plates were originally inserted between common collection chambers within the MCFPE stack, so as to prevent any irregularities with regards to the turbulent recombination of bi-phase product streams, that could otherwise alter the flow dynamics occurring on the surface of the electrode. The diagrams in Figure 6-22 illustrate the difference in dynamics for the two stack configurations.

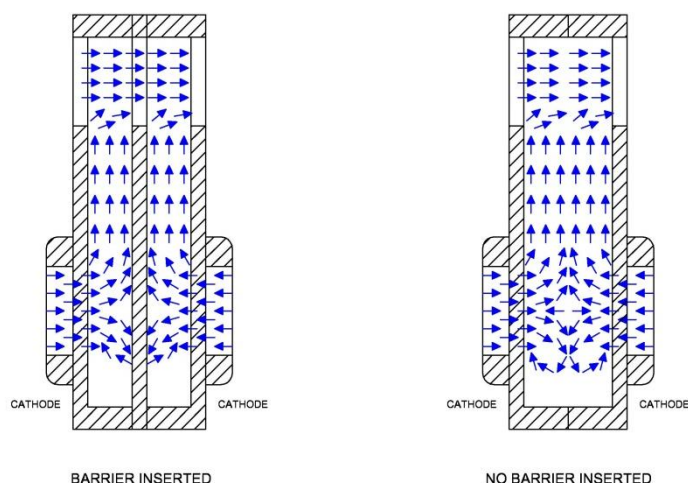


Figure 6-22: Flow configuration of a common bi-phase collection chamber with and without a separation barrier

Through the elimination of the common bi-phase collection chamber, fewer components and seals are required for the assembly of the MCFPE stack. Comparison results (Figure 6-23) reveal surprising improvements in both cell performance and gas purities:

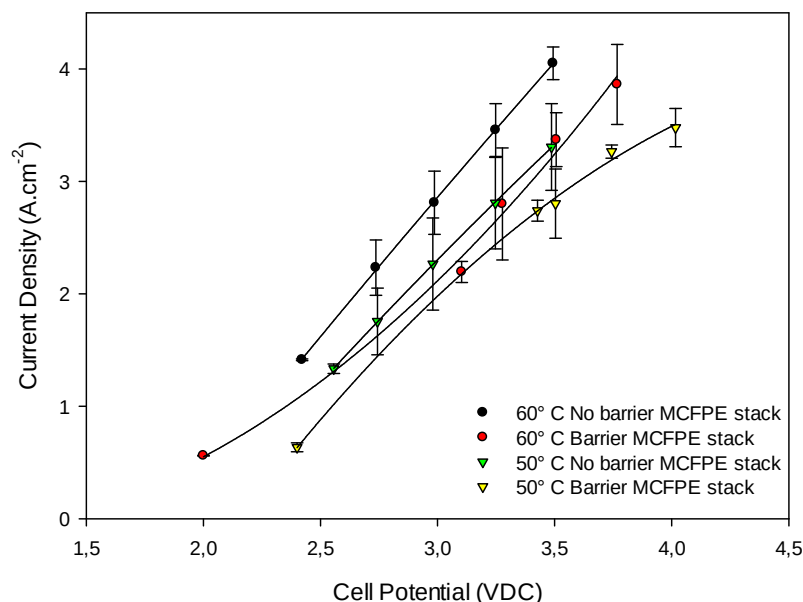


Figure 6-23: Polarisation curves for the MCFPE stack utilising pure nickel electrodes, with and without barriers included between common bi-phase collection chambers for both 50°C and 60°C at a flow velocity of 0.075 m.s⁻¹, 2.5 mm electrode gap and, 30% KOH

After examination of Figure 6-23, the MCFPE stack that does not incorporate barriers, exhibits improved performance over the stack that incorporates barriers for both 50°C and 60°C, and across the tested cell potential range. It is thought that the combining flows, through enhanced turbulence, provides an exerted back pressure toward the rear faces of the electrodes. By doing this, the conventional flow velocity's bullet profile is flattened with evened out flow velocity vectors passing through the mesh material. This implies that current density distributions are improved across the surface of the electrode.

Figure 6-24 depicts an improvement in hydrogen gas purities for the MCFPE stack containing no barriers, and hence the same result can be expected for the oxygen gas. The same phenomenon that leads to an improvement in cell performance for the MCFPE stack can be used to explain the improvement in the product gas qualities. 5-13 (page 98) illustrated a reduction in flow velocities closer to the circumference of the circular electrode, however, internal back pressure will aid in creating a more uniform distribution of flow velocities moving through the mesh electrodes.

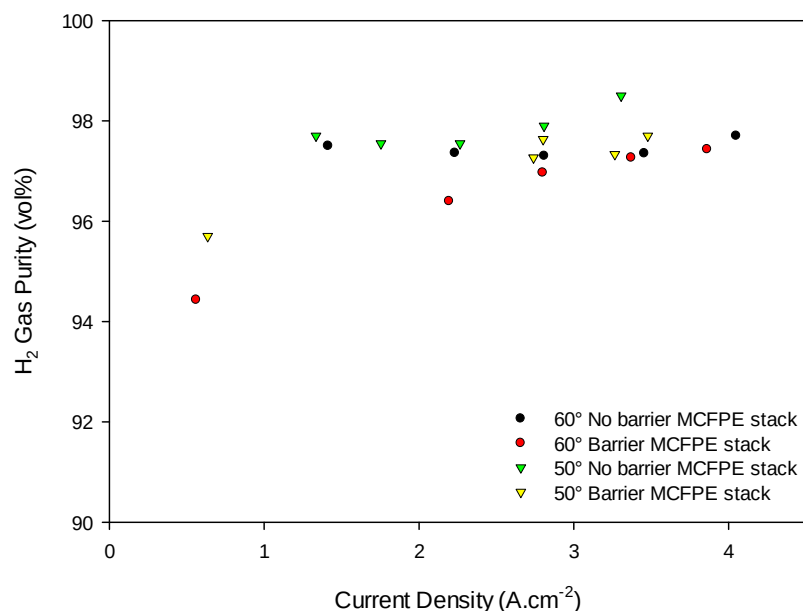


Figure 6-24: Hydrogen gas purity versus current density for 50° and 60°C as a function of an MCFPE stack utilising pure nickel electrodes, containing bi-phase collection chamber barriers and no barriers at 0.075 m.s⁻¹, 2.5 mm electrode gap, and 30% KOH

6.3.7. Methods of improving the active area

Phillips *et al.* (2017) describes that favourable structural electrode configurations, such as meshes and foams, are ideal for enhancing the effective reactive surface area, in contrast to solid smooth plate electrodes [35]. These structures are ideal for use in the DEFT™ process in that they are porous, and ideal for affixing catalysts to the surface to further boost reaction kinetics [35]. Initially, tests performed in Chapter 3 utilised a mesh of the same pore rating, and hence, the same was performed on the MCFPE stack to provide a basis for comparison.

Comparison of the MCFPE stack to the concept optimisation test rig in Figure 6-25a, reveals a notable improvement in current density that is testament to the optimised configuration of the MCFPE stack over previously designed and tested reactor systems. Comparison of Figures 3-10 and 6-25b shows a similar improvement in performance of the reactor making use of two layers of identical mesh in contrast to a single layer. Through applying an electrode configuration, which greatly increases the geometric area with a less effective catalyst, tends to have enhanced improvements in performance, in contrast to a configuration that promotes lower geometric area with an enhanced catalyst coated onto the surface. In the scenario of using cost-effective and corrosion resistant materials, this approach would prove ideal. The pore rating of two 80 µm dutch weave mesh electrodes that are placed in contact with one another, reduces

the prevailing pore rating which will have a negative impact with regard to: (i) the enhanced bubbles formed, and (ii) the ionic resistance, due to the structure becoming clogged with gas [35]. Hence a mesh configuration that does not compromise on pore size, or a metal foam with an optimised porosity rating, would aid in reducing the incidence of the electrode structure becoming clogged with gas.

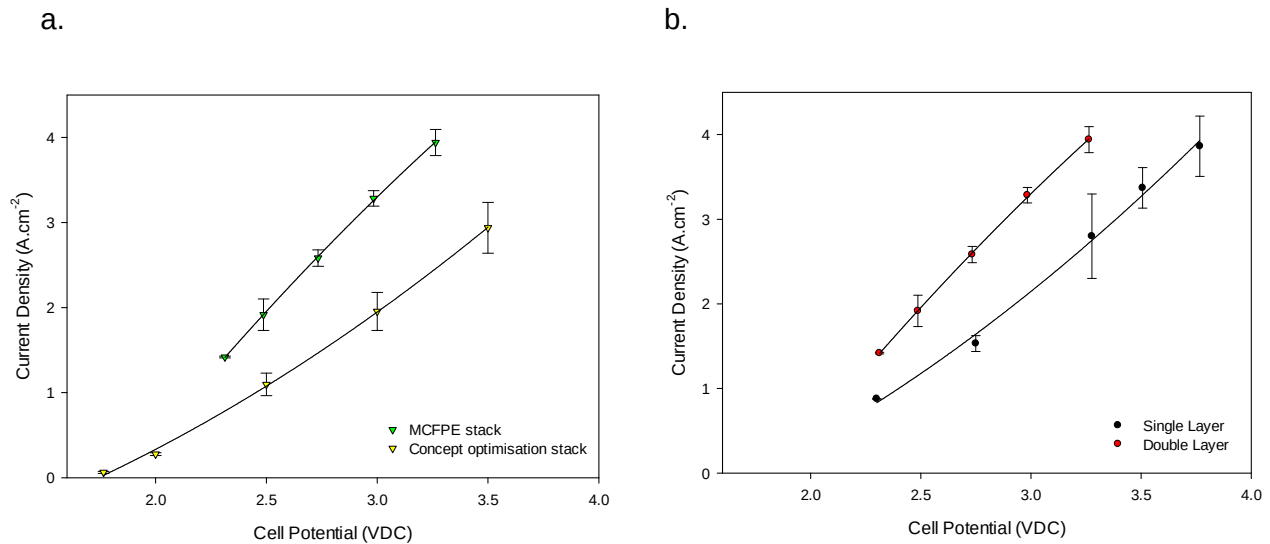


Figure 6-25: Polarisation curves for (a) a double layer of pure nickel 80 μm dutch weave filtration mesh for the MCFPE stack versus the concept optimisation stack, and (b) a single layer versus double layer of pure nickel 80 μm dutch weave filtration mesh for the MCFPE stack, at 60°C, 0.075 $m \cdot s^{-1}$, 2.5 mm electrode gap, and 30% KOH

By placing two layers of dutch weave pure nickel mesh together, of a larger pore diameter of 200 μm , effectively reduces the pore rating of the resulting three-dimensional porous structure. It remains substantially easier for gas and liquid to move through the structure without inhibiting the availability of effective reactive area, in addition to reducing the resolving gas meniscus thickness on the electrode surface. It is observed from Figure 6-26, that the double layer of 80 μm mesh is superior in performance in contrast to the double layer of 200 μm mesh. In calculation of the geometric area of the 80 μm in contrast to the 200 μm mesh, it is determined that per unit of cross sectional area the 80 μm mesh has 4.304 cm^2 in contrast to the 200 μm mesh having 4.007 cm^2 [6]. As a result, it is expected that the 200 μm has a reduced effective reactive area, and resultantly a lower performance can be expected. The double layer of 200 μm mesh remains a viable option in contrast to only using a single layer of 80 μm mesh, as it still promotes elevated performance. By incorporating a third of 200 μm mesh, no effective improvement in performance is gained, and as a consequence, reduced performance, only marginally superior above that of a single layer of 80 μm mesh is observed. A limit is therefore present to how many layers of mesh can be placed

in series with one another before pore diameters are restricted to a point that negatively hampers the ease of fluid and gaseous flow through three-dimensional structures.

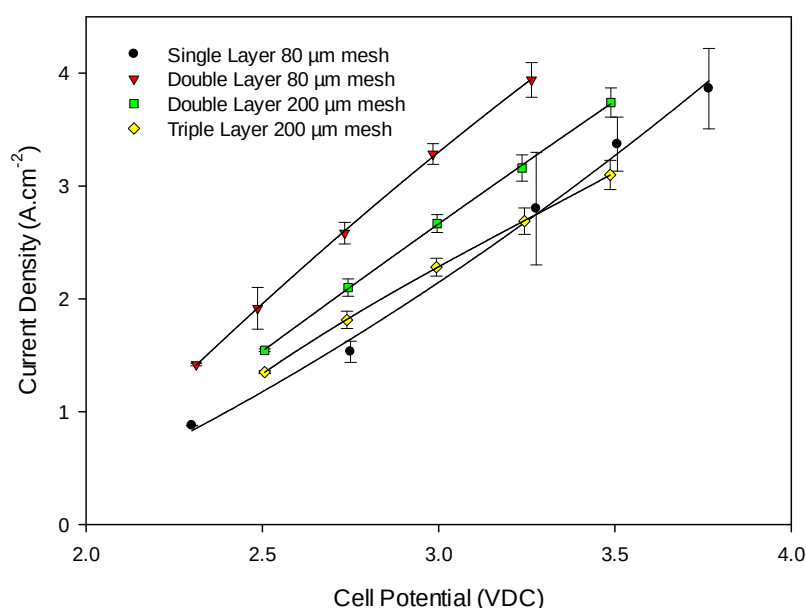


Figure 6-26: Polarisation curve for the comparison of multiple pure nickel dutch weave filtration layers for pore ratings of 80 µm and 200 µm for the MCFPE stack at 60°C, 0.075 m.s⁻¹, electrode gap of 2.5, and 30% KOH

Examination of the gas purity data in Figure 6-27 observes a clear distinction in the advantage of using a larger pore rating of mesh when operating multiple layers of mesh. The double layer of 200 µm mesh demonstrates superior gas qualities, due to the ease with which gas bubbles are capable of passing through the structure. The double layer of 80 µm mesh shows a clear disadvantage due to the severe hindrance to gas quality.

Alternative to mesh structures, metal foams have been used in the development of electrolyzers in order to maximise the performance [75]. Metal foams are advantageous as they promote high porosities, pose little resistance to solution flow, and have significantly more active area in contrast to structures such as woven mesh.

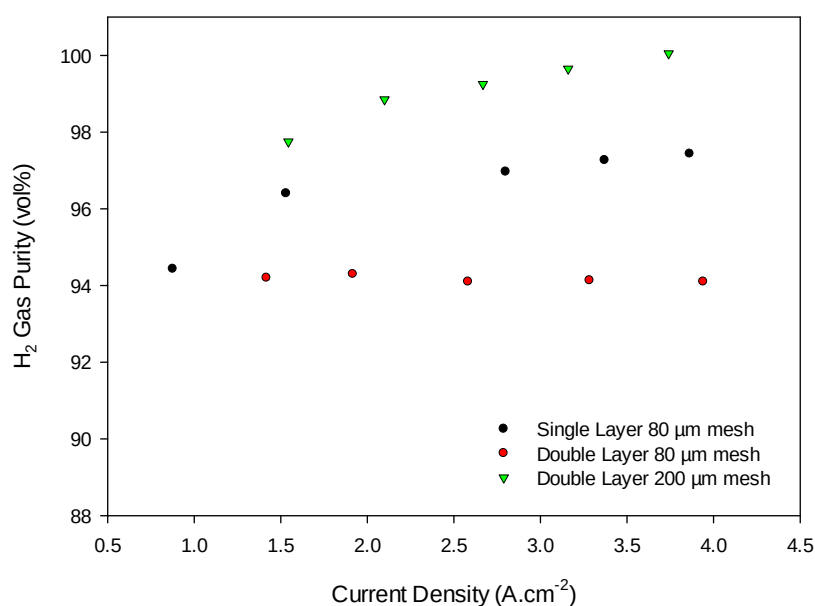


Figure 6-27: Hydrogen gas purity versus current density for the comparison of multiple pure nickel dutch weave filtration layers for the MCFPE stack, at 60°C, 0.075 m.s⁻¹, an electrode gap of 2.5 mm, and 30% KOH

With reference to Figure 6-29, it is expected that since the resultant enhanced geometric area of the metal foam structure is more in contrast to the 80 μm and 200 μm mesh upon observation, that it would enhance the cross sectional current density at set cell potentials for the MCFPE stack. Figure 6-28 suggests the opposite, as it is observed that the single and double layers of metal foam produces performance inferior in comparison to a single layer of 80 μm mesh. Metal foam therefore is ineffective for the DEFT™ operating principle. Due to the irregular pore structures and enhanced voidage for solution flow, the apparent flow velocity through the mesh is likely to be lower than that of the mesh structures. Lower applied forces on accumulating bubbles within the mesh structures, infers that a greater percentage of surface area will be unavailable for the electrolysis reaction. The metal foam structure, comprised of thin metal strands in contrast to the mesh structures, may be limited in forming enhanced current densities. A metal foam, with a lower degree of porosity and thicker wire strand diameters, may be more effective for the DEFT™ principle in conclusion.

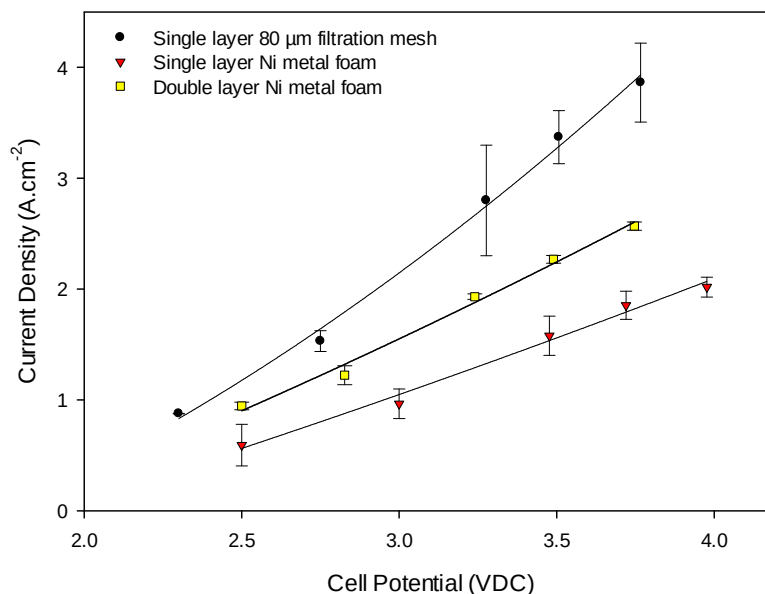


Figure 6-28: Polarisation curve for the comparison of a single pure nickel 80 µm mesh layer to that of a pure nickel single and double metal foam layer for the MCFPE stack, at 60°C, 0.075 m.s⁻¹, an electrode gap of 2.5 mm, and 30% KOH

a.



b.



c.



Figure 6-29: (a) nickel metal foam electrode, (b) a 80 µm nickel mesh electrode, and (c) a 200 µm nickel mesh electrode

6.3.8. Optimised electro-catalyst

The Pt_xNi_zAl_y with metallic ratio 9:56:35 proved highly effective in enhancing the operating performance of the concept optimisation stack in Chapter 3. The same catalyst was applied by vapour deposition to pure nickel electrodes for performance evaluation in the MCFPE stack.

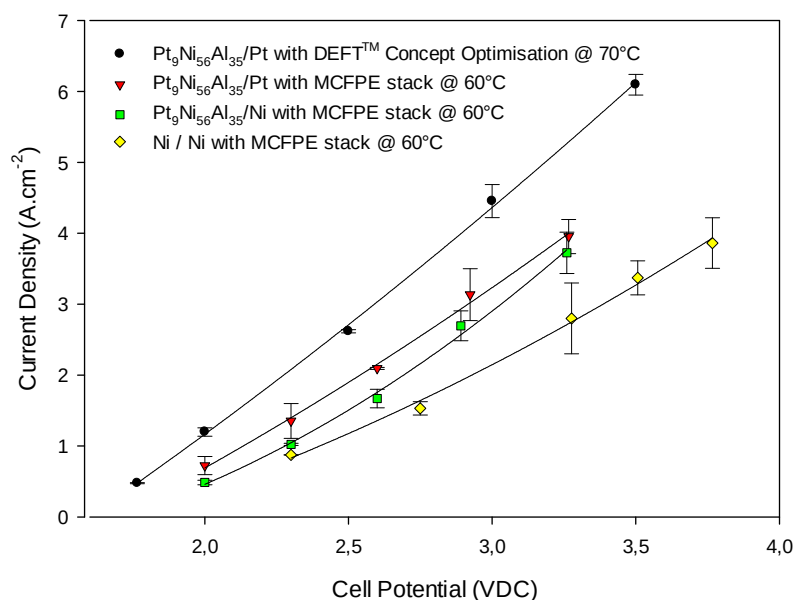


Figure 6-30: Polarisation curves for Pt₉Ni₅₆Al₃₅/Pt catalytic combination for the concept optimisation stack at 70°C, in contrast to the MCFPE stack for the Pt₉Ni₅₆Al₃₅/Pt and Pt₉Ni₅₆Al₃₅/Ni catalytic combinations, at 60°C, 0.075 m.s⁻¹, an electrode gap of 2.5 mm, and 30% KOH

Figure 6-30 depicts a lower performance of the Pt₉Ni₅₆Al₃₅/Pt catalyst combination for the MCFPE stack in contrast to the concept optimisation stack. The catalyst coated onto the electrodes for the MCFPE stack were yet again performed by means of co-sputtering, with the difference being that the alloy composition was not as uniform as the prior catalyst tested in the concept optimisation stack due to time constraints. Adding to the reduction in performance was the lower test temperature, representing the threshold temperature for the MCFPE stack. The performance for the enhanced catalyst still remains superior compared a Ni/Ni catalytic combination. An interesting observation made when comparing the performance of the Pt₉Ni₅₆Al₃₅/Ni and Pt₉Ni₅₆Al₃₅/Pt for the MCFPE stack at the same experimental conditions, is that performance had little difference. The Pt₉Ni₅₆Al₃₅/Pt combination shows a slight improvement in performance in contrast to the Pt₉Ni₅₆Al₃₅/Ni catalyst. It is, however, more economical to utilise non-noble metals to a large extent for both the anodic and cathodic catalytic compositions, as to reduce both CAPEX and OPEX costs.

6.4 CONCLUSION

The mono circular filter press electrode (MCFPE) assembly represents a culmination of all positive design and experimental findings from prior investigations, and proves to be a successful scalable demonstration of the DEFT™ technology. Currently the design allows for a single pole pair per modular plate, however, additional pole pairs can be attributed to a single modular plate so as to reduce stack lengths, and reduce sealing requirements. A long stack length, which subsequently results in extended liquid inlet and outlet feeds, has been found to hinder product gas qualities, and a shorter flow path is preferred. Balanced flow to each electrode pair is integral in ensuring that liquid flows and current densities remain uniform over the electrode surface. The MCFPE stack has shown that it creates a superior balance between flow and current density distribution, in contrast to the prior tested designs, since performance is maximised for similar operating parameters. The stack itself makes use of an automatic purging design that eliminates all air from the system upon start-up, and continually eliminates contaminant gas, that has not passed through the porous electrodes, as operation continues. The design allows for perfect radial injection of fluid into the electrode gap, as each electrode pair has its own independent injection chamber.

The stack has shown that it is capable of producing adequate qualities of gas for extended time durations, with independent gas purity studies revealing that a flow velocity of 0.075 m.s^{-1} , generates adequate gas purities over a wide current density range, from a minimum temperature of 40°C . The stack is capable of generating a maximum hydrogen and oxygen gas purity of 99.81 vol% and 99.5 vol% respectively, at a flow velocity of 0.075 m.s^{-1} , 50°C and $\sim 3.5 \text{ A.cm}^{-2}$. Atmospheric contaminants were observed in the separation system, which implies that gas qualities were offset to a lower value, and could in fact, be greater.

A minimum and maximum electrode gap of 2.5 mm and 4.5 mm, respectively, were tested once again and compared to the electrode gap results for the concept optimisation test rig. Similar trends were observed in comparison to the concept optimisation stack, however, the MCFPE stack showed enhanced current densities at all set cell potentials. It was shown that low temperature operation (40°C) preferred a larger electrode gap due to the presence of a thicker gaseous meniscus. It is therefore preferred to operate at temperatures greater than 40°C to enhance cell performance by employing a smaller electrode gap.

Increasing the number of pole pairs in series with one another has shown a diminished product gas quality, due to the imbalance of solution flowing through each electrode. A shorter stack has

been found to benefit performance at the optimal flow velocity. To allow for a set production volume of hydrogen gas, a number of smaller/shorter stacks can be run in parallel.

Alterations pertaining to the internals of the gas/liquid separation system have revealed distinguishable differences between submerged separation and contact separation. Submerged separation relies on the use of coalescing media and gas exhaust tubes to extract micro-bubbles from a flowing solution. Contact separation distributes the solution in thin films across the surface of media. By doing this it has been shown to efficiently remove entrained gas bubbles from a flowing solution for similar experimental conditions, where the submerged system underperformed.

Furthermore, it has been shown that barriers between common gas collection bi-phase chambers can be removed from the stack assembly, to yield a design of fewer components. A small improvement in performance and gas purity is observed due to the enhancement of flow distribution across the electrode surface.

Up to a 78% improvement in current density, at set cell potentials, has been perceived with regard to tests originally performed with a double layered mesh electrode, of the same mesh rating, utilising the concept optimisation stack. By utilising electrode structures such as multi-layered mesh and metal foams, an enhancement in current density can be attained due to the increase in the effective reactive area. By utilising a double pure nickel 80 μm mesh, a 42-60% improvement in current density at set cell potentials can be attained. A double 80 μm mesh does, however, not promote enhanced gas qualities, and hence, utilising a double mesh with a larger pore rating (200 μm) maximised gas qualities. This has an added benefit of enhancing cell performance in contrast to only using a single layer of mesh. Addition of a third layer of mesh is observed to have a negative effect on both gas quality and operating performance. Metal foams have proven ineffective at maximising cell performance, even when employed in a double layer configuration in contrast to singular-layered mesh structures.

In Chapter 3, the $\text{Pt}_9\text{Ni}_{56}\text{Al}_{35}/\text{Pt}$ catalytic combination served to enhance current densities for the entire tested cell potential range. The same catalytic combination was applied for the MCFPE stack, still maximising performance in contrast to the Ni/Ni catalytic combination. Slight inconsistencies were present, however, the performance resulted to be lower than what was previously generated by the concept optimisation stack. Comparison of the $\text{Pt}_9\text{Ni}_{56}\text{Al}_{35}/\text{Ni}$ and $\text{Pt}_9\text{Ni}_{56}\text{Al}_{35}/\text{Pt}$ catalytic combinations, revealed similar performances with the benefit of utilising lower quantities of platinum metal with regard to the $\text{Pt}_9\text{Ni}_{56}\text{Al}_{35}/\text{Ni}$ catalytic combination.

Take-home observation(s):

- By designing a stack, that provides each individual electrode independently with fluid, located in a chamber that incorporate a gas purge outlet, has yielded a scalable and ideal approach to the DEFT™ operating principle,
- There is a limit to how many pairs can be incorporated into a stack before an imbalance of flow negatively affects gas purities,
- By incorporating a gas/liquid separation system with sufficient residence time and contact area, has provided the necessary separation efficiencies to yield product gases of the appropriate purity,
- Multi-layered mesh electrodes are ideal in boosting stack operating performance with mesh of a larger pore rating promoting improved gas qualities, and
- A flow velocity of 0.075 m.s^{-1} and electrode gap of 2.5 mm are ideal in promoting maximised stack performance while not compromising on gas purity.

7. DEFT™ TECHNOLOGY DESIGN CRITERIA

7.1 OVERVIEW

The two most prominent parameters affecting the DEFT™ technology is: (i) the electrolytic fluid flow velocity and (ii) the electrode gap between the electrodes. It has been found that if the fluid flow velocity is maintained above an optimal flow rate, the gas purity would tend to remain constant despite the chosen operating current density and fluctuations. The chosen operating cell potential will determine the resolving current density dependant on the type of catalyst employed, the reactive surface area, electrode gap, and operating temperature of the liquid electrolyte [35]. By employing an improved catalyst, or high surface area electrode, the overall plant efficiency can be improved by lowering the amount of power required for set gaseous product production. The surface area can be modified by considering catalysts of a porous nature and alternate mesh designs which promote a larger surface area [43]. These parameters have all been investigated taking a high level approach with substantial detailed optimisation still feasible, so as to further improve overall stack and plant efficiencies.

From experimental investigations, the most important design criterion, which has been adequately achieved, is the product gas quality emanating from the DEFT™ technology. All other optimisation parameters are structured around this parameter to produce gas of an appropriate industry standard. Inherent to the DEFT™ technology, the pump remains the single most demanding parasitic load for the DEFT™ system, as higher pumping rates are required compared to regular electrolysis systems. A single pump is employed to service a single reactor and gas/liquid separation system, which is operated in a closed recycle loop. By incorporating the correct separation system within the reactor system, it will be possible to reduce the pumping load on the system by incorporating a multitude of reactor and separation systems in series. The DEFT™ technology relies on a set volumetric quantity of fluid through a reactor module to maintain separation at a minimum flow velocity. These systems, together with their separation systems, are designed to facilitate a low pressure drop. It would then be possible to link a number of these systems in series with one another, reducing the pumping load, and consequently the required operating cell potential benefitting both the overall and stack efficiencies.

7.2 OPTIMAL OPERATING PARAMETER CRITERIA FOR THE DEFT™ TECHNOLOGY

7.2.1. Gas purity

Gas purity is dependent on the following factors, deduced by observations made for the MCFPE pilot plant:

- *Flow velocity*: The greater the flow velocity, the better the stack efficiency and gaseous separation within the reactor module. Increased flow velocity aids in equally distributing flows across electrode surfaces and between electrode pairs. This does, however, have repercussions on the size of gas/liquid separators required,
- *Current Density*: Larger current densities promote the evolution of larger product bubbles, that improves the separation effect at the electrodes, as well as the rise velocity in the gas/liquid separators [27, 65],
- *Mesh type and pore rating*: Large pore ratings or a mesh type that promotes low pressure drops through high porosity, do not promote an even distribution of fluid across the surface, and separation of gases may not be preserved over the entire surface area,
- *Electrode Size*: The larger the electrode, and hence the flow path, the more difficult it may be to maintain an even flow across the surface, and
- *Electrolytic Temperature*: High temperatures promote higher viscosities, which improves the separation mechanism between the electrodes, as well as within the gas/liquid separation system.

The ideal hydrogen gas purity rating is anything above 99 vol%, which would be a typical range found for industrial alkaline electrolysis systems [29]. The ideal oxygen gas purity would be such that it does not promote a flammable mixture of hydrogen gas in oxygen gas, which in this case would mean that the oxygen purity would need to be maintained at > 96 vol% [48].

All inter-related parameters listed above are defined within a range that produces acceptable gas qualities.

7.2.2. Flow velocity

As discussed, flow velocity is considered the essential criterion for maintaining adequate gas purities. Greater flow velocities are required in circumstances where current densities are quite high ($> 3 \text{ A.cm}^{-2}$), and where temperatures are lower than 50°C. It is, however, necessary to integrate a safety factor, to cover the entire operating range of parameters, so that pure separation is always maintained.

The optimal flow velocity has been shown to be 0.075 m.s^{-1} , and should be maintained above 0.0625 m.s^{-1} at all times. The correct separation system needs to be employed to ensure full liberation of micro-bubbles at any operating current density, and within the operating temperature range of $40 - 80 \text{ }^{\circ}\text{C}$.

7.2.3. Gas/liquid separation system

In conjunction with the optimal flow velocity discussed above, it has been found that a contact type vertical separation system, working on the principle of coalescence, and thin film gaseous liberation is ideal for the DEFT™ reactor system. The following parameters apply for such a system:

- A minimum length of at least 600 mm of media filtration,
- 7.5 cm^2 of minimum separator drainage area for every 1 cm^2 of apparent cross-sectional electrode area, with the ideal being 10 cm^2 of minimum separator drainage area for every 1 cm^2 of apparent cross-sectional electrode area,
- a minimum of 7 filtration stages,
- a distance of 100 mm between stages, and
- separator media consisting of 6 mm polypropylene balls.

It is not desired to run the system at pressure as this contributes unnecessarily to the system complexity and capital cost.

The above described system will be capable of handling a reactor system incorporating a flow velocity of 0.075 m.s^{-1} , at any temperature above 40°C , for optimal separation efficiency.

7.2.4. Electrode size and configuration

Computational fluid dynamics modelling has revealed that the optimal fluid path length is 20 mm. Therefore, a maximum electrode diameter that can be incorporated would be 40 mm. To date, however, existential experimental data has exhibited the best results with a fluid path length of 15 mm, with undesirable results associated with non-circular electrodes incorporating a fluid path length of 20 mm. Circumferential flow has been found to be fundamental with non-direct introduction of electrolytic fluid to reduce turbulence at the electrodes themselves. To maintain gas quality, a purge cavity is vital so as to initially purge the reactor of gas, as well as for continued purge gas extraction during operation. The requirements for the electrode configuration have been deduced from results obtained.

- A non-direct circumferential injection of fluid into the electrode gap,

- Any circular design incorporating a fluid path length should not exceed the maximum fluid path as stipulated above, and
- It is vital that the electrode material itself does not present a bottle neck for pressure drop, but rather the injection into the chamber housing the electrode as to balance the pressures and flows, without introducing unwanted turbulence.

7.2.5. Temperature

With increased operating temperatures, an increase in stack electrical efficiency is always observed, and is thus desirable [10]. However, the energy required to ensure that a reaction is maintained always needs to come from a source, whether it be electricity or heat. When linked to solar power, the system needs to start operating from as low a temperature as possible. Based on visual inspection of the clarity of the electrolyte, the minimum temperature for operation is 35°C. With an increase in temperature, solution viscosity alters, with more fluid-like properties prevailing at greater temperatures. Temperatures greater than 60°C have been found to negatively impact gas purities due to enhanced turbulence at the electrodes, disturbing the laminar behaviour of bubbles emanating from the electrode surface. It is therefore desirable to maintain low temperature operation for reliability and extended longevity of plant components.

7.2.6. Current Density

At low current densities, smaller than 1 A.cm⁻², stable operation is possible, however, it places additional strain on the separation mechanism at the electrodes, and the separation efficiency of the gas/liquid separation system. At these current densities, the efficiency of the stack is excellent, however, the overall plant efficiency is lowered due to energy demand of the circulation pump being greater. An optimisation between the pump and the stack load would be required, and is dependent on the system configuration, operating conditions and reactor kinetics. As a general observation from experiments, efficiency is normally maximised for the overall system at current densities from 1.5 A.cm⁻² through to 4 A.cm⁻², depending on the catalyst in use, and other operating parameters. The operating cell potential is a function of the electrolyser configuration and employed catalyst, and can range between 1.75 – 3.5 VDC.

7.2.7. Electrode structure

The electrode structure has been briefly discussed, and relates to the actual geometric form of the electrode along with the surface morphology generated by the catalyst employed. CFD results have suggested that structures with pores ranging from 110 – 200 µm create enough back

pressure to create conditions for uniform current densities and flow velocity vectors across the electrode surface. The back pressure, however, is not excessive to an extent to compromise overall plant efficiency through extensive pumping demands. Pores need to be larger than the micro-bubble bubble size distributions, so as to allow easy passage of bubbles from the frontal surface. Multiple mesh layers could furthermore enhance the back pressure, however, it should be acknowledged that this should be limited, as additional layers will reduce the pore ratings which could hamper the ease at which gasses can pass through the electrode. When utilising multiple layered mesh electrodes, it is vital that no interstitial spaces be left between layers, and that the weave directions be in the same directions. This will ensure that the flow of fluid and gases through the three-dimensional structure is not constricted.

7.2.8. *Electrolytic concentration*

From literature the optimum electrolytic concentration has been confirmed to be 30% by mass for potassium hydroxide [32]. Greater temperatures do, however, allow for greater conductivities at higher concentrations >40% KOH [25].

7.2.9. *Electrode gap*

As already mentioned, the electrode gaps are a very important parameter for the resolving current density and gas purity. Larger electrode gaps promote improved gas qualities, however, this comes at the expense of stack efficiency. It has been found that the compromise of these two factors resolves to yield an optimal electrode gap range of between 2.5 – 3.5 mm. The efficiency difference within this range is limited along with the difference in gas purities. An electrode gap of 3 mm is considered to be ideal. Any gap larger than 4 mm has been found to yield a sharp decline in efficiency.

7.3 PREDICTED EFFICIENCIES FOR VARIOUS PLANT CONFIGURATIONS

Pilot plants tested to date have always made use of a single stage reactor and separation system. A minimum volumetric flow rate is fundamental for adequate gas separation through the electrodes, and with increased production, the flow rate will need to be increased linearly. Whether it is a single system represented by a module of its own, or whether the module is represented by numerous systems conjoined to a single pump in parallel, the result will remain the same for the overall plant efficiency. Figure 7-1 illustrates such a system, and represents the least desirable method of scaling the DEFT™ technology for the purpose of optimising efficiency.

The representation shown in Figure 7-1 can be represented as a single stage system, whether for multiple smaller reactor modules or a singular large reactor module. The only advantage of the configuration depicted in Figure 7-1, is that the multiple stacks could be connected in series with one another to save on electrical conditioning equipment. Efficiency of the overall system will not be optimised substantially, as the ratio between the required fluid flow rate and the gas production rate will resolve to change insignificantly. Therefore, efficiency improvements can only be optimised by improving the kinetics of this system.

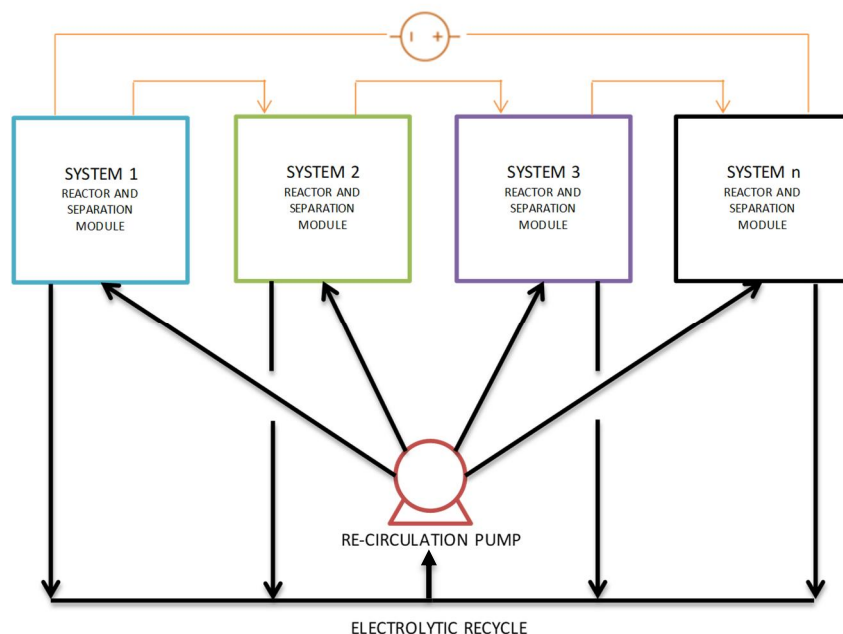


Figure 7-1: n^{th} DEFT™ standardised system modules connected in parallel with one another

Pilot plants tested to date do not represent an optimised configuration of the DEFT™ technology, as each pilot plant has been designed with various parameter flexibilities. Since the power consumption with regard to the pump represents the largest parasitic load, an alteration and optimisation in the plant configuration will be required in order to enhance the overall efficiency of the DEFT™ technology for future pilot plants. It has been noted previously, that conventional electrolysis plants make use of a low flow circulation of fluid to ensure that no concentration gradients form within the electrolytic solution, and for the active extraction of produced gases. The parasitic load contribution from the circulation pump is therefore low. By using a circulation pump to service multiple DEFT™ systems in series, each optimised for minimal pressure head, would represent the simplest and most effective method for enhancing overall system efficiencies.

A more desirable system set-up is depicted in Figure 7-2, whereby standardised system modules are linked in series with one another. Centrifugal pumps are known for naturally providing high

volumetric flow rates at lower pressure heads, whereas positive displacement pumps provide stable high pressures at relatively low flow rates. Centrifugal pumps that are seal-less are ideally coupled to the DEFT™ technology, with pumping energy determined using Bernoulli's equation (equation 17) [76].

$$P_2 + \rho g z_2 + \rho \alpha_2 \frac{v_2^2}{2} + \Delta p_f = P_1 + \rho g z_1 + \rho \alpha_1 \frac{v_1^2}{2} + \Delta p_{\text{lift}} \dots \dots (17)$$

Where, P (N.m^{-2}) is the pressure at the designated system point, ρ (kg.m^{-3}) is the electrolytic density, g (m.s^{-2}) is the gravitational constant, z (m) is the height of the designated system point referenced to the chosen reference point of the system, α is the laminar/turbulent flow correction factor, v (m.s^{-1}) is the fluid velocity at the designated system point, Δp_f (N.m^{-2}) is the friction loss term, and Δp_{lift} (N.m^{-2}) is the pressure head.

For the purposes of determining the overall efficiency of various plant configurations, a basic pump sizing was conducted employing the above equation to determine the pressure head along with employing an electronic pump size calculator (based on magnetically coupled single stage pumps) to obtain an estimation on the pump power demand [77]. The absorbed power was therefore taken into consideration in determining the overall plant HHV% efficiency. The use of multi-stage centrifugal pumps is predicted to have an improvement on the pumping efficiency but is not considered in this study due to the absence of available sizing data [78]. Two catalyst combinations were utilised for the study namely; the $\text{Pt}_9\text{Ni}_{56}\text{Al}_{35}/\text{Pt}$ and Ni/Ni catalytic combinations. The study was performed on the system configuration depicted in Figure 7-2.

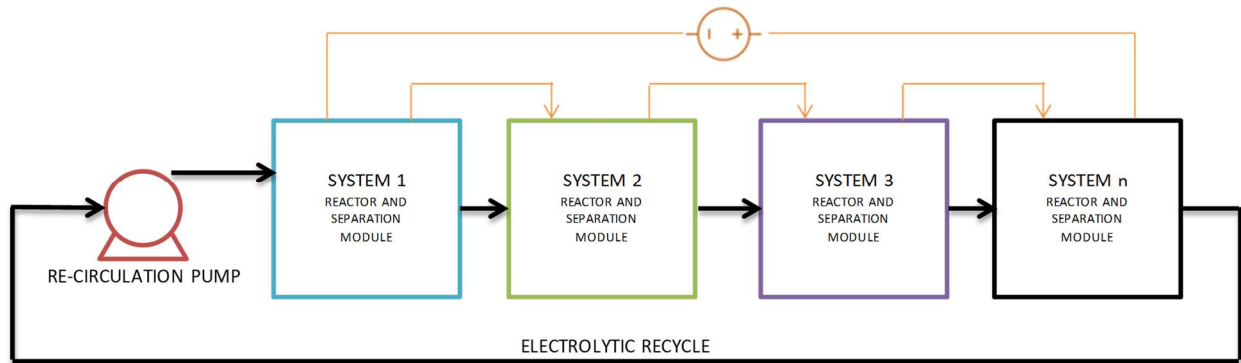


Figure 7-2: n^{th} DEFT™ standardised system modules connected in series with one another

Through connecting standardised modules in series with one another, with fluid passing through all modules from a common circulation pump, the only cumulative factor will be the pressure drop generated by the flow moving through all modules, while the total volumetric flow rate remains constant. This is a factor that can be mechanically designed for and reduced accordingly, to have

a positive effect on the overall plant efficiency. Yet again, this configuration also allows for the advantage of connecting stacks in series with one another. As a function of the chosen catalytic combinations, two scenarios were considered for a maximum of 6 modules stacked in series:

- series stacking of a standard module of the same production capacity, increasing overall capacity with the continual addition of modules, and
- series stacking of progressively smaller modules keeping the overall capacity the same with the addition of modules.

7.3.1. Increasing the overall capacity of the plant

Table 7-1 and 7-2 compare the effect of using a standardised module of the same production capacity, to gradually enhance the total production by incorporating more modules in series.

Table 7-1: Progressively increasing the overall plant capacity by incorporating standardised set production modules utilising the Ni/Ni catalytic combination

Operating Cell Potential (VDC)	Resolving Current Density (A.cm ⁻²)	Stack Efficiency (HHV%)	1 Plant in Series (1x Capacity)		2 Plants in Series (2x Capacity)	
			Power contribution by pump (%)	Overall Efficiency (HHV%)	Power contribution by pump (%)	Overall Efficiency (HHV%)
2.67	1.5	55.43%	34.24%	36.50%	34.38%	36.42%
3.18	2.5	46.54%	17.63%	38.38%	15.88%	39.20%
3.6	3.5	41.11%	12.49%	36.02%	10.88%	36.68%

3 Plants in Series (3x Capacity)		4 Plants in Series (5x Capacity)		5 Plants in Series (5x Capacity)		6 Plants in Series (6x Capacity)	
Power contribution by pump (%)	Overall Efficiency (HHV%)	Power contribution by pump (%)	Overall Efficiency (HHV%)	Power contribution by pump (%)	Overall Efficiency (HHV%)	Power contribution by pump (%)	Overall Efficiency (HHV%)
36.04%	35.50%	33.98%	36.64%	33.77%	36.76%	33.92%	36.67%
17.16%	38.60%	16.58%	38.87%	15.86%	39.21%	16.97%	38.69%
11.07%	36.60%	10.94%	36.66%	10.30%	36.92%	10.17%	36.97%

Table 7-2: Progressively increasing the overall plant capacity by incorporating standardised set production modules utilising the Pt₉Ni₅₆Al₃₅/Pt catalytic combination

Operating Cell Potential (VDC)	Resolving Current Density (A.cm ⁻²)	Stack Efficiency (HHV%)	1 Plant in Series (1x Capacity)		2 Plants in Series (2x Capacity)	
			Power contribution by pump (%)	Overall Efficiency (HHV%)	Power contribution by pump (%)	Overall Efficiency (HHV%)
2.14	1.5	69.16%	39.38%	41.98%	39.53%	41.87%
2.44	2.5	60.66%	21.81%	47.49%	19.74%	48.74%
2.75	3.5	53.82%	15.74%	45.40%	13.78%	46.46%

3 Plants in Series (3x Capacity)		4 Plants in Series (5x Capacity)		5 Plants in Series (5x Capacity)		6 Plants in Series (6x Capacity)	
Power contribution by pump (%)	Overall Efficiency (HHV%)	Power contribution by pump (%)	Overall Efficiency (HHV%)	Power contribution by pump (%)	Overall Efficiency (HHV%)	Power contribution by pump (%)	Overall Efficiency (HHV%)
41.28%	40.66%	39.11%	42.17%	38.88%	42.32%	39.04%	42.21%
21.26%	47.82%	20.57%	48.24%	19.72%	48.75%	21.03%	47.96%
14.02%	46.33%	13.85%	46.42%	13.07%	46.84%	12.91%	46.93%

The results above would hold true to a plant of any production capacity, of the described configuration, and hence no improvement should be demonstrated with larger production plants.

Three current densities were chosen reference to each operating cell potential pertaining to the particular catalyst. The stack efficiency is the same in each case, dependant on the operating cell potential [22]. The only factors impacted are the relative percentage contribution of the pump to the total load of the plant, and as a consequence, the overall efficiency is influenced by this parasitic load and the operating cell potential.

It is observed for both catalytic combinations, that the percentage energy contribution of the pump in relation to the overall power demand, is reduced when increasing the current density. This is because the stack is operating less efficiently, and will be the presiding factor on increasing the total energy consumption. It is expected that an optimal point does exist, or a point where no or little additional improvement is observed, which is specific to a particular setup. After adding an additional module to the first module of the same production capacity, and repeating the process, minimal improvement or change is ascertained in the overall plant efficiency for both catalytic combinations with a maximum HHV% efficiency for the Ni/Ni and Pt₉Ni₅₆Al₃₅/Pt catalytic combinations as 36.97% and 46.93%. It is apparent that the optimal operating current density where efficiency is maximised resolves to be around 2.5 A.cm⁻².

No improvement of consequence is therefore realised by placing plants of the same production capacity in series with one another, due to efficiencies being largely unaffected. The flow and pressure generated from a specific pump can, however, be distributed over a number of modules to reduce the parasitic load contributed by the pump.

7.3.2. Holding overall plant capacity constant and increasing modules

Table 7-3 and 7-4 compare the effect of maintaining the same overall production capacity of a number of modules in series, however, the modules decrease in production capacity with the addition of more modules in series.

Table 7-3: Progressively increasing the number of modules for an overall plant of the same production capacity for the Ni/Ni catalytic combination

Operating Cell Potential (VDC)	Resolving Current Density (A.cm ⁻²)	Stack Efficiency (HHV%)	1 Plant in Series (Same Capacity)		2 Plants in Series (Same Capacity)	
			Power contribution by pump (%)	Overall Efficiency (HHV%)	Power contribution by pump (%)	Overall Efficiency (HHV%)
2.67	1.5	55.43%	34.02%	36.62%	20.33%	44.21%
3.18	2.5	46.54%	19.07%	37.71%	8.43%	42.67%
3.6	3.5	41.11%	11.44%	36.45%	5.84%	38.76%

3 Plants in Series (Same Capacity)		4 Plants in Series (Same Capacity)		5 Plants in Series (Same Capacity)		6 Plants in Series (Same Capacity)	
Power contribution by pump (%)	Overall Efficiency (HHV%)	Power contribution by pump (%)	Overall Efficiency (HHV%)	Power contribution by pump (%)	Overall Efficiency (HHV%)	Power contribution by pump (%)	Overall Efficiency (HHV%)
13.77%	47.86%	12.95%	48.31%	13.22%	48.16%	11.94%	48.87%
6.49%	43.57%	5.74%	43.92%	6.15%	43.73%	5.94%	43.83%
3.91%	39.55%	3.68%	39.65%	3.51%	39.72%	3.46%	39.74%

Table 7-4: Progressively increasing the number of modules for an overall plant of the same production capacity for the Pt₉Ni₅₆Al₃₅/Pt catalytic combination

			1 Plant in Series (Same Capacity)		2 Plants in Series (Same Capacity)		
Operating Cell Potential (VDC)	Resolving Current Density (A.cm-2)	Stack Efficiency (HHV%)	Power contribution by pump (%)	Overall Efficiency (HHV%)	Power contribution by pump (%)	Overall Efficiency (HHV%)	
2.14	1.5	69.16%	39.14%	42.14%	24.15%	52.52%	
2.44	2.5	60.66%	23.49%	46.46%	10.72%	54.22%	
2.75	3.5	59.88%	14.18%	46.88%	7.54%	49.84%	
3 Plants in Series (Same Capacity)		4 Plants in Series (Same Capacity)		5 Plants in Series (Same Capacity)		6 Plants in Series (Same Capacity)	
Power contribution by pump (%)	Overall Efficiency (HHV%)	Power contribution by pump (%)	Overall Efficiency (HHV%)	Power contribution by pump (%)	Overall Efficiency (HHV%)	Power contribution by pump (%)	Overall Efficiency (HHV%)
16.62%	57.74%	15.65%	58.41%	15.97%	58.19%	14.47%	59.23%
8.29%	55.69%	7.35%	56.27%	7.87%	55.95%	7.61%	56.11%
5.06%	51.16%	4.77%	51.32%	4.54%	51.44%	4.48%	51.47%

A significant improvement in efficiency is recognised here, for both catalytic combinations, with improvements in efficiency becoming smaller after the addition of 3 or more modules in series. Yet again results should differ minimally between plants of different production capabilities.

A key factor to promoting the improvement in the overall efficiency is in the reduction of the plant's parasitic load at high and low operating current densities. At 1.5 A.cm⁻², 2.5 A.cm⁻² and 3.5 A.cm⁻², the contribution by the pump is observed to be ~16%, ~8% and ~5% respectively. Contemplating this type of methodology, the efficiency would seem to be maximised at the lower operating current density for both catalysts, after the addition of 3 or more modules. This is due to the low cell potential that promotes enhanced overall efficiency as a result of the significantly lower power demand of the pump. It is therefore clear that the DEFT™ technology has to minimise the operating cell potential wherever possible. It must be mentioned that each plant design and configuration will have its own independent sweet spot, and must be re-calculated separately for each case. The correct design case will be dependent on deciding a set production rate, which will determine the number of modules and production capacity of each, followed by conducting an optimisation of the overall plant efficiency based on the stack configuration and catalyst employed. The above method has revealed that having three modules in series represents the optimal approach, with little additional efficiency gained with the incorporation of more modules in series.

Although the series configuration resolves to be the best method possible for reducing the pump demand, it is acknowledged that the optimal gas/liquid separation system (based on the contact method) will not be compatible with this configuration, due to the lack of a solution driving force that is needed to push the electrolyte at a constant stable rate through all modules. This method can be made to work by ensuring separated gas product lines, that create equal pressure within each separator or by a tiered gravitational configuration. It is clear that an improved gas/liquid separation system is required or an alternative pumping methodology. It is, however, observed

that if efficiency optimisation is not an important criterion, a single stage system coupled to a pump would suffice.

The optimal efficiencies achieved by this study ascertained that the DEFT™ technology is capable of achieving overall plant efficiencies of 48.87 HHV% and 59.23 HHV% with use of the Ni/Ni and Pt₉Ni₅₆Al₃₅/Pt catalytic combinations respectively, utilising 6 system modules in series. Additional improvements, to a limited extent, would be possible with additional modules added in series, however, there will be mechanical limitations present. At these overall plant efficiencies, the energy consumption rates are 80.62 kWh / kg H₂ (6.67 kWh / Nm³) and 66.52 kWh / kg H₂ (5.50 kWh / Nm³) respectively. An illustration from *T. Smolinka* (2014), depicts the typical energy consumptions of common commercial systems for both PEM and AWE systems (Figure 7-3) [58].

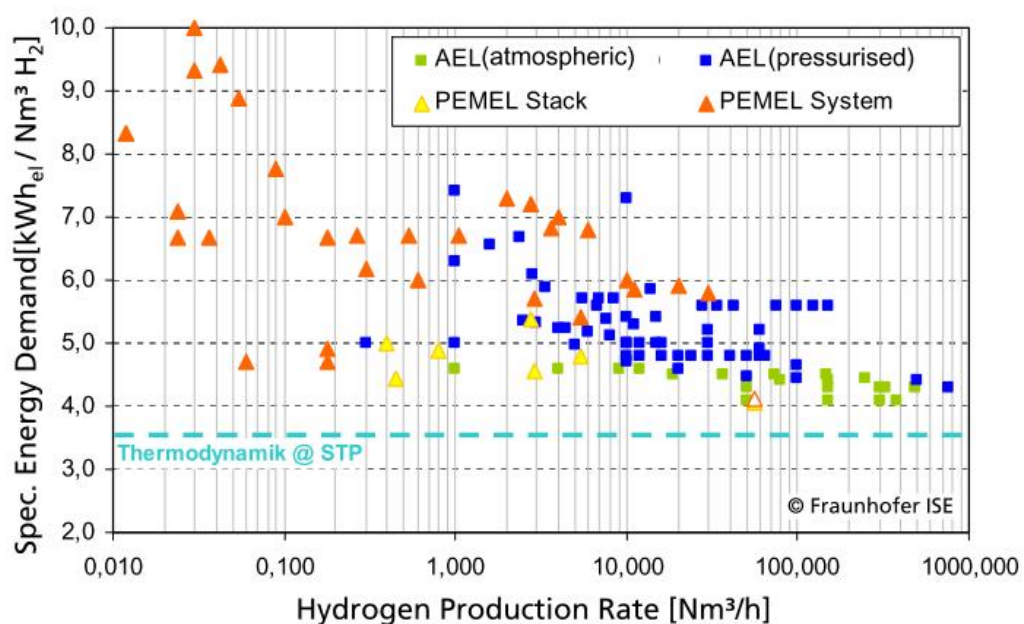


Figure 7-3: Typical energy consumption of PEM and AWE systems as a function of production rate [58]

Figure 7-3 shows an interesting distinction between the energy demand of the PEM stack and the PEM system. When the system is taken into consideration in its entirety, including parasitic power demands, the balance of plant is shown to increase the overall plant energy demand to a significant extent, much greater than common commercialised alkaline technologies. Additionally, pressurised alkaline plants are shown to have a greater energy demand in contrast to their larger atmospheric counterparts. It is clear from the operating points on Figure 7-3, that the energy demand increases for plants of smaller production capacities. In consideration to the energy consumption range of both the PEM and AWE systems, the DEFT™ system can be described as comparable with small and large scale PEM systems considering the DEFT™ technologies'

predicted energy consumption range of 6.67 – 5.50 kWh / Nm³. According to Figure 7-3, the majority of atmospheric commercial plants outperform the current estimated energy consumption rate for the DEFT™ technology, however, there is a definite market for cost-effective small scale alkaline systems for robust decentralised production approaches.

7.4 OPTIMAL DESIGN CRITERIA FOR DEFT™ PLANT AND CRITICAL COMPONENTS

The optimal test parameters have been discussed for the DEFT™ technology, however, a few vital structural parameters have been observed during experimental testing of the DEFT™ test plants with many of them being incorporated into the MCFPE test plant.

7.4.1. DEFT™ modular electrolyser

Throughout this research multiple plant and stack configurations have been developed and tested with each demonstrating a variation in operating performance to the next. This is due to intrinsic variations in flow regimes and electrode configurations. A simple comparison at similar operating conditions reveals which of the demonstrated pilot plants and stacks developed superior performance over its counterparts.

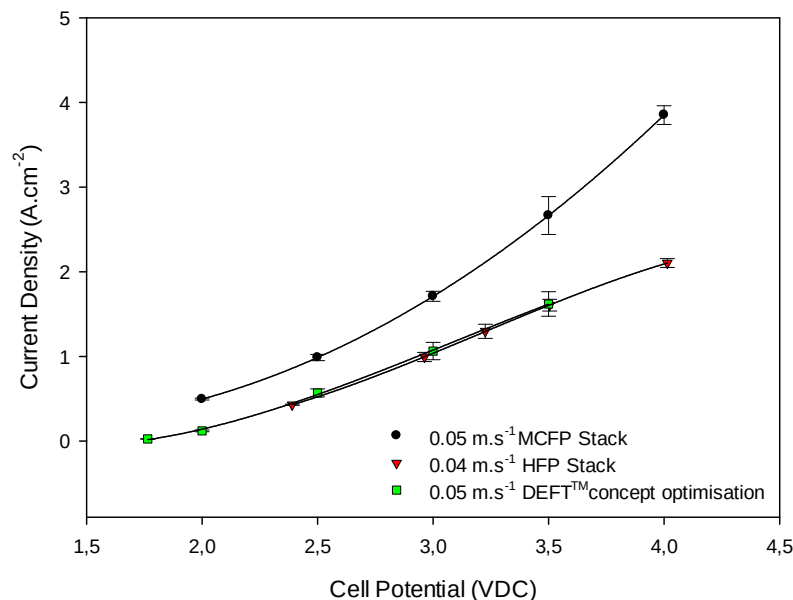


Figure 7-4: Polarisation curves for the comparison of performance from a pure nickel anode and cathode tested in the MCFP stack, HFP stack and DEFT™ concept optimisation stack as a function of flow velocity at temperature of 60°C. electrode gap of 2.5 mm, and electrolytic concentration of 30% KOH

Figure 7-4 illustrates that the MCFP pilot plant demonstrates the best performance when compared to the HFP and DEFT™ optimisation pilot plants using nickel for both the anodic and cathodic electrodes. The MCE pilot plant is not represented in Figure 7-4, as nickel was not utilised as the electrode material of choice. Due to the pure impracticality of the MCE stack, in terms of the number of components utilised in its design, it will inevitably prove economically unviable in the long term. Though the HFP stack is illustrated at a lower flow velocity, the flow velocity difference of 0.1 m.s^{-1} constitutes a small difference, and hence, as found from previous experiments, this small difference would impact operating performance to a negligible extent [6]. It is clear that the HFP stack represents an improvement over the DEFT™ optimisation concept, however, inadequate gas purities discounts the viability of the HFP system [17]. The MCFP stack and system therefore represents an improvement in both operating performance and gas purity, and can therefore be concluded as the concept to base future prototype designs on.

7.4.2. DEFT™ modular electrolyser

Flow

Flow must be balanced between all electrode pair injection chambers, so that similar averaged flow velocities can develop within all electrode pairs. It needs to be done in a manner that promotes equal distributed radial flow for the circular electrodes. The injection slots cannot be orientated in a manner that focuses flow directly at the electrode gap, as this will result in unnecessary turbulence which could alter the separation efficiency of the gaseous product at the electrodes. In addition, back pressure exerted from the rear of the electrode has been proven beneficial, as it allows for a flattened flow velocity profile through the electrode, making for enhanced gas purities and operating performances. An upper 'dead' flow region is ideal for allowing gaseous bubbles, that do not transverse through the porous electrode materials, to collect and be purged from the reactor. This regime is illustrated in Figure 7-5.

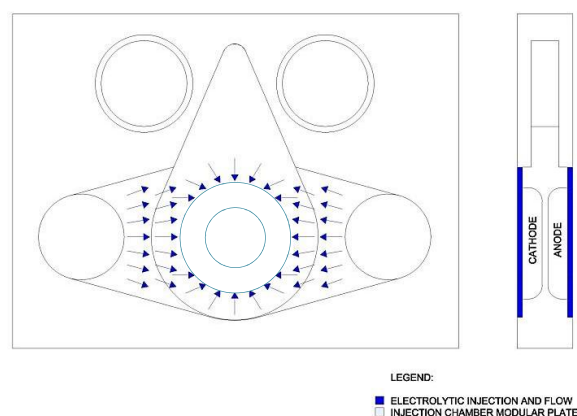


Figure 7-5: Preferred flow regime of the MCFPE reactor

The original concept optimisation DEFT™ reactor made use of a common chamber with a small discrete number of electrodes. The fluid therefore was capable of distributing itself relatively evenly amongst all electrode pairs, preserving gas quality. Performance improvements with regard to the MCFPE reactor over the concept optimisation rig, can be easily accomplished, as a result of the improved balancing of flows and currents between electrode pairs. The HFP reactor was designed to operate on the principle of injecting fluid directly into the electrode gap by means of an injection slot. This created conditions for agitating the surface meniscus formed on the electrode, whereby, instead of most gas bubbles passing through the mesh, some found their way into the electrode gap where they would coalesce to a size that made it impossible for these bubbles to transverse through the mesh material.

Both the HFP and MCE electrolyzers do not utilise product purge chambers, therefore, reliable stable performance was not possible. Collection chambers allow for the direct upward movement of gas and liquid into collection channels to be removed from the reactor. By examining the cross section of the MCE reactor (Figure 4-3 (page 69)), and the HFP reactor (Figure 5-4 (page 92)), if all the produced gas does not flow through the porous electrodes, an accumulation of gas will occur in the injection chamber/slot. The incorporation of a purge cavity is therefore fundamental for stable long term operation. Flow distribution between electrode pairs in the HFP reactor is an improvement over the MCE reactor, as outlet flows from electrodes collecting in a common collection chamber, would be unlikely to resume a balanced flow profile between all electrodes as some will be favoured depending on the ease of flow and pressure drop profiles.

Electrode Structure

It has been concluded from experimental investigations and from computational fluid dynamics simulations, that circular electrodes (with a defined flow path) represent the ideal electrode shape.

Rectangular electrodes can be incorporated either with mono or circumferential injection, however, the irregular shape makes it difficult to promote equal flow across the electrode surface in all areas. From positive design criteria collected from the study, it can be concluded that if the DEFT™ operating principle should be scaled to enhanced production scales greater than laboratory applications, the MCFPE design would work optimally. Larger electrode areas can be incorporated by utilising a donut shaped electrode, which can ensure that the set solution flow path be maintained, in addition to circumferential flow created from both the outside and inside of the electrode shape. The design can therefore be operated at the optimal electrode gap and flow velocity, limited only by the pressure profile of solution moving through the stack, and the capacity of the gas/liquid separation system.

Electrical Connections

Electrical connection to the electrodes themselves is vital to ensure that no external circuit resistance hampers the performance of the electrolyser. The DEFT™ concept optimisation reactor made use of an oversized electrical conduction system, utilising a solid nickel conductive head that forced the mesh electrode to be tort against a conductive surface by means of a self-tightening polypropylene mechanism. The conductive head screwed onto a threaded rod that extended into the reactor, whereby a conductive ring provided power on the exterior of the threaded rod located on the outside of the reactor. To apply this method for a commercial application would be extremely costly, and hence, methods employed by the 'scaled' pilot plants are more practical.

With reference to Figure 7-6, the MCE reactor made use of a solid bus bar linking all electrode structures together, with mesh secured by means of compressions rings. This method ensures a definite low resistance connection of the electrode to the external electrical conducting components. The HFP reactor made use of no compression joints, but rather a pressure connection of the electrode along its entire length to the bus bar. This is not a reliable means of providing an adequate connection of the electrode to the bus bar, and hence, was revised for the MCFPE reactor. The MCFPE reactor obtained power by having the electrode mesh, extending from the circular active region, directly connected to the bus bar by means of a compressed screwed connection. The circular electrode itself is held under pressure by means of a compression ring. This ensures that currents are uniformly distributed, and that a definite electrical connection of low resistance is made in a cost-effective manner. The method by which the bus bars are sealed in the reactor does, however, require additional attention. All tested reactor types made use of a threaded or surface-against-surface methods, that invariably would require the use of sealants to create a seal against opposing surfaces. An O-ring type system would be ideal for

future systems, with bus bars located on the side of reactors to avoid conductors from becoming contaminated with corrosive fluids.

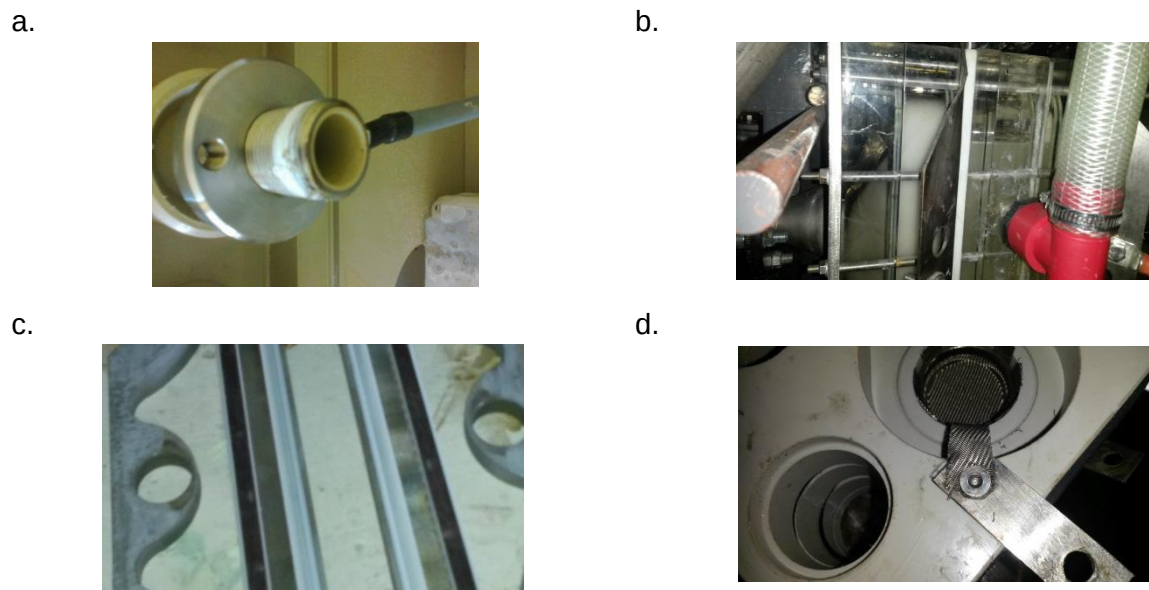


Figure 7-6: (a) Solid electrode conductive head screwed onto a threaded rod for the DEFT™ concept optimisation reactor, (b) bus bar of the MCE reactor penetrating the entire cross-sectional area of the reactor, (c) pressure connection of the electrodes to the bus bar for the HFP reactor, and (d) joined connection of the circular electrode assembly to the bus bar of the MCFPE reactor

7.4.3. Gas/Liquid separation

The removal of entrained micro-bubbles from a flowing electrolytic solution has never been addressed, with the exception of the de-gassing of non-aggressive solutions such as water [79]. Acids and bases, along with other salts have a manner of providing enhanced wettability/fouling to membranes, disallowing them from being de-gassed without substantial solution entering the vacuum side [80]. Although membrane degassing could serve as an effective means of degassing a variety of flowing solutions, the technology is not developed enough to lend itself to the degassing of aggressive solutions such as potassium hydroxide [56].

Due to the necessity of requiring an effective gas/liquid separation solution, a high-level investigation was conducted on the effectiveness of a number of existing and new solutions to extract the micro-bubbles from solution. Cyclonic and submerged separation solutions proved ineffective, with the only working solution in the form of a contact media system whereby flowing solution is flowed over media in thin films, hence controlling the residence time, and allowing the

gaseous entrainment to liberate itself into the surrounding gas by means of the natural buoyant process.

a.



b.



Figure 7-7: (a) Internals of a typical gas/liquid separation system used for the DEFT™ process illustrating the use of purge tubes, and (b) a translucent illustration of the effectiveness of removing micro-bubbles from a bi-phase solution by means of backed media and micronic filters

With reference to figure 7-7, it is observed that each separation stage has a micronic filter located at the top and bottom, with the top stage incorporating a separate purge stage to purge off the collecting gases. It is vital that the purge stage does not have any flowing solution present, as this will hamper the draw off efficiency of the purge system. The packed media is between each stage, serving as collection sites for coalescing gases. As gases collect in the voids, they serve to gather smaller bubbles passing by. Once large enough, they will make their way up to the purge chamber by means of natural buoyancy, once their rise velocity is greater than the solution downward velocity [65].

Gases naturally collect in the upper void of the separation system where the liquid is initially introduced. The gas moves out of the separation system by means of a gas purge valve which only permits the movement of gases out of the system as a safety interlock. Initially, the bi-phase liquid must be distributed across the surface of the initial filter to ensure that the entire available volume of the separation system is used effectively. A small liquid reservoir is located at the base of the separation system where heating can take place, and provide a liquid only suction for the electrolytic circulation pump. With this configuration a highly effective gas/liquid separation system was formulated for the DEFT™ technology, with the additional potential of forming a vacuum within the separation system to enhance the extraction of entrained gas from the flowing electrolytic fluid [79].

8. TECHNO-ECONOMIC ANALYSIS OF THE DEFT™ TECHNOLOGY

8.1 TECHNOLOGY APPLICATION

The DEFT™ technology can be used in conjunction with renewable energy sources with fluctuating power loads. The primary objective of this technology is to deliver cost-effective hydrogen, which is generated from renewable energy sources such as solar panels, wind power, and hydro-electric power, utilising an inexpensive and robust electrolysis plant. It is capable of receiving grid power with the drawback that expensive inverter technologies will be needed, and the cost of electricity will heavily offset the end cost to produce hydrogen. Many cost analysis methods do not take into consideration the inflation of the electricity price over the operating period of the plant [3].

It is envisioned that the technology will be designed to generate gas at low pressure, which will allow the use of plastic only components that would have further cost reductions and positive improvements for plant component life spans in an alkaline environment. A low-pressure storage application would be ideally suited such as that supplied by Hydrogenius (Figure 8.1), which makes use of Liquid Organic Hydrogen Carriers (LOHC's), or by means of low pressure compressed hydrogen storage or metal hydride storage [81]. Additionally, storage of hydrogen can be attained by using the hydrogen as a feedstock to produce liquid fuels [82]. By using processes such as the Fischer-Tropsch process, product liquid fuels can be derived using hydrogen that has properties similar to petroleum or diesel. It is surmised that the production of a liquid fuel in an environmentally friendly way, with the benefit that it can be used by existing infrastructure, will be more easily adopted by the public in contrast to new technologies that will require a slow injection into the market [82].

With the plant produced out of thermo-plastics, it will be relatively well insulated from heat losses, and unlike most electrolysis plants employing a radiator to cool the electrolytic fluid due to the temperature degradation shortcomings of the membrane technology, the technology can utilise the increase in temperature to further improve efficiencies [13]. The technology, when in its infancy and prior to this research) was demonstrated at excessive current densities of 20 A.cm⁻², which implies a significant hydrogen production rate, at high cell potentials if such a scenario presented itself where efficiency is not an important criterion.

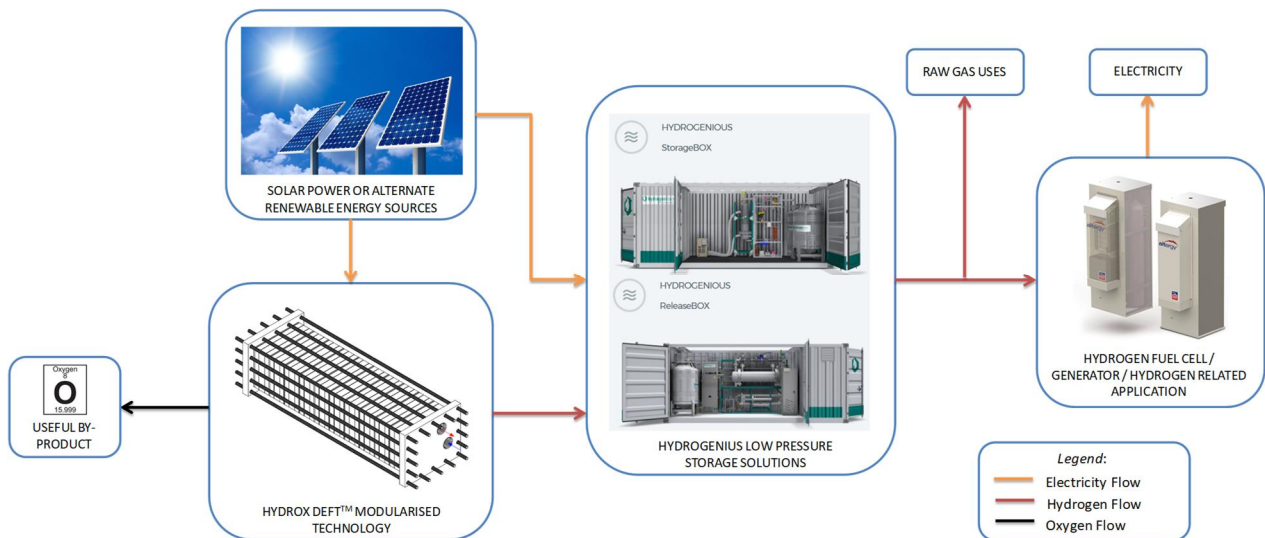


Figure 8-1: Potential application of the DEFT™ in the renewable production of hydrogen and storage in a Liquid Organic Hydrogen Carrier, medium which can be used for a multitude of applications [81]

8.2 THE FUTURE FOR POWER TO HYDROGEN AND HYDROGEN TO POWER TECHNOLOGIES

Fuel cells are considered to be an up-and-coming technology with which stored chemical energy can be converted to electrical energy by means of off-grid energy generation or back-up energy generation in both the automobile and stationary application industries. Through the years 2011 to 2012, fuel cell shipments grew by 86%, mainly in the stationary application sector reaching a total of 166.7 MW installed globally for power generated by means of fuel cells [60]. Twenty-seven hydrogen refuelling stations opened in 2012 alone, which brought the global number of refuelling stations by the end of the year to 208 [60]. The following illustration provides an indication into the total shipped megawatts for fuel cells globally and provides an indication to the growing popularity of the hydrogen to power process [83]:



Figure 8-2: Global fuel cell shipments by mega-watt and sector during the periods 2009-2016 [83]

The hydrogen market for fuel cell and electrolysis technologies in 2015 was valued at USD 415.8 million and is estimated to increase to USD 969.6 million by 2026. Registering an annual growth of 8.1% between the years 2016-2026, with the growth largely being generated by the rise of transportation applications in Europe and North America, and the implementation of 'cleaner energy' requirements in many developed countries [84].

Other than the drive for renewable energy storage and clean energy production applications, current applications for hydrogen include the following major consuming sectors: 63% in the chemical industry, 30% in refineries, 6% in metals processing and 1% in other applications. The total hydrogen consumed by the above sectors accounted for 43 million tonnes of hydrogen annually in 2010 and has been estimated to rise to 50 million tonnes of hydrogen by 2025. Currently, the chemical sector has the largest market share of hydrogen whereby 84% of this sector is involved in the production of ammonia, 12% in the production of methanol, 2% in the production of polyurethanes and 2% in the production of Nylon. The second largest consumer of hydrogen is utilised by refineries, which is used in a hydrogenation process for the production of lighter crudes [85].

The European Union agreed to reduce CO₂ emissions by 80% by 2050 therefore implying that a 95% reduction in the total road carbon production, which can be achieved by a mass transition to fuel cell powered vehicles providing the driving force for change [85].

8.3 COST ANALYSIS

Typical costs involved in producing hydrogen from fossil fuel sources range from between \$2-5 per kg H₂ depending on the production method employed [44]. A cost study performed by the National Renewable Energy Laboratory (NREL) in the US, has provided cost estimations for hydrogen production from electrolytic systems with a variation in scale. The following findings are summarised [3]:

Table 8-1: Depiction of hydrogen selling prices and respective cost contributing portions for different sized electrolyzers

	<i>Neighbourhood Scale (~20 kg H₂ /day)</i>	<i>Small Forecourt Scale (~100 kg H₂ /day)</i>	<i>Forecourt Scale (~1000 kg H₂ /day)</i>
<i>Total Selling Price (US \$ / kg H₂)</i>	19.01	8.09	4.15
<i>Capital (% of Total Cost)</i>	73	35	32
<i>Electricity (% of Total Cost)</i>	17	55	58

The study performed by the NREL reveals that the capital cost represents a larger portion of the total hydrogen selling price for smaller scale operations, which is the focus of the DEFT™ technology. The DEFT™ cost model has been based on real capital costs derived from the MCFPE pilot plant discussed in Chapter 6 with gas evolved at atmospheric pressure, which will be the inevitable future vision for the technology to save costs in the design. Creating a standard modular approach for up-scaled production will lead to further cost reductions and efficiency improvements by reducing parasitic loads. The following cost assumptions have been employed based on facts extracted from literature:

- (i) The expected lifespan of a commercial small scale alkaline electrolysis plant is approximately 60 000 hours before the efficiency drop is too significant and a major overhaul is required. Larger electrolysis plants are capable of longer periods of operation due to their ability to operate in cell potential regions that promote component longevity in excess of 100 000 hours [1],
- (ii) A voltage degradation of 10% of the initial performance over a lifetime of 60 000 hours can typically be expected and has been included in the energy cost. [1],
- (iii) Solar cells have a power output median degradation rate of 0.5% /annum where 20% power loss is considered a failure [86],
- (iv) A US dollar to ZAR exchange rate of R13.05 ~ 1 USD (18/02/2017),
- (v) In the determination of basic operating costs, the following assumptions have been used as described in published literature; Maintenance estimated at 2% of the total capital investment of the plant, with general operating costs (water feedstock and consumables) amounting to 1% of the total capital investment. Electricity costs were determined separately even though it is regarded as an operational cost, however, the balance would relate to labour, which accounts for 68% of the total operating costs determined by the sum of the maintenance, general operating costs and labour [87],

- (vi) Eskom's average commercial electricity price during peak season and standard demand being 94c / kWh¹, not taking into consideration the escalation in the electricity price per annum,
- (vii) The cost of solar technology cost in a Irena solar voltaic cost report has been reported to cost anywhere from US\$ 0.25 / kWh to US\$ 0.65 / kWh in 2011 depending on location and relative radiance levels [88],
- (viii) A South African company specialising in the installation of advanced solar arrays (Solar Track (Pty) Ltd.) was consulted on indicative prices to install solar arrays more accurate to the current value of solar array systems, and the cost per kWh was calculated based on this feedback (Annexure G):
- Two array sized options were cost based on efficiency estimations of a typical 2 kg H₂ / day electrolysis plant, a further 2 options were investigated based on the solar array sizes, that making use of static solar cells, and that making use of a single axis tracking methodology:
 - The total production for the total life of plant was calculated based on power output degradation over the total life of plant:

Table 8-2: Solar array costing based on indicative data provided by Solar Track (Pty) Ltd.

Solar Array Scale (kW)	Solar Array Option	Area Requirements (m ²)	Static Cost (R)	Average Daily Production (kWh)	Average daily production with degradation (kWh)	Total Production over 40 year ¹ Life of Solar Cells (kWh)	Total Cost per kWh (R/kWh)
8	Static	84	224 000	38.4	34.88	509 285	0.44
8	Single Axis Tracking	84	246 000	47.6	43.24	631 301	0.39
12	Static	120	300 000	57.6	52.32	763 928	0.39
12	Single Axis Tracking	120	318 000	71.4	64.86	946 952	0.34

From Table 8-2, the cost per kWh of solar energy reduces with the size increase in the solar array. Single axis tracking methods also have unique cost saving advantages in reducing the cost of solar energy with little added capital cost. Taking into account the above cost basis and

¹Extracted from the Eskom standard 2016/2017 tariffs for commercial electricity (http://www.eskom.co.za/CustomerCare/TariffsAndCharges/Pages/Tariffs_And_Charges.aspx)

assumptions, the following cost method has been used to determine the cost to produce hydrogen from a DEFT™ electrolysis plant:

1. Scenario 1 (Ni/Ni) & 2 (Pt₉Ni₅₆Al₃₅/Pt): Low cost solar at the current R&D CAPEX and efficiency for a short and long LOP (Life of Plant)

- Total capital and fabrication cost of plant: **R 180 000**
- Total kWh consumed with a 32 HHV% efficiency taking into account a 10% degradation:

$$\text{Power Consumed} = \left(\frac{1}{0.32} \right) \left(39.4 \frac{\text{kWh}}{\text{kg H}_2} \text{HHV} \right) = 123.1 \frac{\text{kWh}}{\text{kg H}_2}$$

$$\text{Hours run in a year} = (365 \text{ days})(24 \text{ hours}) = 8\,760 \text{ hours}$$

$$\text{Full time operating hours} = \frac{60\,000 \text{ hours}}{8\,760 \text{ hours}} = 7 \text{ years rounded}$$

Table 8-3: Effect of the degradation of DEFT™ electrolyser efficiency on power consumed by the plant on the basis of 24 hours' continuous power production

Year	Degradation on power consumed (kWh / kg H ₂)
1	124.8
2	126.5
3	128.3
4	130.0
5	131.8
6	133.6
7	135.4
Average Power Consumed (kWh / kg H₂)	130.07

- Cost of solar energy generation based on the 'worst case' cost of R 0.44 / kWh:

$$\text{Total H}_2 \text{ production (short term)} = (0.0416 \text{ kg H}_2)(60\,000 \text{ hours}) = 2500 \text{ kg H}_2$$

$$\text{Total H}_2 \text{ production (long term)} = (0.0416 \text{ kg H}_2)(100\,000 \text{ hours}) = 4166.67 \text{ kg H}_2$$

$$\begin{aligned} \text{Power Consumption of DEFT}^{\text{TM}}(\text{short term}) &= (2500 \text{ kg H}_2) \left(130.07 \frac{\text{kWh}}{\text{kg H}_2} \right) \\ &= 325\,169 \text{ kWh} \end{aligned}$$

$$\begin{aligned} \text{Power Consumption of DEFT}^{\text{TM}}(\text{long term}) &= (4167 \text{ kg H}_2) \left(130.07 \frac{\text{kWh}}{\text{kg H}_2} \right) \\ &= 541\,947 \text{ kWh} \end{aligned}$$

$$\begin{aligned} \text{Capital cost of solar power (short term)} &= \left(0.44 \frac{\text{R}}{\text{kWh}} \right) (325\,169 \text{ kWh}) \\ &= \text{R } 143\,020 \end{aligned}$$

$$\begin{aligned} \text{Capital cost of solar power (long term)} &= \left(0.44 \frac{\text{R}}{\text{kWh}} \right) (541\,947 \text{ kWh}) \\ &= \text{R } 238\,366 \end{aligned}$$

- Operating costs excluding solar power based on continuous operation:

$$\begin{aligned} \text{Theoretical duration that maintenance will be carrier out over (short term)} \\ &= \left(\frac{60\,000 \text{ hours}}{8760 \text{ hours}} \right) = 6.85 \text{ years} \end{aligned}$$

$$\begin{aligned} \text{Theoretical duration that maintenance will be carrier out over (long term)} \\ &= \left(\frac{100\,000 \text{ hours}}{8760 \text{ hours}} \right) = 11.42 \text{ years} \end{aligned}$$

$$\text{Maintenance costs (short term)} = (2\%)(\text{R } 180\,000)(\text{Rounded}(6.85)) = \text{R } 25\,200$$

$$\text{Operating Costs (short term)} = (1\%)(\text{R } 180\,000)(\text{Rounded}(6.85)) = \text{R } 12\,600$$

$$\text{Labour Costs (short term)} = \left(\frac{1}{68\%} \right) (25\,200 + 12\,600) = \text{R } 55\,588$$

$$\text{Total Operating Costs (short term)} = \text{R } 93\,388$$

$$\text{Maintenance costs (long term)} = (2\%)(\text{R } 180\,000)(\text{Rounded}(6.85)) = \text{R } 41\,400$$

$$\text{Operating Costs (long term)} = (1\%)(\text{R } 180\,000)(\text{Rounded}(6.85)) = \text{R } 20\,700$$

$$\text{Labour Costs (long term)} = \left(\frac{1}{68\%} \right) (25\,200 + 12\,600) = \text{R } 91\,324$$

$$\text{Total Operating Costs (long term)} = \text{R } 153\,424$$

- Contingency of 10% for built in revenue:

$$\text{Contingency (short term)} = ((\text{R } 180\,000) + (\text{R } 143\,020) + (\text{R } 93\,388)) * (10\%) = \text{R } 41\,641$$

$$\begin{aligned} \text{Contingency (long term)} &= ((\text{R } 180\,000) + (\text{R } 238\,366) + (\text{R } 153\,424)) * (10\%) \\ &= \text{R } 57\,179 \end{aligned}$$

Total CAPEX and OPEX of the plant are therefore: **R 458 049** for a plant operating on a short term LOP and **R 628 968** on a long term LOP basis.

The above estimated cost does not consider design and cost optimisation of the technology. This is a simple representation of the raw research and development model cost which has considerable room for cost reduction.

- Total cost to produce hydrogen for scenario 1 & 2:

$$\text{Cost of Hydroge short LOP} = \frac{R\ 458\ 049}{2500\ kg\ H_2} = 183.22 \left(\frac{R}{kg\ H_2} \right) \sim 14.04 \left(\frac{\$}{kg\ H_2} \right)$$

$$\text{Cost of Hydrogen long LOP} = \frac{R\ 628\ 968}{4167\ kg\ H_2} = 150.95 \left(\frac{R}{kg\ H_2} \right) \sim 11.57 \left(\frac{\$}{kg\ H_2} \right)$$

Using the same calculation method above, further cost scenario cases were developed based on efficiencies estimated from experimental data for future performance using both the best case and worst case solar technology costs. For the future predicted CAPEX, it is estimated that a 1 kg H₂ / day plant can be constructed at half the cost, calculated conservatively, of the current plant cost when materials, design and cost optimisation is taken into consideration. This does not include the benefits associated with economies of scale.

Table 8-4: Cost scenarios of a DEFT™ power to gas membraneless solution

Scenario	Energy to produce hydrogen (kWh/kg H ₂) and Electricity Consumption (kWh)	Cost of solar power (R)	Operating costs (Water, chemicals, maintenance labour and fixed operating costs) (R)	Contingency (Revenue) (R)	Total Cost of Plant (OPEX + CAPEX) (R)	Cost to produce Hydrogen (R / kg H ₂) / (US\$ / kg H ₂)
LOW COST SOLAR & CURRENT R&D CAPEX						
Scenario 3: Optimal Ni/Ni efficiency for a short LOP	109.53	91 955	93 388	36 534	401 877	160.25
	273 826					12.32
Scenario 4: Optimal Ni/Ni efficiency for a long LOP	109.53	153 258	153 424	48 668	535 350	128.48
	456 377					9.85
Scenario 5: Optimal Pt ₉ Ni ₅₆ Al ₃₅ /Pt efficiency for a short LOP	87.95	73 564	93 388	34 695	381 647	152.66
	219 061					11.70

Scenario 6: Optimal Pt ₉ Ni ₅₆ Al ₃₅ /Pt efficiency for a long LOP	87.95 365 101	122 606	153 424	45 603	501 633	120.39 9.23
Scenario 7: Future estimated optimal efficiency for a short LOP	70.55 176 363	59 225	93 388	33 261	365 875	146.35 11.21
Scenario 8: Future estimated optimal efficiency for a long LOP	70.55 293 938	98 708	153 424	43213	475 345	114.08 8.74
HIGH COST SOLAR & CURRENT R&D CAPEX						
Scenario 9: Current Ni/Ni efficiency for a short LOP	130.07 325 168	143 020	93 388	41 641	458 049	183.22 14.04
Scenario 10: Current Ni/Ni efficiency for a long LOP	130.07 541 947	238 366	153 424	57 179	628 969	150.95 11.57
Scenario 11: Optimal Ni/Ni efficiency for a short LOP	109.53 273 826	120 438	93 388	39 383	433 208	173.28 13.28
Scenario 12: Optimal Ni/Ni efficiency for a long LOP	109.53 456 377	200 729	153 424	53 415	587 568	141.02 10.81
Scenario 13: Optimal Pt ₉ Ni ₅₆ Al ₃₅ /Pt efficiency for a short LOP	87.95 219 061	96 350	93 388	36 974	406 712	162.68 12.47
Scenario 14: Optimal Pt ₉ Ni ₅₆ Al ₃₅ /Pt efficiency for a long LOP	87.95 365 101	160 583	153 424	49 401	543 408	130.42 9.99
Scenario 15: Future estimated optimal efficiency for a short LOP	70.55 176 363	77 570	93 388	35 096	386 054	154.42 11.83
Scenario 16: Future estimated optimal efficiency for a long LOP	70.55 293 938	129 283	153 424	46 271	508 978	122.15 9.36
LOW COST SOLAR & FUTURE R&D CAPEX						
Scenario 17: Current Ni/Ni efficiency for a short LOP	130.07 325 168	109 196	46 694	24 589	270 479	108.19 8.29
Scenario 18: Current Ni/Ni efficiency for a long LOP	130.07 541 947	181 994	76 712	34 871	383 576	92.06 7.05
Scenario 19: Optimal Ni/Ni efficiency for a short LOP	109.53 273 826	91 955	46 694	22 865	251 514	100.61 7.71
Scenario 20: Optimal Ni/Ni efficiency for a long LOP	109.53 456 377	153 258	76 712	31 997	351 967	84.47 6.47

Scenario 21: Optimal Pt ₉ Ni ₅₆ Al ₃₅ /Pt efficiency for a short LOP	87.95 219 061	73 564	46 694	21 026	231 284	92.51 7.09
Scenario 22: Optimal Pt ₉ Ni ₅₆ Al ₃₅ /Pt efficiency for a long LOP	87.95 365 101	122 606	76 712	28 932	318 250	76.38 5.85
Scenario 23: Future estimated optimal efficiency for a short LOP	70.55 176 363	59 225	46 694	19 592	215 511	86.2 6.61
Scenario 24: Future estimated optimal efficiency for a long LOP	70.55 293 938	98 708	76 712	26 542	291 962	70.07 5.37
HIGH COST SOLAR & FUTURE R&D CAPEX						
Scenario 25: Current Ni/Ni efficiency for a short LOP	130.07 325 168	143 020	46 694	27 971	307 685	123.07 9.43
Scenario 26: Current Ni/Ni efficiency for a long LOP	130.07 541 947	238 366	76 712	40 508	445 586	106.94 8.19
Scenario 27: Optimal Ni/Ni efficiency for a short LOP	109.53 273 826	120 438	46 694	25 713	282 845	113.14 8.67
Scenario 28: Optimal Ni/Ni efficiency for a long LOP	109.53 456 377	200 729	76 712	36 744	404 185	97.00 7.43
Scenario 29: Optimal Pt ₉ Ni ₅₆ Al ₃₅ /Pt efficiency for a short LOP	87.95 219 061	96 350	46 694	23 304	256 349	102.54 7.86
Scenario 30: Optimal Pt ₉ Ni ₅₆ Al ₃₅ /Pt efficiency for a long LOP	87.95 365 101	160 583	76 712	32 730	360 025	86.41 6.62
Scenario 31: Future estimated optimal efficiency for a short LOP	70.55 176 363	77 570	46 694	21 426	235 691	94.28 7.22
Scenario 32: Future estimated optimal efficiency for a long LOP	70.55 293 938	129 283	76 712	29 560	325 595	78.14 5.99

Production costs of hydrogen from the DEFT™ technology compares favourably with literary findings. Operating off grid electricity will be found to be considerably more cost intensive when compared to the renewable solar method. For this reason, the majority of alkaline electrolysis plants sacrifice capital cost for reasonable efficiencies in order to keep operating costs to a minimum [16]. From the calculated figures above, it is ideal to operate with a cost-effective solar array, implying that a tracking field is incorporated utilising a reasonable power output. Predicted efficiencies are based on a series configuration utilising an optimal catalyst as mentioned in Chapter 7. The best estimated cost to produce hydrogen proves to be US\$ 5.37 / kg H₂ with a life

of plant of 100 000 hours. A realistic cost for the current status of the technology utilising an optimal catalyst reveals to be 6.47 US\$ / kg H₂, utilising a simple and reliable nickel catalyst.

It is important to take cognisance that the above cost prediction was calculated on the basis of the technology in its current form. This will likely decrease further as the technology evolves towards a more optimal design and function.

Several quoted costs were acquired from prominent suppliers, based on PEM plants of small scale production quantities, for a cost comparison to the DEFT™ technology based on the capital cost to produce 1 kg H₂. This cost represents the capital cost of the plant as it is unknown what operating and electrical demands are involved for each respective plant:

Table 8-5: Cost comparison of the DEFT™ solution to state-of-the-art PEM systems for the same life of plant and similar production capability

<i>Manufacture</i>	<i>Productive Capacity (kg H₂ / 24 hrs.)</i>	<i>Selling Cost (R)</i>	<i>Efficiency Range (HHV %)</i>	<i>Output Pressure (Bar)</i>	<i>Life of Plant (hrs.)</i>	<i>Total Hydrogen Produced for LOP (kg H₂)</i>	<i>Capital Cost (R / kg H₂) excl. OPEX</i>
Hydrox Holdings Ltd.	2	355 000	32-45	1	60 000	5000	71.00
H Generators	2.4	1 227 726.50	40	5	60 000	6000	204.62
Proton Onsite	2.08	1 504 453.20	48.6	13.8	60 000	5200	289.32

The cost estimations for the PEM systems are conservative figures, as the acidic-based smaller systems are generally known to have a life of plant estimated to be in the region of around 20 000 hours. This cost should affectively be increased by a factor of 3 in order to make it realistic with published findings [1]. Therefore, the simple DEFT™ technology has the potential of being order of magnitude more cost-effective compared to state of the art PEM systems.

9. CONCLUSION OF RESEARCH

9.1 OVERVIEW

A membraneless alkaline water electrolysis solution has been investigated for cost-effective renewable hydrogen and oxygen gas production, relying on the manipulation of electrolytic flow in opposing directions (divergent electrode-flow-through, DEFT™), which achieves: (i) separation of the constituent gases, (ii) simplification of the electrolyser design, and (iii) overcoming major limitations of conventional water electrolyzers. Modern alkaline electrolyzers experience cross-diffusion of gases across the membrane/diaphragm and operate with limited current densities. It is a well-developed technology with a number of advantages making use of inexpensive materials of construction: however, it remains capital intensive due to low operating current densities [37]. Proton exchange membrane electrolyzers (PEMELs) overcome some limitations associated with alkaline systems by allowing: (a) efficient performance at high current densities, (b) pressurised operation, and (c) production of superior gas purities. The aggressive acidic regime of PEMELs requires the use of distinct construction materials that are scarce and expensive [37]. The DEFT™ solution incorporates advantages from both alkaline and PEM systems, allowing for high current density operation in an alkaline environment, utilising an inexpensive, simple and, reliable design.

This DEFT™ membraneless technology can be employed in a renewable power to gas or energy scheme. It can receive and handle fluctuating power loads while producing high purity gases at a broad current density range, as long as electrolytic circulation is present at the defined minimum operating velocities. It can solely be used for gas production from renewable energy sources, or as a means of storing excess power generated from the grid for use in industrial applications, or for re-use back into the grid during times of peak energy demand. The majority of current electrolysis applications focus on the centralised deployment of large scale electrolyzers to keep CAPEX and OPEX costs to a minimum. The DEFT™ solution is, however, ideal for decentralised onsite gas production as the technology takes on a low CAPEX, compact, scalable stack, and plant design.

This investigation has discussed, with a detailed proof of concept, optimisation research, and development tests related to four major test rigs. This has culminated into a working prototype with all basic technological components integrated and working well together with defined operational characteristics and constraints. An energy consumption rate of 56 – 73 kWh / kg H₂ has also been defined as the operational benchmark for water electrolysis systems [37]. Although

performance thus far has indicated that the DEFT™ pilot plants have not been capable of operating within this efficiency region, an efficient design of the technology in the correct configuration will most certainly allow operation within this range. Neighbourhood scale water electrolysis plants have been reported having an overall efficiency range of 43 – 52 HHV% [1]. DEFT™ pilot plants used in this study have come within close reach of this number, and a small degree of optimisation would need to be done in order for it to operate within this benchmark. The following points define the most prominent conclusions from the research:

- (i) From the four pilot plants fabricated and tested, a reactor making use of; 30 mm circular electrodes in a pressurised chamber, counter current flow, indirect electrolytic introduction, and contaminant gas purge chambers with reactors of defined length coupled to a contact type vertical separation system, provided the best product gas purities and performance using similar electrodes and experimental conditions,
- (ii) Gas purities are greatly dependant on reactor set-up, flow velocity, temperature and operating current densities. Optimal gas purities were achieved with the refined MCFPE DEFT™ reactor amounting to 99.81 vol% H₂ and 99.5 vol% O₂ at an operating current density of 3.5 A.cm⁻², optimal electrode gap of 2.5 mm, 50°C and the optimal flow velocity of 0.075 m.s⁻¹,
- (iii) The optimal catalyst tested is a combination catalyst consisting of aluminium nickel and platinum in the mass ratio 36:55:9 respectively for the anode, and pure plated platinum for the cathode, providing 0.477 A.cm⁻² at 1.77 VDC and 2.617 A.cm⁻² at 2.5 VDC, at a temperature of 70 °C, flow velocity of 0.075 m.s⁻¹, and an electrode gap of 2.5 mm,
- (iv) It was shown that using structures that maximise the available electrode area in relation to the flow of electrolyte, proved successful in enhancing stack performances. Double mesh layers of a few configurations and metal foam are ideal for this application,
- (v) Temperature is important on enhancing stack efficiencies, however, to facilitate quick start up times, and to enhance material longevities, the technology would be able to start operating from 35°C with a recommended maximum temperature of 60°C, and
- (vi) Nickel and its oxides have proven themselves as reliable catalytic constituents and stand-alone materials, with PGM based catalysts proving unstable for long term optimal performance.

The current form of the DEFT™ membraneless electrolysis technology is still within the early developmental stages with performance holding promise to potentially outperforming current industry solutions in the market for hydrogen production by water electrolysis. CAPEX and OPEX, related to the DEFT™ membraneless electrolysis technology, are highly competitive with current industry benchmarks, with estimations coming within close range of forecourt production systems.

With optimisation of the technology through continued research and development, it is poised to become competitive with current fossil fuel derived methods of hydrogen production.

The technology is currently classified to be in TRL (Technology Readiness Level) 5 and needs to progress to TRL 6. For the next step, the system components need to be mechanically designed to operate more efficiently and to the correct safety standards. This will progress the technology to a representative engineering prototype designed specifically for operation in a real application environment as to study long term operational characteristics.

DEFT™ membraneless alkaline electrolysis has the potential to be a unique disruptive technology, that not only lowers the cost to produce hydrogen, but could accelerate the move toward clean and renewable energy for the future.

9.2 RECOMMENDATIONS

Based on literature and experimental findings made in this research, the following recommendations are made to further improve the DEFT™ technology:

- (i) The majority of research conducted for the DEFT™ technology has commonly dealt with filtration mesh and limited testing with metal foam as electrode material. A greater variation of tests can be performed with regards to alternate porous metal materials, which promote enhanced surface areas on which water electrolysis can take place,
- (ii) A variable programmable DC power supply was used to provide the stack with power, and though loads were altered continuously throughout the tests, tests involving a load from a solar array would be beneficial in order to study all the intricacies with regards to coupling the DEFT™ technology to solar or alternate renewable energy sources,
- (iii) HHV% efficiencies were calculated in instances where pilot plants are not optimised for best stack efficiencies, lowest pressure drop, and hence lowest parasitic load designs. The MCFPE stack can be integrated into a balance of plant that promotes energy efficiency in order to obtain accurate estimations toward efficiency,
- (iv) Larger circular electrode diameters need to be tested along with their relationship to flow velocity and resolving gas purity to maximise the production rate per unit volume of the reactor,
- (v) Enhanced catalysts must be continually tested and adhered to surfaces such as metal foam to establish greater stack efficiencies,
- (vi) The effects of catalyst corrosion and degradation will require further study in order to develop a suitable long term catalyst, and

(vii) Though tests have only been performed up to 80 °C, the DEFT™ technology has the potential to run at high temperatures to boost stack efficiencies even higher. This aspect can be investigated in order to determine complexities dependent on high temperature operation.

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ANNEXURE A – GAS PURITY REPORT FOR CONCEPT OPTIMISATION TEST PLANT



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TEST REPORT

REPORT NO.: AS-14-302

PAGE 1 OF 2

SUMMARY

Customer	DemcoTech		
	P O Box 9624, Edenglen, 1613, SOUTH AFRICA		
Test Required	Hydrogen and Oxygen	Study number	DCT 14-302
TEST ITEM			
Description	Gas sample	Condition	Gas
Identification	Flow rate	Date of Receipt	18/06/2014
Number of Samples	6	Storage conditions	At room temperature
Storage date	None – taken from unit and analysed	Date of Analysis	18/06/2014
Method/s used	Standard methods of Analysis as specified.		
Environmental Conditions with analysis	Temperature: 20 °C	Humidity: 41 %RH	

TEST ITEMS

On 18 June 2014 Airsep Laboratory tested gas samples on site from a unit supplied by DemcoTech Engineering.

The request was to issue a COA for the gas content in the samples.

Before the start of the analyses, each test item was examined visually to determine if any foreign material was present. Odour, colour and any other physical aspects were noted. A representative sample was taken for analysis.

ANALYTICAL METHODS AND TEST GUIDELINES

The methods/instruments used for the analysis are all part of an on-going quality control system and were standardized before the analysis took place.

Analyses was performed with on and Agilent 6890 gas chromatograph with a suitable capillary column. Certified standards were utilized prior and during analysis.

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REPORT NO.: AS-14-302
 PAGE 2 OF 2

CERTIFICATE OF ANALYSIS 14-302/001
ANALYSIS OF GAS SAMPLES FROM ELECTROLYSER

Test Item	Test Result (%)			Uncertainty of result
	Flow 3 m ³ /hr	Flow 2 m ³ /hr	Flow 1.5 m ³ /hr	
H ₂ outlet	99.83	99.78	98.98	± 0.1 %
O ₂ outlet	98.84	96.69	97.60	± 0.1 %

The total balance of the O₂ outlet is nitrogen, and of the H₂ outlet, the balance is mostly nitrogen.

OBSERVATIONS

1. The gas was sampled directly from the outlets on the electrolyser unit before injection directly into the gas chromatograph.
2. Electrolyte level adjusted for lower flow rates.

Indemnity Clause

"No warranties or guarantees are given by Airsep SA cc, its employees, affiliates, consultants, sub-contractors or representative regarding the accuracy or correctness of the above tests and Airsep SA cc, its employees, affiliates, consultants, sub-contractors or representatives are therefore indemnified against any and all damages, losses, claims and demands, including legal fees and expenses of whatsoever nature in respect of any damages suffered, directly or indirectly, resulting from the above tests."

Dr RF van de Water
 Responsible Laboratory Manager

Date : 19 June 2014

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ANNEXURE B – GAS PURITY REPORT FOR MCFPE STACK BATCH A



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TEST REPORT

REPORT NO.: AS-17-065
PAGE 1 OF 2

SUMMARY

Customer	Hydrox Holdings		
	P O Box 8365, Centurion, 0046, SOUTH AFRICA		
Test Required	Hydrogen and Oxygen	Study number	Hydrox 17-065
TEST ITEM			
Description	Gas sample	Condition	Gas
Identification	A, B, C, D	Date of Receipt	31/05/2017
Number of Samples	4	Storage conditions	At room temperature
Storage date	None – taken from unit and analysed	Date of Analysis	5/06/2017
Method/s used	Standard methods of Analysis as specified.		
Environmental Conditions with analysis	Temperature: 23 °C	Humidity: 33 %RH	

TEST ITEMS

On 05 June 2017 Airsep Laboratory tested gas samples from Gas Sampling Bags supplied by Hydrox Holdings.

The request was to issue a COA for the gas content in the sample.

Before the start of the analyses, each test item was examined visually to determine if any foreign material was present. Odour, colour and any other physical aspects were noted. A representative sample was taken for analysis.

ANALYTICAL METHODS AND TEST GUIDELINES

The methods/instruments used for the analysis are all part of an on-going quality control system and were standardized before the analysis took place.

Analyses was performed with on and Agilent 6890 gas chromatograph with a suitable capillary column. Certified standards were utilized prior and during analysis.

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CERTIFICATE OF ANALYSIS 17-065/001

ANALYSIS OF GAS SAMPLES

Sample	Test Result (%)			Uncertainty of result
	H ₂	O ₂	N ₂	
"A"	99.20	0.12	0.68	± 0.2 %
"B"	< 0.2	99.5	0.47	± 0.2 %
"C"	<0.2	98.8	1.16	± 0.2 %
"D"	99.81	0.06	0.13	± 0.2 %

OBSERVATIONS

1. The gas was sampled directly from the gas sampling bags supplied before injection directly into the gas chromatograph.
2. Some residual air may be due to the sampling bags and the injection technique.

Indemnity Clause

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Dr RF van de Water
 Responsible Laboratory Manager

Date: 05 June 2017

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ANNEXURE C – GAS PURITY REPORT FOR MCFPE STACK BATCH B



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TEST REPORT

REPORT NO.: AS-17-066
PAGE 1 OF 2

SUMMARY

Customer	Hydrox Holdings		
	P O Box 8365, Centurion, 0046, SOUTH AFRICA		
Test Required	Hydrogen and Oxygen	Study number	Hydrox 17-066
TEST ITEM			
Description	Gas sample	Condition	Gas
Identification	A, B, C, D	Date of Receipt	28/06/2017
Number of Samples	4	Storage conditions	At room temperature
Storage date	None – taken from unit and analysed	Date of Analysis	29/06/2017
Method/s used	Standard methods of Analysis as specified.		
Environmental Conditions with analysis	Temperature: 21 °C	Humidity: 47 %RH	

TEST ITEMS

On 28 June 2017 Airsep Laboratory tested gas samples from Gas Sampling Bags supplied by Hydrox Holdings.

The request was to issue a COA for the gas content in the sample.

Before the start of the analyses, each test item was examined visually to determine if any foreign material was present. Odour, colour and any other physical aspects were noted. A representative sample was taken for analysis.

ANALYTICAL METHODS AND TEST GUIDELINES

The methods/instruments used for the analysis are all part of an on-going quality control system and were standardized before the analysis took place.

Analyses was performed with on and Agilent 6890 gas chromatograph with a suitable capillary column. Certified standards were utilized prior and during analysis.

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CERTIFICATE OF ANALYSIS 17-066/001

ANALYSIS OF GAS SAMPLES

Sample	Test Result (%)			Uncertainty of result
	H ₂	O ₂	N ₂	
"A"	94.94	4.51	0.55	± 0.2 %
"B"	< 0.2	99.40	0.60	± 0.2 %
"C"	96.02	3.65	0.33	± 0.2 %
"D"	< 0.2	99.14	0.86	± 0.2 %

OBSERVATIONS

1. The gas was sampled directly from the gas sampling bags supplied before injection directly into the gas chromatograph.
2. Some residual air may be due to the sampling bags and the injection technique.

Indemnity Clause

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Dr RF van de Water
 Responsible Laboratory Manager

Date: 30 June 2017

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ANNEXURE D – FIRST PUBLISHED ARTICLE IN THE JOURNAL OF POWER SOURCES

Journal of Power Sources 293 (2015) 228–235



Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour



Performance evaluation of a membraneless divergent electrode-flow-through (DEFT) alkaline electrolyser based on optimisation of electrolytic flow and electrode gap



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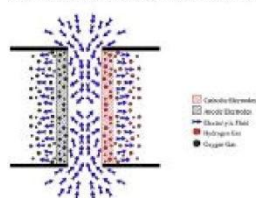
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HIGHLIGHTS

- Membraneless alkaline electrolysis (MAE) reduces capital and maintenance costs.
- Gas separation by directing the flow of electrolyte in directly opposing directions.
- An HHV% efficiency of 75% below 2.00 VDC for the electrolyser stack alone.
- Hydrogen purity of 99.83% realised at electrolyte flow of 0.2 m s^{-1} .
- Current densities of $219.99 \text{ mA cm}^{-2}$ (1.80 VDC) and $474.40 \text{ mA cm}^{-2}$ (2.00 VDC).

GRAPHICAL ABSTRACT

Membraneless Divergent Electrode-Flow-Through (DEFT) Electrolysis



ARTICLE INFO

Article history:

Received 14 December 2014

Received in revised form

14 May 2015

Accepted 18 May 2015

Available online 23 May 2015

Keywords:

Alkaline water electrolysis

Membraneless

Hydrogen production

ABSTRACT

A membraneless divergent electrode-flow-through (DEFT) alkaline electrolysis design and operating principle is investigated, which allows for the ohmic drop contribution and performance threshold limitations of a conventional membrane barrier to be overcome. Employing mesh electrodes of 30 mm diameter, operation of the electrolyser at an electrolytic flow velocity of $0.075\text{--}0.1 \text{ m s}^{-1}$, resulted in an optimal electrode gap of $\sim 2.5 \text{ mm}$, while operating at greater velocities ($>0.1\text{--}0.2 \text{ m s}^{-1}$) allows for the employment of a smaller optimal gap of $\sim 0.8 \text{ mm}$. At an electrode gap of 2.5 mm and current densities of 3500 mA cm^{-2} , hydrogen purity of 99.83% has been recorded. With pure nickel electrodes current densities of $101.19 \text{ mA cm}^{-2}$ (at 1.80 VDC) and $326.33 \text{ mA cm}^{-2}$ (at 2 VDC) have been achieved, while the use of superior catalysts, namely, $\text{RuO}_2/\text{IrO}_2/\text{TiO}_2$ and Pt for the anode and cathode respectively, resulted in the current densities to increase to $219.99 \text{ mA cm}^{-2}$ (at 1.8 VDC) and $474.40 \text{ mA cm}^{-2}$ (at 2 VDC) at an electrode gap of 2.5 mm and a minimum flow velocity of 0.075 m s^{-1} . The test rig is capable of generating hydrogen at a rate of 63.6 L/hr at normal temperature and pressure (NTP). The production rate follows current density linearly at high overpotentials.

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<http://dx.doi.org/10.1016/j.jpowsour.2015.05.077>

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1. Introduction

Water electrolysis has proved to be an effective method of producing hydrogen employing renewable sources of energy [1].

ANNEXURE E – MCFPE PLANT COSTING

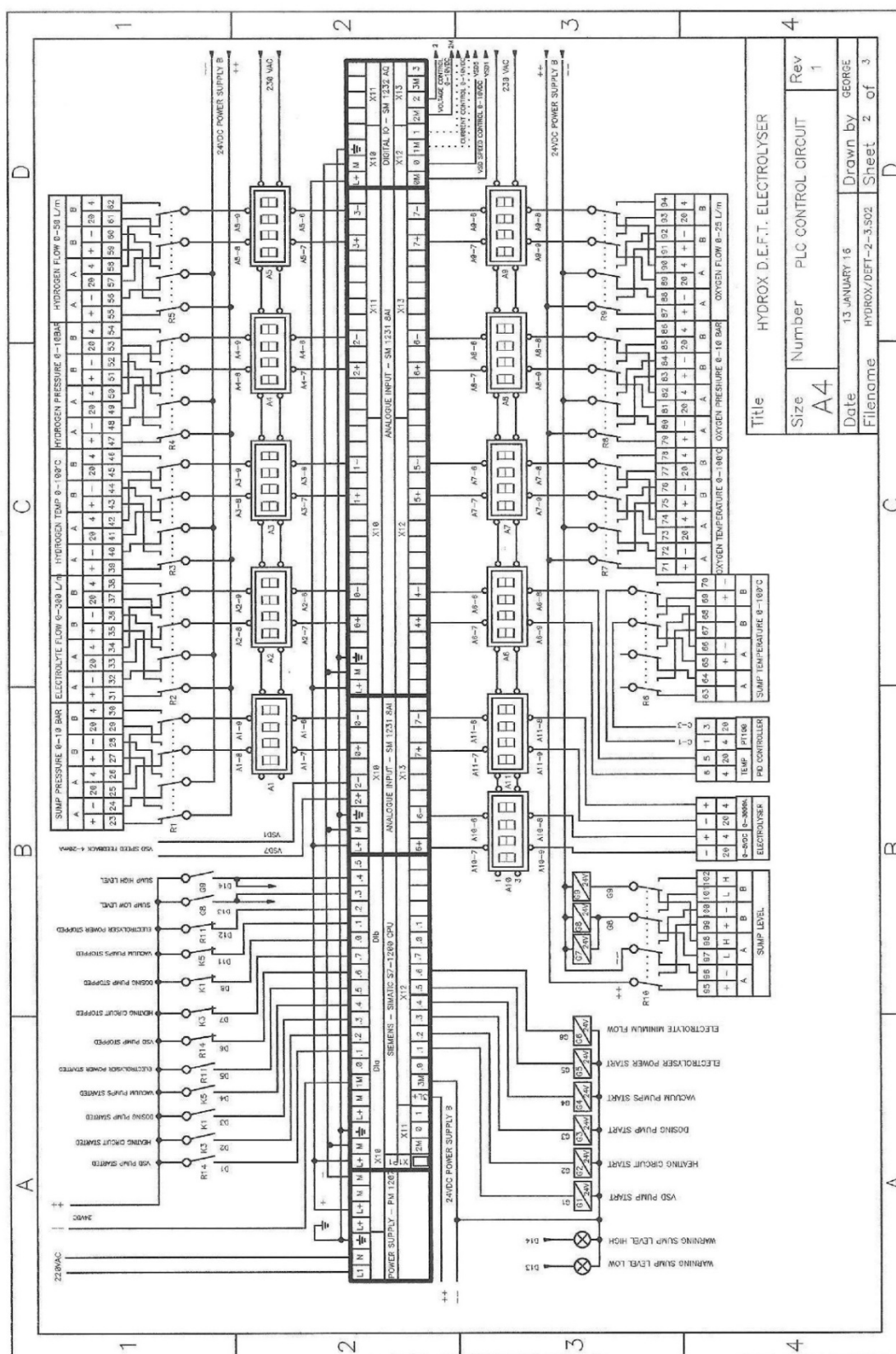
HYDROGEN PROJECT PHASE 3 WATER ELECTROLYSIS PILOT PLANT A									
Title: Breakdown by Equipment Type									
Date: 17/02/2017									
Document Number: DE12-039-F3 - Plant C Equipment List									
Revision: 1									
A									

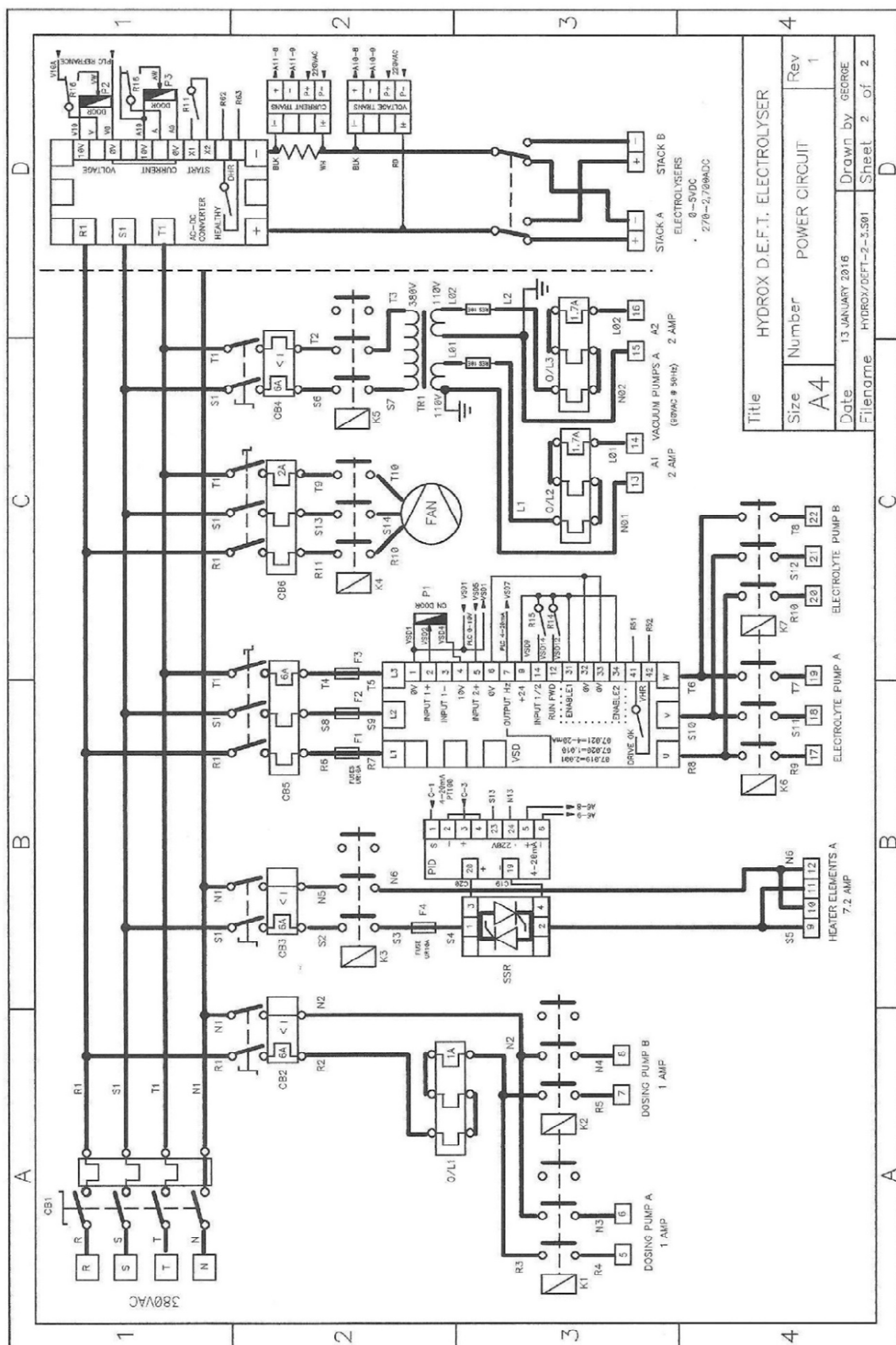
1. ELECTROLYSER C COMPONENTS AND MACHINING COSTS									
Raw Materials and Equipment Items									
Item Number	Description	Supplier / Fabricator	Quantity	Invoice Unit Description	Unit Cost / Man Hour Cost (Excl.) / (R)	VAT (R)	Total Cost (Incl.) / (R)	Comments	
1.1	20mm Thick Polypropylene Sheet	SO 00982948	1m*2m	1.00	R 436.00	R 86.38	R 522.38		
1.2	30mm Thick Polypropylene Sheet	SO 00982959	2m	2.00	R 386.01	R 77.20	R 463.21		
1.3	50mm Diameter Polypropylene Round Bar	SO 00982960	1m	1.00	R 120.00	R 24.00	R 144.00		
1.4	Ni 120 (60) Nickel Mesh	?	0.02 m ²	0.05	R 100.00	R 5.00	R 105.00		
1.5	40mm Diameter Polypropylene Round Bar	SL 00984812	21m	21.00	R 140.00	R 29.40	R 169.40		
1.6	5mm ID SS Washers	?	64	64	R 1.00	R 0.21	R 1.21		
1.7	2mm Thick Neoprene Rubber Foam Sheet	?	2m x 1m	2	R 437.15	R 87.43	R 524.58		
1.8	Set Screw Gals M5x60	RN0000974479	4	4	R 0.70	R 0.14	R 0.84		
1.9	Set Screw Gals M5x60	RN0000974479	4	4	R 0.70	R 0.14	R 0.84		
1.10	Set Screw Gals M5x60	RN0000974479	4	4	R 0.70	R 0.14	R 0.84		
1.11	Nuts M5	RN0000974479	22	22	R 0.12	R 0.02	R 0.22		
1.12	Washers M5	RN0000974479	44	44	R 0.04	R 0.01	R 0.44		
1.13									
Total (Incl.)							R 9,611.21		

2. STRUCTURE AND LABOUR									
Labour Cost Items									
Item Number	Description	Supplier / Fabricator	Quantity	Invoice Unit Description	Unit Cost / Man Hour Cost (Excl.) / (R)	VAT (R)	Total Cost (Incl.) / (R)	Comments	
1.1	Machining of Collection Plate A	1974/Hydrog	20	20	150	R 21.00	R 3,210.00		
1.2	Machining of Collection Plate B	1974/Hydrog	20	20	150	R 21.00	R 3,210.00		
1.3	Electrolyte Injection Plate	5.8 R Engineering	20	20	200	R 28.00	R 5,600.00		
1.4	Collection Plate	5.8 R Engineering	18	18	200	R 28.00	R 5,040.00		
1.5	Collection Plate	LANI Service Center	40	40	12	R 1.68	R 517.20		
1.6	Electrode Housing	5.8 R Engineering	152	152	4	R 0.56	R 851.20		
1.7	Locust Rings	1974/Hydrog	40	40	4	R 0.00	R 0.00		
1.8	Injector Plate Gaskets Profile	LANI Service Center	40	40	4	R 0.00	R 0.00		
1.9	Collection Chamber Gaskets Profile	LANI Service Center	40	40	4	R 0.00	R 0.00		
1.10	Machine Electrolyser Rings	LANI Service Center	40	40	4	R 0.00	R 0.00		
1.11									
1.12	Electrodes Nickel Plate Electrolyser Rings	?	40	40		R 0.00	R 0.00		
Total (Incl.)							R 13,552.32		

3. RIGHT SIDE SEPERATORS AND LABOUR									
Labour Cost Items									
Item Number	Description	Supplier / Fabricator	Quantity	Invoice Unit Description	Unit Cost / Man Hour Cost (Excl.) / (R)	VAT (R)	Total Cost (Incl.) / (R)	Comments	
1.1	Welding done	In House	24	24	R 4,854.82	R 679.67	R 5,534.49		
1.2									
1.3									
1.4									
1.5									
1.6									
1.7									
1.8									
1.9									
1.10									
1.11									
1.12									
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1.16									
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1.19									
1.20									
1.21									
1.22									
1.23									
1.24									
1.25									
1.26									
1.27									
1.28									
1.29									
Total (Incl.)							R 7,503.51		

Acknowledgement of George Anagnostopoulos from Power Dynamics (Pty) Ltd





ANNEXURE G – SOLAR TECHNOLOGY COST EMAIL

about:blank

----- Forwarded Message -----

Subject:Re: Solar collaboration

Date:Thu, 2 Mar 2017 15:55:59 +0200

From:Russ Bowden <russell@solartrack.co.za>

To:Malcolm <malcolm.gillespie@demcotech.com>

Hi Malcolm,

Herewith some indicative pricing to work on. Economies of scale are not good on small installations like this and cost per kW can be as low as R14 000 on installs above 1 MW, just something to bear in mind.

I have also not taken into account possible costs for health and safety compliance requirements when doing installations on mine property, these can add R50 000 to an installation if their requirements are stringent. Also excluded are travel and subsistence costs for out of town work.

12 kW array

Static - Area required approximately 120 sqm (10m x 12m)

Static Cost- R300 000

Average daily production -57.6 kWh

Single axis - Area required approximately 120 sqm (48 x 2.5)

Single axis cost - R318 000

Average daily production - 71.4 kWh

8 kW array

Static - Area required approximately 84 sqm (12 m x 7m)

Static cost - R224 000

Average daily production - 38.4 kWh

Single axis - Area required approximately 80 sqm (32 x 2.5)

Single axis cost - R246 000

Average daily production - 47.6 kWh

Kind regards

Russ Bowden

CEO Solar Track (Pty) Ltd



ANNEXURE H – KARAMANEV METHOD AND BOZZANO AND DENTE METHOD

H.1. Karamanev Method

The following is the solution method to calculate the bubble rise velocity using the Karamanev method. Initially the Reynolds number is determined to show whether deformation of the product gas bubble from a spherical shape will prevail:

$$Re_B = \frac{\rho_f u_t d_e}{\mu_f} \dots \dots \dots (H1)$$

Where, ρ_f (kg.m^{-3}) is the solution density, u_t (m.s^{-1}) is the required bubble rise velocity, d_e (mm) is the equivalent bubble diameter and μ_f ($\text{kg.m}^{-1}.\text{s}^{-1}$) is the solution viscosity.

The expressions corresponding to the deformation of the bubble shape can now be determined using the Tadaki number and Morton's number:

$$M = \frac{g \mu_f^4 (\rho_l - \rho_g)}{\rho_l^2 \sigma_l^3} \dots \dots \dots (H2)$$

$$Ta = Re_B M^{0.23} \dots \dots \dots (H3)$$

Where, g (m.s^{-2}) is the acceleration due to gravity, ρ_l (kg.m^{-3}) is the density of solution, ρ_g (kg.m^{-3}) is the density of the gas and σ_l (N.mm^{-1}) is the surface tension of the liquid.

The bubble shape correlation used within the rise velocity equation is then determined:

$$\frac{d_e}{d_h} = a.Ta^b \dots \dots \dots (H4)$$

Co-efficients a and b can be substituted respectively by examining the table below:

Table H-1: Depiction of hydrogen selling prices and respective cost contributing portions for different sized electrolyzers

a	b	Condition
1	1	When $Ta < 2.11$
1.14	-0.176	When $2.11 < Ta < 5.46$
1.36	-0.28	When $5.46 < Ta < 16.53$
0.62	0	$16.53 < Ta$

In order to determine the drag coefficients, a quantity referred to as the Archimedes number needs to be determined:

$$Ar = \frac{g\rho_f d_e^3}{\mu_f^2} (\rho_f - \rho_g) \dots \dots \dots (H5)$$

The Archimedes number can then be substituted in order to determine the drag co-efficient:

$$C_D = \frac{432}{Ar} \left(1 + 0.0470 Ar^{\frac{2}{3}} \right) + \frac{0.517}{1 + 154 Ar^{-\frac{1}{3}}} \dots \dots \dots (H6)$$

The terminal rise velocity of a gas bubble for any size and shape is then subsequently determined:

$$u_t = \sqrt{\frac{4gd_e}{3C_D} \frac{d_e}{d_h}} \dots \dots \dots (H7)$$

H.2. Bozzano and Dente Method

Like Karamanev, the Bozzano and Dente method is valid for the entire Reynolds number range and bubble shape. Equation 9 above can similarly be used to determine the terminal rise velocity upon determination of the drag co-efficient. The method for determining the drag coefficient is as follows:

Initially the quantities for the Morton's number (Equation H2) and Eotvos number need to be determined:

$$Eo = \frac{g\Delta\rho d_e^2}{\sigma} \dots \dots \dots (H8)$$

A factor, f , needs to be determined for latter substitution into the drag co-efficient equation:

$$f = \frac{48}{Re} \left(\frac{1 + 12M^{\frac{1}{3}}}{1 + 36M^{\frac{1}{3}}} \right) + 0.9 \frac{Eo^{\frac{3}{2}}}{1.4 \left(1 + 30M^{\frac{1}{6}} \right) + Eo^{\frac{3}{2}}} \dots \dots \dots (H9)$$

Additionally, another factor, or factor a , needs to be determined for substitution into the drag co-efficient expression:

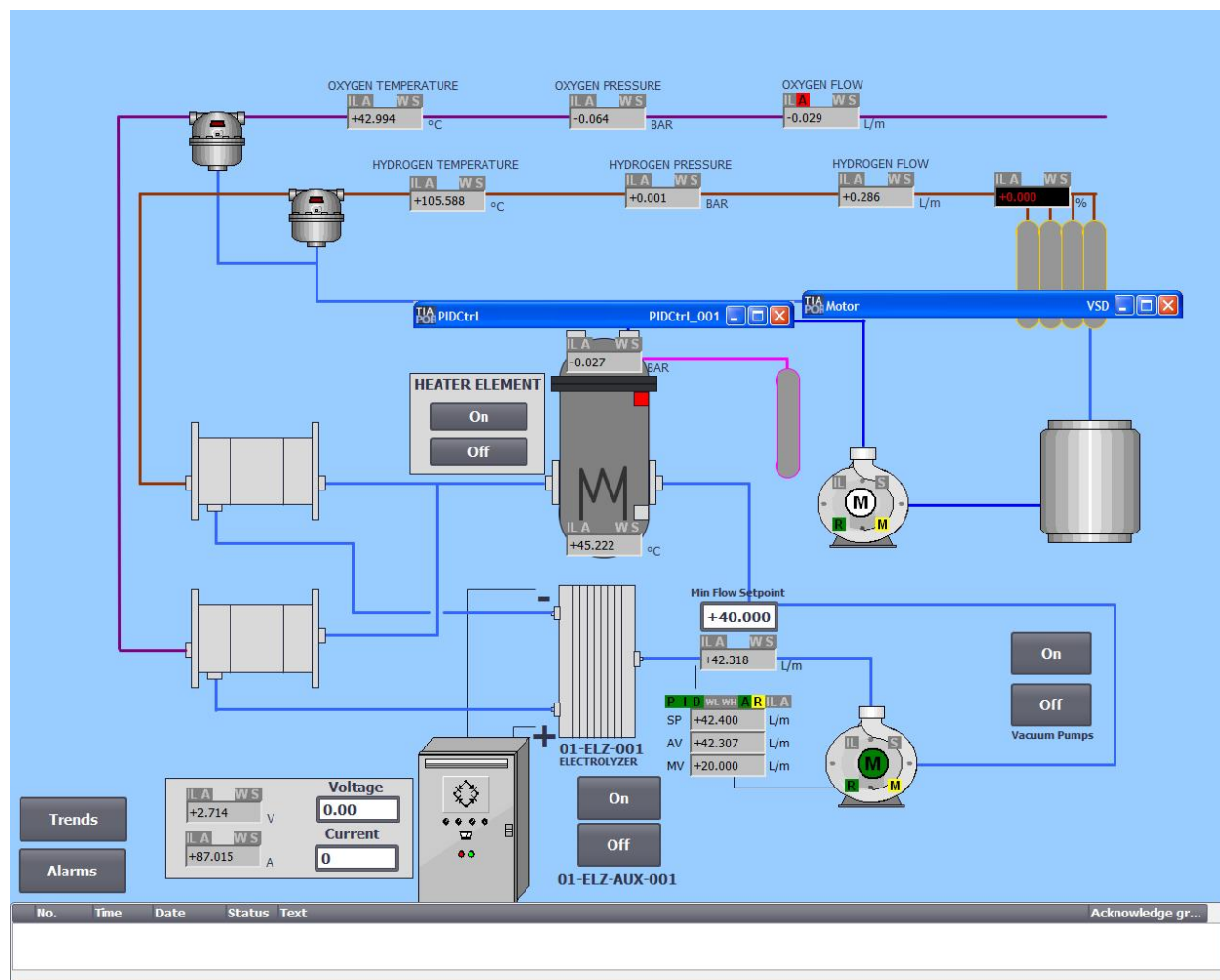
$$a = R_0 \sqrt{\frac{10 \left(1 + 1.3M^{\frac{1}{6}} \right) + 3.1Eo}{10 \left(1 + 1.3M^{\frac{1}{6}} \right) + Eo}} \dots \dots \dots (H10)$$

Where, R_0 (mm) is the equivalent bubble radius.

The drag co-efficient can now be calculated for the Bozzano and Dente method and then subsequently substituted into Equation H7 (above).

$$C_D = f \left(\frac{a}{R_0} \right)^2 \dots \dots \dots (H11)$$

ANNEXURE I – SCADA VIRTUAL INSTRUMENT PANEL



ANNEXURE J – REFERENCE PERMISSIONS

Permission for use of Table 3-1, Figures 1-1, 2-4, 3-1, 3-2 and 3-12

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Journal of Power Sources 372 (2017) 252–259



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Hydrogen production from a rectangular horizontal filter press Divergent Electrode-Flow-Through (DEFT™) alkaline electrolysis stack



M.I. Gillespie^{a,*}, R.J. Krick^{b,**}

^a Demcotech Engineering, P.O. Box 9624, Edenglen, Johannesburg 1645, South Africa

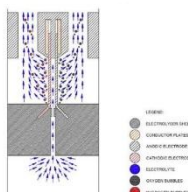
^b Electrochemistry for Energy & Environment Group, Research Focus Area: Chemical Resource Beneficiation (CRB), North-West University, Private Bag X6001, Potchefstroom 2520, South Africa

HIGHLIGHTS

- A DEFT™ membraneless alkaline electrolyser operates at high energy densities.
- A NiO anode and Ni cathode yields 508 mA cm⁻² at a cell potential of 2 VDC.
- Geometric electrode area of 344.32 cm² for a single electrode.
- Ideal for renewable energy sources as it can receive fluctuating energy loads.

GRAPHICAL ABSTRACT

Divergent Electrode-Flow-Through (DEFT™) Electrolyser.
Divergent Electrode-Flow-Through (DEFT™) Electrolyser



ARTICLE INFO

Keywords:

Alkaline water electrolysis
Membraneless
Hydrogen production

ABSTRACT

A membraneless Divergent Electro-Flow-Through (DEFT™) alkaline electrolyser, for unlocking profitable hydrogen production by combining a simplistic, inexpensive, modular and durable design, capable of overcoming existing technology current density thresholds, is ideal for decentralised renewable hydrogen production, with the only requirement of electrolytic flow to facilitate high purity product gas separation.

Scale-up of the technology was performed, representing a deviation from the original tested stack design, incorporating elongated electrodes housed in a filter press assembly. The pilot plant operating parameters were limited to a low flow velocity range (0.03 m s⁻¹–0.04 m s⁻¹) with an electrode gap of 2.5 mm. Performance of this pilot plant demonstrated repeatability to results previously obtained.

Mesh electrodes with geometric area of 344.32 cm² were used for plant performance testing. A NiO anode and Ni cathode combination developed optimal performance yielding 508 mA cm⁻² at 2 VDC in contrast to a Ni anode and cathode combination providing 467 mA cm⁻² at 2.26 VDC at 0.04 m s⁻¹, 30% KOH and 80 °C. An IrO₂/RuO₂/TiO₂ anode and Pt cathode combination underwent catalyst deactivation.

Owing to the nature of the gas/liquid separation system, gas qualities were inadequate compared to results achieved previously. Future improvements will provide qualities similar to results achieved before.

1. Introduction

Globally, around 40.5 million metric tons of hydrogen is produced

annually for major uses in oil refining, food production as a hydrogenating agent, treatment of metals, and production of ammonia [1]. Only 4% of this global figure is produced by means of water electrolysis

* Corresponding author.

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<http://dx.doi.org/10.1016/j.jpowsour.2017.10.080>

Received 4 September 2017; Received in revised form 22 October 2017; Accepted 23 October 2017
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