Green Hydrogen Production for Fuel Cell Applications and Consumption in SAIAMC Research Facility

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A thesis submitted in fulfilment of the requirements for the degree of Doctor Philosophiae, in the Department of Chemistry, University of the Western Cape.

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ABSTRACT

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PhD Thesis, Department of Chemistry, University of the Western Cape

Today fossil fuels such as oil, coal and natural gas are providing for our ever growing energy needs. As the world's fossil fuel reserves fast become depleted, it is vital that alternative and cleaner fuels are found. Renewable energy sources are the way of the future energy needs. A solution to the looming energy crisis can be found in the energy carrier hydrogen. Hydrogen can be produced by a number of production technologies. One hydrogen production method explored in this study is electrolysis of water.

The proposed study aims to investigate the integration of a hydrogen production, compression and dispensing system. Hydrogen will be produced using a solid polymer electrolyte (SPE) electrolyser powered by both photovoltaic and grid power. The produced hydrogen will be compressed using a metal hydride compressor and stored in the SAIAMC gas storage facility. A dispensing system will be developed to fuel various FC prototypes, amongst others the golf cart, forklift, fuel cell bicycle and fuel cell chargers. It is expected that this study will contribute in promoting use of clean fuel, hydrogen derived from renewable energy sources that will facilitate the transition to the hydrogen economy. A crucial aspect of the proposal is the establishment of design and operation protocols around hydrogen safety.

18 May 2020

KEY WORDS

Metal hydride

Electrolyser

Hydrogen economy

Renewable energy

Hydrogen compression

Hydrogen safety

Efficiency

Electrode

Stack

DECLARATION

I declare that *Green hydrogen production for fuel cell applications and consumption in SAIAMC research facility* is my own work, that it has not been submitted for any degree or examination in any other university, and that all the sources I have used or quoted have been indicated and acknowledged by complete references.

Stanford Chidziva. 18 May 2020

Signed.......................................

DEDICATION

I dedicate this thesis to my wife Patience Chidziva, son Emmanuel Chidziva, daughter Elizabeth Chidziva

&

My mother Cornelia Chidziva and late father Richard Garikayi Chidziva

ACKNOWLEDGEMENTS

Firstly, I would like to express my sincere gratitude to my supervisor Dr Mykhaylo Lototskyy for the continuous support of my Ph.D. study and related research, for his patience, motivation, and immense knowledge. His guidance helped me in all the time of research and writing of this thesis. I could not have imagined having a better advisor and mentor for my Ph.D. study.

Besides my supervisor, I would like to thank my core supervisors Professor Bernard Bladergroen & Professor Sivakumar Pasupathi, for their insightful comments and encouragement, but also for the hard questions, which incensed me to widen my research from various perspectives.

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ACADEMIC OUTPUT REPORTED IN THIS RESEACH

PUBLISHED PAPERS

1. Mykhaylo Lototskyy, Yevgeniy Klochko, Moegamat Wafeeq Davids, Lydia Pickering, Dana Swanepoel, Gerhard Louw, Burt van der Westhuizen, **Stanford Chidziva**, Cordelia Sita, Bernard Bladergroen, Vladimir Linkov, Industrial-scale metal hydride hydrogen compressors developed at the South African Institute for Advanced Materials Chemistry; Materials Today: Proceedings 5 (2018) 10514-10523;

2. Mykhaylo Lototskyy, Moegamat Wafeeq Davids, Dana Swanepoel, Gerhard Louw, Yevgeniy Klochko, Fahmida Smith, Fatema Haji, Ivan Tolj, **Stanford Chidziva**, Sivakumar Pasupathi, Vladimir Linkov, Hydrogen refuelling station with integrated metal hydride compressor: layout features and experience of three-year operation; International Journal of Hydrogen Energy 45 (2020) 5415-5429

3. Mykhaylo Lototskyy, Moegamat Wafeeq Davids, Ivan Tolj, Yevgeniy Klochko, Bhogilla Satya Sekhar, **Stanford Chidziva**, Fahmida Smith, Dana Swanepoel, Bruno G. Pollet. Metal hydride systems for hydrogen storage and supply for stationary and automotive low temperature PEM fuel cell power modules; International Journal of Hydrogen Energy: 40 (2015) 11491-11497

DRAFTED PAPERS

1. **Stanford Chidziva**, Marek Malinowski, Bernard Bladergroen, Sivakumar Pasupathi, Mykhaylo Lototskyy; PEM water electrolysis system performance and system safety integration; **Przeglad Elektrotechniczny registration: PE5891**
2. Boris Tarasov; Pavel V. Fursikov; Alexey A Volodin; Mikhail S Bocharnikov; Yustinas Y Shimkus; Aleksey M Kashin; Volodymyr A Yartys; **Stanford Chidziva**; Sivakumar Pasupathi; Mykhaylo V Lototskyy. Metal hydride hydrogen storage and compression systems for energy storage technologies; International Journal of Hydrogen Energy; **Manuscript HE-D-20-01322**

PROTOTYPE

- HySA 2 Nm^3/h PEM Water Electrolyser system

POSTER PRESENTATION

1. Industrial-Scale Metal Hydride Hydrogen Compressors Developed At South African Institute For Advanced Materials Chemistry on the 15th International Symposium on Metal-Hydrogen Systems August 2016, Interlaken – Switzerland

NOMENCLATURE

PEM – Proton Exchange Membrane

FC – Fuel cell

SAIAMC – South Africa Institute of Advanced material Chemistry

PLC – Programmable Logic controller

HHV – Higher Heating Value

LHV – Lower Heating Value

MH – Metal Hydride

PEMEC – Proton Exchange Membrane Electrolysis Cell

UPW – Ultra-Pure Water

PV- Photovoltaic

DC – Direct Current

HAZOP – Hazard Operability Study

BOP – Balance of plant

BOP – Balance of Plant

HCF - Hydrogen content factor

GF - Greenization Factor

EIF - Environmental Impact factor

SPE - Solid Polymer Electrolyte

P&ID - Process & Instrumentation Diagram

CHAPTER 1 – GENERAL INTRODUCTION

1.1INTRODUCTION

This chapter introduces the study and brings out the overview of the study. During this chapter the research objectives, the hypothesis of the study are highlighted, as well as the design and methodology approach for the study. The research outline, framework of the study and delimitations are included in this chapter.

1.2 BACKGROUND

The world has a looming energy crisis; the traditional non-renewable energy in form of fossil fuels is facing extinction. The reality of fossil fuel depletion, environmental pollution leading to global warming, climate changes, and a need for alternative energy supply with low carbon footprint has opened research for alternative energy sources.

The energy crisis has given birth to the Hydrogen economy. Hydrogen is an alternative energy source to the current energy crisis. A wide range of technologies can generate hydrogen such as: reforming of natural gas, liquefied petroleum gas, gasoline. etc.; gasification of coal and biomass; electrolysis of water using nuclear, fossil or renewable energy sources; photo electrochemical/photo catalytic splitting of water; thermolysis and thermo-chemical cycles (Conte, Lacobazzi, Ronchetti, & Vellone, 2001), (Badwal, Giddey, & Phair, 2006)

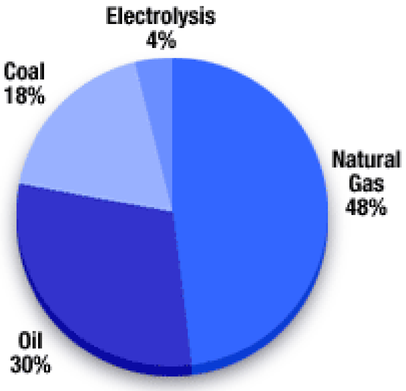


Figure 1: Current main hydrogen production routes (Molkov V. , 2012).

It is clear from Figure 1 that the majority of hydrogen used today is produced from fossil fuels. About 95% of the total global hydrogen production is captive meaning it is used at the site where it is produced. Renewable hydrogen does not yet make up a significant part of the market, hopefully more renewable hydrogen will become available as customers demand renewable fuel and the cost of renewable power becomes more competitive (Molkov V. , 2012).

Fossil fuels are non-renewable energy source that currently account for about 90 percent of world energy consumption (including manufacturing, heating, cooking, electricity and fuel for cars). Petroleum leads with a share of about 40% of total world energy consumption, followed by coal (24%) and natural gas (22%) (enviroliteracy.org, 2007)

The problem with humanity's heavy reliance on these sources of energy is that reserves are finite, and are rapidly running out. There are also health and environmental concerns surrounding the use of fossil fuels e.g. greenhouse gas emissions leading to global warming and climate changes. An estimated 4.6 million people die each year due to air pollution (enviroliteracy.org, 2007) and global warming is widely regarded as one of the most critical issues facing the planet. Additionally, given the market volatility of the oil price and the tenuous political climate surrounding oil production and delivery, researching cleaner, renewable energy alternatives to fossil fuels will contribute to a sustainable, stable energy future for South Africa and the world.

A solution to world energy crisis can be found in the energy carrier hydrogen. Hydrogen is the most abundant element in the universe; it possesses a high energy density and it can be produced from water using almost any primary energy source. Many scientists believe that hydrogen is the best way to store renewable energy, especially solar and wind power (Awad & Veziroglu, 1984).

From the global energy systems transition as shown in Figure 2 below hydrogen is emerging as the alternative energy source that will meet the ever increasingly sustainable economic growth beyond 2050. The most important consequence of a hydrogen economy is the replacement of the 20th century 'hydrocarbon society' by a sustainable one based on hydrogen (Dincer & Zamfirescu, 2012).

This replacement occurs at a time when 90 percent of the energy worldwide is being delivered primarily by fossil fuels, and most experts now agree that sometime during the early to middle decades of the twenty-second century, and perhaps much earlier, sustainable sources transformed into hydrogen and electric currencies will dominate civilisation's energy system (Sperling & Cannon, 2004)

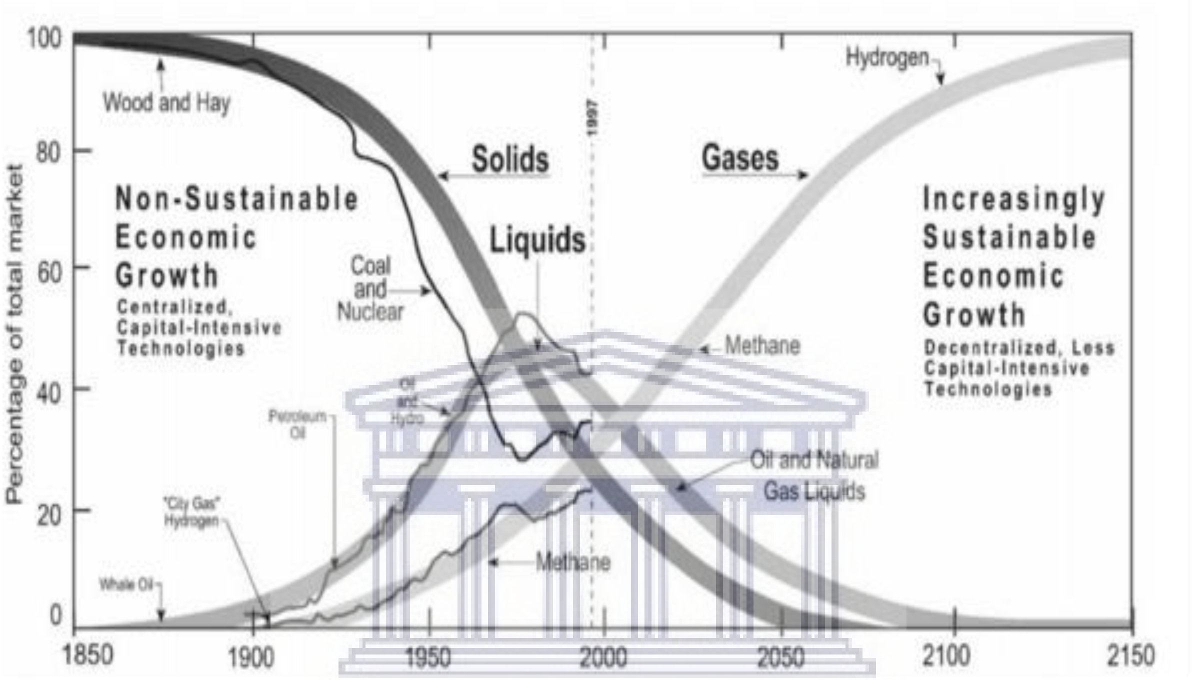


Figure 2: Global energy systems transition in the period from 1850 to 2150 (Dunn, 2002, Volume 27) (Jordan, 2006)

Hydrogen production from renewable energy sources is an environmental friendly initiative that leads to a climate of clean future industry. High-quality hydrogen (approximately 99.999% purity) can be produced by the electrochemical conversion of water to hydrogen and oxygen through a process known as water electrolysis (Carmo, Fritz, & Mergel, 2013). In this hydrogen generation process, electricity is applied to the electrode assembly and water is split at the anode into oxygen and protons. The protons diffuse through the conducting membrane to the cathode to form hydrogen (Khan, et al., 2006).

Anode: $H_2O_{(L)} \rightarrow 1/2O_2\,(g) + 2H^+ + 2e^-$ (1)

Cathode: $2H^+ + 2e^- \rightarrow H_2\,(g)$ (2)

Full reaction $H_2O_{(L)} \rightarrow H_{2\,(g)} + 1/2O_{2\,(g)}$ (3)

When the electricity is provided by a renewable source of energy (e.g. wind or solar), then a truly zero emission hydrogen supply is achieved. Solid Polymer Electrolysers (SPE) can be coupled to distributed, intermittent renewable electricity sources (e.g. wind generators or solar panels), in order to store energy generated from excess electricity as hydrogen in gas cylinders or in metal hydrides (Khan, et al., 2006) . The stored hydrogen can later be used in hydrogen fuel cells to generate electricity at one's convenience (like a battery). Advantages of a Proton Electrolyte Membrane (PEM) electrolyser are that they produce much higher current densities; smaller mass – volume characteristics; high degree of gas purity; increased level of safety (no circulation of caustic electrolyte); possibility of combining fuel cell and Electrolyser modes (Khan, et al., 2006). The low gas crossover rate of the polymer electrolyte membrane (yielding hydrogen with high purity), allows the PEM Electrolyser to work under a wide range of power input (economical aspect). This is because the proton transport across the membrane responds quickly to the power input, not delayed by inertia as in liquid electrolytes.

1.3PROBLEM STATEMENT

Heavy dependence on fossil fuels and the environmental effects caused by the consumption of fossil fuels has resulted in global warming. The depletion of fossil fuels has resulted in increased research and development of alternative energy to replace fossil fuels. A substantial amount of funding has been released by governments and private sector to try and find a solution to a possible energy crisis looming in the near future. Hydrogen has been identified as an alternative energy source due to its high energy density and easy of production. Hydrogen is a renewable clean energy that is environmentally friendly as it promotes reduction of global warming. South Africa's economy has a drive to reduce carbon footprint through initiatives like the White Paper on Renewable Energy of 2003 released by the Department of Energy which is one of the policy documents that laid foundation for the promotion of renewable energy technologies in the country.

1.4 MOTIVATION OF STUDY

Global energy systems transition in the period from 1850 to 2150 (Dunn, 2002, Volume 27) (Jordan, 2006), see Figure 2, clearly shows a serious depletion of fossil fuels and a need of alternative energy to meet the increasing global sustainable economic growth. There is a market niche for systems that produce renewable energy in the form of hydrogen in the world at large. The systems must supply clean hydrogen to the growing hydrogen economy. Competitive safe technology for hydrogen production technology is a key to the growth of hydrogen economy. The cost of complete and certified systems is relatively high, and it creates sufficient room for the development of a low cost integrated system. Hydrogen is a highly flammable gas, the integration of a system that produces hydrogen does have several safety challenges which must be mitigated and at the same time create a positive public awareness that will result in acceptance of such systems as safe to operate.

1.5 HYPOTHESIS OF THE STUDY

Safe operation of integrated complex hydrogen production, compression and storage, technical viability under certain constrains.

1.6 NOVELTY OF THE STUDY

Several hydrogen production methods are available on the market (Dincer, Green methods for Hydrogen productions, 2012). During this study one hydrogen production method, namely electrolysis is used. Electrolysis using a Polymer Electrolyte Membrane (PEM) electrolyser is investigated in this study. The novelty of this study emanates from the integration of a prototype PEM electrolyser coupled to a metal hydride compressor and the application of hydrogen safety on the integration of hydrogen production and compression systems. The success of this project creates job opportunities through production and sales of such locally produced systems that can also ultimately result in growth of the economy of our country, South Africa.

1.7AIMS AND OBJECTIVES

This project aims at feasibility study of the integration of fuel cell and hydrogen storage technologies, demonstrating South African competencies in the renewable hydrogen space, by the development and preliminary tests of a prototype green hydrogen production, compression and dispensing system for fuel cell applications including general hydrogen consumption at SAIAMC research facility. Special attention is paid to the operation safety of the prototype system.

The main objectives of the study include:

- The design of an 8.4kW Polymer Electrolyte Membrane Water Electrolyser (PEMWE) with a hydrogen production rate of 2 Nm^3/hr and hydrogen discharge pressure of 20 bars.
- Construction and commissioning of a 8.4kW PEMWE prototype system
- A HAZOP study on the integration of PEM Water Electrolyser prototype system with the balance of plant.
- Integration of PEM water electrolyser prototype system with a locally developed 5 Nm^3/h MH compressor.
- Integration of PEM water electrolyser prototype system to a locally produced 4.2kW Photovoltaic supply.

1.8 RESEARCH QUESTIONS

To achieve the above aims and objectives during this study the following research questions are going to be answered:

i. What are the optimum technical parameters at which the integrated system can operate safely with high productivity?
ii. What is the system optimum operation point when efficiency is at maximum?
iii. What design or operational measures in integrated system is required to mitigate hazards at high productivity?
iv. What recommendations could be suggested for further development of integrated system?

1.9 RESEARCH FRAMEWORK

To answer the above research questions extensive literature review has been carried out and explained in the Chapter 2, literature review. However, a structure needs to be formulated in order to meet all the specified objectives of the study. The following framework is used in accordance with the objectives of the study, it's outlined as follows:

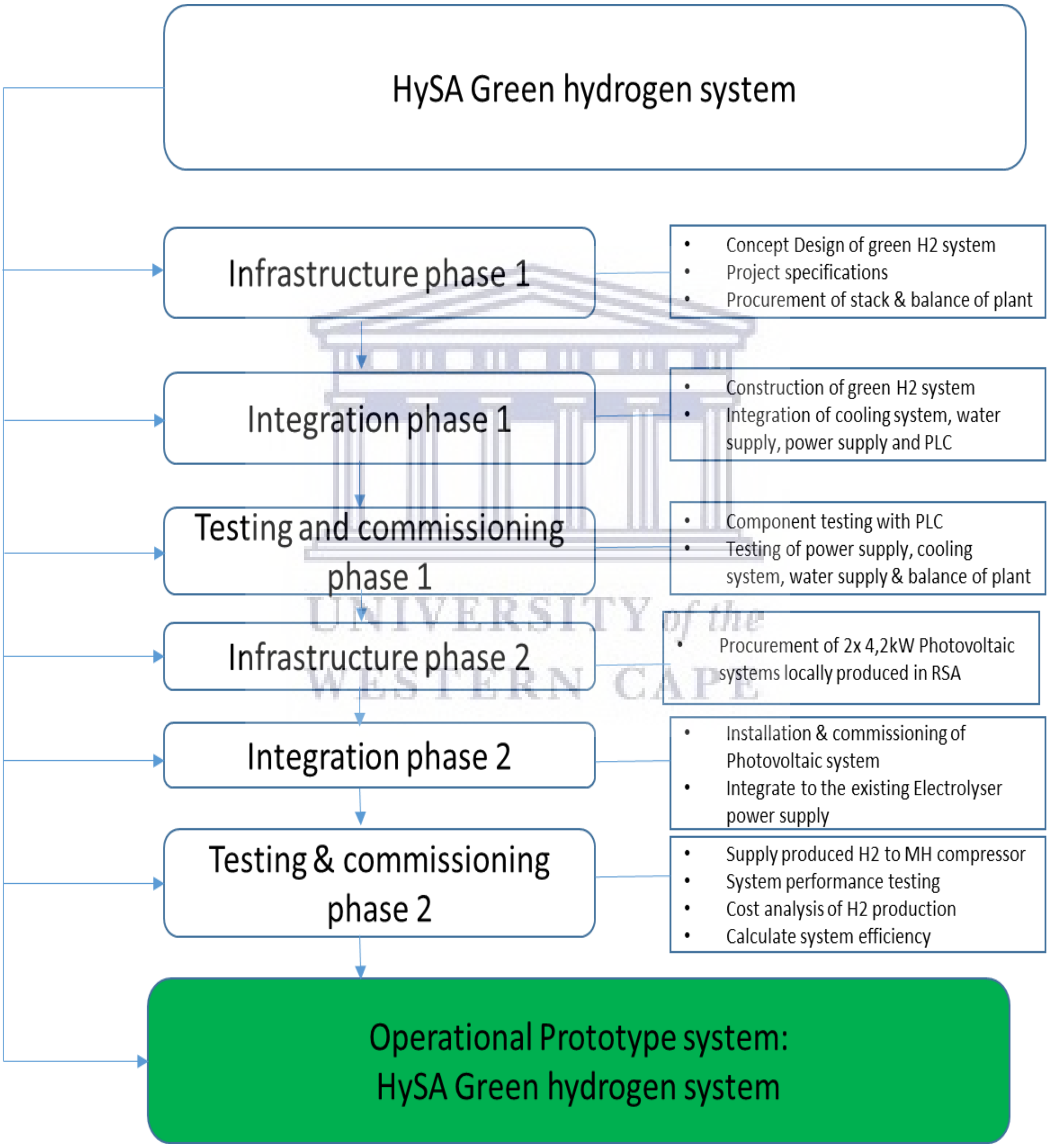


Figure 3: Research Framework

1.10 SCOPE AND DELIMITATION OF THE STUDY

Due to time and funding challenges, some modifications to our prototype system have been recommended for further development if funding is secured.

1.11 THESIS STRUCTURE

The thesis is comprised of six chapters including this introduction chapter, which gives an overview of the study. The chapters unfold in a chronological sequence from chapter one to six.

CHAPTER 2 - LITERATURE REVIEW

Renewable energy is the future energy source of the world. Considerable resources and expertise is being harnessed worldwide to address the future energy crisis. Governments and the private sector have all agreed in funding research of renewable energy as the alternative future energy source. In this study, we are going to look into the literature of one of the renewable energy source hydrogen. The literature is going to address two key areas namely hydrogen production and storage.

2.1WHAT IS HYDROGEN?

As a unique gas, Henry Cavendish discovered hydrogen in 1766. It was given the name ‘’water forming’’ by Antoine Lavoisier seven years later, who proved that water was composed of hydrogen and oxygen. The word ‘’hydrogen’’ originates from the Greek word *hydor* (water) and *gignomai* (forming). However, it has to be mentioned that hydrogen was observed and collected by Robert Boyle in 1671, who dissolved iron in diluted hydrochloric acid, i.e. long before it was recognised as a unique gas by Henry Cavendish (Molkov V. , 2012).

Hydrogen is one of the main components of water and of all organic matter and it’s widely spread not only in the Earth but also in the entire Universe. It is the most abundant element in the universe representing 75% by mass or 90% by volume of all matter. Hydrogen forms 0.15% of the Earth crust (Molkov V. , 2012).

Atomic number of hydrogen (symbol H) in the periodic table is one and atomic mass is 1.008 g/mol. The hydrogen atom is formed by a nucleus with one unit of positive charge (proton) and one electron. In normal conditions hydrogen is a gas formed by diatomic molecules, H_2 (molecular mass 2.016) in which two hydrogen atoms have formed a covalent bond (Molkov V. , 2012).

Standard properties of Hydrogen (Molkov V. , 2012)

- Colourless
- Odourless
- Nontoxic
- Non-metallic
- Tasteless
- Highly combustible diatomic gas with molecular formula H_2.

There are three hydrogen isotopes namely Protium (found in more than 99.985% of the natural element; only a proton in the nucleus), Deuterium (found in nature in 0.015% approximately; a proton and a neutron in the nucleus) and Tritium (appears in small quantities in nature, but can be artificially produced by various nuclear reactions; a proton and two neutrons in the nucleus) with atomic mass 1, 2 and 3 respectively (Molkov V. , 2012).

a) HYDROGEN AS FUEL

Hydrogen is a promising fuel, can be obtained from different sources of raw materials, including water. This is a renewable and sustainable source, which can obtain a high hydrogen purity via electrolysis. Among the processes for obtaining hydrogen from the water, the electrolytic conversion is the best known, in which two electrodes are responsible for conducting electricity and production of this gas. However, to promote this segregation, some technological challenges must be overcome, as the efficiency of electrolysers, efficiency and durability of the main fuel cells and the integration of the electrolysis systems for supply and energy, aiming to reduce production costs (Santosa, Eckerta, & Eduardo De Rossia, 2017).

The production of H_2 is an environmentally attractive process and can occur via routes considered sustainable, as the electrolysis of water, charcoal and biomass gasification, photo-electrolysis, biological processes and reforming (Kasai, 2014). This fuel can be obtained from a variety of methods, the main are characterized by production from fossil and renewable sources by steam reforming, dry reforming, thermal decomposition and cracking natural gas, petroleum hydrocarbon oxidation and coal gasification. These methods require the use of high energy load to which the process occurs (Kelly, 2014).

Reducing the dependence on fossil fuels and minimizing environmentally harmful emissions can be achieved by sustainable energy sources. With near-zero or zero end-use emissions and continually replenished resources, hydrogen can be an ideal sustainable energy carrier. Some of the advantages of hydrogen can be listed as (Acar & Dincer, 2014):

b) ADVANTAGES OF USING HYDROGEN AS A FUEL

1. High energy conversion efficiencies.
2. It can be produced from water with no emissions
3. It is abundant
4. Hydrogen can be stored in different forms like gas, liquid, or in combination with metal hydrides)
5. Hydrogen can be transported over long distances
6. Hydrogen can be easily converted to other forms of energy
7. Hydrogen has both a higher HHV and LHV compared to conventional fossil fuels. See Table 1 below.

On the other hand, a number of hydrogen production methods are still under development, this results in high production costs and low system efficiencies (Acar & Dincer, 2014).

Fuel	**HHV (kJ/g)**	**LHV (kJ/g)**
Hydrogen	141.9	119.9
Methane	55.5	50.0
Gasoline	47.5	44.5
Diesel	44.8	42.5
Methanol	20	18.1

Table 1: Higher (HHV) and Lower (LHV) heating values of Hydrogen and common fuels at 25 degrees and 1 atm (Dincer, 2012)

Here, we go further to compare hydrogen with other conventional fuels in terms of Environmental Impact Factor (EIF), Greenization Factor (GF) and Hydrogen Content Factor (HCF) to emphasize the importance of hydrogen as a unique option, through the following equations:

$$EIF = \frac{kg\ CO_2\ product\ of\ combustion\ reaction}{kg\ fuel} \qquad (4)$$

$$GF = \frac{EIF_{max} - EIF}{EIF_{max}} \qquad (5)$$

$$HCF = \frac{kg\ of\ H_2 in\ the\ fuel}{kg\ fuel} \qquad (6)$$

Where EIF_{max} is the maximum value of EIF among the evaluated options. In this specific case with 3.6, coal is selected as the EIF_{max}. As can be seen from Figure 4 below, with increasing hydrogen content (HCF), the energy sources become greener (increasing GF) and the environmental impact (EIF) decreases. This is a clear advantage of hydrogen in terms of reducing carbon-related emissions. In order to take full advantage of the hydrogen economy, it needs to be produced from renewable or vast sources at low costs (Dincer & Acar, Review and evaluation of hydrogen production methods for better sustainability, 2015)

Among the possible hydrogen production methods studied in the literature, natural gas steam reforming is the most commonly used process, resulting in heavy GHG emissions. Around 50% of the global hydrogen demand is met by natural gas steam reforming, 30% comes from oil reforming, 18% from coal gasification, 3.9% from water electrolysis, and 0.1% from other sources (Muradov & Veziroglu, 2005).

In order to remove the adverse effects of fossil fuel utilization on the environment, human health, and the climate, hydrogen should be produced from clean and abundant sources with environmentally benign methods (Levin & Chahine, 2010) and (Awad & Veziroglu, 1984). This concept is called as “green hydrogen production”.

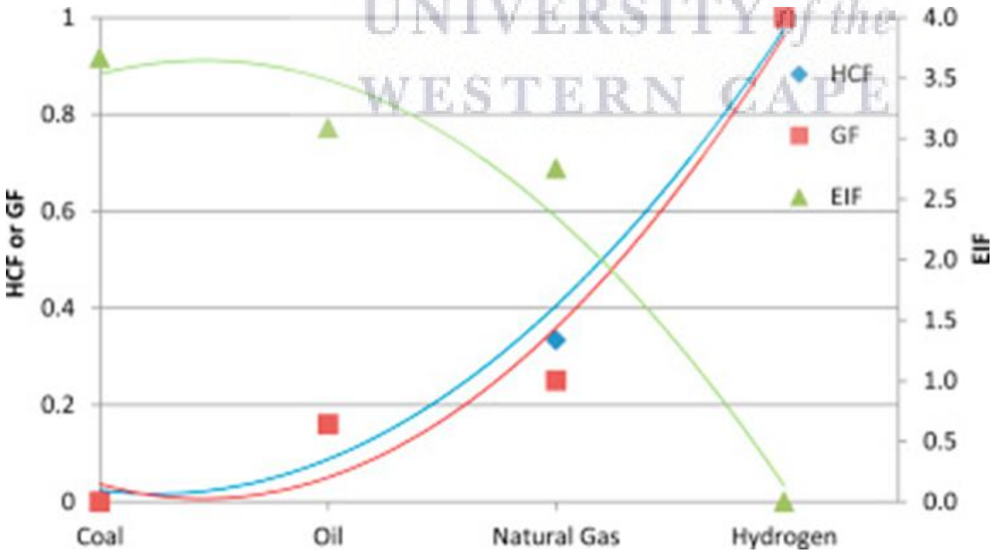


Figure 4: Hydrogen Content Factor (HCF), Greenization Factor (GF) and Environmental Impart Factor (EIF) of hydrogen and other fossil fuels. (Yilanci, Dincer, & Ozturk, 2009)

Green hydrogen technologies are not quickly accessible with sensible effectiveness and expense. For instance, studies on effectiveness and cost of PV electrolysis for large and small scale hydrogen production show that PV electrolysis is currently expensive (>$5/kg for H_2) and it cannot reach high conversion efficiencies (with energy and exergy efficiencies less than 5%) (Yilanci, Dincer, & Ozturk, 2009).

A total of 19 hydrogen production methods are compared based on energy and exergy efficiencies, production cost, global warming potential (GWP), acidification potential (AP), and social cost of carbon. (Acar & Dincer, 2015)

2.2 HYDROGEN PRODUCTION METHODS

Hydrogen can be produced by a number of technologies using renewable and non-renewable sources.

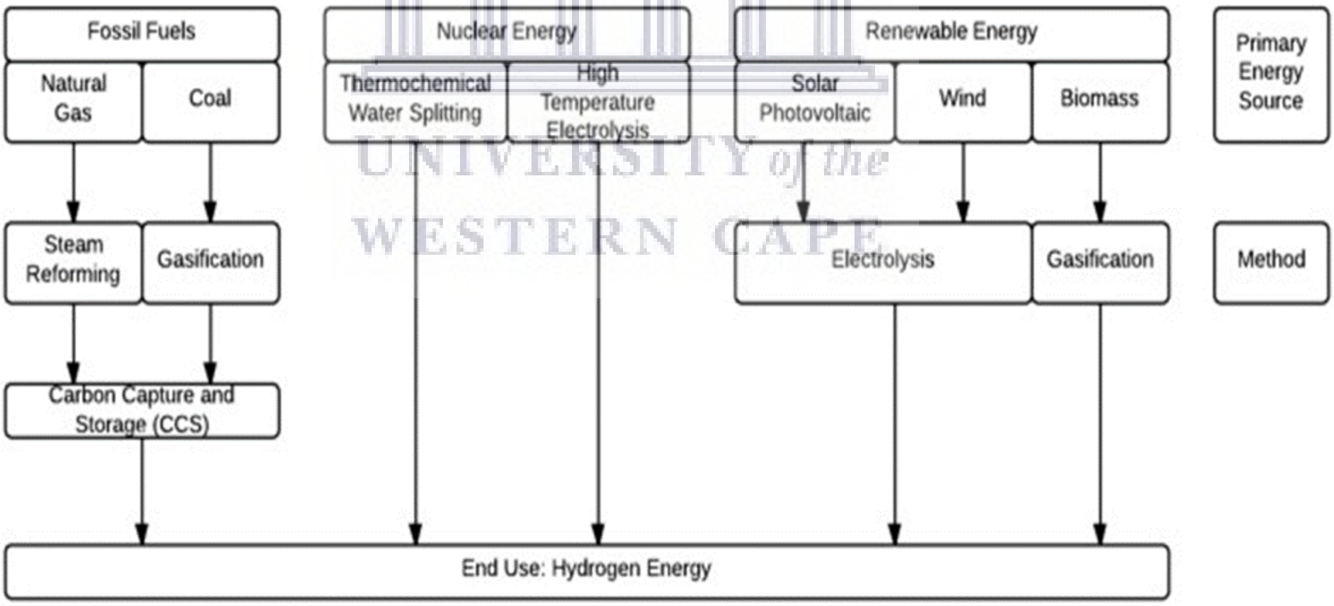


Figure 5: Selected hydrogen production methods (Dincer, 2012).

Figure 5 summarises the current methods used to produce hydrogen. Hydrogen is an abundant element found in many substances in nature like fresh and sea water, biomass, hydrogen sulphide, and fossil fuels.

With the aim of producing hydrogen with zero or low environmental impact, green hydrogen, all carbon dioxide and other pollutants must be removed when hydrogen is extracted from fossil fuels. Some other sources to generate hydrogen are thermal, electrical, photonic, and biochemical energy.

In Table 2 below, the overview and brief description for hydrogen production process from primary energy and material origins. The electrical and thermal energy can be harnessed from fossil fuels (should be processed to be regarded as “clean”), renewable energies such as solar, wind, hydro, wave, ocean, and thermal, biomass, nuclear, or recycled energy (Acar & Dincer, 2015).

The photonic energy comes from solar irradiation, while biochemical energy is recovered from organic matter. In addition to four major primary sources listed in Table 2 (electrical, thermal, biochemical, and photonic), there are also hybrid forms of energy such as electrical-thermal, photonic-biochemical, and electrical-photonic. Water, biomass, and fossil fuels are the material sources evaluated. In cases where fossil fuel is utilized, hydrogen production process includes CO_2 separation and sequestration (Acar & Dincer, 2015).

A total of 19 hydrogen production methods are compared based on energy and exergy efficiencies, production cost, global warming potential (GWP), acidification potential (AP), and social cost of carbon.

Method		**Source**		**Brief Description**
		Primary energy	**Material**	
M1	Electrolysis	Electrical	Water	Direct current is used to split water into O_2 and H_2 (electrochemical reaction)
M2	Plasma arc decomposition		Fossil Fuel	Cleaned natural gas is passed through plasma arc to generate H_2 and carbon soot
M3	Thermolysis	Thermal	Water	Thermal decomposition of water (steam) at temperatures over 2500 K

M4	Thermochemical process: Water Splitting		Water	Cyclical chemical reactions (net reaction: water splitting into H_2)
M5	Thermochemical process: Biomass		Biomass	Thermo-catalytic conversion
M6	Thermochemical process: Gasification			Conversion of biomass into syngas
M7	Biomass Reforming			Conversion of liquid biomass (biofuels) into H_2
M8	PV Electrolysis	Photonic	Water	PV panels are used to generate electricity
M9	Photo catalysis			Water is split into H_2 by using the electron-hole pair generated by the photo catalyst
M10	Photo-electrochemical method			A hybrid cell simultaneously produces current and voltage upon absorption of light
M11	Dark fermentation	Biochemical	Biomass	Biological systems are used to generate H_2 in the absence of light
M12	High temperature electrolysis	Electrical +Thermal	Water	Electrical and thermal energy are used together to drive water splitting at high temperatures
M13	Hybrid thermochemical cycles			Electrical and thermal energy are used together to drive cyclical chemical reactions
M14	Coal gasification			Conversion of coal into syngas

M15	Fossil fuel reforming			Fossil fuels are converted to H_2 and CO_2
M16	Bio photolysis	Photonic + Biochemical	Biomass+ water	Biological systems (microbes, bacteria, etc.) are used to generate H_2
M17	Photo fermentation			Fermentation process activated by exposure to light
M18	Artificial Photosynthesis			Chemically engineered systems mimic photosynthesis to generate H_2
M19	Photo electrolysis	Electrical + Photonic	Water	Photo electrodes and external electricity are used to drive water electrolysis

Table 2: Hydrogen production methods from primary energy and material sources (Acar & Dincer, 2015)

The following is a summary overview of the current hydrogen production methods:

i. ELECTROLYSIS

Currently the most basic industrial process for almost pure hydrogen production is water electrolysis, and its significance is expected to increase in the future. Water electrolysis is based on the movement of electrons which are supported by an external circuit. Alkaline, polymer membrane, and solid oxide electrolyser are the key electrochemical hydrogen production technologies (Santosa, Eckerta, & Eduardo De Rossia, 2017).

ii. PLASMA ARC-DECOMPOSITION

Plasma is an ionized state of matter which contains electrons in an excited state and atomic species. Plasma has a potential to be used as medium for high voltage electric current release due to the presence of electrically charged particles. Natural gas (mostly methane) dissociates to hydrogen and carbon black (soot) as a result of thermal plasma activity. Carbon black is in solid phase which remains at the bottom while hydrogen is collected in gas phase. The decomposition reaction of methane to hydrogen and carbon is written as (Fulcheri, et al., 2002):

$$CH_4 \rightarrow C_{(s)} + 2H_{2_{(g)}}, \quad \Delta H = 74.6\ MJ/kmol \qquad (7)$$

Reaction (7) is studied by Fulcheri et al (Fulcheri, et al., 2002); their thermal plasma reactor has 3 electrodes connected to a 3 phase voltage. Plasma gas is introduced to 2 of the 3 electrodes and methane is inserted from the top of the reactor. Their results show a 100% pure hydrogen production with zero CO_2 emissions (solid state carbon black remains at the bottom of the reactor). Plasma arc decomposition can be classified as “high temperature pyrolysis”. (Gaudernack & Lynum, 1998) State that plasma cracking has a potential to reduce hydrogen production cost by at least 5%, compared to large scale steam methane reforming with carbon dioxide sequestration.

iii. H_2O THERMOLYSIS

Water thermolysis, also known as single step thermal dissociation of water, reaction can be written as:

$$H_2O \xrightarrow{heat} H_2 + \frac{1}{2}O_2 \qquad (8)$$

In order to accomplish a reasonable degree of dissociation, the reaction requires a heat source which could provide temperatures above 2500 K. For instance, at 3000 K and 1 bar, the degree of dissociation is 64%. One of the challenges of this production method is the separation of H_2 and O_2. Therefore, the mixture needs to be cooled down before being sent to the separation process. The experimental solar thermolysis of water study conducted by Baykara (Baykara, 2004) achieves 90% of the equilibrium at a residence time of 1 ms and temperature of 2500 K. The results also show that if the product gases are rapidly cooled to 1500–2000 K (in few milliseconds); recombination of H_2 and O_2 can be avoided by effective hydrogen separation with the use of palladium membranes.

iv. THERMO-CHEMICAL H_2O SPLITTING

Thermochemical water splitting cycles have a major advantage of not requiring catalysis to drive the individual chemical reactions. Except water, which is the material source of hydrogen production, all chemicals used in the thermochemical cycle can be recycled. Other advantages of thermochemical water splitting cycles can be listed as (Dincer, 2012):

a. No need for O_2–H_2 separation membranes,
b. Reasonable temperature requirement range of 600–1200 K, and
c. Zero or low electrical energy requirement.

Balta et al (Balta, Dincer, & Hepbasli, 2009) summarized the review articles on thermochemical water splitting available in the literature. Being fully developed and demonstrated in Japan and the US, the S–I cycle are considered as technically viable. On the other hand, the commercial viability of these cycles needs to be proven. The first reaction of S–I cycles is thermally driven and it can be written as.

$$H_2SO_{4(aq)} \xrightarrow{heat\ (300-500^\circ C)} H_2O_{(g)} + SO_{3(g)} \qquad (9)$$

The product gases (H_2O and SO_3) are separated and heated up to 800–900 °C. Then SO_3 gas is decomposed thermally according to:

$$SO_{3(g)} \xrightarrow{heat\ (800-900^\circ C)} \frac{1}{2}O_{2(g)} + SO_{2(g)} \qquad (10)$$

After separation from O_2, SO_2 undergoes an exothermic reaction with iodine and water which occurs at low temperatures spontaneously:

$$SO_{2\,(g)} + I_{2\,(g)} + 2H_2O_{\,(l)} \rightarrow 2HI_{\,(g)} + H_2SO_{4\,(aq)} \qquad (11)$$

Lastly, HI thermally decomposes into H_2 at temperatures around 425–450 °C:

$$2HI_{(g)} \xrightarrow{heat\ (425-450^\circ C)} H_{2(g)} + I_{2(g)} \qquad (12)$$

Since there are no side reactions happening during S–I cycle, it is reasonably straightforward to separate and reuse the chemicals used in (9), (10), (11) and (12) Because of the relatively high reaction temperature requirements of S–I cycles, there are not many sustainable thermal energy sources available to drive the individual reactions in the cycle. Nuclear, concentrated solar, and biomass combustion heat can be listed as possible sustainable thermal energy sources to drive the S–I cycle reactions. In the hybrid version of S–I cycles, hydrogen generating reaction is supported electrochemically (Balta, Dincer, & Hepbasli, 2009).

Thermochemical conversion of biomass, gasification, and biofuel reforming

When using biomass to extract hydrogen, the moisture content should be kept below a certain level by drying or supercritical steam gasification. Some of the examples of biomass are wood sawdust and sugar cane. The general biomass conversion is:

$$\alpha C_l H_m O_n + \beta H_2O \xrightarrow{heat} aH_2 + bCO + cCO_2 + dCH_4 + eC + f\mathrm{Tar} \qquad (13)$$

Where $C_l H_m O_n$ is the general chemical symbol of the biomass. Tar is the undesired product of this reaction since it has adverse effect on the process (i.e. slugging and fouling). There are numerous catalysts used to control, minimize, and prevent the formation of tar as a result of reaction 13.

In order to produce hydrogen, solid biomass undergoes the following gasification reaction:

$$C_x H_y + xH_2O \xrightarrow{high\ temperature\ heat} \left(\frac{y}{2} + x\right) H_2 + xCO \qquad (14)$$

In this regard, fixed bed, moveable bed and fluidized bed are treated as the common types of gasifiers used in the gasification process. Based on the amount of provided heat, the process is called either auto thermal or thermal. In auto thermal gasification, the required heat is provided by the partial oxidation in the gasifiers. Hydrogen production from liquid biofuels (i.e. ethanol and methanol) occurs via thermochemical processes (Dincer, 2012).

v. PV ELECTROLYSIS, PHOTO CATALYSIS, AND PHOTO ELECTROCHEMICAL METHOD

PV based electrolysis process includes photovoltaic (PV) panels, DC bus bar, AC grid, accumulator battery set, Electrolyser and hydrogen storage canisters. PV based electrolysis is one of the most expensive hydrogen production methods; with current technology, the cost of hydrogen from PV electrolysis is about 25 times higher than that of fossil fuel alternatives. However, the cost of this process has been continuously decreasing and this factor is estimated to go down to six (Rand & Dell, 2009).

The photo catalysis converts photonic energy (comes from solar irradiation) to chemical energy (hydrogen). The energy carried by the photon is proportional to the frequency of the radiation and given by hv where h is the Planck constant and v is the frequency. When a photon hits the photo catalyst, an electron-hole pair is generated and the obtained electrical charge is utilized to dissociate water. In order for a photo catalyst to split water and generate hydrogen, it should have an appropriate band gap and properly located conduction and valance bands for oxidation/reduction reactions (Dincer, 2012).

Furthermore, rapid generation and separation of electron-hole pairs is essential when picking an appropriate photo catalyst. In the literature, semiconductors (i.e. TiO_2) and metal oxides (i.e. Fe_2O_3) are heavily studied as photo catalysts. Also, chemically modified and engineered complex supramolecular devices are utilized to perform photocatalytic reactions. Acar et al. (Acar, Dincer, & Zamfirescu, 2014) reviewed and assessed various simple and complex photo catalysts based on their H_2 production yield, efficiency, and impact on human health and the environment. The photo-reduction and photo oxidation reactions can be written as.

$$\text{Photo} - \text{reduction}: \; 2H_2O + 2e^- \xrightarrow{h\nu} H_2 + 2OH^- \qquad (15)$$

$$\text{Photo} - \text{oxidation}: \; 2H_2O \xrightarrow{h\nu} O_2 + 4H^+ + 4e^- \qquad (16)$$

Here, photo-electrochemical cells (PEC) convert solar energy to an energy carrier via light stimulated electrochemical processes. In a PEC, solar light is absorbed by one or both of the photo-electrodes and at least one of them is a semiconductor. PECs can produce either chemical or electrical energy. They are also used to treat hazardous aqueous wastes (Quan, Yang, Ruan, & Zhao, 2005). The working principle of the semiconductor in a PEC is similar to a PV cell.

In both cases, photons with higher energy than the band gap generate electron-hole pairs and this electric field is used to oxidize/reduce water. PEC systems combine solar energy absorption and water electrolysis into a single unit. This is a clear advantage of PEC because they do not require a separate power generator such as a PV cell and therefore they are more compact (Dincer, 2012).

There are many kinds of photosensitive semiconductors investigated in the literature. The most promising option so far is agreed to be TiO_2. In addition to TiO_2, several other semiconductors have been studied, such as, ZnO, Fe_2O_3, $BiVO_4$, and WO_3 (Dincer, 2012).

vi. DARK FERMENTATION

Biochemical energy, which is stored in organic matter, can be used by living creatures to extract hydrogen in the absence or presence of light. Dark fermentation is the conversion of biochemical energy stored in organic matter to other forms of energy in the absence of light (this case might happen when there is reduced supply of light) (Dincer, 2012).

The bioreactors used for dark fermentation are simpler and cheaper compared to photo fermentation since the process does not require solar input processing. Hydrogen production by dark fermentation has several other advantages such as the ability to produce hydrogen from organic waste and therefore control and stabilize biological waste which has a potential danger of contamination (Dincer, 2012).

For instance, dark fermentation can be integrated into wastewater treatment systems to produce H_2 from wastewater. Producing hydrogen from organic waste has a potential to reduce hydrogen production costs since organic waste (including wastewater) is cheap and easily available. Hydrogen production from water diluted olive oil by study by Koutrouli et al. (Koutrouli, et al., 2009) Shows a maximum 640 g of H_2 per tonne of olive pulp. A hydrogen production yield of around 77 g H_2 per kg of glucose is reported by Das and Veziroglu (Das & Veziroglu, 2008).

Low production capacity per unit of (production facility) capital investment is one of the major challenges of anaerobic digestion. Some of the advantages and disadvantages of dark fermentation compared to bio photolysis and photo fermentation as well as the future prospects of these methods are listed in Table 3 below:

Process	**Advantages**	**Disadvantages**	**Future prospects**
Bio photolysis	Abundant supply(water)	Separation of H_2 and O_2	Near term incremental improvement possible
	Carbon independent pathway	Low conversion efficiencies	Immobilisation might bring some improvement
	Only products are H_2 and O_2	Large surface area requirement	Material science breakthrough
	Readily available waste streams as supply	Low volumetric production rate	Metabolic engineering is required
Photo fermentation	Nearly complete substrate conversion	Low conversion efficiencies	Near term incremental improvement possible
	Can use variety of streams	Large surface area requirement	Material science breakthrough
		Large amounts of by products	Metabolic engineering is required
Dark fermentation	Simple reactor technology	Reactor to reactor variation	Two stage systems can extract additional energy,
	High production rates	Low COD removal	Decrease COD

Table 3: Comparison: dark and bio-photolysis Photo fermentation (Hallenbeck, Abo-Hashesh, & Ghosh, 2012)

vii. HIGH TEMPERATURE ELECTROLYSIS

High temperature electrolysis is a method of electrolysis where steam is dissociated to H_2 and O_2 at temperatures between 700 and 1000 °C. This method is generally considered as more efficient than conventional room temperature electrolysis (efficiency increases with increasing temperature). In high temperature electrolysis, water is converted to steam by using thermal energy (Dincer, 2012).

The system components are either heated directly by the steam supply or indirectly by heat transfer. Thus the electrical energy need of this type of electrolysis is lower than that of conventional electrolysis methods. Another advantage of this method is the possibility of achieving zero greenhouse gas emissions when a clean heat source (i.e. solar, geothermal, and/or nuclear) is used as external heat source (Dincer, 2012).

However, due to high operating temperatures, the system components have to meet specific requirements for an efficient hydrogen generation. Current challenges of high temperature electrolysis can be listed as (Dincer, 2012):

a. Chemically stable electrolyte development with high ionic and low electronic conductivity,
b. Porous, chemically stable electrode research in highly reducing/oxidizing environments with good electronic conductivity and coefficient of thermal expansion similar to the electrolyte.
c. Engineering chemically stable materials at high temperatures and highly reducing/oxidizing environments.

viii. HYBRID THERMOCHEMICAL CYCLES

Hybrid thermochemical cycles operate at lower temperatures compared to thermally driven water splitting cycles mentioned in thermochemical Water Splitting. External energy needs of the individual electrochemical reactions are met by thermal and electrical energies. Since hybrid cycles operate at lower temperatures, other sustainable thermal sources apart from solar, high temperature nuclear and biomass combustion (such as recovered waste heat from nuclear and geothermal facilities) can be used to drive the involved processes (Acar & Dincer, 2014).

Cu–Cl cycle is proposed as an outstanding hybrid cycle as investigated in the literature. The operating temperature of this cycle does not exceed 550 °C. Among different types of Cu–Cl cycles, “five-step” version is the most studied one. This version is composed of three thermally driven chemical reactions, one electrochemical reaction, and one physical drying step. In Cu–Cl cycles, the thermal energy source is used partially to drive the cycle directly and partially to generate the required electricity. The major advantage of Cu–Cl cycles is hydrogen generation from low grade temperature sources, especially those which can be considered as sustainable thermal energy. Nuclear heat, industrial heat, waste heat recovered from power plants, concentrated solar heat, heat resulting from municipal waste incineration, and geothermal heat can be listed as sustainable thermal energy sources (Acar & Dincer, 2014).

ix. COAL GASIFICATION

With current state of technology and worldwide coal reserves, coal is an economical and technically practical option to produce hydrogen in large scale plants. Compared to the existing methods (i.e. electrolysis), gasification is more suitable for converting coal to hydrogen. In gasification, coal is partially oxidized with steam and O_2 in a high-temperature and high-pressure reactor and the products are mainly H_2, CO, mixed with steam and CO_2 (syngas). This syngas goes through a shift reaction in order to increase the hydrogen yield (Acar & Dincer, 2014).

The gas product can be processed and cleaned in cases where there is a need to recover elemental sulphur or sulphuric acid. Some of the syngas can further be processed and used in gas turbines to generate electricity. Despite some advantages of coal gasification, due to high carbon content of coal, this method causes higher CO_2 emissions compared to other available hydrogen production technologies. Carbon capture and storage technologies are currently developed in order to address this issue (Acar & Dincer, 2015).

At present, hydrogen production cost of coal gasification is slightly higher than that of natural gas steam reforming. However, coal gasification techniques are less well-defined than those used in the steam reforming of natural gas. In terms of economics, making hydrogen from coal differs from other fossil fuels: the unit raw material costs are lower while the unit capital costs are higher for the coal gasification plants (Acar & Dincer, 2014).

x. FOSSIL FUEL REFORMING

Steam reforming, partial oxidation, and auto-thermal reforming are three main fossil fuel reforming technologies to produce hydrogen. The advantages and challenges of each of these processes are listed in Table 4 below.

Technology	**Advantages**	**Disadvantages**
Steam Reforming	Most developed industrial process	Highest air emissions
	No oxygen requirement	
	Lowest operating temperature	
	Best H_2/CO ratio	
Auto thermal Reforming	Lower process temperature than partial oxidation	Limited commercial experience
	Low methane slip	Air/oxygen requirement
Partial Oxidation	Reduced desulfurization requirement	Low H_2/CO ratio
	No catalyst requirement	High operating temperatures
	Low methane slip	Complex handling process

Table 4: Fossil fuel reforming technologies comparison (Parthasarathy & Narayanan, 2014).

In addition to H_2, CO and CO_2 are emitted in the end of a reforming process. Steam reforming generally requires an external heat source but it does not demand oxygen to drive the process. It has a lower operating temperature and higher H_2/CO ratio than partial oxidation and auto thermal reforming.

In partial oxidation, hydrocarbons are partially oxidized with oxygen to produce hydrogen. The source of heat to drive this process is derived from the partial oxidation (combustion) reaction. There is no catalyst requirement in partial oxidation and it is more sulphur tolerant compared to steam and auto thermal reforming. The pressure requirement of auto thermal reforming is lower than partial oxidation (Parthasarathy & Narayanan, 2014).

Auto thermal reforming and partial oxidation do not need an external heat source. However, both of these processes require pure oxygen feed which increases complexity and cost with the addition of oxygen separation units. Compared to other fossil fuel reforming technologies, steam reforming (particularly steam methane reforming) is the least expensive and most common method to produce hydrogen (Holladay, Hu, King, & Wang, 2009).

xi. BIO PHOTOLYSIS AND PHOTO FERMENTATION

Bio photolysis and photo fermentation are photonic-driven biochemical hydrogen production processes from water. Kotay and Das (Kotay & Das, 2008) categorize hydrogen production via bio photolysis into direct, indirect, and photo fermentation.

In bio photolysis, some light-sensitive microorganisms are used as biological converters in a specially designed photo-bioreactor. Among possible microorganisms, the most suitable ones are microalgae since they can be cultured and have a potential to generate hydrogen in closed systems which permits hydrogen capture. Cultured micro-algal strains show high hydrogen yields (Kotay & Das, 2008).

The major advantage of bio photolysis is the ability to produce hydrogen from water in an aqueous environment at ambient temperature and pressure. However, it was only demonstrated at laboratory scale and not yet fully developed for commercial use.

The general hydrogen generation reactions with the help of photo-activated enzymes are (Dincer, Green methods for Hydrogen productions, 2012):

$$6H_2O + 6CO_2 \xrightarrow{h\nu} C_6H_{12}O_6 + 6O_2 \qquad (17)$$

$$C_6H_{12}O_6 + 6H_2O \xrightarrow{h\nu} 6CO_2 + 12H_2 \qquad (18)$$

xii. ARTIFICIAL PHOTOSYNTHESIS

Artificial photosynthesis is a bio-mimetic process mimicking the natural photosynthesis process to accomplish the following (Dincer, Green methods for Hydrogen productions, 2012):

- PV-based electricity generation: to support the grid system.
- Dry agriculture: with this method, carbohydrates (food), liquid fuels, chemical feed stocks, and polymers for fibre manufacture can be produced with near or absolute chemical minimum water usage. This amount is thousands of times

lower than the conventional agriculture water usage. The system has an enzyme bed reactor system which fixes CO_2 from the air (or other convenient sources) and it is powered by hydrogen and bioelectric transducers.

- Hydrogen production: electrolytic decomposition of water into H_2 and O_2 can be achieved by mimicking photosynthesis.

Although the technology is not mature enough to be applied to large scale manufacturing, artificial photosynthesis has a significant potential to lower global water usage and support clean energy systems by generating electricity and hydrogen from photonic energy (Kotay & Das, 2008).

xiii. PHOTO ELECTROLYSIS

The process where heterogeneous photo catalysts is applied on one or both of the electrodes is called photo electrolysis. In addition to solar irradiation exposure, the electrolysis cell should be supported by electrical energy to conduct photo electrolysis. Therefore, in photo electrolysis, both photonic and electrical energies are converted to chemical energy (hydrogen) (Acar & Dincer, 2014).

The photo electrolytic hydrogen production mechanism includes the following steps:

a. Generation of an electron-hole pair with the help of a photon that has sufficiently high energy (higher than the band gap of the p–n junction),
b. Flow of electrons from the anode to the cathode generating electricity current,
c. Decomposition of water into hydrogen ions and gaseous oxygen,
d. Reduction of hydrogen ions at the cathode to form hydrogen in gas form,
e. Separation of the product gases, processing, and storage.

The performance of a photo electrolytic system depends on the type of photon absorbing material, their crystal structure, surface properties, corrosion resistance, and reactivity. There usually is a trade–off between photo electrode stability and photon energy–to hydrogen conversion efficiency: the high efficiency photo electrodes generally have poor stability in electrolytes while the chemically stable photo electrodes show poor water splitting efficiencies (Acar & Dincer, 2015)

In the end, in order to be able to move to a sustainable and clean energy supply, hydrogen should be produced from clean energy sources instead of fossil fuels.

Production quantity, efficiency, cost, system reliability and environmental impact are some of the major concerns of hydrogen energy research.

It is now widely accepted that carbon-free society is not possible without hydrogen economy. This study reviews and assesses current efforts to produce hydrogen with minimum cost, environmental and social impact as well as maximum efficiency. These efforts are to help address adverse effects of excessive fossil fuel utilization and any energy crisis that might happen in the near future with green solutions (Acar & Dincer, 2015).

The key benefits and critical challenges of the selected hydrogen production method are summarised in Table 5 below.

Fossil Fuel Reforming	**Biofuel Reforming**	**Coal and biomass gasification**	**Thermochemical method**	**Water electrolysis**	**Photo electrochemical method**	**Biological method**
Critical Challenges						
High capital costs	High capital costs	High reactor costs	Cost effective reactor	Low system efficiency	Effective photocatalytic material	Efficient microorganisms for sustainable production
Design	High operation and maintenance costs	System efficiency	Long term technology	High capital costs	Low system efficiency	Optimal microorganism functionality
High operation and maintenance costs	Design feedstock quality	Feedstock impurities Carbon capture and storage	Effective and durable material	System integration Design issues	Cost effective reactor Long-term technology	Reactor material selection Long term technology
Major R&D Needs						
Efficiency and cost	Hydrogen yield and efficiency	Low cost and efficient purification	Robust, low cost materials	Durable and cheap materials	Durable and efficient photo catalyst	Microorganism functionality

Low cost and efficient purification	Low temperature production	Co-fed gasifiers	Ease of manufacture and application	Corrosive-resistant membranes	Low cost materials	New organisms
Feedstock pre-treatment	Low cost and efficient production	Carbon capture and storage	System optimization	Durable, active and cheap catalyst	Active, stable and cheap supporting materials	Inexpensive methods
Optimization	Optimization	Hydrogen quality	High volume, low cost, flexible system design	Large scale applications	High volume production	Low cost and durable material
Automated process control	Regional best feedstock	Cost of feedstock preparation	Efficient heat transfer	Storage and production rate	System control	System optimization
Reliability	Feedstock pre-treatment	Tolerance of impurities	Reliability	Reliability	Power loses	High capacity and low costs system
Key Benefits						
Most viable approach	Viability	Low cost syngas production	Clean and sustainable	No pollution with renewable energy sources	Low operation temperature	Clean and sustainable
Lowest current cost	Existing infrastructure	Abundant and cheap feedstock	Recycled chemicals	Existing infrastructure	Clean and sustainable	Tolerant of diverse water conditions
Existing infrastructure				Integration with fuel cells		Self-sustaining

Table 5: Benefits and challenges for H_2 production mechanisms (Acar & Dincer, 2014)

2.3 FINANCIAL COMPARISON OF HYDROGEN PRODUCTION METHODS

When it comes to calculating the cost of hydrogen production, there are several uncertainties since the cost is strongly affected by the production technology's advancement level, availability of existing infrastructure, and the feedstock prices (Acar & Dincer, 2014).

The literature survey results of average hydrogen production costs (per kg of hydrogen) are presented in Figure 3 below for the nineteen hydrogen production methods identified. Among the selected methods, hydrogen production cost of water electrolysis, thermochemical water splitting, biomass gasification, photo catalysis, coal gasification, and fossil fuel reforming are taken from Parthasarathy and Narayanan (Parthasarathy & Narayanan, 2014). Plasma arc decomposition, thermochemical biomass conversion and reforming, dark fermentation, bio photolysis, photo fermentation, artificial photosynthesis, and photo electrolysis cost data is compiled from Uddina et al (Uddina, Dauda, & Abbas, 2013).

Thermolysis, PV electrolysis, high temperature electrolysis, and hybrid thermochemical cycles' hydrogen production cost data are obtained from Ngoha and Njomo (Ngoha & Njomo, 2012). And the hydrogen production cost of photo electrochemical method is attained from Trainham et al (Trainham, Newman, Hoertz, & Akunuri, 2012).

According to Figure 6 below, the most financially advantageous methods for hydrogen production are steam methane reforming, coal and biomass gasification, and plasma arc decomposition. Thermochemical cycles and biomass conversion, as well as hybrid thermochemical cycles also seem to be competitive to fossil fuel and biomass prices. It should be noted that in this study the average of production costs are taken from the literature (Dincer, 2012).

Photo electrochemical systems give the highest production cost per kg of hydrogen. However, this method is in early R&D phase and one of the major advantages of this method is its local applications. Therefore, the production costs related to PEC operation are expected to decrease in the future as PEC systems technology gets more advanced (Trainham, Newman, Hoertz, & Akunuri, 2012).

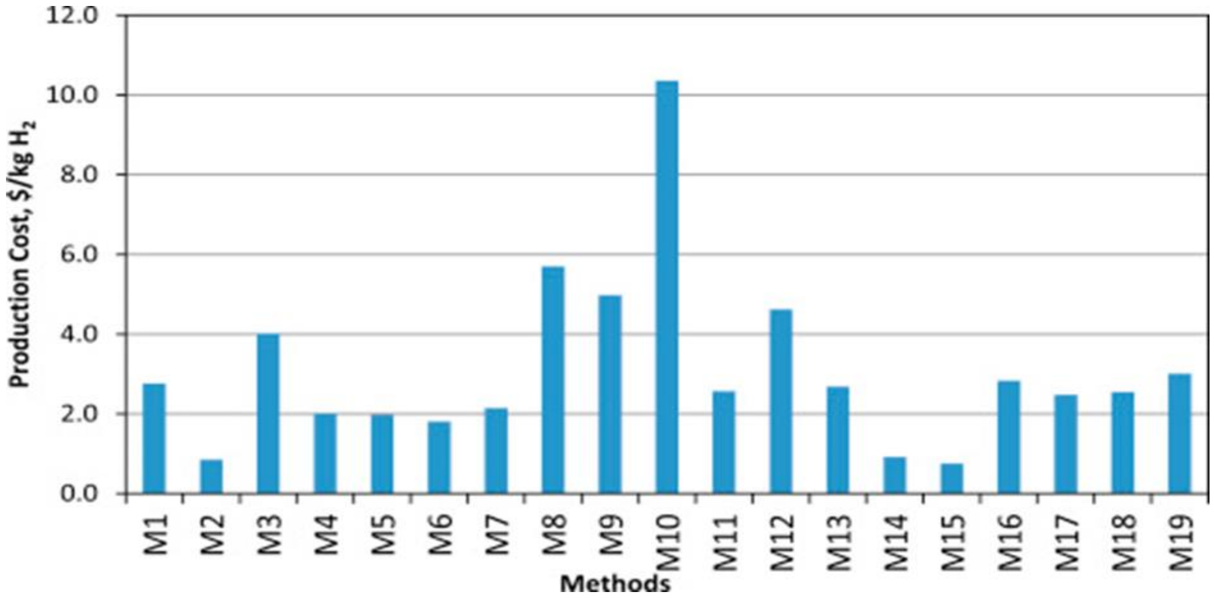


Figure 6: Production cost of selected hydrogen production methods (per kg of hydrogen) (Acar & Dincer, 2014).

a. ENERGY AND EXERGY EFFICIENCIES COMPARISON OF HYDROGEN PRODUCTION METHODS

Efficiency is defined as useful output by consumed input. Energy efficiency of a hydrogen production method can be calculated as.

$$\eta = \frac{\dot{m}LHW_{H_2}}{\dot{E}_{in}} \qquad (19)$$

Where $\dot{m}$ the mass flow rate of produced hydrogen, LHV is the lower heating value of hydrogen (121 MJ/kg) and $\dot{E}_{in}$ is the rate of energy input to the process. The following equation is used for exergy efficiency:

$$\psi = \frac{\dot{m}ex^{ch}_{H_2}}{\dot{Ex}_{in}} \qquad (20)$$

Here, $ex^{ch}_{H_2}$ is the chemical exergy of hydrogen and $\dot{Ex}_{in}$ is the rate of exergy input into the process. The efficiency data used in this study are taken from (Holladay, Hu, King, & Wang, 2009), (Ismail & Bahnemannc, 2014), (Singh & Wahid, 2015), (Karunadasa, Chang, & Long, 2010), (Ibrahim, Kamarudina, & Minggua, 2014), and (Dincer & Zamfirescu, 2012).

Figure 7 presents the energy and exergy efficiency data of selected hydrogen production methods from which it can be seen that fossil fuel reforming, plasma arc decomposition, and coal and biomass gasification are advantageous over other methods. On the other hand, photonic energy based hydrogen production methods show the poorest performance among the selected production methods (Acar & Dincer, 2014).

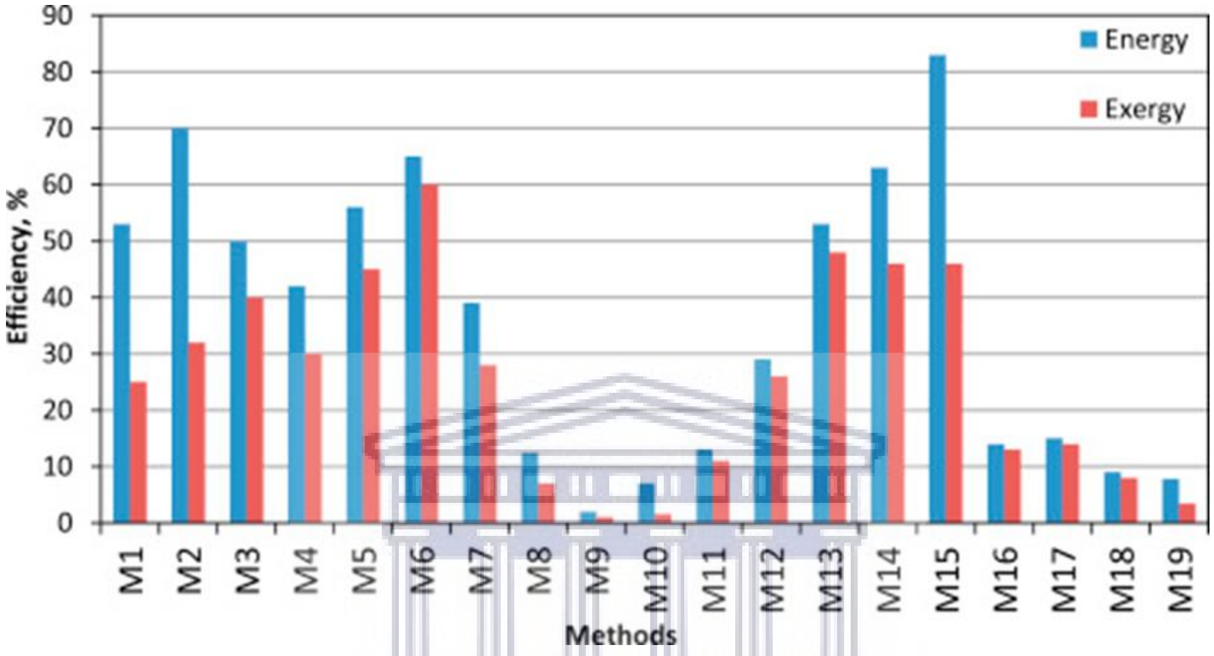


Figure 7: Energy and exergy efficiencies of selected hydrogen production methods (Acar & Dincer, 2014).

b. OVERALL COMPARISON OF HYDROGEN PRODUCTION METHODS

In this section, the environmental, social, financial, and technical assessment results are normalized in order to compare each method effectively. GWP, AP, SCC and production costs are normalized based on the following equation (Acar & Dincer, 2014):

$$Rank\ (Method\ i) = \frac{Maximum - Method\ i}{Maximum} \times 100 \qquad (21)$$

The ranking is between 0 and 10, where 0 means poor performance and 10 indicates the ideal case (zero-cost and zero-emissions). Lower costs and emissions are given higher rankings. “0” is assigned to the highest cost and emissions in selected categories. For example, in terms of GWP, coal gasification method gives the highest emissions; therefore, the GWP ranking of coal gasification is assigned to be “0”. Efficiencies are normalized based on the following equation:

$$Efficiency\ Rank\ (Method\ i) = Efficiency\ (Method\ i) \times 10 \qquad (22)$$

The ranking range is again between 0 and 10, 0 means poor performance and 10 indicate the ideal case (100% efficiency). Higher rankings mean higher efficiencies. The normalized emissions, cost, and efficiency rankings are presented in table 7.

The hypothetical ideal case refers to zero-cost and emissions, which also means zero SCC. The energy and exergy efficiency of this ideal case is 100%. In terms of energy and exergy efficiency, closest performance to the ideal case is reached by fossil fuel reforming and biomass gasification. However, biomass gasification gives considerably high AP (low AP ranking) compared to other selected methods. SCC rankings of biomass gasification are also low (Acar & Dincer, 2014).

2.4 MOST EFFICIENT HYDROGEN PRODUCTION METHOD: ELECTROLYSIS

From the literature the most energy efficient hydrogen production method has emerged to be electrolysis. The most common technology of electrolysis include:

- Alkaline electrolyser
- Proton exchange membrane (PEM) electrolyser
- Solid oxide electrolysis cells (SOEC)

Table 6 summarizes the typical specifications of alkaline, polymer membrane (PEM), and solid oxide electrolysers (SOE). Of the parameters listed in Table 6, efficiency and the current density are the most important parameters. Efficiency of an electrolysis cell is calculated based on the ideal and actual energies needed to drive the reaction.

Specification	**Alkaline**	**PEM**	**SOE**
Technology maturity	state of the art	Demonstration	R&D
Cell temperature, °C	60 - 80	50 - 80	900 - 1000
Cell pressure, bar	<30	<30	<30
Current density, A/cm^2	0,2 - 0,4	0,6 - 2,0	0,3 - 1,0
Cell voltage, V	1,8 - 2,4	1,8 - 2,2	0,95 - 1,3
Power Density, W/cm^2	Up to 1,0	Up to 4,4	-
Voltage efficiency, %	62 - 82	67 - 82	81 - 86
Specific system energy consumption, kWh/Nm^3	4,5 - 7,0	4,5 - 7,5	2,5 - 3,5
Hydrogen production, Nm^3/hr	<760	<30	-

Table 6: Standard specifications for alkaline, PEM and SOE Electrolysers (Santosa, Eckerta, & Eduardo De Rossia, 2017)

Catalysts are used in order to increase current density and rate of electrolysis reactions. Platinum is one of the most commonly used heterogeneous catalysts – applied to the surface of the electrodes. Homogeneous catalysts can also be used during electrolysis. Due to their high turnover rates, homogeneous catalysts are less expensive than the heterogeneous ones (Karunadasa, Chang, & Long, 2010)

a. ELECTROLYSIS

Electrolysis is the production of a chemical reaction by means of an electric current (Jones & Atkins, 2002) Electrolysis is a method used for quantitative separations. The electrolytic method can be applied to the quantitative removal and determination of one or more different metallic ions from solution or maybe used, with carefully controlled conditions, to effect a separation of ions of one metal from those of several metals (Frank., 1967).

They are fundamental laws related to electrolysis:

The Coulomb is the quantity of electricity that will cause the deposition or removal of 0.001118g of silver at an electrode. An Ampere, the unit of current is 1 coulomb per second. The Ohm is the unit of resistance. The Volt or unit of electromotive force (emf) causes a current of 1 Ampere to flow through a resistance of 1 Ohm. The Volt-Coulomb or Joule is the unit of electrical energy and the Volt-Ampere or Watt is the unit of electrical power (Frank., 1967).

Ohm's law gives the relation between current, resistance and electromotive force.

$$\text{Current}, (I) = \frac{\text{Voltage}, (V)}{\text{Resistance}, (R)} \text{ in Amperes}, (A) \qquad (23)$$

Where I is in Amperes, electromotive force in Volts V, and resistance R in Ohms.

The Faraday, 96 493 coulombs, is the amount of electricity equivalent to Avogadro's number of electrons transferred in either an oxidation or a reduction process. Because this quantity of electrons must be removed to oxidise a gram equivalent of any substance and the same number of electrons must be taken to reduce a gram equivalent, a Faraday is that quantity of electricity used in transforming a gram equivalent of any substance at an electrode (Frank., 1967).

The two laws of electrolysis, usually referred to as a Faraday's law, can be stated as follows (Frank., 1967):

2.1 The quantity of a given substance that is liberated at an electrode is proportional to the quantity of electricity that is passed through the system.

2.2 The amounts of different substances that are deposited by the same quantity of electricity are proportional to the chemical equivalent weights of these substances.

These laws are only applicable if the current efficiency does not vary and is 100% for the substance being measured.

b. ELECTRODE POTENTIALS

If any chemical element that is a conductor of electricity is placed in contact with a solution containing its ions, a potential difference develops at the interface between the electrode and solution. The magnitude and sign or direction of this potential depend upon the relative tendency of the atoms of the element to give off or accept electrons to form ions of the element. Depending on the nature of the element and the concentration of its ions in solution, the potential of the electrode may be positive, zero or negative relative to the solution (Frank., 1967).There are two major factors that determine the electrode potential relative to another electrode. First is the activity of the electrolytic solution pressure of the element which is the tendency of the element to furnish ions. Ata a given temperature and pressure this is a characteristic constant for a stable form of an element but varies if the electrode is strained mechanically or if a metastable crystalline form of the metal is present (Frank., 1967).

Second is the activity of the dissolved ions of the element, which in turn varies with the concentration at constant temperature. A table of standard potentials at a 25 ºC that apply to the condition unit activity (approximately 1 molar) of the ions and one atmosphere pressure for gases given in Table 7.

Reduction Half-Reaction	**Standard Reduction Potential (V)**
$F_2(g)+2e^- \rightarrow 2F^-(aq)$	+2.87
$S_2O_8^{2-}(aq)+2e^- \rightarrow 2SO_4^{2-}(aq)$	+2.01
$O_2(g)+4H^+(aq)+4e^- \rightarrow 2H_2O(l)$	+1.23
$Br_2(l)+2e^- \rightarrow 2Br^-(aq)$	+1.09
$Fe^{3+}(aq)+e^- \rightarrow Fe^{2+}(aq)$	+0.77
$I_2(l)+2e^- \rightarrow 2I^+(aq)$	+0.54
$Cu^{2+}(aq)+2e^- \rightarrow Cu(s)$	+0.34
$Sn^{4+}(aq)+2e^- \rightarrow Sn^{2+}(aq)$	+0.15
$S(s)+2H^+(aq)+2e^- \rightarrow H_2S(g)$	+0.14
$2H^+(aq)+2e^- \rightarrow H_2(g)$	**0.00**
$Sn^{2+}(aq)+2e^- \rightarrow Sn(g)$	-0.14
$V^{3+}(aq)+e^- \rightarrow V^{2+}(aq)$	-0.26
$Fe^{2+}(aq)+2e^- \rightarrow Fe(s)$	-0.44
$Cr^{3+}(aq)+3e^- \rightarrow Cr(s)$	-0.74
$Zn^{2+}(aq)+2e^- \rightarrow Zn(s)$	-0.76
$Mn^{2+}(aq)+2e^- \rightarrow Mn(s)$	-1.18
$Na^+(aq)+e^- \rightarrow Na(s)$	-2.71
$Li^+(aq)+e^- \rightarrow Li(s)$	-3.04

Table 7: Standard Reduction Potentials at 25ºC (Frank., 1967)

The potentials shown above are standard reduction potentials and all reactions are written as reductions. For oxidations, which is the same as considering the reactions in table 1 written in the opposite direction, the magnitude of the potential will remain the same but the sign will be opposite (Frank., 1967).

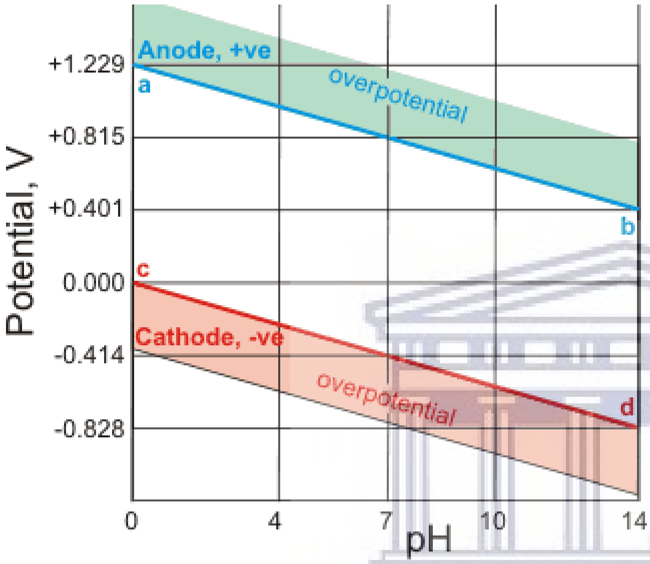
Creating an electric potential through water causes positive ions, including the inherent hydrogen ions H_3O^+, to move towards the negative electrode (cathode) and negative ions, including the inherent hydroxide ions OH^-, to move towards the positive electrode (anode). At sufficient potential difference, this may cause electrolysis with oxygen gas being produced at the anode and hydrogen gas produced at the cathode (Marini, et al., 2012). The electrolysis of water usually involves dilute, or moderately concentrated, salt solutions in order to reduce the power loss driving the current through the solution, but the presence of salt is not a requirement for electrolysis.

Thus (Chaplin, 2017),

Anode	+ve	$6H_2O_{(l)} \longrightarrow O_{2(g)} + 4H_3O^+_{(aq)} + 4e^-$(to anode)	$E°$ = +1.229 V, pH 0	$E°'$ = +0.815 V
Cathode	-ve	$4e^-$(from cathode) + $4H_2O_{(l)} \longrightarrow 2H_{2(g)} + 4OH^-_{(aq)}$	$E°$ = -0.828 V, pH 14	$E°'$ = -0.414 V

Where (l), (g) and (aq) show the states of the material as being liquid, gas or aqueous solution, and with the electrical circuit passing the electrons back from the anode to the cathode. The reactions are heterogeneous, taking place at the boundary between the electrode and the electrolyte with the aqueous boundary layer subject to concentration and electrical potential gradients with the presence of the generated gaseous Nano bubbles and microbubbles (Chaplin, 2017).

Generally the water next to the electrodes (Pedroza, Poissier, & Fernández-Serra, 2015)will change pH due to the ions produced or consumed. If the electrode compartments are separated by a suitable porous membrane then the concentration of H_3O^+ in the anolyte and OH^- in the catholyte (and hence the increase in the respective conductivities) are both expected to increase more than if there is free mixing between the electrodes, when most of these ions will neutralize each other. Small but expected differences in the solutions' pHs next to the anode (anolyte) and cathode (catholyte) cause only a slight change to the overall potential difference required (1.229 V). Increasing the acid content next to the anode due to the H_3O^+ produced will increase its electrode potential (for example: pH 4 *E* = +0.992 V) and increasing the alkaline content next to the cathode due to the OH^- produced will make its electrode potential more negative (for example: pH 10 *E* = -0.592 V). If the anode reaction is forced to run at pH 14 and the cathode reaction is run at pH 0 then the electrode potentials are +0.401 V and 0 V respectively as shown on Potential vs pH table below (Chaplin, 2017).



Potential vs pH table (Chaplin, 2017)

a)	Anode	pH 0	$2\ H_2O \longrightarrow O_2 + 4H^+ + 4e^-$	E°= +1.229 V
b)	Anode	pH 14	$4\ OH^- \longrightarrow O_2 + H_2O + 4e^-$	E°= +0.401 V
c)	Cathode	pH 0	$4\ H^+ + 4e^- \longrightarrow 2H_2$	E°= 0.0 V
d)	Cathode	pH 14	$4\ H_2O + 4e^- \longrightarrow 2H_2 + 4OH^-$	E°= -0.828 V

This does not mean that because the electrolysis can be achieved with a (minimum) voltage of +0.403 V (c and b, above right) (Chen, Dong, Wang, Wang, & Xia, 2016), it breaks the thermodynamic requirement of 1.229 V as there is a further input of energy required in keeping the electrode compartments at the required pHs and solute concentration.

The current flowing indicates the rate of electrolysis. The amount of product formed can be calculated directly from the duration and current flowing, as 96,485 Coulombs (i.e. one Faraday) delivers one mole of electrons; with one Faraday ideally producing 0.5 moles of H_2 plus 0.25 moles of O_2. Thus, one Ampere flowing for one second (one Coulomb) produces

5.18 µmol H_2 (10.455 µg, 0.1177 mL at STP) and 2.59 µmol O_2 (82.888 µg, 0.0588 mL at STD; 4.9 kW h/m^3 H_2 at 60% efficiency), if there are no side reactions at the electrodes (Chaplin, 2017); that is:

- Number of moles = Coulombs/ (unsigned numeric charge on the ion ^{x} Faraday)
- Number of moles = (Current in Amperes ^{x} time in seconds)/ (unsigned numeric charge on the ion ^{x} Faraday)

The gases produced at the electrodes may dissolve, with their equilibrium solubility proportional to their partial pressure as gases in the atmosphere above the electrolytic surface. Oxygen gas is poorly soluble (~44 mg kg^{-1}, ~1.4 mM at 0.1 MPa and 20 °C, but only ~0.29 mM against its normal atmospheric partial pressure). Hydrogen gas is less soluble (~1.6 mg kg^{-1}, ~0.80 mM at 0.1 MPa and 20 °C but only ~0.44 nM against its very low normal atmospheric partial pressure). It may take considerable time for the solubility to drop from their initially-super-saturated state to their equilibrium values after the electrolysis has ended (Chen, Dong, Wang, Wang, & Xia, 2016).

Although theoretically as described above, the current passing should determine the amounts of hydrogen and oxygen formed, several factors ensure that somewhat lower amounts of gas are actually found. Some electrons (and product) are used up in side reactions, some of the products are catalytically reconverted to water at the electrodes particularly if there is no membrane dividing the electrolysis compartments, some hydrogen may absorb into the cathode (particularly if palladium is used) and some oxygen oxidizes the anode. Finally some gas remains held up in the Nano-bubbles for a considerable time and some gas may escape measurement (Chaplin, 2017).

The above description hides much important science and grossly over-simplifies the system. The actual potential required at any position within the electrolytic cell is determined by the localized concentration of the reactants and products including the local pH of the solution, instantaneous gas partial pressure and effective electrode surface area loss due to attached gas bubbles. In addition, a greater potential difference (called over potential) is required at both electrodes to overcome activation energy barriers and deliver a significant reaction rate (Chaplin, 2017).

Typically at good electrodes, such as those made of platinum, that may total an addition of about half a volt to the potential difference between the electrodes. In addition a further potential difference is required to drive the current through the electrical resistance of electrolytic cell and circuit; for a (typical) one Ohm cell circuit resistance, each Ampere current flow would require a further one Volt and waste one Watt of power. This power (and consequent energy) loss (~20 %,) (Carmo, Fritz, & Mergel, A comprehensive review on PEM water electrolysis, 2013)causes the electrolyte to warm up during electrolysis.

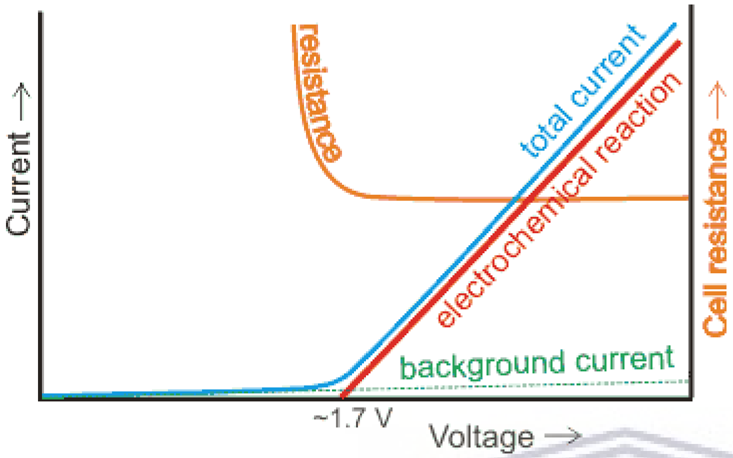


Table 8: Current and Voltage (Chen, Dong, Wang, Wang, & Xia, 2016)

To clarify:

- The minimum necessary cell voltage to start water electrolysis is the potential 1.229V.
- The potential necessary to start water electrolysis without withdrawing heat from the surroundings is -ΔH°'/nF = 1.481 V.

This results in at least a 21% unavoidable loss of efficiency. Normally further heat is generated, and efficiency lost, from the over potentials applied (Chaplin, 2017).

The efficiency of electrolysis (Mazloomi, S.K, & Sulaiman, 2012)increases with the temperature as the hydrogen bonding reduces. If the pressure over the electrolysis is increased, then more current passes for the same applied voltage. However the output of gas per Coulomb and the heating effect are both decreased.

This is due to the increased solubility of the gases and smaller bubbles both reducing the cell resistance and increasing recombination reactions. Although reducing the distance between electrodes reduces the resistance of the electrolysis medium, the process may suffer if the closeness allows a build-up of gas between these electrodes (Mazloomi, S.K, & Sulaiman, 2012).

Low to higher pulsed potential increases the reaction (current) and accelerates both the movement of bubbles from the electrode surface and the mass transfer rate in the electrolyte, which lowers the electrochemical polarization in the diffusion layer and further increases hydrogen production efficiency (Hourng, Lin, & L.-W., 2014). The rate of change of the current density (and hence efficiency) can be increased using a magnetic field (Hourng, Lin, & L.-W., 2014).

Pure water conducts an electric current very poorly and, for this reason, is difficult (slow) to electrolyse. However, usually some salts will be added or present in tap and ground waters which will be sufficient to allow electrolysis to proceed at a significant rate.

However such salts, and particularly chloride ions, may then undergo redox reactions at an electrode. These side reactions both reduce the efficiency of the electrolysis reactions (above) and produce new solutes. Other electrolytic reactions may occur at the electrodes so producing further solutes and gases (Chaplin, 2017).

In addition, these solutes may react together to produce other materials. Together the side reactions are complex and this complexity increases somewhat when the voltage applied to the cell is greater than that required by the above reactions and processes. The likely reactions within the electrode compartments are described below. Some of these may only occur to a very small extent and other reactions may also be occurring that are not included. Standard electrode potentials are shown below (Chaplin, 2017):

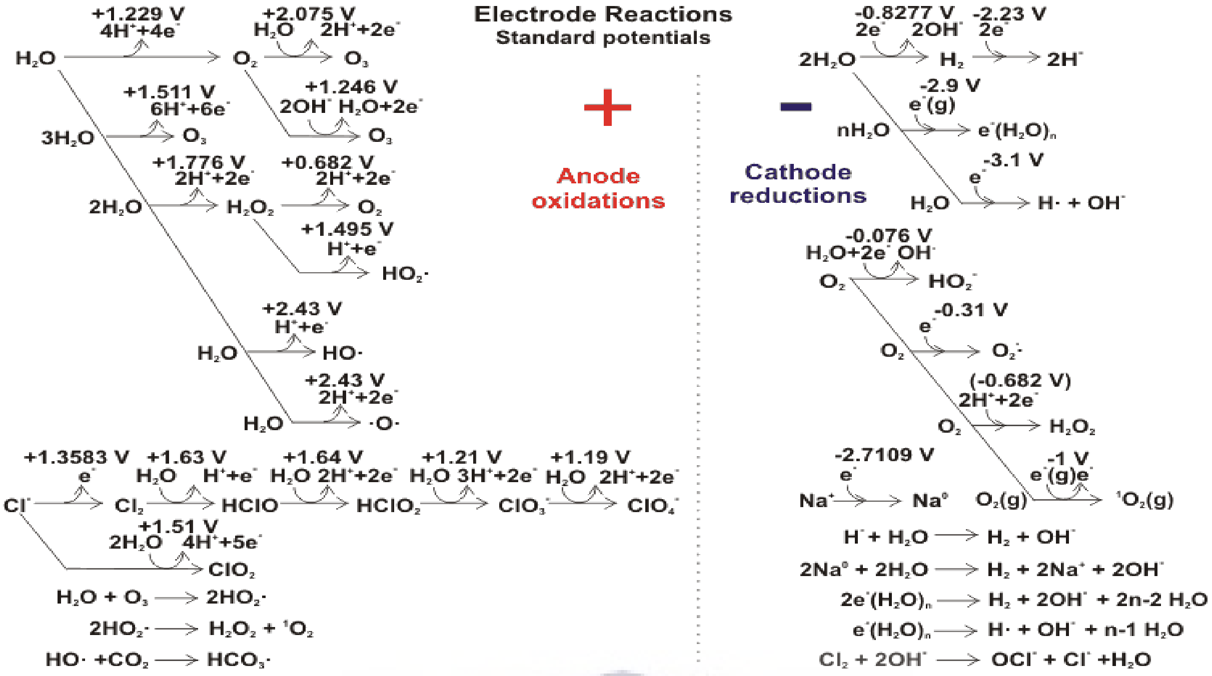


Figure 8: Electrode Standard Potentials (Chaplin, 2017)

d. ELECTROLYSIS COMPARTMENT.

Cathode and anode reactions in the electrolytic cell with some of their constituent molecules, ions and radicals are given below. Other materials may be present and some of the materials given may be at very low concentrations and/or have short half-lives.

The amount of O_3 produced (relative to molecular oxygen) depends on the over potential, pH, radicals present and anode material. O_2 evolution is greater than that for O_3 due to the lower potential required. At low over potentials, very little O_3 may be produced but at high current densities and over potentials, up to a sixth of the oxidized molecules may be O_3 in total. As O_3 is more much more soluble than O_2, there may twice the dissolved O_3 than O_2 but the bubble gas will contain about 20 times the O_2 than O_3 (Naya & Okada, 2012).

Tin oxide anodes have proved useful for the production of O_3, particularly if doped with Sb and Ni, as they bind both oxygen molecules and hydroxyl radicals to facilitate the O_3 production (Chen, Wang, & Q.-Y., 2013). Decomposition of ozone gives rise to several strong oxidants including hydroxyl radicals (·OH); an extremely strong oxidizer capable of killing viruses, amoebae, algae and dangerous bacteria, such as MRSA and Legionella.

Although charged ions are attracted into the compartments by virtue of the applied potential, oppositely charged ions are created in both compartments due to the electrolytic reactions. Thus for example, Na^+ ions enter the catholyte from the anode compartment but excess OH^- is produced at the same time at the cathode.

The concentration of the OH^- ions will be generally expected to be greater than the increase in cations in the catholyte and the concentration of the H_3O^+ ions will be generally expected to be greater than any increase in anions in the anolyte. Often a conductive but semi-permeable membrane (nafion, a strongly hydrated sulfonated tetrafluoroethylene based copolymer (Ito, Maeda, Nakano, & Takenaka, 2011), for example) is used to separate the two compartments and reduce the movement of the products between the electrode compartments; a process that improves the yield by reducing back and side reactions (Carmo M. , Fritz, Mergel, & Stolten, 2013). Due to the easier electrolysis of water containing ^1H rather than ^2H (D) or ^3H (T), electrolysis can be used for producing water with reduced or enriched isotopic composition.

When electrolysis uses short voltage pulses of alternating polarity at above 100 kHz the Nano-bubbles produced contain both H_2 and O_2 gases that can spontaneously react (combust) to form water whilst producing pressure jumps (Postnikov, Uvarov, Lokhanin, & Svetovoy, 2017).

e. ELECTROLYSIS THROUGH ELECTROLYTIC CELLS

Electrolysis of water is regarded as a promising technology because of its simplicity, low maintenance requirement and handling in the renewable energy space. Electrolysis involves the oxidation and reduction reactions producing hydrogen gas separated from the oxygen gas in a controlled environment.

However, even if sustainable usually is used only to obtain hydrogen with high purity (Wang, Wang, & Gong, 2014). The generation of energy as a supplement, not an alternative to fossil fuel sources, and hydrogen may have various destinations as the production of ammonia, methanol, pharmaceuticals, etc. Hydrogen energy carrier has low gas emissions that drastically reduce global warming.

Electrolysis occurs with power supply (Figure 9), being necessary to dissolve an ionic substance, but which in turn does not participate in the reactions involved. This decomposition of water occurs due to the electric potential which makes the chemically feasible reaction.

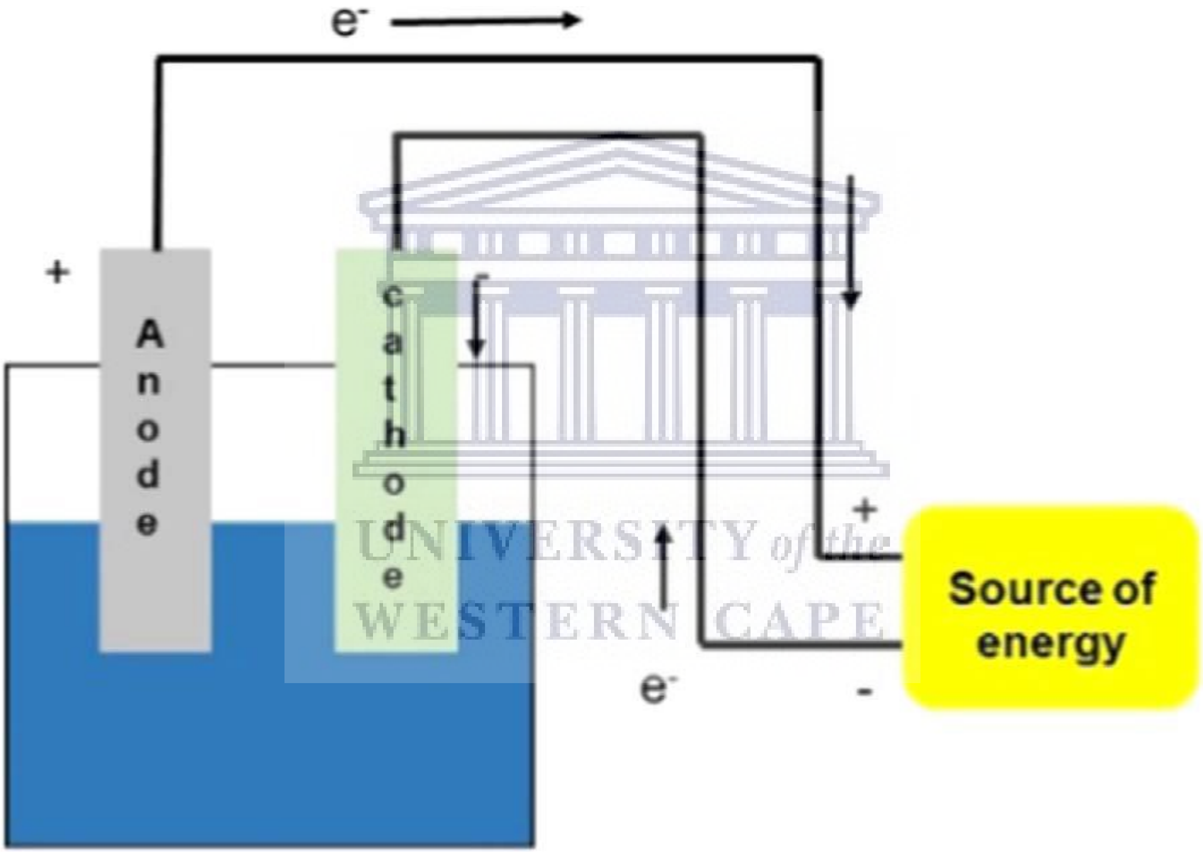


Figure 9: Electrolysis System (Santosa, Eckerta, & Eduardo De Rossia, 2017)

According Stefanelli (Stefanelli, 2015), the electrolytic cells consist of two electrodes, and these are determined according to the electrolyte present in each. The electrolysers are classified into unipolar (type tank) and bipolar (filter press). One way to improve efficiency of the electrolysis process is the increase in electrode surface area and changes in its composition (Lim RJ, 2014). Between the electrodes there is a membrane acting as an electrolyte that blocks electrons (Stefanelli, 2015). These electrolytes are responsible for the dissociation of oxygen.

2.5 ELECTROLYSERS

The most widespread electrolysis system are based on alkaline and PEM electrolysers. The alkaline electrolysis is one of the most developed technologies, and is considered a simple method where the electrolytes have basic character (Santosa, Eckerta, & Eduardo De Rossia, 2017). The electrolysis may alternatively be performed with a so-called polymer electrolyte membrane (PEM), one of the most promising technologies for decomposing water, providing greater efficiency and purity of the gas. However, it is little explored (Carmo, Frit, Mergel, & Stolten, 2013). Figure 10 shows the systems of alkaline Electrolyser and PEM, respectively.

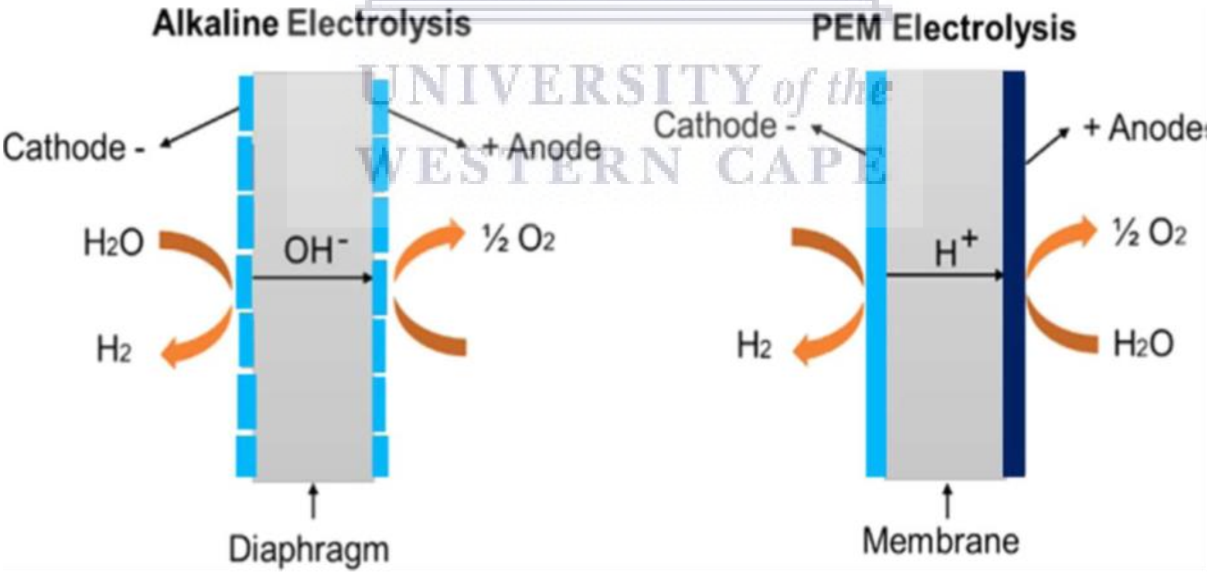


Figure 10: Operating System of Alkaline and PEM Electrolysers (Santosa, Eckerta, & Eduardo De Rossia, 2017)

a) PEM ELECTROLYSERS

Proton Exchange Membrane (PEM) electrolysis, based on a solid polymer electrolyte (i.e., usually Nafion). PEM electrolysis is attractive for small-size plants, mainly because it has an easier plant management and it does not require the use of hazardous chemicals. Moreover, PEM cells are more compact (usually, one third of volume compared to alkaline), have a faster response time and better dynamic behaviour characterized by high partial-load performance compared to the alkaline ones, thus they are more suitable for the integration with fluctuating renewable energy sources such as wind and solar (Ferrero & Santarelli, 2017).

Among the various technological applications of electrolysis, the production of hydrogen at high pressure is attracting more and more interest, especially when considering the necessary storage requirements. In fact, high pressure electrolysis – both PEM and alkaline – requires less electricity per unit of produced (and stored) hydrogen compared to the atmospheric water electrolysis with subsequent hydrogen compression (Onda, Kyakuno, Hattori, & Ito, 2004).

The high-temperature operation enhances both the kinetics of electrolysis reactions, thus allowing a lower electricity demand of the process, and also the tolerance to fuel impurities; moreover, the availability of recoverable high-temperature waste heat improves the overall system efficiency (Ferrero & Santarelli, 2017).

The PEM Electrolyser membrane has thickness around 20–300 μm and has the following advantages (Acar & Dincer, 2015):

- Provides high proton conductivity,
- Is compact and operates under high pressure.
- The electrolyte is thinner than the alkaline,
- Operating costs of electrolysis are smaller because the PEM can operate with high energy density, the gases have a high purity,
- Effective at high voltages.

b) ALKALINE ELECTROLYSERS

The disadvantages in alkaline electrolyser application are (Acar & Dincer, 2015):

- the electrolyte used is corrosive;
- operating pressures are low;

- high cost of components,
- low durability
- Lower efficiency due to diffusion of oxygen to the cathode chamber and the diffusion of hydrogen into the chamber of oxygen.

Character	Alkaline Electrolyser	PEM Electrolyser
Temperature (°C)	40 - 90	20 - 100
Pressure (bar)	< 30	< 30
Voltage (V)	1.8 – 2.4	1.8 – 2.2
Efficiency (%)	62 -82	67 - 82
H_2 Production Nm^3/h	< 760	< 10
Decay rate (mV/h)	< 3	< 4
Power Consumption (kW h Nm^3)	4.5 - 7	4.5 – 7.5

Table 9: Alkaline and PEM Electrolysers main characteristics (Holladay, Hu, King, & Wang, 2009)

c) ELECTROLYSIS AND SAFETY CONSIDERATIONS

The most important consideration with electrolysers is to prevent mixing of hydrogen and oxygen and the development of a flammable atmosphere within flammability and detonability limits of hydrogen and oxygen mixtures. Hydrogen and oxygen are generally separated by the membrane thus a key consideration when considering electrolyser safety is ensuring the membrane is intact and having a strategy in place in the event that either the membrane or a seal/gasket ruptures (Molkov V. , 2012)

Considering first the membrane several factors may contribute to its degradation or rupture these include (Molkov V. , 2012):

- ❖ Gradual blocking up of the protonic exchange sites, this is generally as a result of water of a poor quality being used with the electrolysers. The result of this is a gradual increase in the electrolyser voltage and eventually the system will prevent the electrolyser from operating any further.

- Uneven mechanical stresses due to stacks being unevenly tightened can also lead to degradation.
- Contaminants in the water or uneven catalyst layer distribution (porosity, thickness etc.) can have a negative effect on the electrolyser membrane and cause what are known as hotspots. Hotspots ultimately may lead to thinning of the membrane or worst case, perforations within the membrane both of which lead to an increase in the exchange of gases across the membrane. If gases are exchanged across the membrane there is the potential to create a potentially explosive atmosphere.
- Hotspots may also be caused by poor water management across the membrane as insufficient water will result in parts of the membrane not being sufficiently hydrated, leading to hotspots.
- Sub-zero temperatures can cause pinhole damage and micro-cracking of the membrane as well as damage to other components within the stack.
- For every one mole of oxygen produced two moles of hydrogen is produced, thus meaning either twice the volume of hydrogen or twice the pressure. This as potential to lead to an unbalanced system, the increased pressure of the hydrogen could potentially lead to a rupture in the membrane.

Mitigation methods should be employed to detect degradation of the membrane, or a hydrogen leak. Sensors can be employed to detect crossover of the hydrogen to the anode of the electrolyser. In addition to hydrogen sensors, the use of voltage and current can be used to monitor and to detect any short circuits.

A further safety issue arises with high pressure electrolysers. Whilst they may have advantages there are safety disadvantages in that the inventory of hydrogen in the system is increased, this becomes significant in the case of a leak (Molkov V. , 2012).

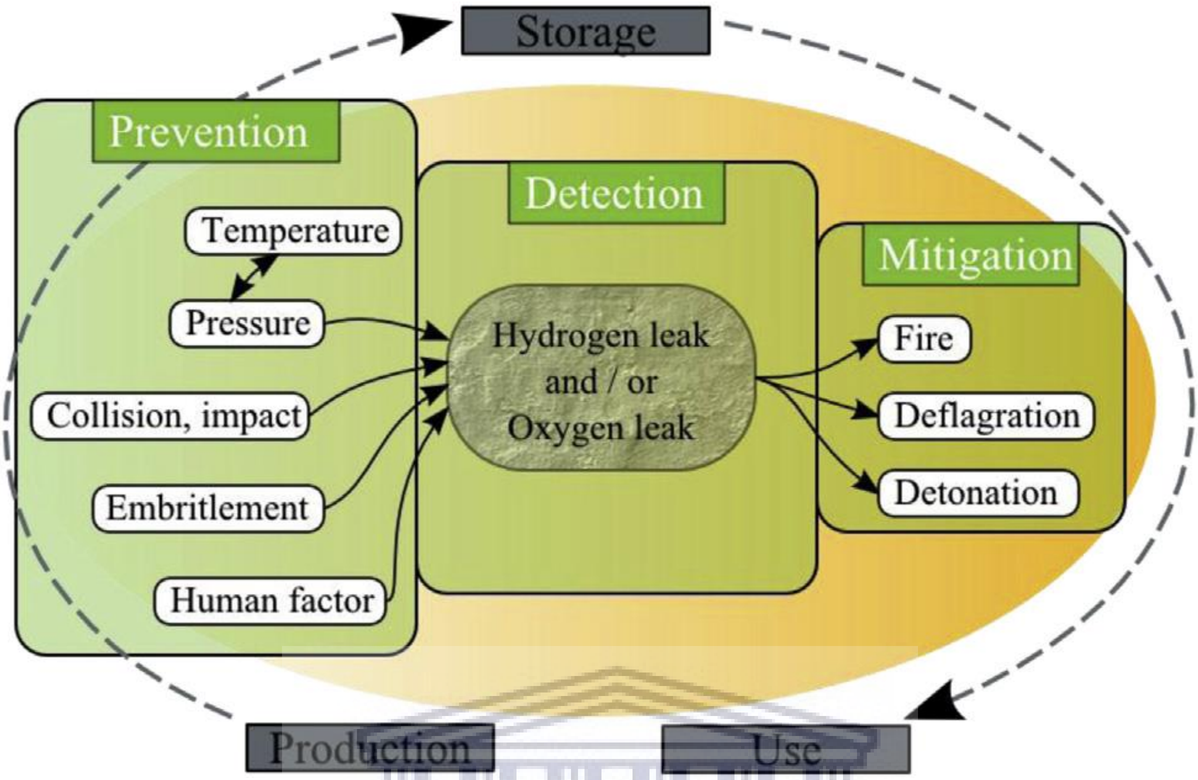


Figure 11: Types of risks related to H2 production, storage and use (Dubois, et al., 2013)

Figure 11 shows a schematic and non-exhaustive representation of risks that may be encountered along a hydrogen chain (production, storage and use). The three main control means categories (prevention, detection and mitigation) are also represented.

2.6 HYDROGEN STORAGE

There are currently three hydrogen storage technologies namely:

i. Compressed gaseous storage
ii. Cryogenic (Liquid) storage
iii. Solid state storage

2.6.1 GASEOUS HYDROGEN STORAGE

At present hydrogen is most commonly stored as a compressed gas. Hydrogen gas may be compressed to 20-100 MPa. This makes sense as many applications need hydrogen at higher pressure levels anyway. Compression of hydrogen also increases the volumetric capacity.

Limitations for storing hydrogen in a compressed form are the real gas effects which make compression to even higher pressures inefficient, and the availability and additional weight of high pressure vessels. Especially above 15 MPa the deviations from ideal gas behaviour become evident (more than 10% in density).

The primary issues with storing hydrogen as a compressed gas are the energy required to compress the gas, the inherent safety issues with storing hydrogen at such high pressure and the additional cost and weight of cylinders designed to store hydrogen at such pressures. Issues such as permeation and embrittlement are proportional to gas pressure therefore at higher pressures these may be a greater issue.

Issues with compressed hydrogen gas tanks revolve around high pressure, weight, volume, conformability and cost. The highest pressure gas tanks tend to be for automotive applications where type IV tanks are currently used (Molkov V. , 2012).

SAFETY ISSUES OF GASEOUS STORAGE

a. LOSS OF CONTAINMENT

A major concern with high pressure hydrogen storage is loss of containment, either through partial or full rupture. While it is a requirement that vehicle tanks are equipped with pressure relief devices this is not always the case with stationary applications. The extent of a flammable jet or a jet fire and hence the consequences is directly proportional to the pressure of the hydrogen in the tank and thus will affect the associated safety distances (Molkov V. , 2012).

b. MATERIALS – BLISTERING

The issue of hydrogen interaction with the materials used for hydrogen storage should be considered. Where metallic tanks are used hydrogen attack and embrittlement are important considerations. In type IV tanks, which are commonly used for vehicle applications “blistering” and delamination of the polymeric liner may occur. The polymeric liner is prone to permeation of the stored hydrogen and this is a result of dissolution and diffusion in the polymer matrix. Due to this permeation, hydrogen can accumulate between the liner and the composite and cause a blister. The accumulated hydrogen between the liner and the composite layer will initially be at a pressure lower than the internal pressure of the liner and thus only a blister will occur between the liner and composite, however as the pressure within the liner is reduced the pressure in the blister may eventually become greater than the pressure within the liner. The result of this can be localised collapse of the liner and in extreme cases full collapse of the liner.

The permeation issues of the liner have led to the development of polyamide liners for use with hydrogen. These liners will minimise the permeation and reduce this effect. Other methods of avoiding this from happening would be regular inspection of the cylinder and/or replacement (Molkov V. , 2012).

c. FILLING ORIENTATION

Interesting work presented in the paper by Barral et al (Barral, Pregassame, & Renault, 2004) describes experimental investigations which indicate that the orientation of a cylinder during filling can affect the temperature rise in the tank. The study takes the example of a cylindrical tank and considers filling in a horizontal and vertical orientation. In the vertical case, two fill directions are considered: top to bottom and bottom to top.

The case where the tank is orientated vertically and filled from the top shows a similar trend in temperature rise to the case of the horizontally orientated tank. In the case of horizontal filling small hot spots were observed for a short duration of time, this hot spot was attributed to the fast compression of the low pressure gas present in the tank at the beginning of the filling.

The higher the filling rate the higher the temperature of the hotspot. Similar behaviour was observed in the vertical case whereby the cylinder was filled from top to bottom. However, in the case where a vertical tank is filled from bottom to top a permanent and growing temperature gradient appears. The temperature increases significantly at the top of the tank, above the recommended level in the tank. The phenomenon also depends on the filling rate. Horizontal filling or vertical filling from top to bottom are recommended for safety purposes. When the cylinder is rapidly filled the result is near adiabatic compression, leading to a significant increase in temperature of the gas (Barral, Pregassame, & Renault, 2004).

d. PRESSURE RELIEF DEVICES

Thermally and pressure activated pressure relief devices are a means of addressing safety issues. It is important to note that the inclusion of such a device can mitigate against a potentially catastrophic scenario, indeed such safety technologies should be considered in all forms of hydrogen storage. It is better to vent hydrogen in a controlled manner than to have a situation where complete rupture of the tank occurs (Molkov V. , 2012).

e. HEATING EFFECTS DURING FILLING

The rapid filling of a compressed hydrogen tank is most relevant to on-board storage, this fast filling results in a temperature rise within the cylinder due to the heat of the compression effects. The temperature of the gas and especially that of a vessel needs to be closely controlled during the filling process in order to avoid detrimental effects on the vessel materials of the vessel (85 °C is generally considered to be the temperature limit (Wuechner, 2009).

Furthermore, without compensation, this heating effect results in reduced density of hydrogen in storage tank. Standards allow containers to be pressurised such that, when gas stored gas temperature stabilised, a complete fill is achieved based on the prevailing ambient conditions. It therefore becomes necessary to dissipate the heat or perhaps even cool the tank to enable more hydrogen to be transferred into it (Wuechner, 2009).

2.6.2 *LIQUID HYDROGEN STORAGE*

The boiling temperature of hydrogen is 20.39 K at 0.1013 MPa for ortho-H_2 and 20.26 K for para-H_2. Therefore in order to store hydrogen in liquid form the temperatures are cryogenic and the tanks must be sufficiently insulated. Cryogenic hydrogen is the second major category of hydrogen storage. Although volumetrically cryogenics is an excellent technology for storing and transporting hydrogen, it does take a significant amount of energy to cool the gas down to -243 °C, around 30% of the energy contained in the hydrogen (Aceves, et al., 2010).

Hydrogen compressed to 70 MPa has a density of about 60 g/l, while that of liquid hydrogen is about 68 g/l. But there is a penalty to be paid by the insulated and even more tightly sealed cryogenic tanks, reducing both volumetric and gravimetric capacities of the system. Nevertheless, liquid hydrogen storage offers unprecedented energy density, which makes it so popular in airspace applications. But when the hydrogen must be justified commercially and is competing with still-cheap petrol, the energy cost might be too high.

Hydrogen may be liquefied for a simplified transport or storage. Compared to compressed gaseous hydrogen (CGH_2), LH_2 has a considerably higher volumetric energy density. The liquefaction is achieved by cooling below the boiling temperature. The cost and weight of suitable materials to store and maintain the hydrogen at this temperature must also be considered. On average, 15 times more energy is needed compared to the liquefaction of a kilogram of nitrogen. The energy density of hydrogen can be improved by storing hydrogen in a liquid state. However, the issues with LH2 tanks are hydrogen boil-off, the energy required for hydrogen liquefaction, volume, weight, and tank cost. The energy requirement for hydrogen liquefaction is high; typically 30% of the heating value of hydrogen is required for liquefaction (Aceves, et al., 2010).

SOME SAFETY ISSUES LIQUID HYDROGEN STORAGE

a. LOSS OF CONTAINMENT

As with CGH_2 loss of containment should be avoided wherever possible and is mentioned here for completeness. A worst case scenario which may result in heating and subsequent pressure rise and a loss of containment is loss of the vacuum due to puncture of the outer tank (Molkov V. , 2012).

b. BOIL OFF

The main problem with liquid hydrogen tanks from safety perspective is hydrogen boil-off. It must be minimised or eliminated not only for reason of cost, efficiency and vehicle range, but also for safety, especially when the vehicle is parked in confined spaces. The dormancy, period of inactivity before a vessel releases hydrogen to reduce pressure build up, is 5 days at the operating pressure of today's liquid hydrogen tanks (~6 atm).
With liquefied hydrogen there is also an issue of boil-off and evaporation via a pressure limiting valve. The boil-off may correspond to a loss of 1.5% of the stored energy per day. Thus the typical stored mass of about 7kg will be lost in 2 months if the car was not used in this phase.

The involved temperatures are demanding not only regarding the design of the actual storage but also regarding the compatibility of all connected technologies, like measurement techniques, armatures, valves, and piping (Molkov V. , 2012).

Boil-off losses can occur as a result of several mechanisms (Molkov V. , 2012) these include:

i. Ortho-para conversion: The conversion of ortho-hydrogen to para-hydrogen is an exothermic reaction. The heat of conversion is related to the change of momentum of the hydrogen nucleus when the direction of spin changes. The amount of heat given off in this conversion process is temperature dependent. If the unconverted normal hydrogen is placed in a storage vessel, the heat of conversion will be released within the container, which leads to the evaporation of the liquid.

ii. Thermal stratification and self-pressurisation: Heat transfer from the sidewalls and bottom to a liquid hydrogen storage vessel will always result in an increase of the sensible enthalpy of the liquid. When the heat flux is small enough and the inside wall of the vessel is smooth, boiling is unlikely to occur. In this case, the added energy tends to get distributed non- uniformly because the imposed heat flux usually produces a free convective flow. The warm liquid hydrogen becomes buoyant and rises to the top.

iii. Heat leaks: This is a common cause of boil-off. The heat leakage losses are generally proportional to the ratio of surface area to the volume of the storage vessel (S/V).The most favourable shape of cryogenic vessel is therefore spherical since it has the least surface to volume ratio. A big cause of heat leaks in cryogenic storage is through the support struts in the vessel.

iv. Sloshing: Another process which leads to boil-off during liquid hydrogen transportation by tankers is sloshing. Sloshing is the motion of liquid in a vessel due to acceleration or deceleration. Some of the impact energy of the liquid against the vessel is converted to thermal energy.

v. Flashing: Another source of boil-off is flashing. This problem occurs when liquid hydrogen, at a high pressure (2.4 to 2.7 atm), is transferred from trucks and rail cars to a low pressure Dewar (1.17 atm). This problem can be reduced if transportation of liquid hydrogen is carried out at atmospheric pressures.

c. ICE FORMATION

The cold temperatures involved may result in ice build-up on structures (valves, Dewar’s) which can in turn produce excessive exterior pressures, rupturing storage systems.

2.6.3 SOLID STATE HYDROGEN STORAGE

Hydrogen can be stored either within the structure or on the surface of certain materials. There are presently three generic mechanisms known for storing hydrogen in materials: absorption, adsorption, and chemical reaction.
These methods do not require the high pressures or low temperatures of the previous methods; this offers advantages regarding the safety of the materials. In addition solid storage has a high volumetric energy density. Also unlike compressed and liquefied hydrogen accidental loss of confinement may only occur if the materials are heated and further hydrogen is released (Molkov V. , 2012).

Examples of advanced materials are metal hydrides which are based on metallic compounds, which store hydrogen via chemical bonding. The solid reaction during loading the hydrogen releases heat at relatively moderate pressure. To release the hydrogen again the pressure has to be decreased and heat has to be delivered. These loading and unloading cycles may be repeated without reducing the storage capacity.

The hydrogen storing materials are separated into three broad categories (Molkov V. , 2012):

a. Chemical Hydrides (i.e., hydrogen containing materials with strong chemical bonding exhibiting “irreversible” hydrogen release that usually require catalysts for desorption. These materials typically involve off-board regeneration, requiring chemical reactions and/or high pressure/temperature.).
b. Metallic Hydrides (i.e., materials that absorb hydrogen within the host itself by the dissociation of hydrogen molecules and usually exhibit “reversible” reactions with hydrogen gas under moderate conditions of temperature and pressure that can be done on-board. These materials are typically limited by low hydrogen storage density per unit weight.

c. Hydrogen storage via physical adsorption of hydrogen species with rather weak bonding that generally permits storage only at much lower “cryogenic” temperatures.

Volumetric capacities of these materials are typically very limited at ambient temperatures.

There are also some “borderline” materials with behaviour intermediate between any two of these categories. The weight of the capturing element can be significant, so one of the parameters for measurement of the effectiveness of a compound is the percentage by mass of hydrogen that it absorbs. Common hydrides can hold about 3-8%. Any amount greater than 6% is considered attractive. It means that in order to store 4 kg of hydrogen a state-of-the-art hydride tank would perhaps weight 80 kg (Molkov V. , 2012).

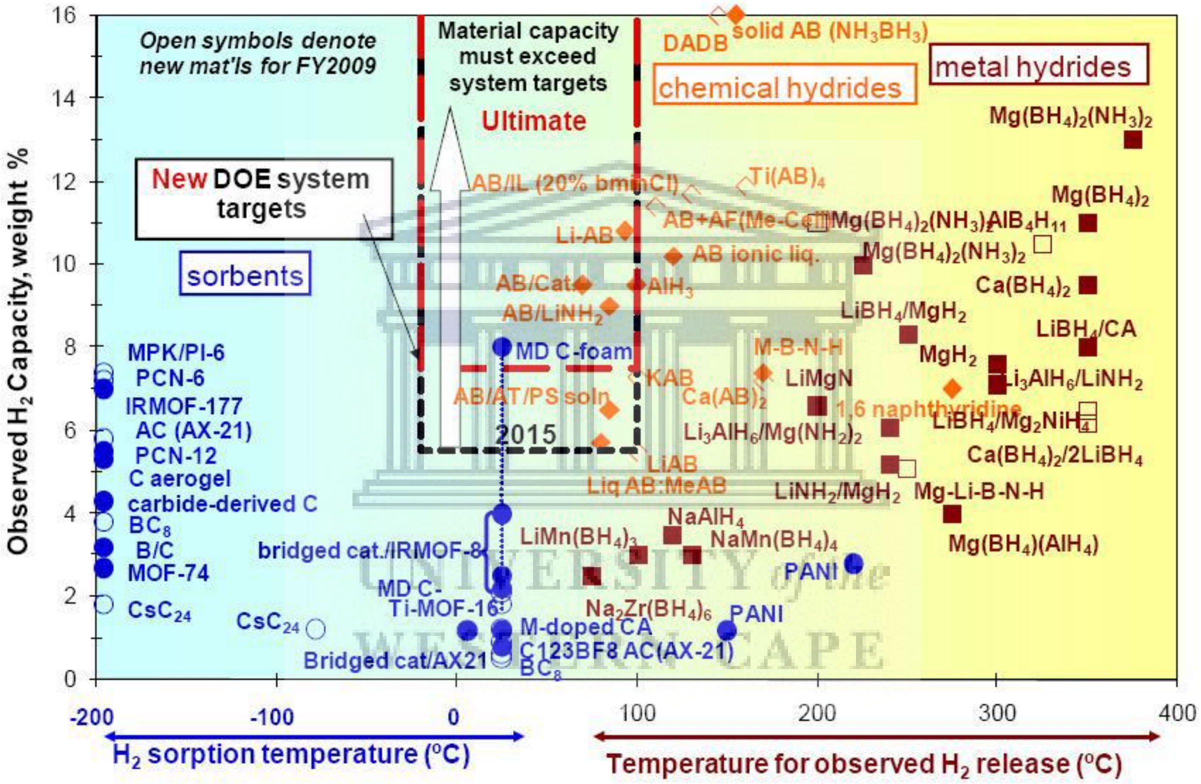


Figure 12: Hydrogen storage gravimetric capacity versus temperature for different materials investigated within DOE programme in 2007-2009 (Energy, 2009).

SOME POTENTIAL SAFETY ISSUES OF METAL HYDRIDES

a. PYROPHORIC MATERIALS

The materials used for solid storage tend to be pyrophoric. A pyrophoric material is one which can ignite spontaneously in air. Therefore there is a danger with solid state storage that damage to the storage may results in a vigorous reaction upon exposure to air releasing hydrogen, heat, and with probable ignition (Molkov V. , 2012).

b. RISK OF EXPLOSION

Loss of containment could lead to a potential dust cloud explosion. However, it is worth noting that even non-pyrophoric materials, such as flour or sawdust, are prone to deflagrate with a minimal spark energy and can cause a disastrous accident when their fine powder forms a dust cloud in air. Complex hydrides, in general, are powdery substances with a low density; therefore, they can easily form a dust cloud (Molkov V. , 2012).

c. HEAT MANAGEMENT

Materials used in solid hydrogen storage typically release a lot of heat upon hydrogen uptake. This heat must thus be managed by sound engineering and thermodynamics applications. Thus use of a cooling fluid (oil, water) is a common approach.

d. TOXICITY

Metal hydrides can typically be toxic to humans and thus damage to the storage is highly undesirable. They must be handled with caution and properly disposed.

2.7METAL HYDRIDE HYDROGEN COMPRESSORS

Metal hydride (MH) thermal sorption compression is an efficient and reliable method allowing a conversion of energy from heat into a compressed hydrogen gas. The most important component of such a thermal engine - the metal hydride material itself should possess several material features in order to achieve an efficient performance in the hydrogen compression. Apart from the hydrogen storage characteristics important for every solid H storage material (e.g. gravimetric and volumetric efficiency of H storage, hydrogen sorption kinetics and effective thermal conductivity), the thermodynamics of the metal-hydrogen systems is of primary importance resulting in a temperature dependence of the absorption/desorption pressures. Several specific features should be optimised to govern the performance of the MH-compressors including synchronisation of the pressure plateaus for multi-stage compressors, reduction of slope of the isotherms and hysteresis, increase of cycling stability and life time, together with challenges in system design associated with volume expansion of the metal matrix during the hydrogenation (Lototskyy, Yartys, Pollet, & Bowman Jr, 2014)

Metal Hydride (MH) hydrogen compression utilises a reversible heat-driven interaction of a hydride-forming metal, alloy or intermetallic compound with hydrogen gas to form MH and is considered as a promising application for hydrogen energy systems. This technology, which initially arose in early 1970s, still offers a good alternative to both conventional (mechanical) and newly developed (electrochemical, ionic liquid pistons) methods of hydrogen compression. The advantages of MH compression include simplicity in design and operation, absence of moving parts, compactness, safety and reliability, and the possibility to consume waste industrial heat instead of electricity (Lototskyy, Yartys, Pollet, & Bowman Jr, 2014).

2.7.1 METAL-HYDROGEN SYSTEM

Applications of metal hydrides, including hydrogen compression, utilise a reversible heat-driven interaction of a hydride-forming metal/alloy, or intermetallic compound (IMC) with hydrogen gas, to form a metal hydride:

$$M(s) + x/2\,H_2(g) \underset{\text{desorption}}{\overset{\text{absorption}}{\rightleftharpoons}} MH_x(s) + Q; \qquad (24)$$

Where M is a metal/alloy (e.g., V or a BCC solid solution based upon it), or an intermetallic compound (IMC; $LaNi_5$, TiFe, etc.); (s) and (g) relate to the solid and gas phases, respectively. The direct interaction, an exothermic formation of the metal hydride/hydrogen absorption, is accompanied by a release of heat, Q. The reverse process, endothermic hydride decomposition/hydrogen desorption, requires supply of approximately the same amount of heat (Lototskyy, Yartys, Pollet, & Bowman Jr, 2014).

2.7.2 GENERAL LAYOUT OF A METAL HYDRIDE SYSTEM

The simplest apparatus realising thermally driven hydrogen compression using MH is shown in Figure 13(a). Metal hydride material (A) thermally coupled to a heat supply/ removal accessory (B) is placed into a pressure container (C) comprising a gas pipeline (D) which allows supply or removal of hydrogen gas to/from MH (A). The gas pipeline (D) can have a built-in filter element (not shown) which provides a uniform hydrogen distribution within the

MH bed, and also prevents contamination of gas pipelines with fine powder of the MH (Lototskyy, Yartys, Pollet, & Bowman Jr, 2014).

The assembly A-D called the metal hydride compression element, or generator-sober, provides periodic suction of low-pressure hydrogen (H_2 @ PL) when the MH is cooled (-Q) down to the lower temperature, TL, followed by a discharge of high-pressure hydrogen (H_2 @ PH) in the course of heating (+Q) of MH to the upper temperature, TH. This solution first patented in 1970 by Wiswall and Reilly (USA Patent No. US3516263, 1970) Allows periodically operated hydrogen compression that restricts its application from the continuous technological processes.

The simplest continuously-operated metal hydride hydrogen compressor (Figure 13(b)) comprises two compression elements (A1-D1, A2-D2) similar to the one shown in Figure 12(a). The gas pipelines D1 and D2 are connected to a gas distributing system (E) equipped with a port (F) for the supply of hydrogen at low pressure, P_L, and a port (G) for the output of hydrogen at high pressure, P_H. The operation of the compressor includes two steps, 1 and 2. During Step 1 the heat supply/removal accessory (B1) of the first compression element provides heat removal (-Q) from the MH (A1) at a lower temperature level, T_L; simultaneously, the accessory (B2) of the second compression element provides heat supply (+Q) to the MH (A2) at a higher temperature level, T_H. During the next Step 2 the heating/cooling modes of the accessories B1 and B2 are reversed, so that B1 operates in the heat supply, and B2 in heat removal mode. Thus, a periodic reversal of the operating modes of the heat supply/removal accessories B1 and B2 synchronised with switching gas flows by the gas distributing system (E) provides the continuous operation resulting in the suction of low-pressure hydrogen to the port F and the release of high-pressure hydrogen from the port G (Lototskyy, Yartys, Pollet, & Bowman Jr, 2014).

An approach to generate high H_2 pressures at modest operating temperatures is the use of multi-stage hydride compressors, a concept developed at Ergenics Inc. (Golben, Multi-stage hydride hydrogen compressor, 1983). The multistage compressor uses a series of two or more alloys differing by thermal stabilities of their hydrides. Figure 13(c) shows an example of layout of two-stage MH compressor. The alloy forming the most stable hydride is placed in the compression elements of the first stage (A1.1, A1.2), and other MH are loaded to the compression elements belonging to the next stages, in the order of decrease of their thermal stability (A2.1, A2.2). The multistage operation allows achievement of higher overall compression ratios using the same or smaller temperature swing. For example, five-stage MH compressor developed by Ergenics allows H_2 compression from 7 to 250 bar in the temperature range 30-90 C with water as a heating/cooling agent (Lototskyy, Yartys, Pollet, & Bowman Jr, 2014).

The gas distributing system (E) can be made as a one-way (check) valve arrangement; the periodic heating/cooling of heat supply/removal accessories (B) is conveniently controlled by timing relays (USA Patent No. US4402187, 1983), (Patent No. EP0094202 A2, 1983), (USA Patent No. US 4505120, 1985).

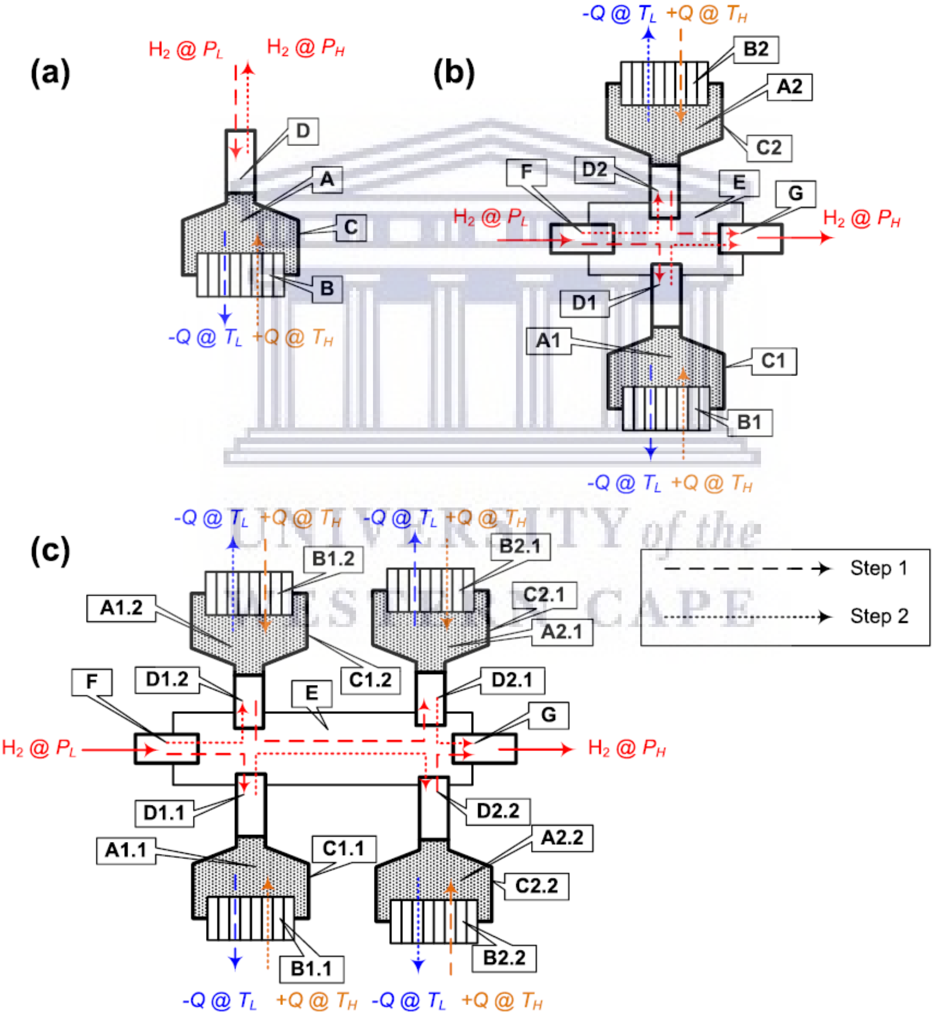


Figure 13: General layouts of MH Compressors: (a) Periodically operated, (b) One-stage continuously operated, (c) Two stage continuously operated

2.7.3 APPLICATION OF METAL HYDRIDE H_2 COMPRESSORS

Below is the list of current applications of MH compressors

a. ISOTOPE HANDLING

Metal hydrides have been used internationally in the research laboratories, nuclear energy and defence industries for decades to store and process hydrogen isotopes, protium, deuterium, and tritium (Mueller, Blackledge, & Libowitz, 1968) (Beavis, 1968). Prior to 1970 the binary hydrides of titanium, zirconium, palladium, and uranium were only utilised (Bowman Jr, Carlson, & DeSando, 1976). Often these metal hydrides served concurrent roles of collecting, storing, purifying, transporting, and isotope separation rather than to serve as explicit compression applications.

b. CRYOGENICS/SPACE

In 1972, van Mal was the first to report that metal hydride compressors could be used to form liquid hydrogen via Joule Thomson (J-T) expansion (Lototskyy, Yartys, Pollet, & Bowman Jr, 2014). Subsequently, a number of laboratory demonstrations of hydrogen liquefaction using metal hydride compression is being practised worldwide and is recorded in a number of journal publications.

c. UTILISATION OF LOW-GRADE HEAT

The main advantage of MH hydrogen compressors is in the conversion of waste heat ($T < 200$ °C) into the energy of compressed hydrogen which can be further utilised. In 1979 Nomura et al. (Nomura, Ishido, & Ono, 1979) developed and successfully tested a piston engine which used one stage MH compressor on the basis of $LaNi_5$ and operated at 20-80 °C providing efficiency of energy conversion of 7.7%, or about 50% of the Carnot efficiency. A year later the first prototype of MH-based ($LaNi_{4.63}Al_{0.37}$) water pump operating in the same temperature range was developed at Sandia National Laboratories (Northrup Jr & Heckes, 1980).

Use of MH compressors for water pumping driven by solar heat was intensively studied in the early 2000s. The systems were shown to be promising in distributed stand-alone applications capable of daily pumping up to 3000 L of water over a height of 15 m using 1 m^2 solar collector area (Lototskyy, Yartys, Pollet, & Bowman Jr, 2014).

d. THERMALLY DRIVEN ACTUATORS

Developments of pneumatic actuators on the basis of MH hydrogen compression were considered in earlier MH applications. Their advantages include compactness, ability to develop high forces, smooth actuation, silent and vibration-free action, simplicity in design and operation. As a rule, the actuators are driven by thermoelectric/Peltier elements used for heating and cooling of the MH; pressure transmission from compressed H_2 to mechanical or hydraulic actuating mechanism is provided by bellows (Lototskyy, Yartys, Pollet, & Bowman Jr, 2014).

e. HYDROGEN REFUELLING STATIONS

Hydrogen refuelling infrastructure takes a significant part of the capital investments for the introducing fuel cell powered vehicles and must be taken into account in the assessment of their economic feasibilities. Despite a certain number of hydrogen refuelling stations operating worldwide, they are not introduced broadly enough, mainly because of their high costs ranging between $500,000 and $5,000,000 per installation (Rare, 2008). The most expensive H_2 refuelling components originate from:

i. On-site hydrogen production and
ii. Hydrogen compression.

According to techno-economic analysis presented in Reference (Weinert, Shaojun, Ogden, & Jianxin, 2007), the contribution of hydrogen compression to the total station cost is about 20%.

Cost-performance optimisation of the H_2 refuelling infrastructure can be achieved by the improvement of hydrogen compression technology. A promising way for that is the application of thermally-driven metal hydride hydrogen compressors characterised by simplicity in design and operation, reliability and minimum maintenance, with potentially low price and ability to utilise waste heat, instead of electricity, for the H_2 compression (Lototskyy, Yartys, Pollet, & Bowman Jr, 2014).

2.8 PHOTOVOLTAIC ELECTROLYSIS

The photovoltaic driven water electrolysis comprises photovoltaic (PV) panels, DC bus bar, AC grid, accumulator battery set, and electrolyser and hydrogen storage canisters. The cost of PV-generated electricity is in continuous decline. The efficiency of the solar cell can range from 12 to 15% typically for the silicon solar cell. However, it is as high as 25-30% for GaAs solar cells. The total efficiency of solar radiant energy transformed to chemical hydrogen energy is nearly 16% (Yilanci, Dincer, & Ozturk, A review on solar hydrogen/fuel cell hybrid energy systems for stationery applications, 2009). The exergy efficiency of the PV-electrolyser system is calculated as the product of exergy efficiency of the PV system ψ_{PV} and the exergy efficiency of the electrolyser ψ_{EL} and it is:

$$\psi = \psi_{PV}\psi_{EL} = \frac{V_m I_m - \left(1 - \frac{T_0}{T_{cell}}\right) hA(T_{cell} - T_0)}{\dot{E}x_{solar}} \times \frac{\dot{E}x_{H_2} + \dot{E}x_{O_2}}{V_m I_m}, \qquad (25)$$

Where $V_m I_m$ is the electrical power accounting of all electrical losses of the PV panel, associated electronics and electrical lines. This power is the same as that retrieved at the input of the electrolyser. The quantity $hA(T_{cell} - T_0)$ represents the heat losses between the PV panel and the ambient due to heat transfer; some exergy losses are associated with this heat as indicated in the numerator of above equation 25 (Dincer, Green methods for Hydrogen productions, 2012).

2.9 HYDROGEN SAFETY

Hazard can be defined as a chemical or physical condition that has the potential for causing damage to people, property and the environment. Hydrogen accident could have different hazards, e.g. asphyxiation due to release in closed space, frostbite by liquefied hydrogen, thermal hazards from jet fire, pressure effects from deflagrations and detonations, etc. Hazard could lead to no damage, if the proper safety measures are applied, or could lead to costly consequences up to fatalities if the system or infrastructure has been designed and used without professional knowledge in hydrogen safety (Molkov V. , 2012).

The modern definition of risk is provided by ISO/IEC Guide 73:2002 (2002) stating that it is the combination of the probability of an event and its consequence while safety is defined as the freedom from unacceptable risk. This means that safety is a societal category and cannot be numerically defined while risk is a technical measure that can be calculated. Society in consequence establishes acceptable levels of risk or risk acceptance criteria (Molkov V. , 2012).

An analysis shall be conducted to identify all fire and explosion hazards and accomplish the following (Molkov V. , 2012):

Significant hazards shall be eliminated or reduced to acceptable risk levels

- Where the hazard cannot be eliminated or reduced, the system components associated with the hazard shall be relocated to an area less threatening to people and property as directed by the Authority having jurisdiction;
- Where the hazard cannot be eliminated, reduced or removed the system components associated with the hazard shall be isolated within the facility so as not to pose a danger to the remainder of the structure or its occupants;
- Where the hazard cannot be eliminated, reduced, relocated or isolated, protection shall be provided to ensure adequate levels of human and structural safety. Should an incident / accident occur, the occupants of the facility shall be provided with protection to enable them to leave the area safety and the structure will be protected to ensure its continued integrity

Hydrogen safety engineering (HSE) is defined as the application of scientific and engineering principles to the protection of life, property and environment from the adverse effects of incidents/accidents involving hydrogen. HSE can be applied to existing and new hydrogen systems, including but not limited to stationery, e.g. Combined heat and power systems, or portable e.g. mobile phones and computers, applications for indoor and outdoor use, hydrogen transportation and refuelling infrastructures, power generation, hydrogen production and distribution units, storage, infrastructure (Daniel & Young-Do, 2007).

A hydrogen system could be defined as an equipment dealing with hydrogen e.g. storage, production, delivery, distribution, consumption, etc. Hydrogen should remain contained within hydrogen system from its production/ delivery to its final use (Molkov V. , 2012) .

2.9.1 PHYSICAL AND CHEMICAL PROPERTIES OF HYDROGEN

a. BUOYANCY AS SAFETY ASSET

The main hydrogen safety assert, i.e. its highest on the earth buoyancy, confers the ability to rapidly flow out of an incident scene and mix with the ambient air to a safe level below the lower flammability limit (LFL) of 4% by volume of hydrogen in air. Indeed, hydrogen has a density of 0.0838 kg/m^3 (NTP) which is far below than air density of 1.205 kg/m^3 at the same conditions. The unwanted consequences of hydrogen releases into the open atmosphere and in partially confined geometries where no conditions to allow hydrogen to accumulate exist are drastically reduced by buoyancy (Molkov V. , 2012).

Contrary, heavier hydrocarbons are able to form a huge combustible cloud. In many practical situations, hydrocarbons may pose stronger fire and explosion hazards than hydrogen. Hydrogen high buoyancy affects its dispersion considerably more than its high diffusivity.

Pure hydrogen is positively buoyant above a temperature of 22K, i.e. over almost the whole temperature range of its gaseous state. Buoyancy provides comparatively fast dilution of released hydrogen by the surrounding air below the lower flammability level. In unconfined conditions, only small fraction of released hydrogen would be able to deflagrate. Indeed a hydrogen-air cloud evolving from the inadvertent release upon the failure of a storage tank or pipeline liberates only a small fraction of its thermal energy in case of a deflagration which is in the range 0.1 -10% and in most cases below 1% of the total energy of released hydrogen. This makes safety considerations of hydrogen accident with large inventory at the open quite different from that of other flammable gases with often less or no harmful consequences at all (Molkov V. , 2012).

b. DIFFUSIVITY AND VISCOSITY

Diffusivity of hydrogen is higher compared to other gases due to small size of the molecule. Data on diffusion coefficient of hydrogen in air at Normal Temperature and Pressure (NTP) is 6 x 10^{-5} m^2/s. The low viscosity of hydrogen and small size of the molecule cause a comparatively high flow rate if the gas leaks through fittings, seals, porous material etc. This negative effect is to a certain extent offset by low energy density (volumetric) of hydrogen in comparison with e.g. methane or other hydrocarbon gases. Viscosity of gaseous hydrogen (µPoise): 89.48 NPT (Molkov V. , 2012).

c. INTERACTION WITH METALS

Hydrogen can cause a significant deterioration in the mechanical properties of metals. This effect is referred to as hydrogen embrittlement. Hydrogen embrittlement involves a large number of variables such as temperature and pressure of the environment, the purity, concentration and exposure time of the hydrogen and the stress state, physical and mechanical properties, microstructure, surface conditions and nature of the crack front of the material. Many hydrogen material problems involve welds or the use of an improper material (Molkov V. , 2012).

Many metals absorb hydrogen especially at high pressure. Hydrogen absorption by steel can result in embrittlement, which can lead to fails in the equipment. There is an atomic solution of hydrogen in metals. Permeated through a metal atomic hydrogen recombines to molecules on the external surface of storage to diffuse into surrounding gas afterwards. The choice of material for hydrogen system is an important part of hydrogen safety (Molkov V. , 2012).

d. COMBUSTION PROPERTIES

At normal temperature hydrogen is not a very reactive substance, unless it has been activated somehow e.g. by an appropriate catalyser. Hydrogen reacts with oxygen to form water at ambient temperature extraordinarily slow. However if the reaction is accelerated by a catalyser or a spark, it proceeds with high rate and explosive violence (Molkov V. , 2012).

Hydrogen burns in a clean atmosphere with an invisible flame. It has a somewhat higher adiabatic premixed flame temperature for a stoichiometric mixture in air of 2403 K compared to other fuels. This temperature can be a reason for serious injury at an accident scene, especially at clean laboratory environment where the hydrogen flame is practically invisible. However hydrogen combustion and hot currents will cause changes in the surroundings that can be used to detect the flame. Although the non-luminous hydrogen flame makes visual detection difficult, there is a strong effect of heat and turbulence on the surrounding atmosphere and raising plume of hot combustion products. These changes are called the signature of the fire (Molkov V. , 2012).

e. STOICHIOMETRIC MIXTURE, EQUIVALENCE RATIO AND MIXTURE FRACTION

Stoichiometric mixture is a mixture in which both fuel and oxidiser are fully consumed to form combustion product(s). For example, the two diatomic gases hydrogen (H_2) and oxygen (O_2) can combine to form water as the only product of an exothermic reaction between them, as described by the equation:

$$2H_2 + (O_2 + 3.76N_2) = 2H_2O + 3.76N_2 \qquad 26$$

Thus, the stoichiometric hydrogen- oxygen mixture is composed of 66.66% by volume of hydrogen and 33.33% of oxygen. Thus the stoichiometric concentration of hydrogen in air (assuming 21% of oxygen and 79% of nitrogen) is 29.59% by volume (2/ (2 + 1 + 3.76) = 0.2959) with air content of 70.41% (Daniel & Young-Do, 2007)

f. HEAT OF COMBUSTION

The lower heating value (LHV) (heat of combustion) of hydrogen is 241.7 kJ/mol and the higher heating value (HHV) is 286.1 kJ/mol. The difference of about 16% is due to the heat of condensation of water vapour and this value is larger compared to other gases (Carmo, Fritz, & Mergel, A comprehensive review on PEM water electrolysis, 2013).

g. FLAMMABILITY LIMITS

The flammability range of hydrogen is wider compared to most hydrocarbons i.e. 4 to 75 % by volume in air at NTP. The flammability range of hydrogen expands with temperature e.g. the lower flammability limit drops from 4% at NTP to 3% at 100 °C (For an upward propagating flame) and depends on pressure (Molkov V. , 2012).

h. QUENCHING

Hydrogen flames are difficult to quench. For example premixed hydrogen-air combustion can be aggravated by heavy sprays of water due to induced turbulence and ability of mixture to burn around the droplets. Hydrogen has the lowest quenching distance compared to other flammable gases. Quenching of any flame occurs when heat loses from flame are comparable with heat generation due to combustion and then the chemical reactions cannot be sustained. Usually quenching distance is reported as the minimum pipe diameter through which a premixed flame can pass. The quenching distance decreases with increase of pressure and temperature, depends of mixture composition, etc. Hydrogen fires normally are not extinguished until the supply of hydrogen has been shut off because of danger of re-ignition and explosion (Molkov V. , 2012).

2.9.2 HYDROGEN HEALTH HAZARDS

Hydrogen is not expected to cause mutagenicity, teratogenicity, embryo toxicity or reproductive toxicity. There is no evidence of adverse effects if skin or eyes are exposed to hydrogen, it cannot be ingested (unlikely route). However, inhaled hydrogen can result in a flammable mixture within the body (Daniel & Young-Do, 2007)

Hydrogen is classified as a simple asphyxiate, has no threshold limit value (TLV) and it is not a carcinogen. High concentration of hydrogen in air can cause an oxygen-deficient environment. Individuals breathing such atmosphere may experience symptoms that include headaches, dizziness, drowsiness, unconsciousness, nausea, vomiting, depression of all the senses, etc. A victim may have a blue colour skin and under some circumstances, death may occur. If hydrogen is inhaled and above symptoms observed, then remove a person to fresh air give oxygen if breathing is difficult or apply artificial respiration if not breathing (Molkov V. , 2012).

The system design shall prevent any possibility of asphyxiation of personnel in adjacent area. The system design shall provide for prevention of personnel entering the enclosure unless confined space entry procedures are strictly followed. It is recommended to check oxygen content before entering an incident/accident area. Hydrogen concentrations have to be measured with a suitable detector (Molkov V. , 2012).

Oxygen concentration below 19.5% by volume are biologically inactive for humans and no effects of oxygen deficiency are usually observed. At concentrations below 12%, immediate unconsciousness may occur with no prior warning symptoms. Stages of asphyxiation have been noted based on the oxygen concentrations as follows (Molkov V. , 2012):

- 15-19% by volume – decreased ability to perform tasks, may induce early symptoms in person with heart, lung or circulatory problems
- 12-15% - deeper respiration, faster pulse, poor coordination
- 10-12% - giddiness, poor judgement, slightly blue lips
- 8-10% - nausea, vomiting, unconsciousness, ashen face, fainting, mental failure
- 6-8% - death in 8 min(50% death and 50% recovery with treatment in 6 min, 100% recovery with treatment in 4 to 5 min)
- 4% - Comma in 40 s, convulsions, respiration ceases, death

2.9.3 DETECTION AND HYDROGEN SENSORS

The addition of an odorant to hydrogen would ease the detection of small leaks. However this is not practicable in most situations, e.g. this would poison an expensive catalyst in fuel cells. Moreover, this is not feasible to be added to hydrogen. Hydrogen fire detection can be based on registration of infrared radiation of flames which are not seen in a day light (Gandia, Arzamedi, & Dieguez, 2013). They are various types of hydrogen sensors in the market today, they include the following:

- Optical fibre hydrogen sensors
- Electrochemical hydrogen sensors
- MEMS hydrogen sensors
- Thin Film sensors
- Thick Film sensors
- Chemo chromic hydrogen sensors
- Diode based Schottky sensor
- Metallic La-Mg_2-Ni hydrogen sensors

Hydrogen sensors are calibrated during manufacturing and they must be calibrated periodically to maintain sensitivity. Depending with the operating conditions the end user can use any type of sensor that meet his system specifications and compatibility.

CHAPTER 3 RESEARCH DESIGN AND METHODOLOGY

INTRODUCTION

This chapter explains in detail the research, design and methodology used in the present study. It explains the research objectives and a suitable design and methodology to achieve these objectives. The objectives of this study were:

i. The design of an 8.4kW Polymer Electrolyte Membrane Water Electrolyser (PEMWE) with a hydrogen production rate of 2 Nm^3/hr and hydrogen discharge pressure of 20 bars.
ii. Construction and commissioning of a 8.4kW PEMWE prototype system
iii. A HAZOP study on the integration of PEM Water Electrolyser prototype system with the balance of plant.
iv. Integration of PEM water electrolyser prototype system with a locally developed 5 Nm^3/h MH compressor.
v. Integration of PEM water electrolyser prototype system to a locally produced 4.2kW Photovoltaic supply.

3.1PROJECT DESIGN & SPECIFICATIONS

This involves an exhaustive design process, integration and commissioning of a prototype that has an application of hydrogen safety at its core. The produced hydrogen will be compressed using an existing 5Nm^3/h metal hydride compressor and stored in the SAIAMC gas storage facility. An existing hydrogen dispensing system was used to refuel various FC prototypes, amongst others the golf cart, forklift, fuel cell bicycle and fuel cell chargers. This study will contribute in promoting use of clean fuel, hydrogen derived from renewable energy sources that will facilitate the transition to the hydrogen economy. A crucial aspect of the study is the establishment of design and operation protocols around hydrogen safety. The stack specifications for the PEM water electrolyser is a hydrogen production rate of 2 Nm^3/hr and hydrogen discharge pressure of 20 bars. The project implementation summarised as follows:

- Project Design & Specifications
- Infrastructure & Integration
- Prototype Testing and commissioning

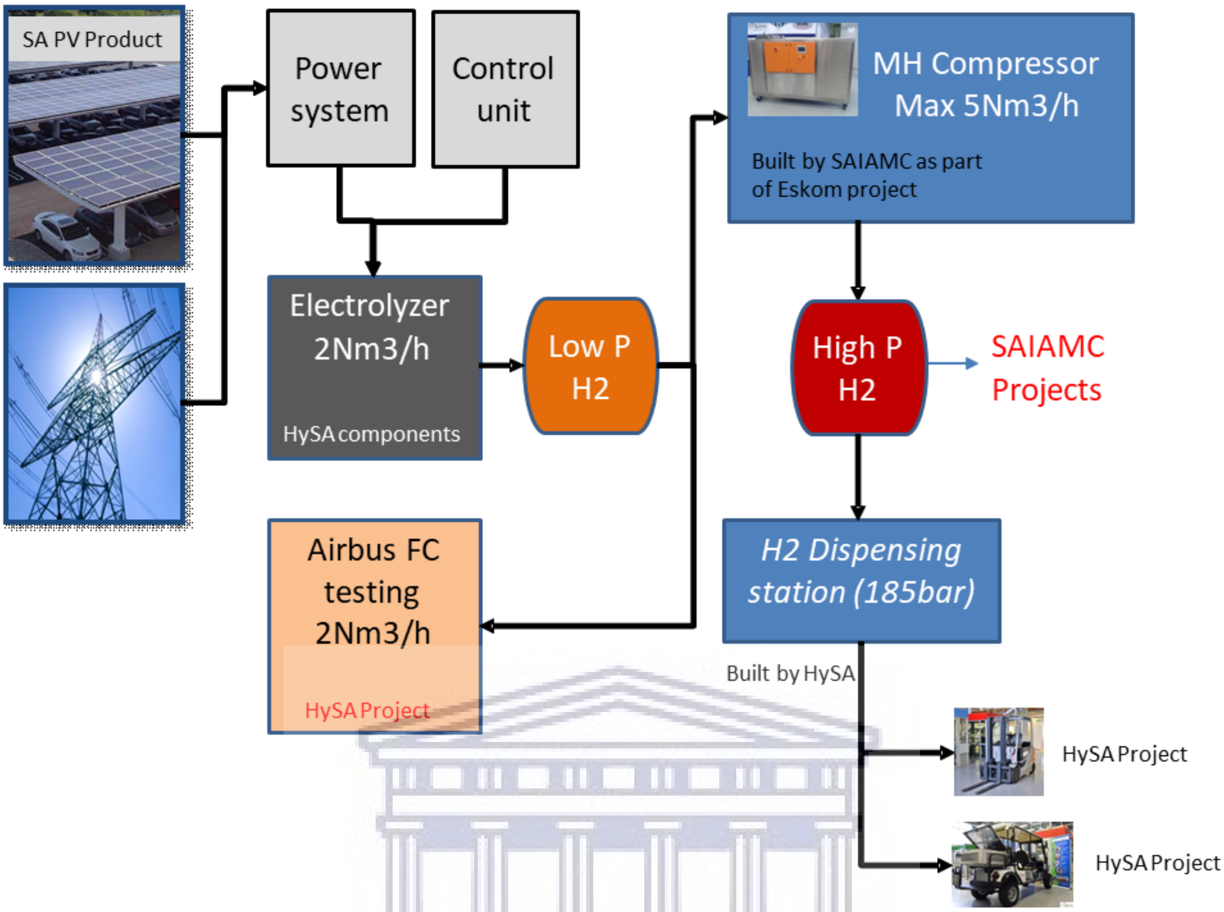


Figure 14: Project concept Overview

Following the project concept overview in Figure 14, a critical thinking process begins. During this phase, the design of the PEM electrolyser system commenced. The system is broken down into the following subsystems:

- Stack specification
- Cooling system
- Water supply
- Design of balance of plant

The PEM water electrolyser block diagram in Figure 15 evolved following the project concept overview in Figure 14. A detailed process and instrumentation diagram detailing all processes and controls is summarised in Figure 23.

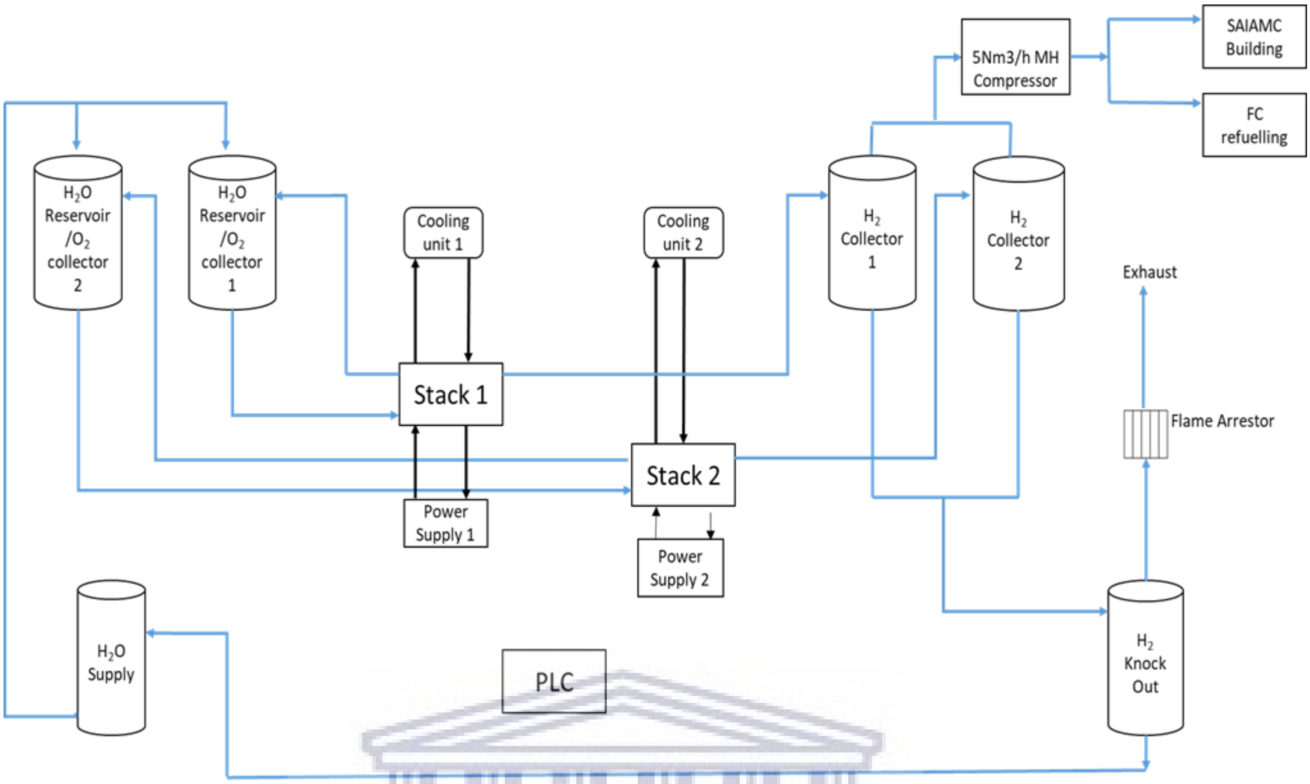


Figure 15: PEMWE System Block diagram

a. STACK SPECIFICATIONS

The project specification requires a stack that can produce hydrogen at 2 Nm^3/h, a discharge pressure of 20 bars and a power rating of average of 4.3kW. The stack specifications are specific because the hydrogen produced by the system is designed to be consumed downstream by SAIAMC projects, FC testing systems and refuelling fuel cell prototypes. A commercial stack with the above specification was sourced from prospective suppliers. The specifications were given out to international reputable companies for electrolyser suppliers namely:

- Hydrogenics,
- Proton,
- Pure Energy Centre and
- Hydron Energy B.V.

A number of challenges were encountered, some suppliers could not quote only on the stack, and they wanted to supply a complete Electrolyser stack unit due to various reasons which include the issue of intellectual property rights on stack design, loss of business and after sales technical support. Only three companies managed to quote on the specification provided but under different business conditions. We evaluated the business conditions and the cost of the stack and we ominously chose the supplier Hydron Energy B.V based on the specifications, cost and business conditions. The specifications of the stack from Hydron is as follows:

Specifications EL100		
Electrolyser type	Polymer Electrolyte Membrane	
Stack model	EL100	
Number of cells	24	
	Specifications for 24 cell stack	
H_2 production rate (nominal)	1	Nm^3/hr
O_2 production rate (nominal)	0,5	Nm^3/hr
Maximum H_2 discharge pressure[2]	20	bar
Maximum O_2 discharge pressure	5	bar
Beginning of life (BoL)	4,3	kW
End of life (EoL)	5,8	kW
Stack efficiency (ηth - BoL at	84%	HHV
Power supply requirements	30 -60 VDC	0 -150 A
Ambient temperature range	5 - 40	°C
Stack temperature range	5 - 80	°C
Process water specification (a)	18 MΩ/cm	
Process water consumption	0,9	L/hr
Thermal conditioning fluid	DI- water, 50/50 ethylene	
Stack Dimensions (HxWxD)	300 x 154 x 154	mm
Stack Weight	30	kg

Table 10 Stack Specifications

In order to meet the system output production of $2Nm^3/H$, two of the EL100 stacks were purchased and integrated into the prototype HySA PEM Electrolyser system.

The image of the EL100 stack top view is as follows:

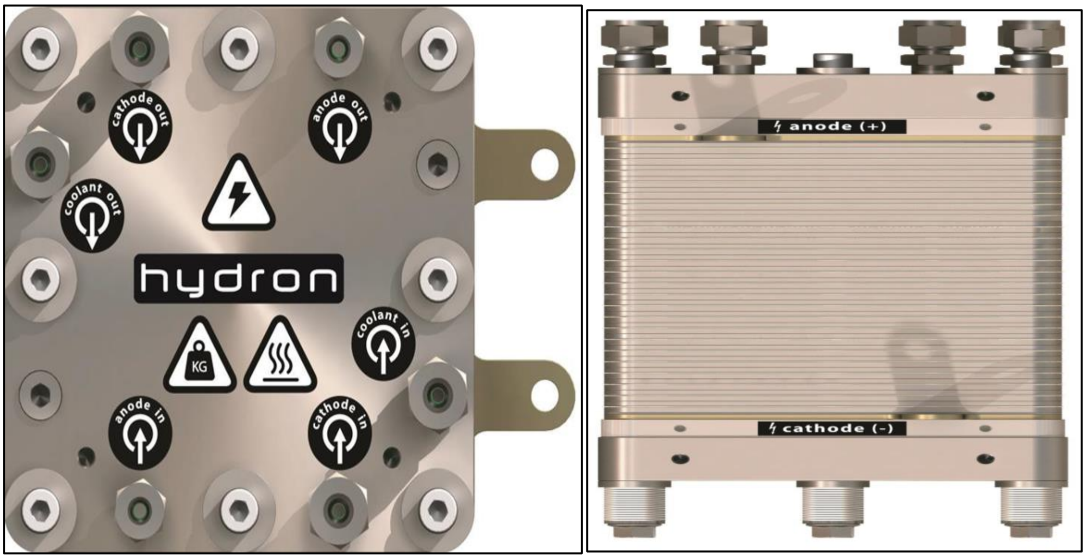


Figure 16: Process connections of the EL100 cell stack Sticker nearest to fitting designates the process connection

The EL100 stack features 6 process connections (see Figure 16), which are identified by stickers:

- **Anode in:** process water inlet
- **Anode out:** oxygen / process water outlet
- **Cathode in:** process water inlet (if cathode process water circulation is adopted, otherwise the connection can be utilised as a hydrogen / proton water discharge)
- **Cathode out:** hydrogen / proton water discharge
- **Coolant in:** thermal exchange fluid inlet
- **Coolant out:** thermal exchange fluid outlet

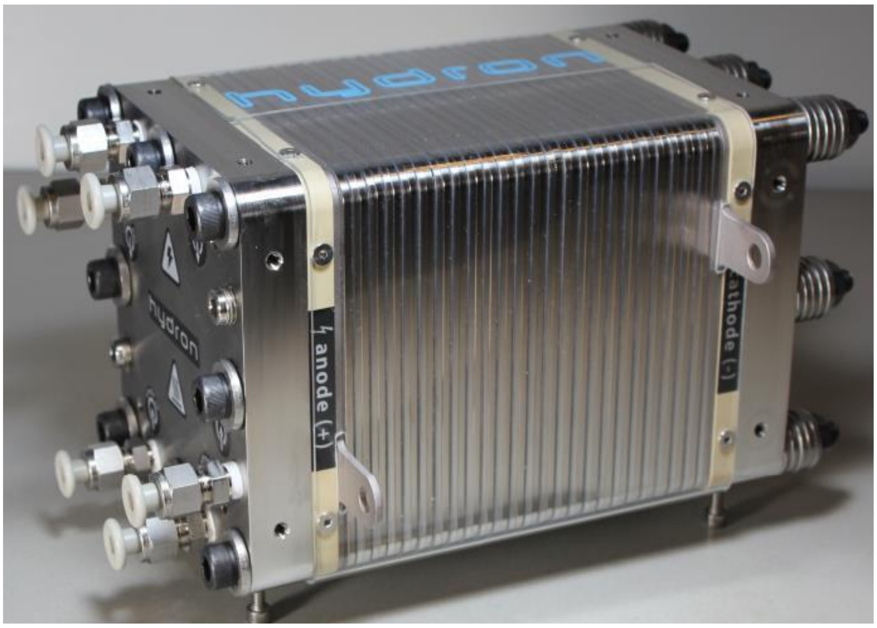


Figure 17: EL 100 Stack

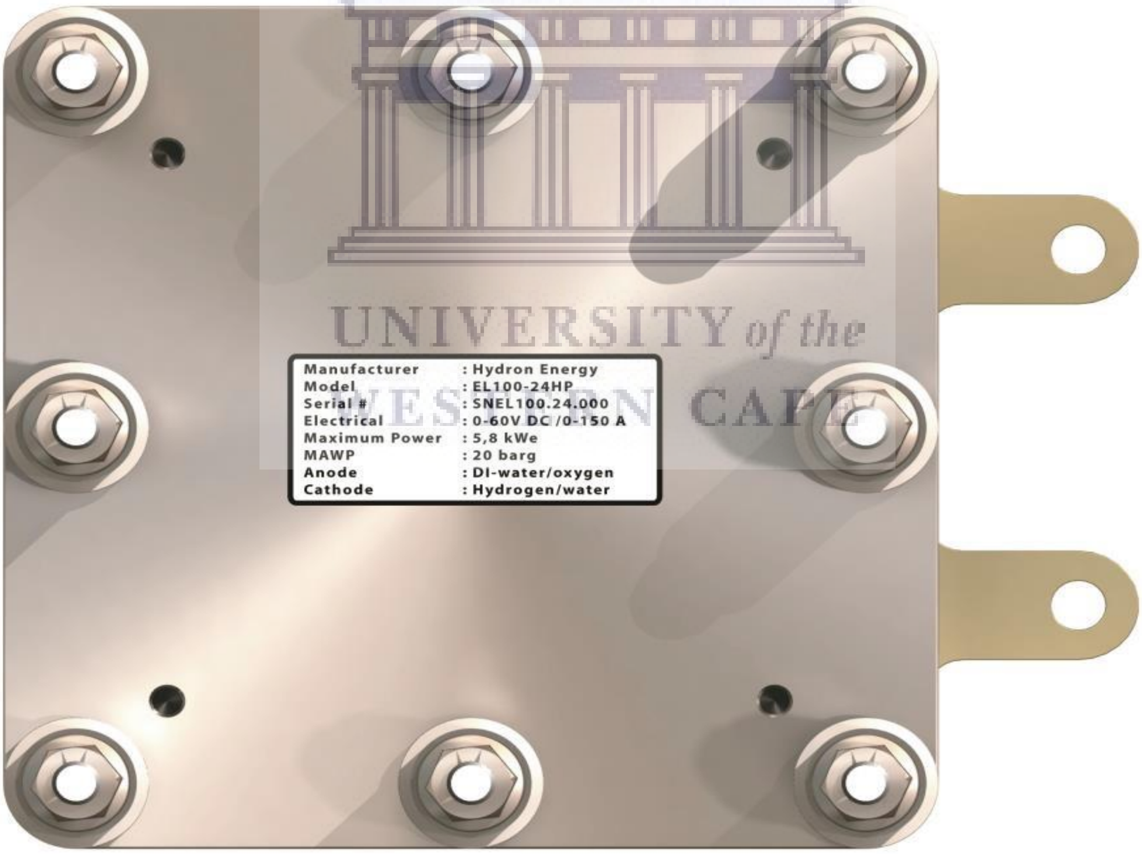

Manufacturer : Hydron Energy
Model : EL100-24HP
Serial # : SNEL100.24.000
Electrical : 0-60V DC /0-150 A
Maximum Power : 5,8 kWe
MAWP : 20 barg
Anode : DI-water/oxygen
Cathode : Hydrogen/water

Figure 18: Type plate and electrical leads of the EL100 stack

b. COOLING SYSTEM

The cooling system is essential in order to manage heat within the stack during operation. Below is the design of the cooling system that will ensure that the stack temperature does not go beyond 80°C in operation.

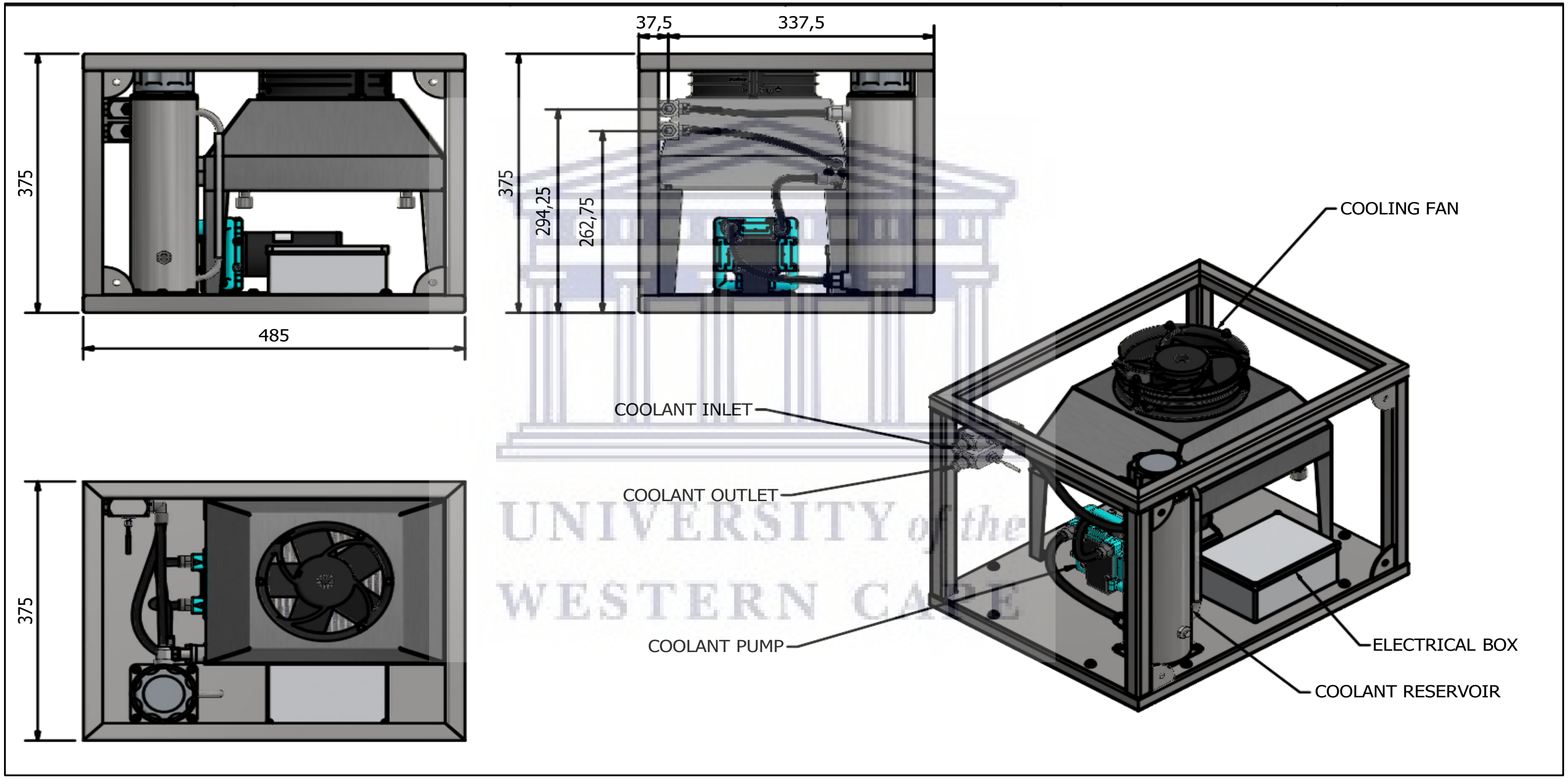


Figure 19: Stack cooling System

The water electrolysis process generates heat as current is applied to the EL100 stack. The production of excess heat is related to the rated current (Ohmic heating). Therefore a thermal management subsystem should be applied in the electrolysis system. The EL100 stack features a dedicated thermal management means: the exchanging of excess process heat is facilitated by circulating thermal conditioning fluid through the stack.

A coolant inlet and outlet process port is available on the stack. The maximum operational temperature of the stack is 80˚C. The set points for the coolant inlet and outlet temperature are related to the operational temperature of the stack and the flow rate of the cooling. The heat production by the process can be calculated by assuming a thermal efficiency of approximately 20% as specified by Hydron Energy.

c. WATER SUPPLY SYSTEM

Hydron Energy recommends to supply the anode loop with Ultra-Pure Water (UWP) of 18 MΩ/cm quality. The stack should not be operated with water with a higher conductivity than 1, 5 µS/cm. Operation the EL100 stack with process water above this conductivity will lead to rapid degradation of the internal parts and will irreversibly decrease lifetime of the EL100 stack.

Continuously monitor the process water quality and trip at the threshold value of 1,5 µS/cm once reached. A Milli-Q water purification system was used to supply water to the Electrolyzer system. It produces Type 1 ASTM water (18 MΩ), which provides substantially low conductivity of the water required. The water supply system design below:

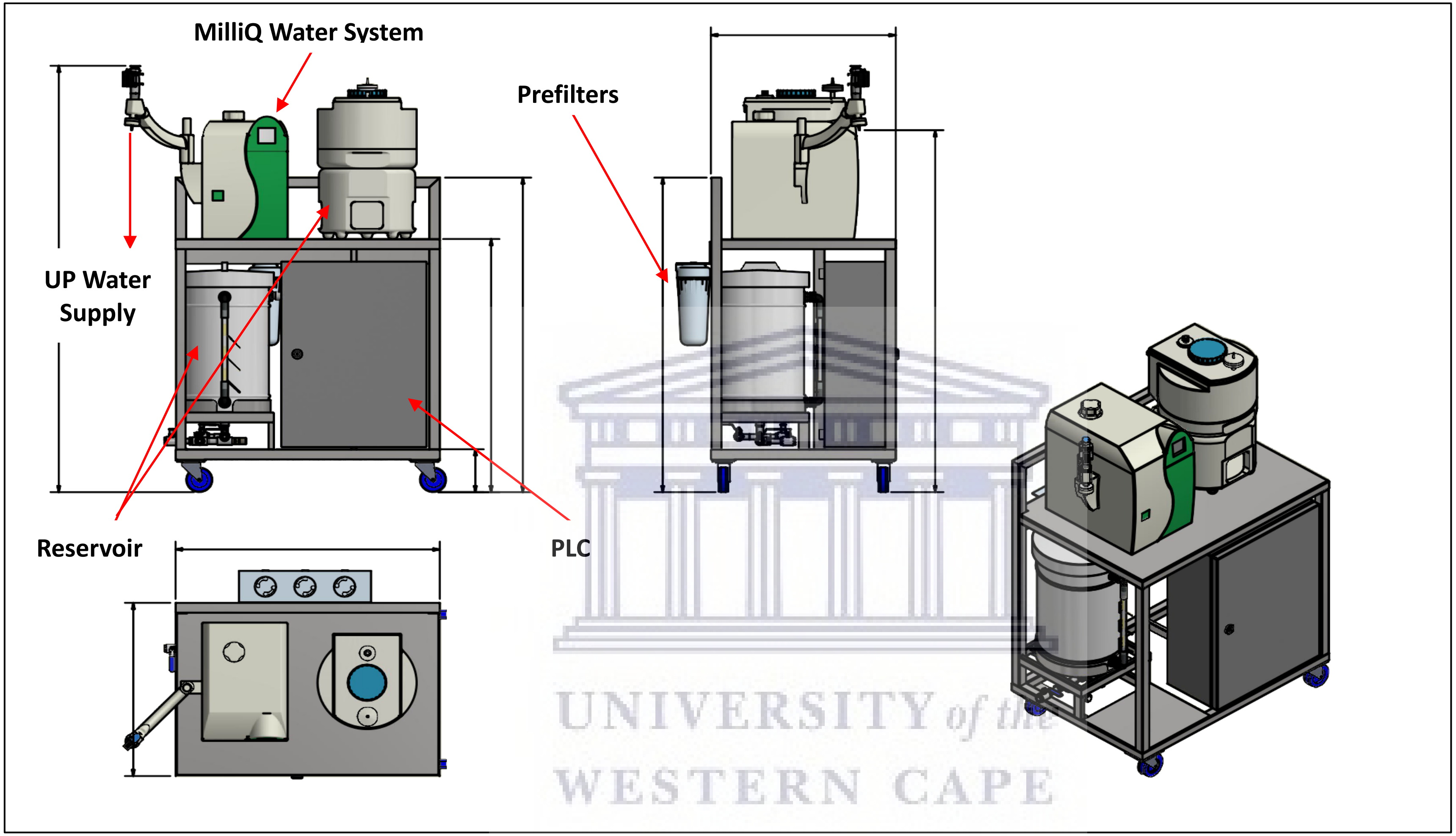


Figure 20: Ultra-pure water supply system

d. BALANCE OF PLANT

A PEM water electrolysis stack operated with Balance of Plant components. Below a basic process and instrumentation diagram for a PEM, water electrolysis system (Figure 21).

The prototype system is comprised of the following subsystems

- Water/oxygen subsystem
- Hydrogen subsystem
- Feed water subsystem
- Thermal management subsystem
- Electrical subsystem
- Control subsystem
- Electrical layout

e. HYSA SYSTEMS PEMWE PROTOTYPE P&ID

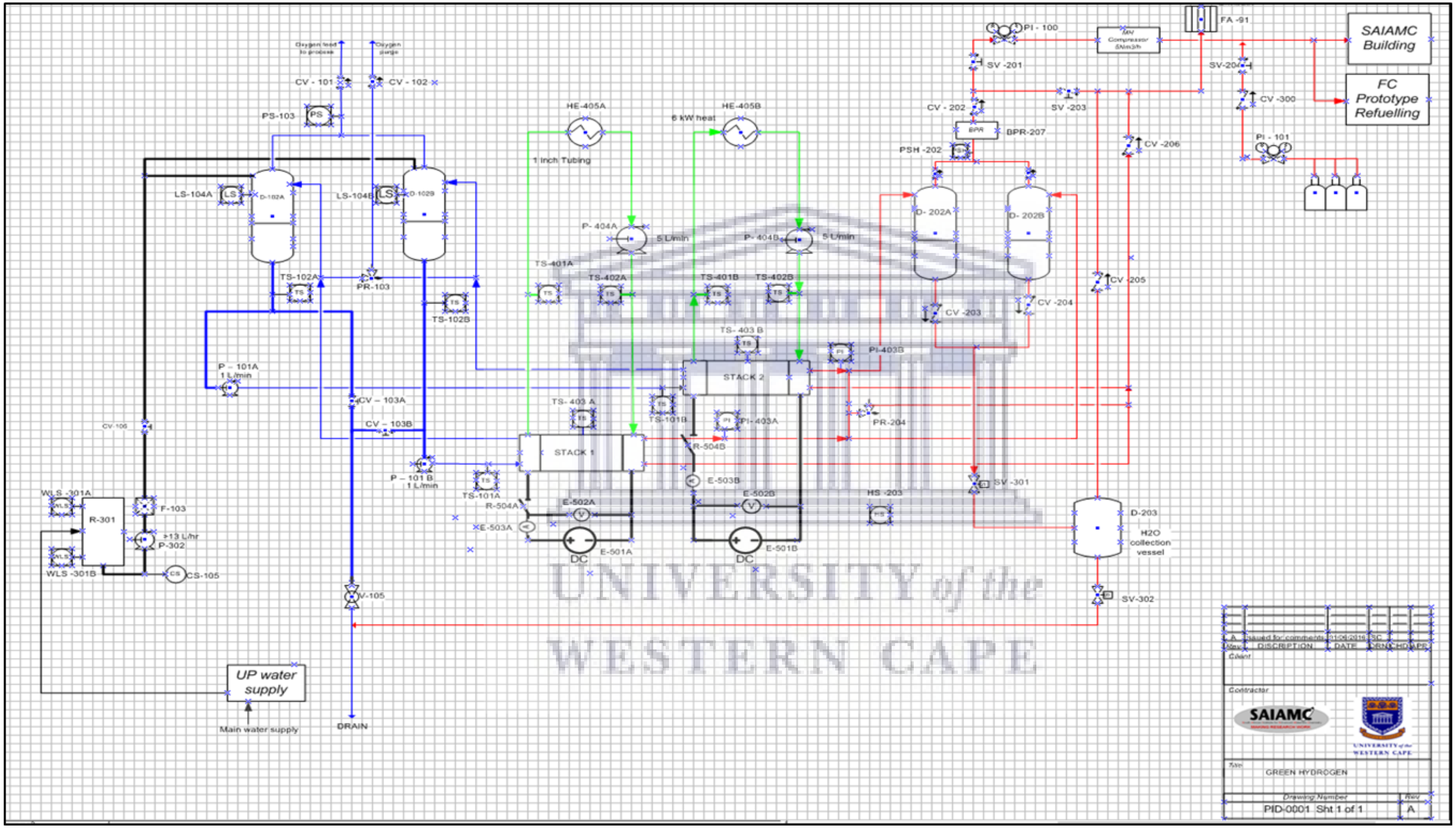


Figure 21: Process and instrumentation diagram (P&ID) PEMWE

f. HYSA SYSTEMS PEMWE PROTOYPE ASSEMBLY LIST AS PER P&ID

Subassembly	P&ID tag	Function
0. electrolyser stack	n/a	PEM water electrolysis stack
1. water/oxygen subsystem		
main gas solenoid valve	CV-101	opens/closes off oxygen flow to application
check valve	CV-102	prevents backflow into anode loop
purge solenoid valve		opens/closes off oxygen flow to purge
check valve / flame arrestor	CV-103	prevents backflow into anode loop/ flash back
manual drain valve water	V-105	drains process water loop
pressure relief valve	PR-103	prevents pressure build up in anode loop above threshold
temperature sensor stack in	TS-101A TS- 101B	measures process water temperature entering the stack
temperature sensor stack out	TS-403A TS-403B	measures process water temperature exiting the stack
pressure sensor oxygen	PS-103	measures oxygen/process water pressure in anode loop
level sensor water	LS-104A	measures process water upper level in D-102
Level sensor water	LS- 104B	measures process water lower level in D-102
conductivity sensor	CS-105	measures conductivity of process water
water circulation pump	P-101A	circulates process water through stack
water circulation pump	P-101B	circulates process water through stack
water/gas separator	D-102	separates process water and oxygen
water polishing filter	F-103	keeps water quality at specification (low conductivity)
2. hydrogen subsystem		
main gas solenoid valve	SV-201	opens/closes off hydrogen flow to application
check valve check valve / flame arrestor	CV-202	prevents back flow into cathode loop / flash back
purge solenoid valve	SV-203	opens/closes off hydrogen flow to purge

check valve / flame arrestor	CV-206	prevents backflow into cathode loop/ flash back
automatic drain valve condensate	SV-301	actively drains proton water out D-202
back pressure regulator	BPR-207	regulates cathode pressure in stack
pressure relief valve	PR-204	prevents pressure build up in cathode loop above threshold
temperature sensor	TS-201	measures water temperature of cathode
pressure sensor hydrogen	PSH-202	measures hydrogen pressure in cathode loop
hydrogen sensor	HS-203	measures hydrogen concentration in process Cabinet
water/gas separator	D-202	separates proton water and hydrogen
Check Valve	CV-203	Prevents backflow into water/gas separator D202A
Check Valve	CV-203	Prevents backflow into water/gas separator D202B
Pressure Indicator	PI-403A	Measures pressure of hydrogen from the stack 1
Pressure Indicator	PI-403B	Measures pressure of hydrogen from the stack 2
ion exchange filter	F-203	keeps proton water quality at specification (low conductivity)
check valve	CV-206	prevents backflow of process water
3. feed water subsystem		
level sensor feed water reservoir	WLS-301A	measures process water upper level in R-301
level sensor feed water reservoir	WLS-301B	measures process water lower level in R-301
feed water pump	P-302	feeds anode loop with process water loop
feed water reservoir	R-301	provide storage for process water
check valve	CV-303	prevents back flow of process water to R-301
4. thermal management subsystem		
temperature sensor cooling in	TS-401A	measures coolant temperature entering the stack 1

temperature sensor cooling in	TS-401B	measures coolant temperature entering the stack 2
temperature sensor cooling out	TS-402A	measures coolant temperature exiting the stack 1
temperature sensor cooling out	TS-402B	measures coolant temperature exiting the stack 2
temperature sensor stack	TS-403A	measures stack temperature stack 1
temperature sensor stack	TS-403B	measures stack temperature stack 2
coolant pump	P-404A	circulates coolant trough stack 1 and heat exchanger
coolant pump	P-404B	circulates coolant trough stack 2 and heat exchanger
heat exchanger	HE-405A	radiates excess heat of stack 1
heat exchanger	HE-405A	radiates excess heat of stack 2
5. electrical subsystem		
power supply	E-501A	provides DC power to stack 1
power supply	E-501B	provides DC power to stack 2
voltage sensor	E-502A	measures stack voltage Stack 1
voltage sensor	E-502B	measures stack voltage Stack 2
current sensor	E-503A	measures stack current Stack 1
current sensor	E-503B	measures stack current Stack 2
high power relay	R-504A	circuit breaker for emergency shutoff
high power relay	R-504B	circuit breaker for emergency shutoff

Figure 22: Equipment list

g. ELECTROLYSER ELECTRICAL CONNECTIONS LAYOUT

In order to supply power to the stack as per manufactures requirements and the various balance of plant equipment they is a need of two distinct power supplies. The first power supply is a dedicated power supply for each stack 1 & 2. The second power supply is for the various balance of plant equipment. Below is a list of electrical connections layout which includes:

i. Stack electrical connections
ii. Anode water supply pumps electrical connections
iii. PLC + Display & General Power supply
iv. Solenoid valves & Pressure Transducer Electrical Connections
v. Fans and Relays Electrical Connections

i. STACK ELECTRICAL CONNECTIONS

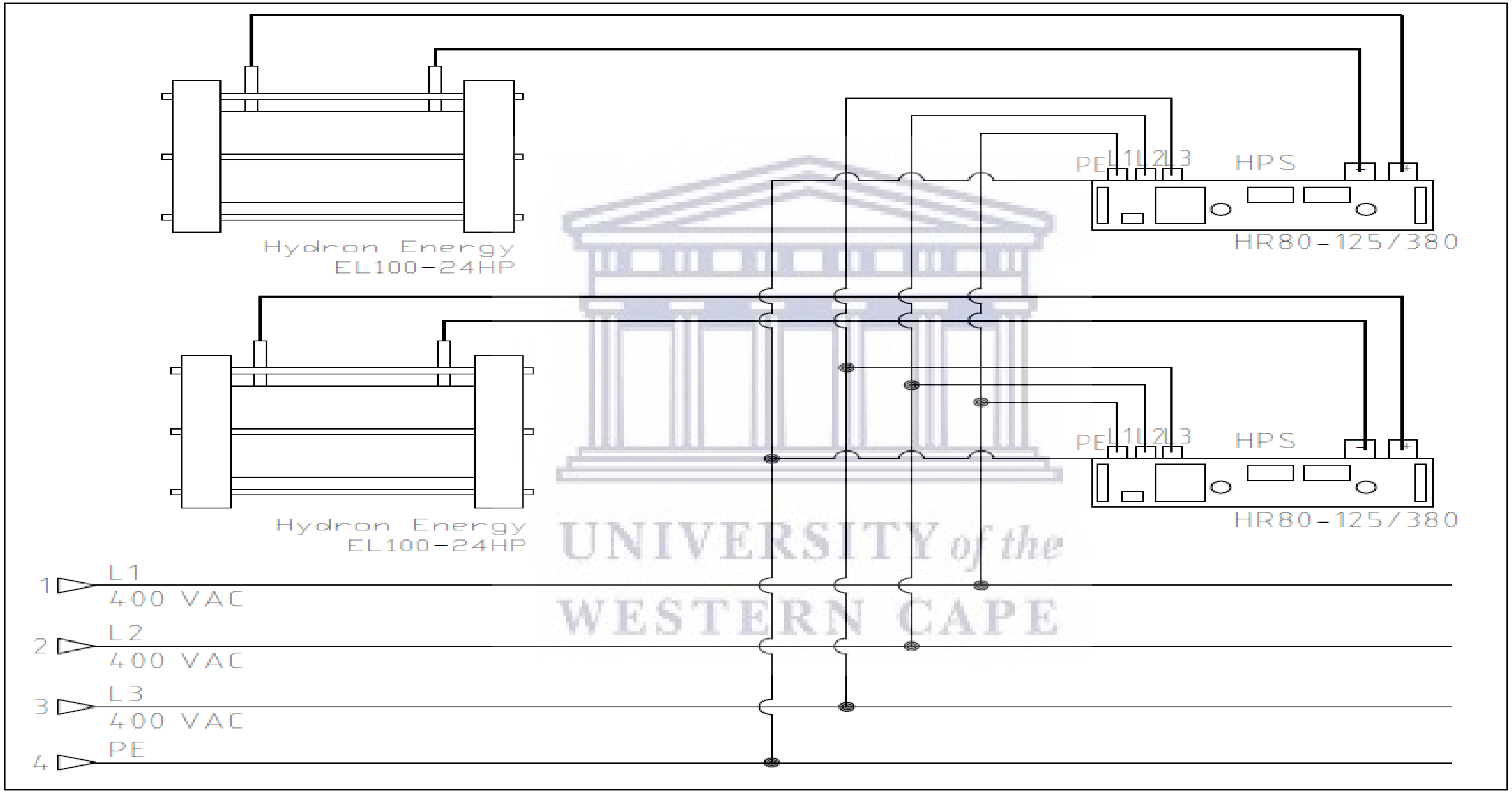


Figure 23: Stack Electrical Connections

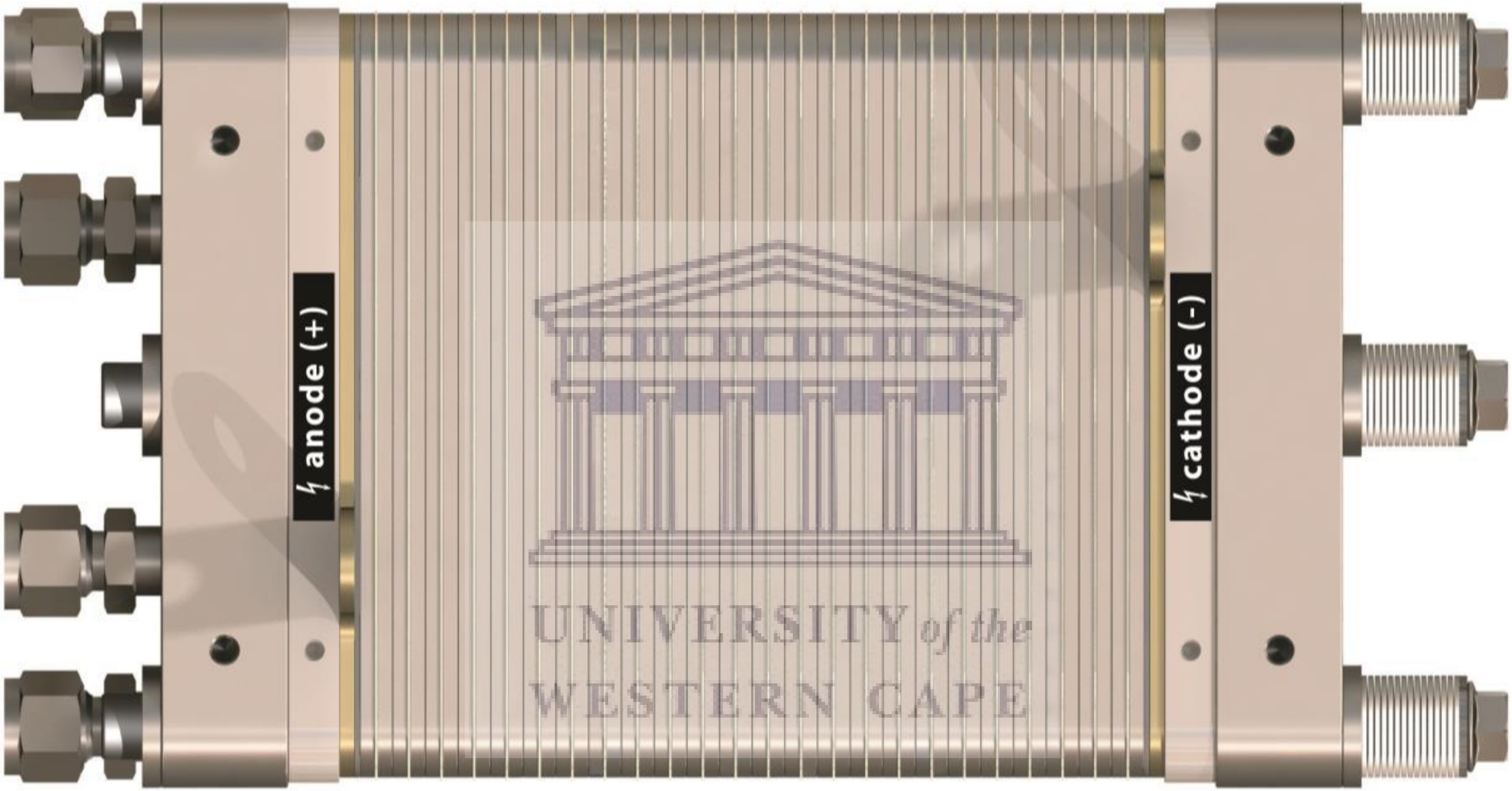


Figure 24: Electrical leads of EL100 stack positive and negative polarity designated by sticker. Electrical grounding of stack facilitated by M6 bores of stainless steel compression plates

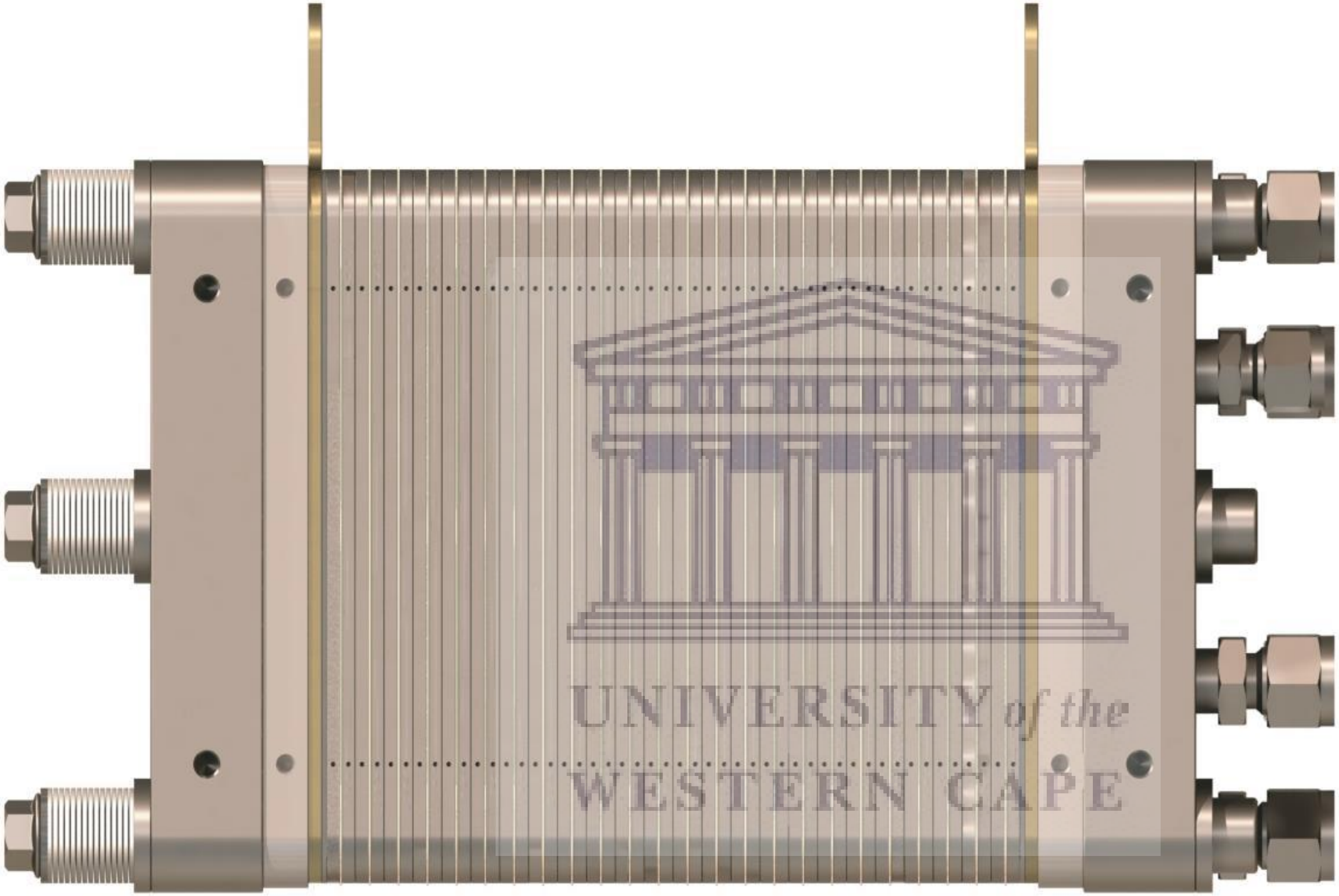


Figure 25: Cell Voltage Monitoring & thermocouples; the bores can feature voltage probes, temperature sensors

ii. ANODE WATER SUPPLY PUMPS ELECTRICAL CONNECTIONS

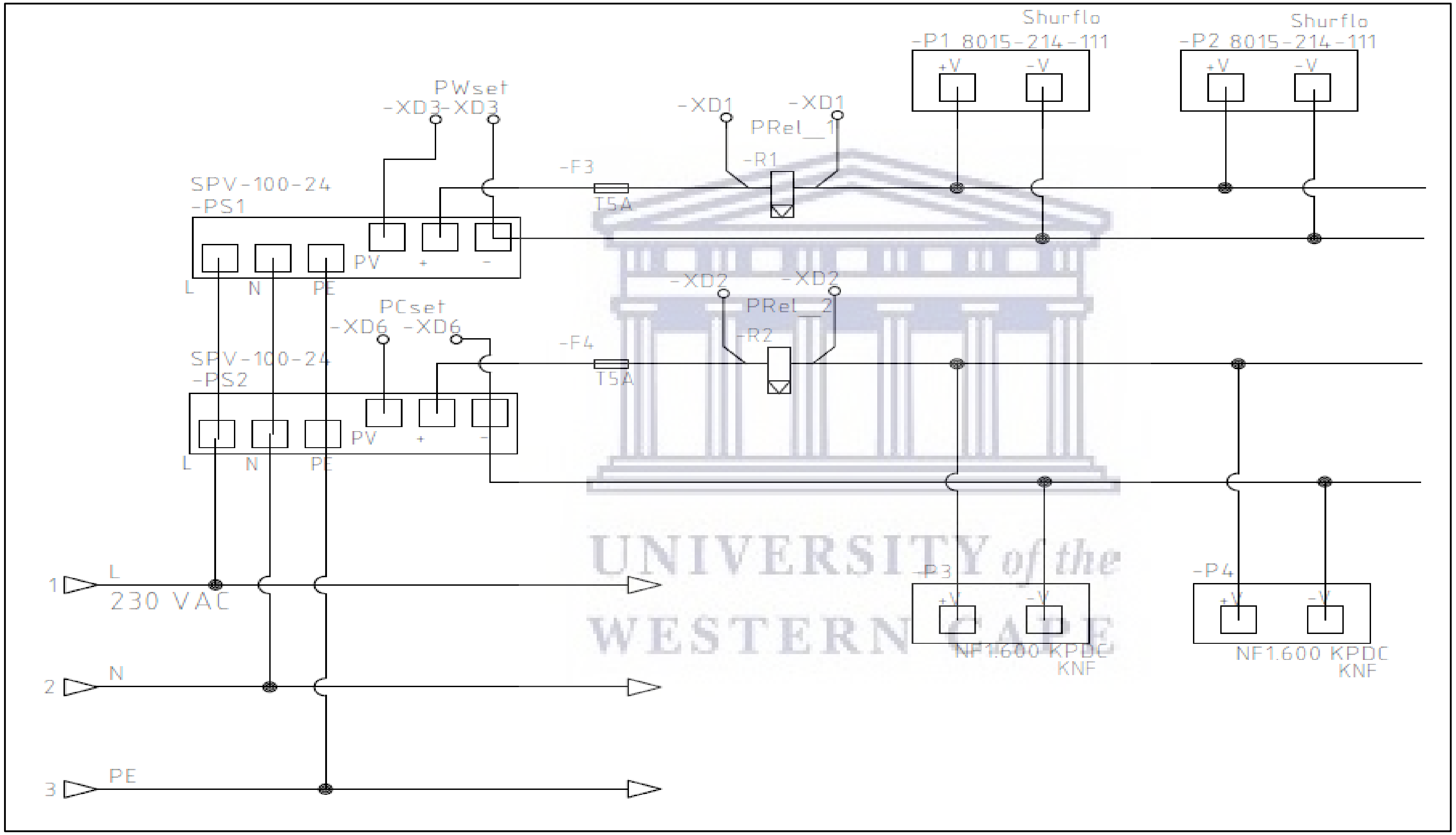


Figure 26: Anode water supply pumps Electrical connections

iii. PLC + DISPLAY & GENERAL POWER SUPPLY

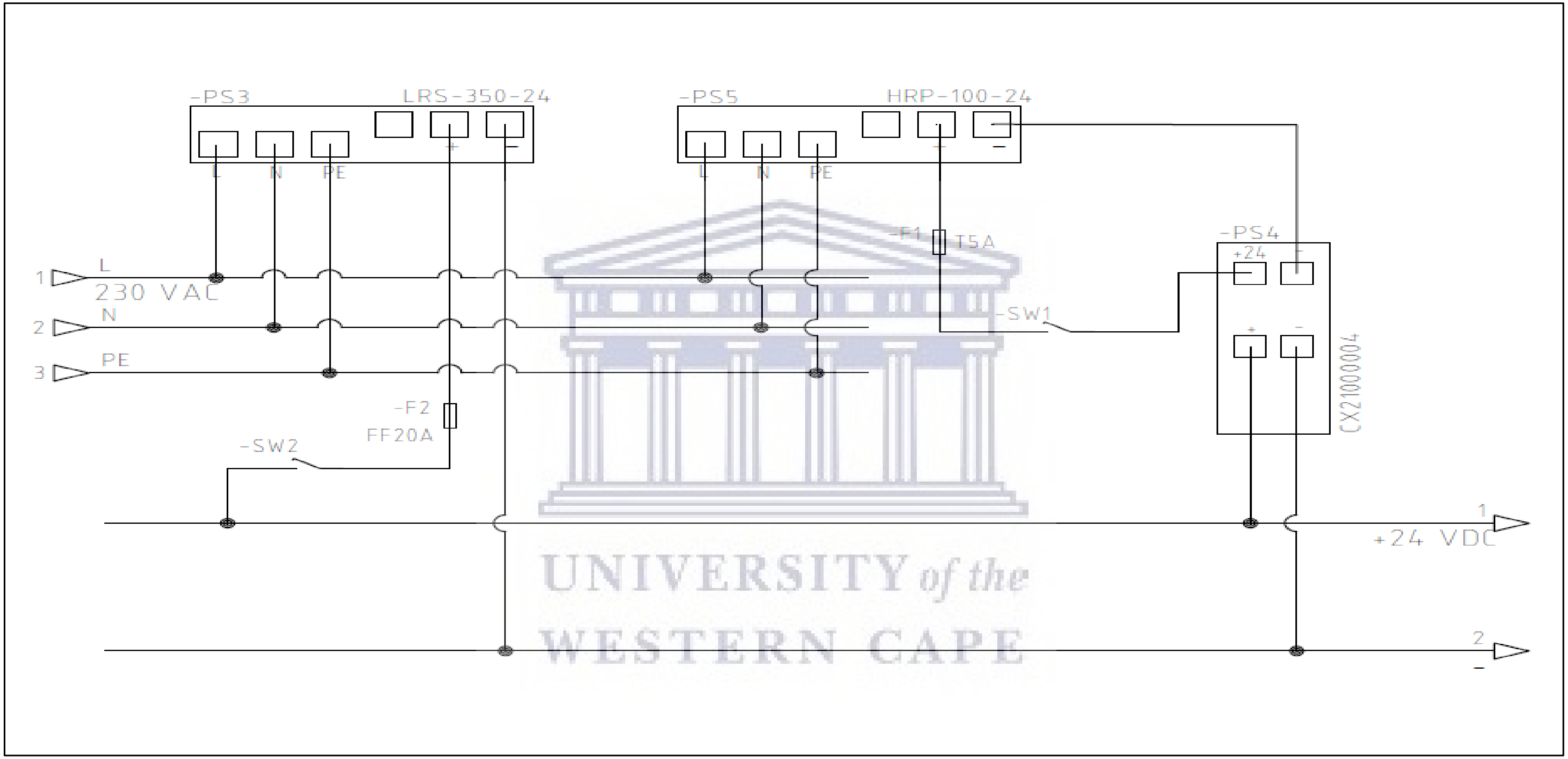


Figure 27: PLC + Display & General Power supply

iv. SOLENOID & PRESSURE TRANSDUCER ELECTRICAL CONNECTIONS

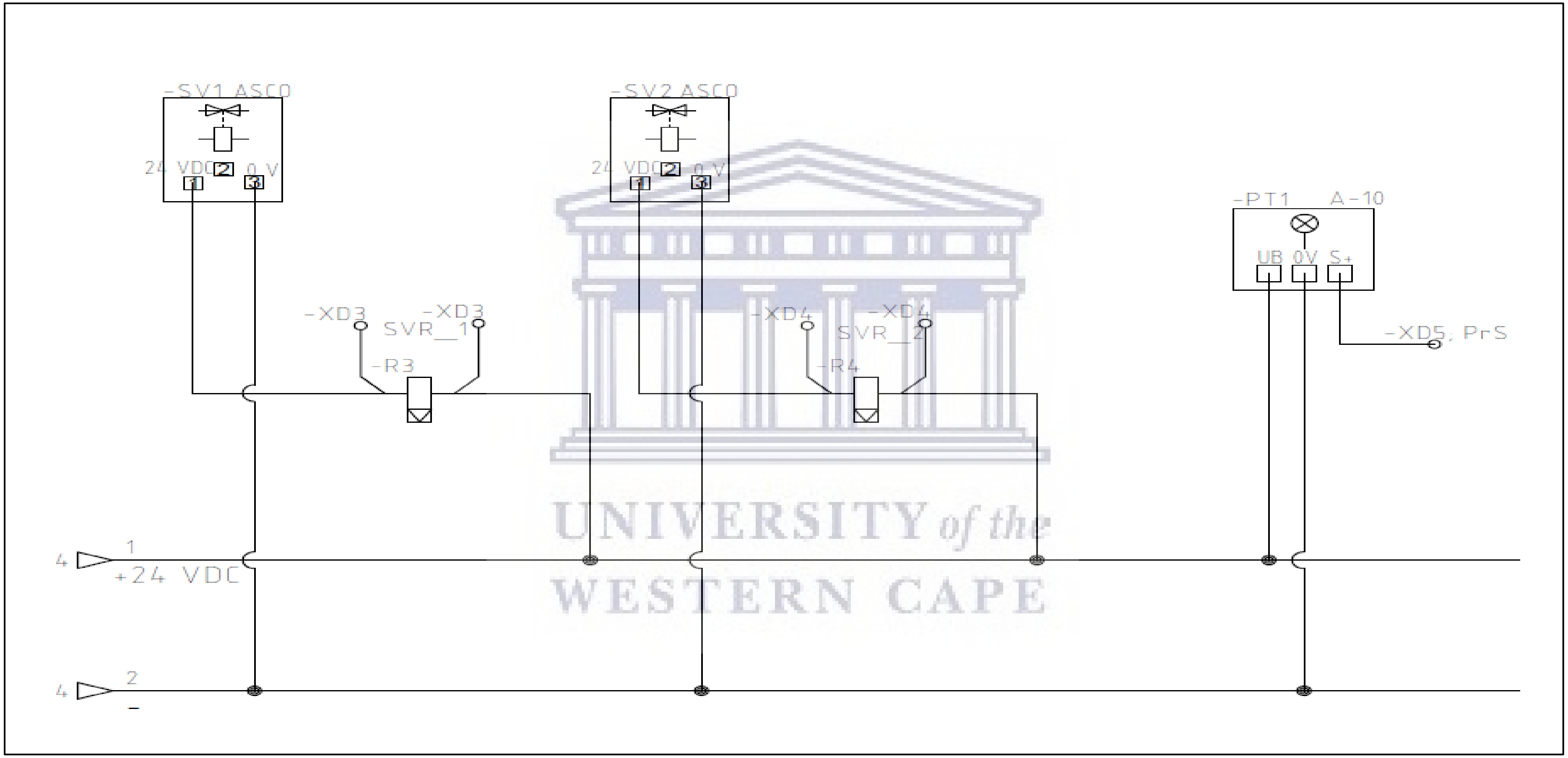


Figure 28: Solenoid valves & Pressure Transducer Electrical Connections

v. FANS AND RELAYS ELECTRICAL CONNECTIONS

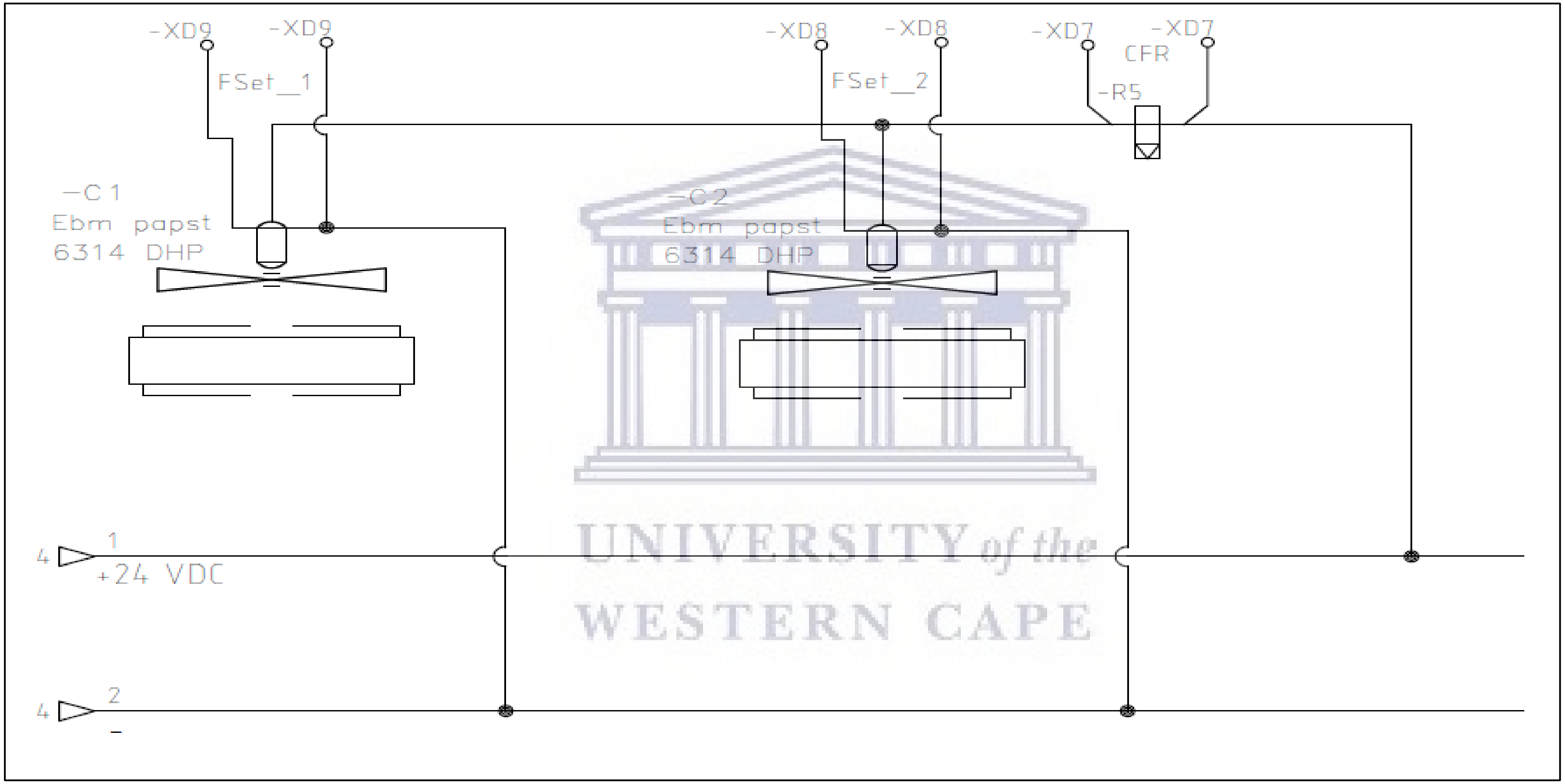


Figure 29: Fans and Relays Electrical Connections

3.2 INTEGRATION PHASE 1

During this phase the Prototype water Electrolyzer was constructed together with the balance of plant as per design specifications. All material and connections are put together and resulted in the following system:

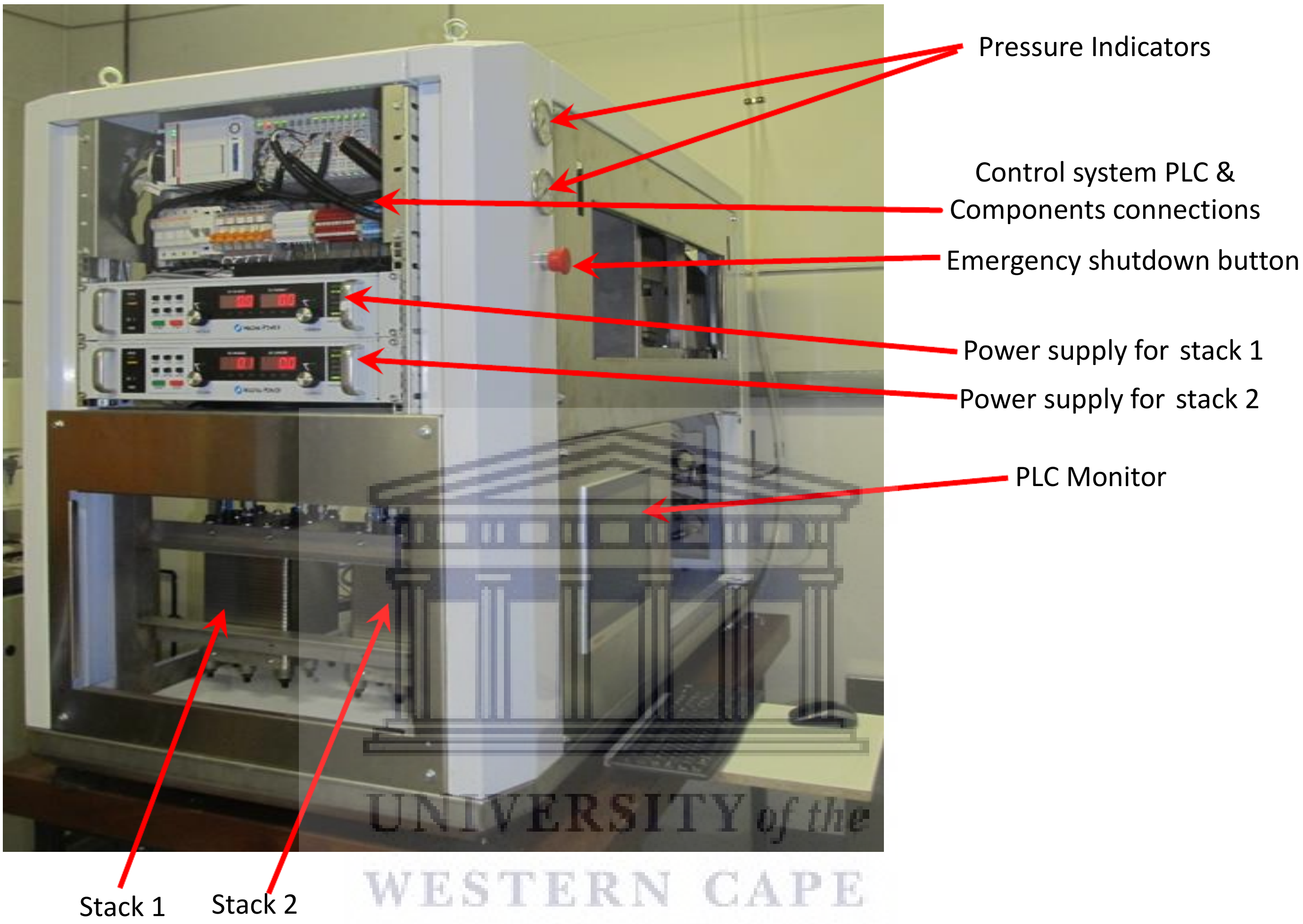
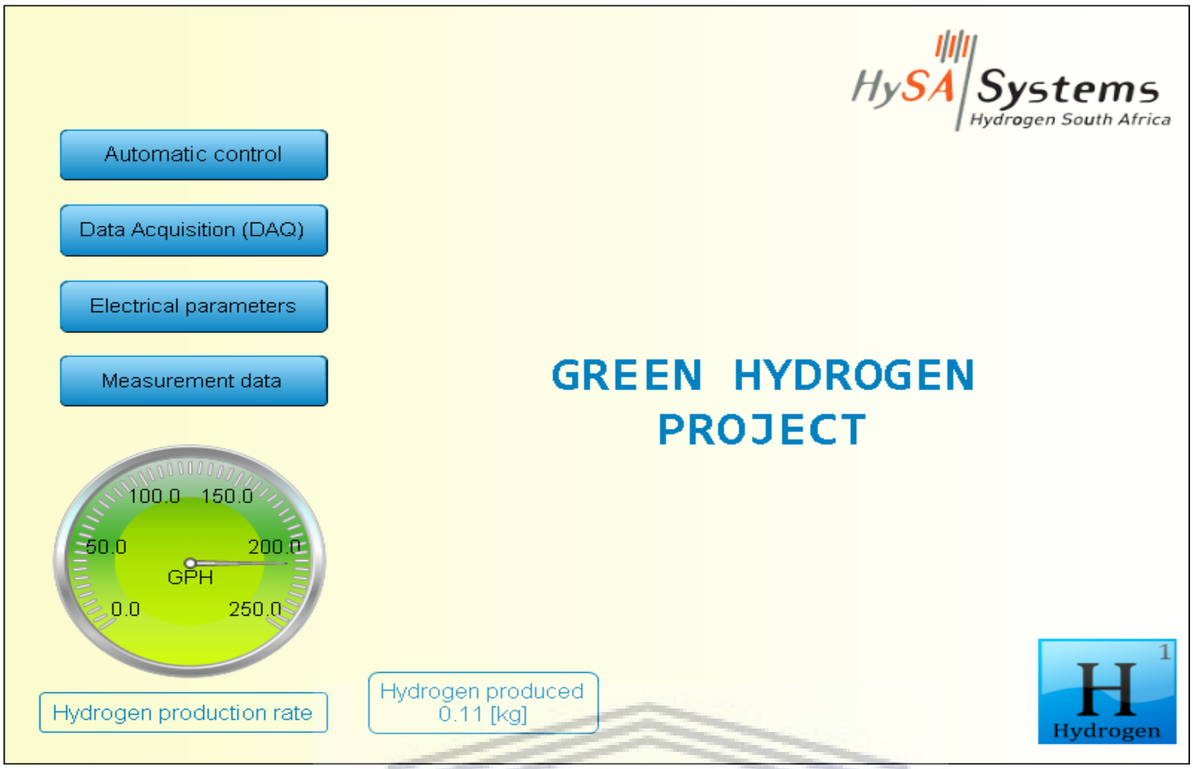


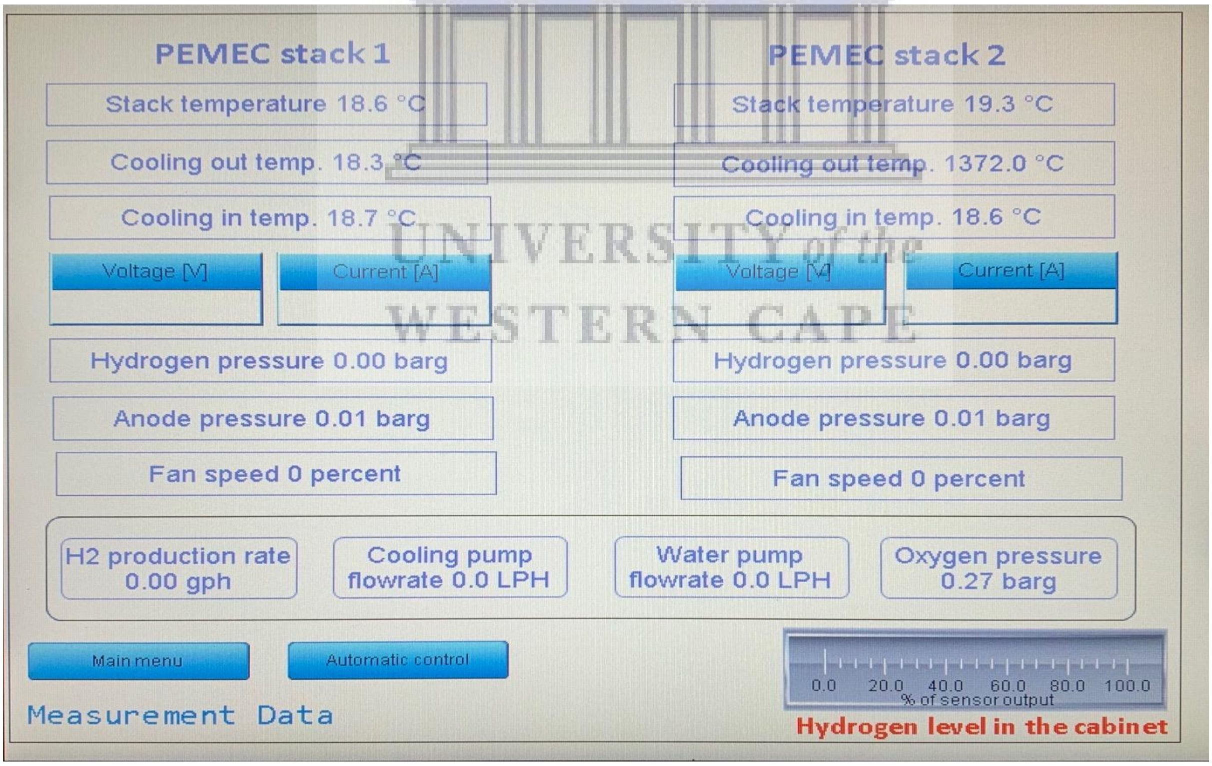
Figure 30: HySA systems PEM Water Electrolyser Overview



GREEN HYDROGEN PROJECT

Hydrogen produced 0.11 [kg]

Figure 31: HySA systems PEMWE PLC home screen



PEMEC stack 1

Stack temperature 18.6 °C

Cooling out temp. 18.3 °C

Cooling in temp. 18.7 °C

Hydrogen pressure 0.00 barg

Anode pressure 0.01 barg

Fan speed 0 percent

PEMEC stack 2

Stack temperature 19.3 °C

Cooling out temp. 1372.0 °C

Cooling in temp. 18.6 °C

Hydrogen pressure 0.00 barg

Anode pressure 0.01 barg

Fan speed 0 percent

H2 production rate 0.00 gph

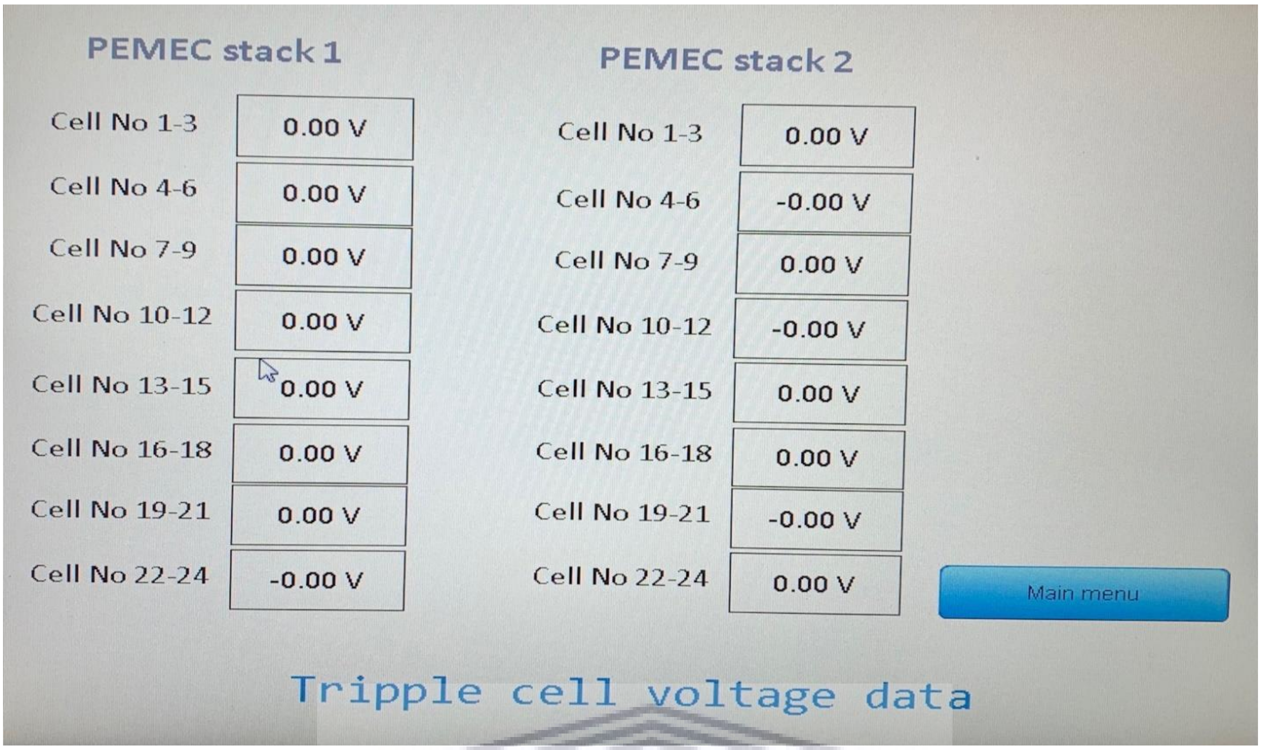
Cooling pump flowrate 0.0 LPH

Water pump flowrate 0.0 LPH

Oxygen pressure 0.27 barg

Measurement Data

Figure 32: HySA systems PEMWE PLC- Measurement Data screen



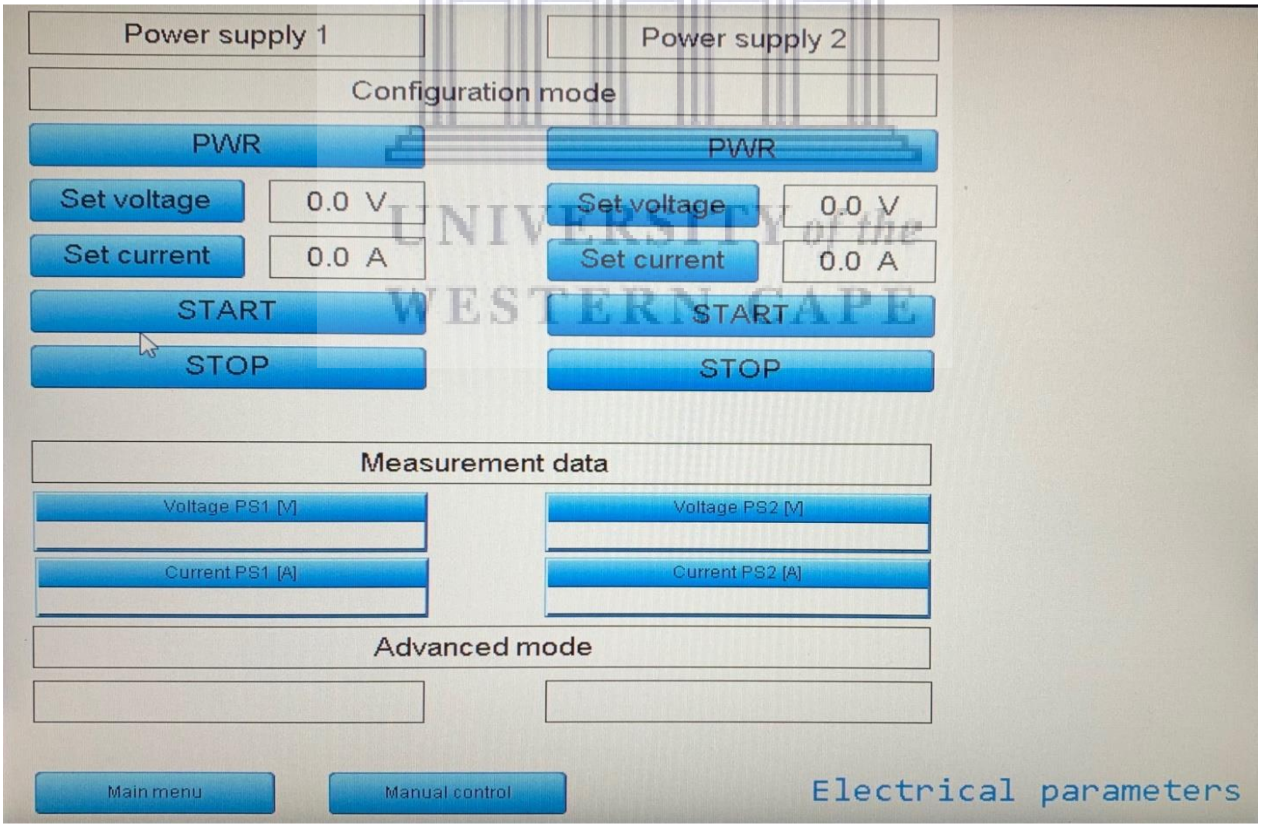
PEMEC stack 1

Cell No 1-3 0.00 V
Cell No 4-6 0.00 V
Cell No 7-9 0.00 V
Cell No 10-12 0.00 V
Cell No 13-15 0.00 V
Cell No 16-18 0.00 V
Cell No 19-21 0.00 V
Cell No 22-24 -0.00 V

PEMEC stack 2

Cell No 1-3 0.00 V
Cell No 4-6 -0.00 V
Cell No 7-9 0.00 V
Cell No 10-12 -0.00 V
Cell No 13-15 0.00 V
Cell No 16-18 0.00 V
Cell No 19-21 -0.00 V
Cell No 22-24 0.00 V

Figure 33: HySA systems PEMWE PLC- Cell Voltage screen



Power supply 1

Set voltage 0.0 V
Set current 0.0 A

Power supply 2

Set voltage 0.0 V
Set current 0.0 A

Figure 34: HySA systems PEMWE PLC- Electrical parameters screen

Figure 35: HySA Systems Prototype PEMWE Overview

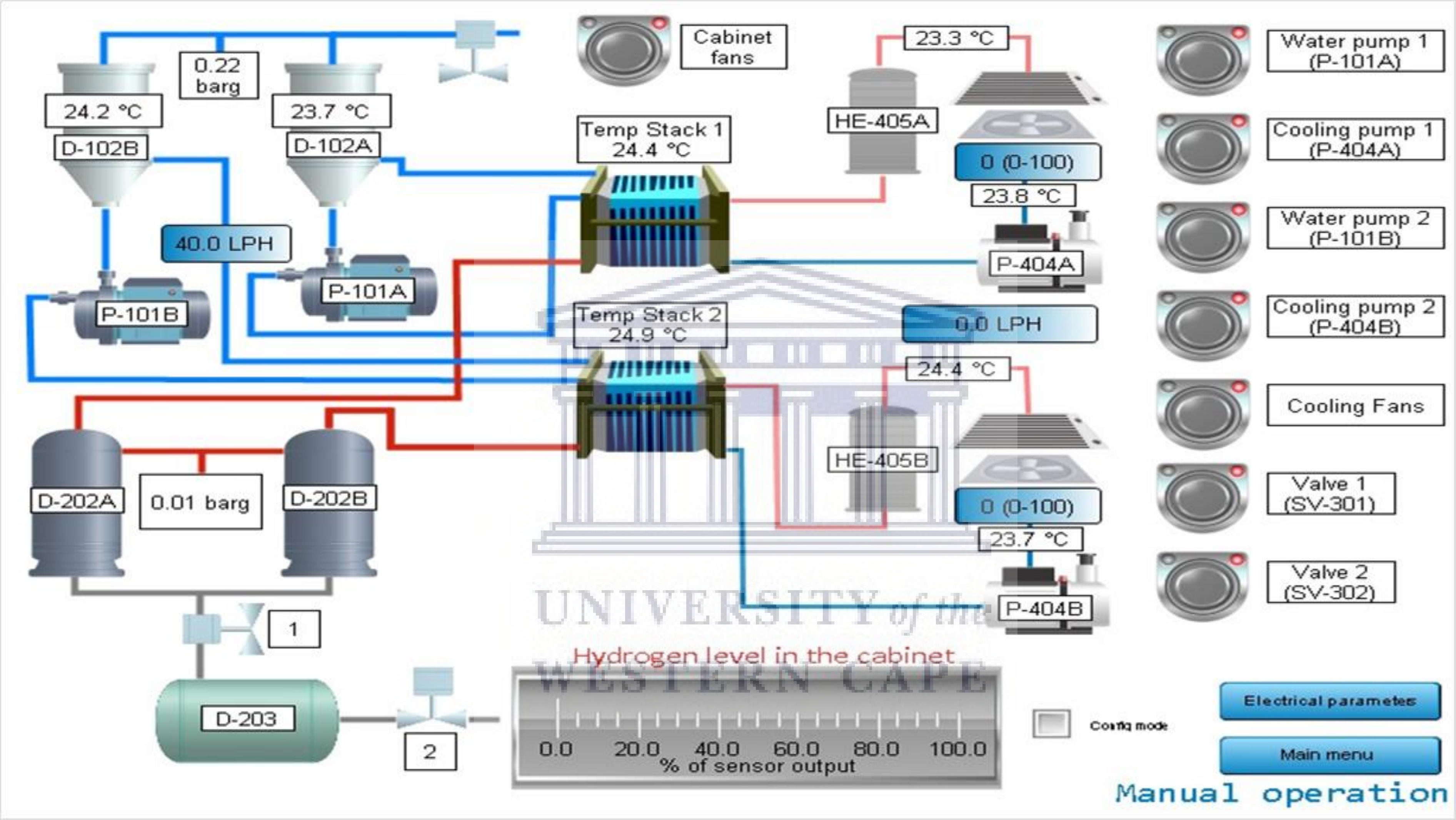


Figure 36: HySA Systems PEM Water Electrolyser prototype PLC windows

a. PROTOTYPE SYSTEM PLC OPERATION

The system operation window as shown in Figure 32 taken from the PLC. The prototype system was programmed to operate in either the automatic mode or manual mode from the PLC while an embedded data logger continually logs system data. Figure 33 shows system parameter loggings.

b. PLC CONTROLLER WITH DEDICATED ALGORITHM

The electrolysis system managed based on an implemented Programmable Logic Controller (PLC). It includes embedded personal Windows-based computer, signal input and output terminals (as well as digital and analogy for connections of measurement sensors and controlling of BoP devices), digital extension modules (including energy meter and data acquisition unit) and communication modules as well as based on internal communication protocol and external GSM/Ethernet-capable communication processor for remote management. Additionally, dedicated terminal couplers and 24 VDC power supplies installed according to the PLC architecture requirements. The basic control panel in the form of HMI display for on-site management and maintenance integrated with PLC controller.

PLC control algorithm written according to IEC 61131-3 standard and Structured Text (ST) - standardized programming language (Twin CAT environment). The general description of the algorithm structure depicted as a flowchart in Figure 38. The PLC controller operates in a closed infinite loop. Once the electrolyser switched on, the inspection of critical parameters takes place. This includes but is not limited to hydrogen leaking detection, maximum allowable output pressures of gases and temperature of the stacks, feed water pressure and temperature, cooling water presence, and PEM electrolysis cells voltage measured independently (every three cells combined).

If the failure detected, the system reconnects to the safe operational mode and the electrolysis process is suspended. Each cycle of the infinite loop triggers reading and writing of PLC terminals that includes temperature and pressure readings and setting of analog and digital voltage signals (e.g. water pumps, electric relays). Control algorithm includes both manual and automatic operation modes. The manual mode used in case of testing and maintenance while automatic mode is fully autonomous enabling the uninterrupted long-term operation. The system allows on sensitive data acquisition, writing CSV files as well as displaying data based on virtual or embedded HMI. Self-testing and remote upgrading of the control algorithm implemented in the system to optimise system efficiency.

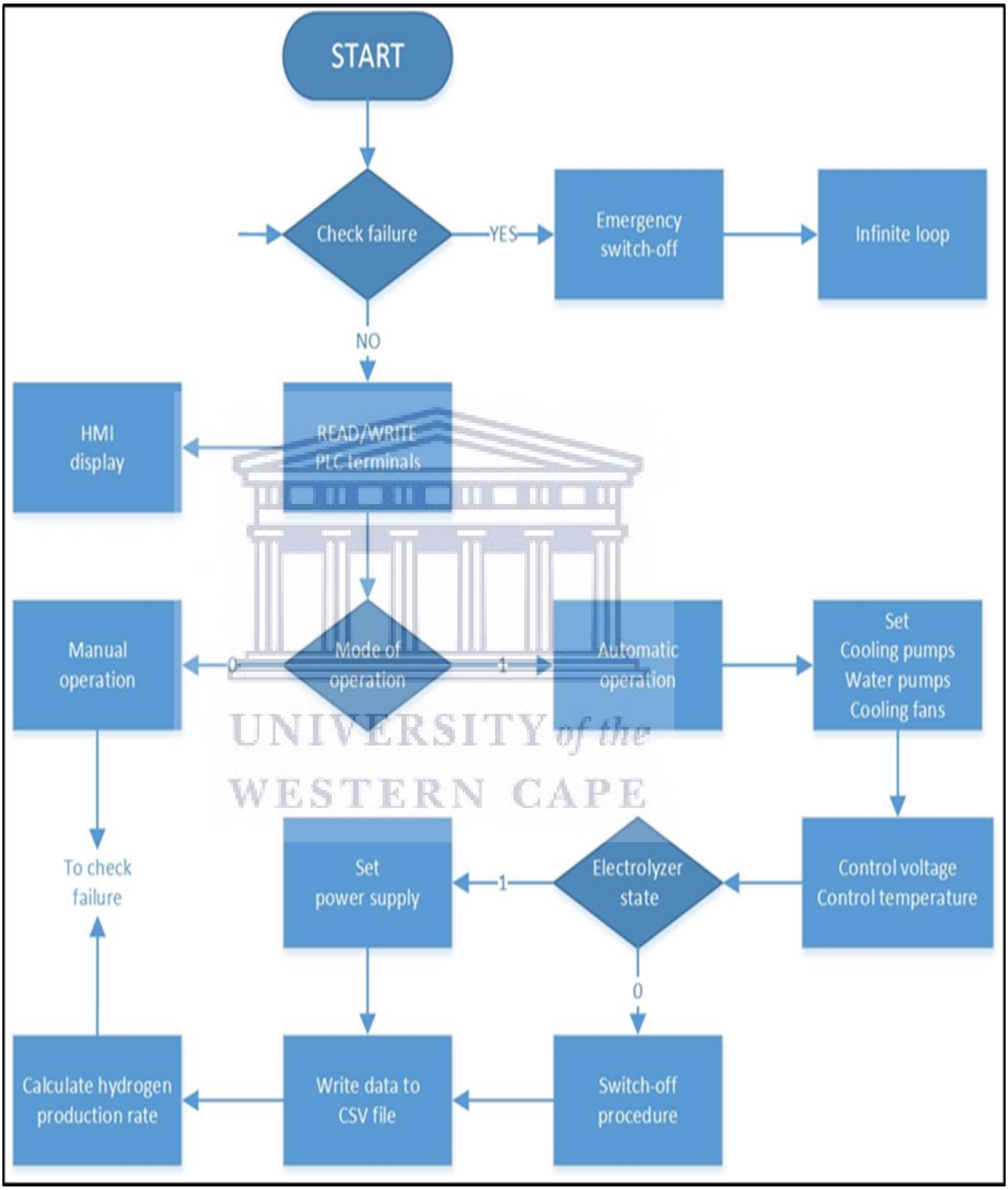


Figure 37 Flowchart of control algorithm, PLC managed, manual or automatic operation

3.3 PROTOTYPE TESTING AND COMMISSIONING

After success integration of the prototype system a detailed operating manual was complied. Emphasis has been put on safety in order to assure the user(s) of the safety of the prototype but however common sense need to be applied in all instances.

PROTOTYPE PEMWE OPERATING MANUAL

This manual features safety guidelines and recommendations. However, it is not intended to cover all possible operational conditions, faults, troubleshooting topics and incidents. It is the responsibility of the user(s) of the prototype equipment to meet all local safety requirements and to ensure safety during operation, maintenance and storage of the prototype polymer electrolyte membrane water Electrolyzer (PEMWE) stack. Although all efforts have been made to ensure the accuracy and completeness of the information contained in this document, HySA systems reserves the right to change the information at any time and assumes no liability for its accuracy.

⚠ → **WARNING: HIGH HYDROGEN CONCENTRATION**

⚠ → **WARNING: HIGH OXYGEN CONCENTRATION**

⚡ → **WARNING: HIGH DIRECT CURRENT**

⚠ → **WARNING: HOT SURFACES**

⚠ → **WARNING: PRESSURISED OPERATION**

3.3.1 GENERAL INFORMATION

The prototype PEM water **Electrolyzer** product is a single cell /multi cell water electrolysis stack platform developed for hydrogen (H_2) and Oxygen (O_2) generation.

Electrolysis of water in PEMWE cell is the decomposition of water (H_2O) into oxygen (O_2) and hydrogen gas (H_2) due to an electric current being passed through the water as shown in Figure 39. The (liquid) water is supplied to the anode of the Electrolyzer and is decomposed into hydrogen ions (protons: H^+) and molecular oxygen (O_2). This reaction is called Oxygen Evolution Reaction (OER). The protons are transported through the membrane from the anode to the cathode under the influence of an applied potential. At the cathode the protons and electrons are recombined to form molecular hydrogen. This reaction is called the Hydrogen Evolution Reaction (HER).

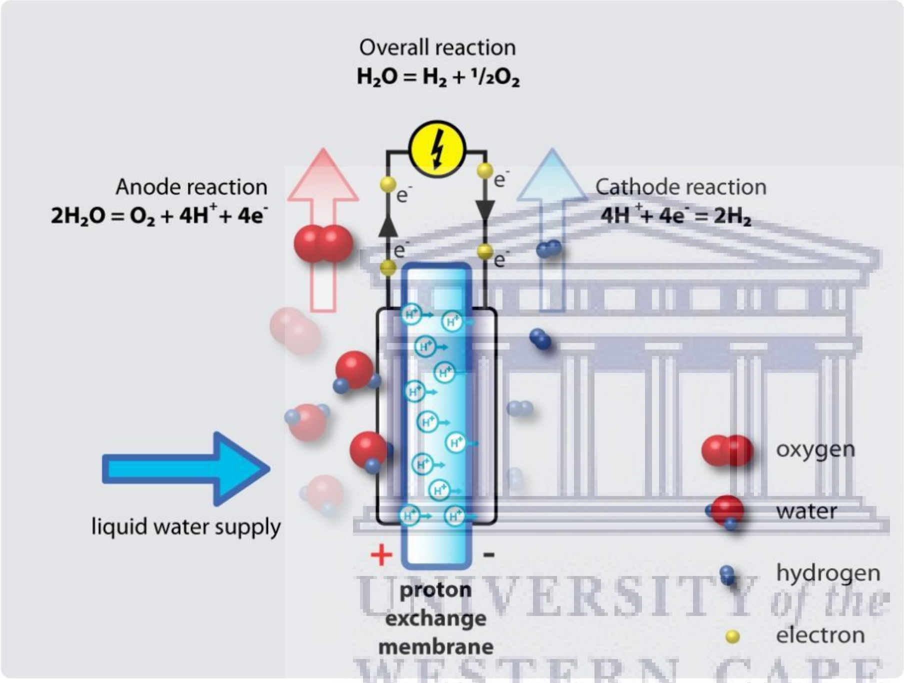


Figure 38: Electrolyse cell operating principle

a) SAFETY

Please read all instructions carefully prior to the **HySA systems** water electrolyser stack operation and use. It is important for any operator to be aware of, understand, and follow all safety requirements related to the handling of hydrogen, oxygen and compressed gases. Ensure that you read the material safety data sheet (MSDS) of hydrogen and oxygen. Familiarise yourself with the Hazard Operability study (HAZOP) of prototype HySA systems PEM water electrolyser. The safety guidelines included here may not cover every situation. **PLEASE USE COMMON SENSE**

b) HYDROGEN GENERATION

WARNING! FIRE OR EXPLOSION

Keep all sources of ignition away from hydrogen. The **Electrolyzer** generates pure hydrogen and oxygen gas. Hydrogen is a colorless, odorless and flammable substance. It is highly combustible in the presence of oxygen and burns with a colorless flame. The explosion range (in air) is 4 -77% and the gas auto-ignites at 560˚C. Leaking gas may be hot and pose a burn danger. Furthermore hydrogen is subject to igniting spontaneously if it flows out at high speed.

If an incident with hydrogen occurs: immediately turn the electrolysis stack/system off and - if you are not in danger - use water to cool the area. If fire occurs, do not attempt to extinguish flames, allow the fire to burn out. Prevent personal overexposure to hydrogen. Hydrogen is non-toxic but can act as a simple asphyxiate by displacing the oxygen in the air. There are no warnings before unconsciousness results.

When operating the prototype Electrolyzer system in a laboratory set up:

- Ensure ventilation/extraction is on;
- Operate the system (and especially the PEMWE stack) within the temperature and pressure limits stated in this manual;
- Never operate the system if a hazardous and/or alarm condition exists;
- If the system is operated at elevated pressures, close the process cabinet and use personal safety glasses;
- It is highly recommended that the working area in which hydrogen is used is equipped with safety systems (e.g. hydrogen sensor, forced ventilation etc.).

c) OXYGEN GENERATION

WARNING! FIRE OR EXPLOSION

The normal oxygen concentration in air is approximately 21% by volume. Air containing less than 19,5% or more than 23.5% oxygen constitutes a hazardous working environment. Oxygen is not combustible, but it promotes very rapid combustion of flammable materials and some materials that are normally regarded as being relatively non-flammable.

Although a source of ignition energy is always necessary in combination with flammable materials and oxygen, control or elimination of flammables is a precautionary step. Lubricating oils and other hydrocarbon materials can react violently with higher concentrations of oxygen. Personnel should not be exposed to an oxygen-enriched atmosphere because of increased risks of fire. As concentrations increase above 23,5% oxygen, ease of ignition of clothing increases dramatically.

Once ignited by even a relatively weak ignition source such as a spark or cigarette, clothing can burst into flame and burn rapidly. Above approximately 60% oxygen, the nap on clothing and even body hair and oil are subject to flash fire that spreads rapidly over the entire exposed surface.

d) WATER SPECIFICATIONS

The anode loop should be supplied with Ultra-Pure Water (UWP) of 18 MΩ/cm quality (according to ISO 3696). The stack should not be operated with water with a higher conductivity than 1, 5 µS/cm. Please note that operation the EL100 stack with process water above this conductivity will lead to rapid degradation of the internal parts and will irreversibly decrease lifetime of the PEM stack. Sensor CS-105 should continuously monitor the process water quality and trip at the threshold value of 1, 5 µS/cm.

e) PROCESS WATER UTILISATION

In the water electrolysis process the rated current is directly related to the hydrogen and oxygen production of the PEM stack. When operating the stack at 100 Ampere, a single cell of the PEM water electrolysis stack will utilize ~0, 54 mL/min for the production of hydrogen and oxygen (please refer to Table 11 for other current set points). To calculate the total process water utilization in the electrolysis process, one should sum the number of cells in the stack and multiply with the ‘process water utilization’ figure at a given current set point. For example a 10 cell stack operated at 120 Ampere will consume 6, 5ml/min of process water. HySA systems prototype Electrolyzer system has **24 cell stack operated at 120 Ampere will consume 15, 6 ml/min of process water.**

Current	H2 production	O2 production	H2O utilization	H2O utilization	Proton water
[A]	[LPM/cell]	[LPM/cell]	[mLPM/cel	[mLPM/cel	[mLPM/cel
0	0,00	0,00	0,00	0,00	0,00
10	0,07	0,03	0,05	0,54	0,24
20	0,14	0,07	0,11	1,09	0,47
30	0,21	0,10	0,16	1,63	0,71
40	0,28	0,14	0,22	2,18	0,95
50	0,35	0,17	0,27	2,72	1,18
60	0,42	0,21	0,33	3,27	1,42
70	0,49	0,24	0,38	3,81	1,66
80	0,56	0,28	0,44	4,36	1,89
90	0,63	0,31	0,49	4,90	2,13
100	0,70	0,35	0,54	5,44	2,37
110	0,77	0,38	0,60	5,99	2,60
120	0,84	0,42	0,65	6,53	2,84

Table 11: Mass balance of EL100 electrolysis process

f) PROCESS WATER TEMPERATURE DIFFERENTIAL

The temperature differential between the process water entering the stack and exiting the stack should be between 5 - 15 ˚C (5 ˚C being the most optimum value). The maximum temperature of process water exciting the stack is 80˚C

g) PROTON WATER PRODUCTION

When performing the water electrolysis process in the PEM stack, proton water is produced in the hydrogen compartment of the stack (cathode loop) due to a process called electro-osmotic drag. The proton water production is - similar to the hydrogen and oxygen production rate - directly related to the rated current (and dependent on the stack temperature). In Table 10the proton water production correlated to the rated current is given. When operating the stack at 120 Ampere, a single cell of the PEM water electrolysis stack will produce ~2, 8 mL/min of proton water in the hydrogen compartment (please refer to Table 10 for other current set points). To calculate the total proton water production in the water electrolysis process, one should sum the number of cells in the stack and multiply with the proton water production figure at a given current set point. For example a 10 cell stack operated at 120 Ampere will produce 28 ml/min of proton water. HySA systems prototype Electrolyzer system has 24 cell stack operated at 120 Ampere will consume 68.16ml/min of proton water.

h) PROTON WATER RECIRCULATION

The produced proton water can be circulated back to the anode loop of the PEM stack or drained out of the system. When recirculating the proton water to the anode loop, one should make sure that the flow is properly degassed (and containing no gaseous hydrogen) and sufficiently pure (low conductivity). Degassing the proton water flow in a dedicated degassing means and purifying the proton water by means of an ion-exchange resin filter results in the removal of all ion acquired during electrolysis. Alternatively the proton water flow - after degassing and purification - can be circulated back to the main process water storage vessel (R-301)

→ PLEASE NOTE THAT GASEOUS HYDROGEN MUST NEVER ENTER THE ANODE LOOP OF THE EL100 STACK: A HIGHLY EXPLOSIVE MIXTURE OF HYDROGEN/OXYGEN IS FORMED

i) SPECIFICATION PROCESS WATER FLOW RATE

The flow of process water by means of circulation pump P-101 will feed the electrolysis process and in some extend influence the temperature profile and distribution within the stack (and exchange some heat within the anode loop). Hydron Energy recommends to utilize a stoichiometry of 10 -20 for the process water circulation flow.

To calculate the required flow at a given rated current the following calculation applies:

Process water flow rate at rated current [ml/min] = number of cell in the stack [n] * stoichiometry (λ) * (process water utilization at rated current [ml/min] + proton water production at rated current [ml/min])

For example, when operating a 10 cell stack at 100 Ampere and a process water stoichiometry of λ=10 the process water flow rate should be set on: 10 * 10 * (0, 54 + 2, 37) = 291 ml/min.

HySA PEM Electrolyzer **24 *10 * (0.65 +2.84) = 837.6 ml/min**

Please observe the following requirements for selecting the proper process water circulation pump:

- Fluid compatibility: UPW

- Fluid temperature range: 5 - 90˚C
- Fluid flow rate range: calculate according to formula presented above - stoichiometry flow 10-20
- Head at maximum flow rate: 6 bars

j) DC POWER SUPPLY

A DC power supply (E-501) is to be connected to the stack by means of power cables. Magna power supply will be supplying DC power supply that can operate in both constant current and constant voltage modus. 90 mm^2 power cables are used for hooking up the stack (in order to avoid excessive heating up of cables and current collectors/poles of the stack).

The EL100 stack is preferably operated in a constant voltage modus. The power supply should be shut off when the rated current exceeds 120 Ampere.

k) PRESSURE SENSORS

Pressure sensor PS-103 and PS-202 are employed to monitor the oxygen and hydrogen pressure of the electrolysis process. When operating the EL100 stack, pressure levels should never exceed the rated values displayed on the type plate and stack traveler.

l) TEMPERATURE SENSORS

Temperature probes (e.g. K-type thermocouple) can be placed in the empty bores of the cell. Please note that the sensor needs to be electrically insulated from interfacing data acquisition equipment. Hydron Energy recommends placing at least one thermocouple in the middle cell of a multi cell stack to monitor the stack temperature. The temperature of the stack must never exceed 80 ˚C.

m) THERMAL MANAGEMENT SUBASSEMBLY

The water electrolysis process generates heat as current is applied to the EL100 stack. The production of excess heat is related to the rated current (Ohmic heating). Therefore a thermal management subsystem should be applied in the electrolysis system. The EL100 stack features a dedicated thermal management means: the exchanging of excess process heat is facilitated by circulating thermal conditioning fluid through the stack. To this extend a coolant inlet and outlet process port is available on the stack. The maximum operational temperature of the stack is 80˚C. The set points for the coolant inlet and outlet temperature are related to the operational temperature of the stack and the flow rate of the cooling. Hydron Energy recommends employing a PID type of monitoring and control strategy for the thermal management subassembly (flow rate control). The heat production by the process can be calculated by assuming a thermal efficiency of approximately 20%.

3.4 HYSA SYSTEMS GREEN HYDROGEN SYSTEM HAZOP

The development of hydrogen economy and its growth are directly dependent on safety and public perception and therefore safety mitigation into Electrolyzer system is of paramount importance. Most of the hazards have been mitigated during design of the system and those hazards that could not be eliminated by design have been mitigated by the operating procedure and instructions. Hydrogen is a colorless and odorless gas a hydrogen detector HS-203 has been installed in the system to detect any hydrogen leaks. Once any hydrogen leaks are detected the PLC automatically switches to the emergency mode and the system is intrinsically safe.

a) HYSA SYSTEMS PROTOTYPE PEMWE HAZOP

Hazard and operability study is a technique used to study the hazards of a system and operability of a system by exploring the effects of any deviations from designed conditions. The study will first identify and subsequently analyses possible scenarios that can cause accidents of different severity. The following study was done our prototype PEM water Electrolyzer:

b) HYSA SYSTEMS PEM WATER ELECTROLYSE HAZOP STUDY

PARAMETER	DEVIATION	CAUSES	CONSEQUENCE	EXISTING SAFETY MECHANISM	ACTION
H_2 Pressure	low	Electrolysis rate low due to: • Water quality above 1.5µS. • Low voltage <1.5V per cell.	Low pressure hydrogen output	Automatic emergency mode[1] activation	• Check water supply conductivity CS-105 • Check power supply E-501A & E-501B and PLC Electrical parameters
	low	Undetected leakages	Low pressure hydrogen output	Hydrogen sensor HS-203 installed	• Use liquid spray to detect leak replace pipe work.
	High	• Closed exhaust valve	Pressure built up	Pressure sensor PSH-202 monitors pressure	• Open the exhaust valve CV-202

		• Closed regulator outlet • Faulty pressure indicator		and pressure relieve valve PR-204 rapture at 22 bars System switches into emergency mode[1] at 20.8 bars	• emergency mode[1] from the PLC activation • Replace faulty pressure indicator
O$_2$ Pressure	low	Electrolysis rate low due to • Water quality above 1.5µS. • Low voltage <1.5V per cell	Low pressure oxygen output	Automatic emergency mode[1] activation	• Check water supply conductivity CS-105 • Check power supply E-501A & E-501B and PLC Electrical parameters
	High	• Closed exhaust	Pressure build up	Pressure relieve valve PRP-103 prevent	• Open exhaust valve CV-101

				pressure build up in anode loop over 5 bars	
Temperature	Low	H_2 production very low	Little hydrogen production	PLC get into emergency mode	• Check the stack thermocouple TS-403A/B and monitor during course of operation. • Check the power supply E-501A & E-501B and electrical parameters on PLC
	Higher >80^{O}C	Faulty temperature indicator	Damage the stack.	PLC get into emergency mode[1]	• Increase the speed of the cooling fan and pump P-404A & P-404B to maximum • Check the stack thermocouple TS-403A/B and

					monitor during course of cooling until 30^oC
Others	H_2 Leak in BOP	Mechanical failure/ Leaking fittings	Potential fire and explosion	Hydrogen HS-203 installed to detect leaks. Once leaks detected PLC switches to emergency mode[1]	- Press Emergency alarm button
	H_2 leak in Electrolyser	Overpressure causing rapture of membrane	Potential fire and explosion	Hydrogen HS-203 installed to detect leaks. Once leaks detected PLC switches to emergency mode	- Press Emergency alarm button
	Fire and Explosion	Ignition in the vicinity of H_2 and O_2 mixture	Equipment damage and possible injuries	Fire detection system installed which will extinguish the fire and trigger UWC	- Escape the room for personal safety and call for Emergency assistance X2100

				Campus emergency services	
	Short circuit	Cut wires, burned wires, overload	Opening of safety valves	Earth leakage will trip power for the whole system	• Earth leakage switch trips • Emergency mode[1] switched on
	Alarm	Gas sensor limit reached	H_2 leak	PLC switches in the emergency mode	• System switches into emergency mode

c) PROTOTYPE PEM ELECTROLYSER SYSTEM SAFETY

The system has multiple levels of built-in operator and stack safety redundancy. Control and safety systems monitor all flows, levels and temperatures of significance. All fault conditions are failsafe and duplicated, triggering relays, which shut the system down. Process indicators monitor several key variables and allow operating limits to be adjusted in response to experience of system performance automatically in the automatic mode and manually in the manual mode.

The prototype PEM electrolyser operating system demonstrates successful integration of all aspects of the design, including safety and control systems, into a single functioning entity embedded in the PLC. The following safety protocols in addition to a detailed HAZOP to mitigate any accidents, the following detailed procedures to increase prototype PEM Electrolyser safety have been implemented:

- Pre start up
- Start up
- Shutdown
- Emergency
- Post Shutdown
- Purging the system with Nitrogen gas lead to inertisation of the Stack

Safety materials are also provided within the facility, like extinguishers, sand buckets and fire hoses. Facility operations are supervised by a person designated by the main operator. This will bring knowledge on the facility functioning and feedback on hydrogen and oxygen storage in the facility housing the Prototype PEM Electrolyser.

Operation manual is in Appendix 1

3.5 HYDROGEN COMPRESSION AND STORAGE

Hydrogen compression technology combined with application of sound engineering practice produced a safe and efficient hydrogen compression system. Our extensive work on Industrial scale metal hydride hydrogen compressors developed at the South African Institute for Advanced Material Chemistry has been developed and published (Lototskyy, et al., 2018). The thermally driven Metal Hydride Hydrogen Compressor is intended for compression of hydrogen gas from 3 to 200 bar with the productivity up to 5 Nm^3/h.

Hydrogen compression is a main contributor in the capital and operation costs of the H_2 refuelling or production infrastructure. The efficient solution to mitigate this challenge is found in thermally driven MH compression. The success of thermally driven compressors and has been seen in metal hydride compressor developed and commissioned at Impala Platinum Holdings in Springs, Johannesburg South Africa. The work was published in our article entitled Hydrogen refuelling station with integrated metal hydride compressor: Layout feature and experience of three- year operation (Lototskyy, et al., 2019).

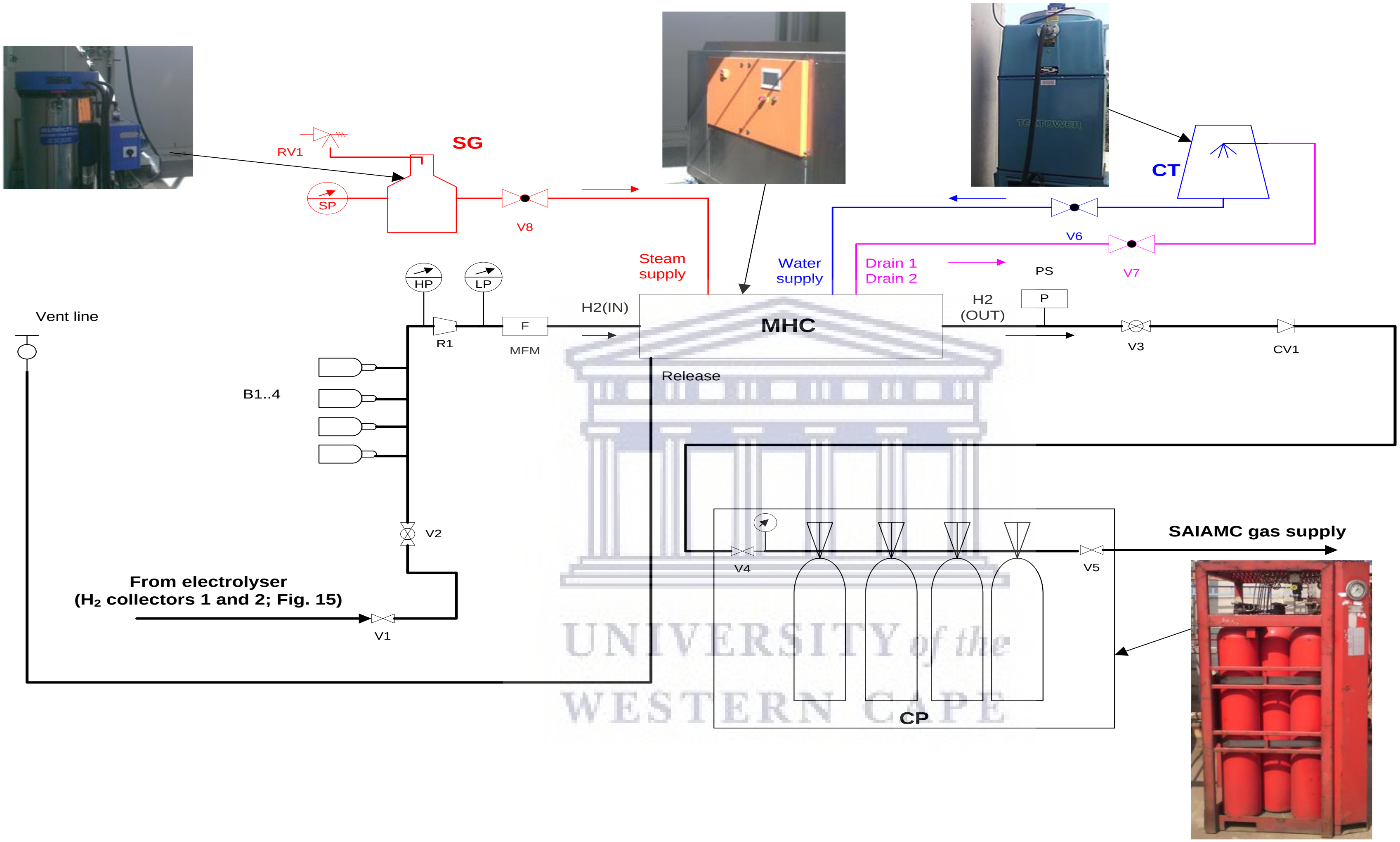


Figure 39: MH compressor (MHC) installed at SAIAMC hydrogen supply facilities; the insets show main system components. SG – steam generator; CT – cooling tower; CP – cylinder pack

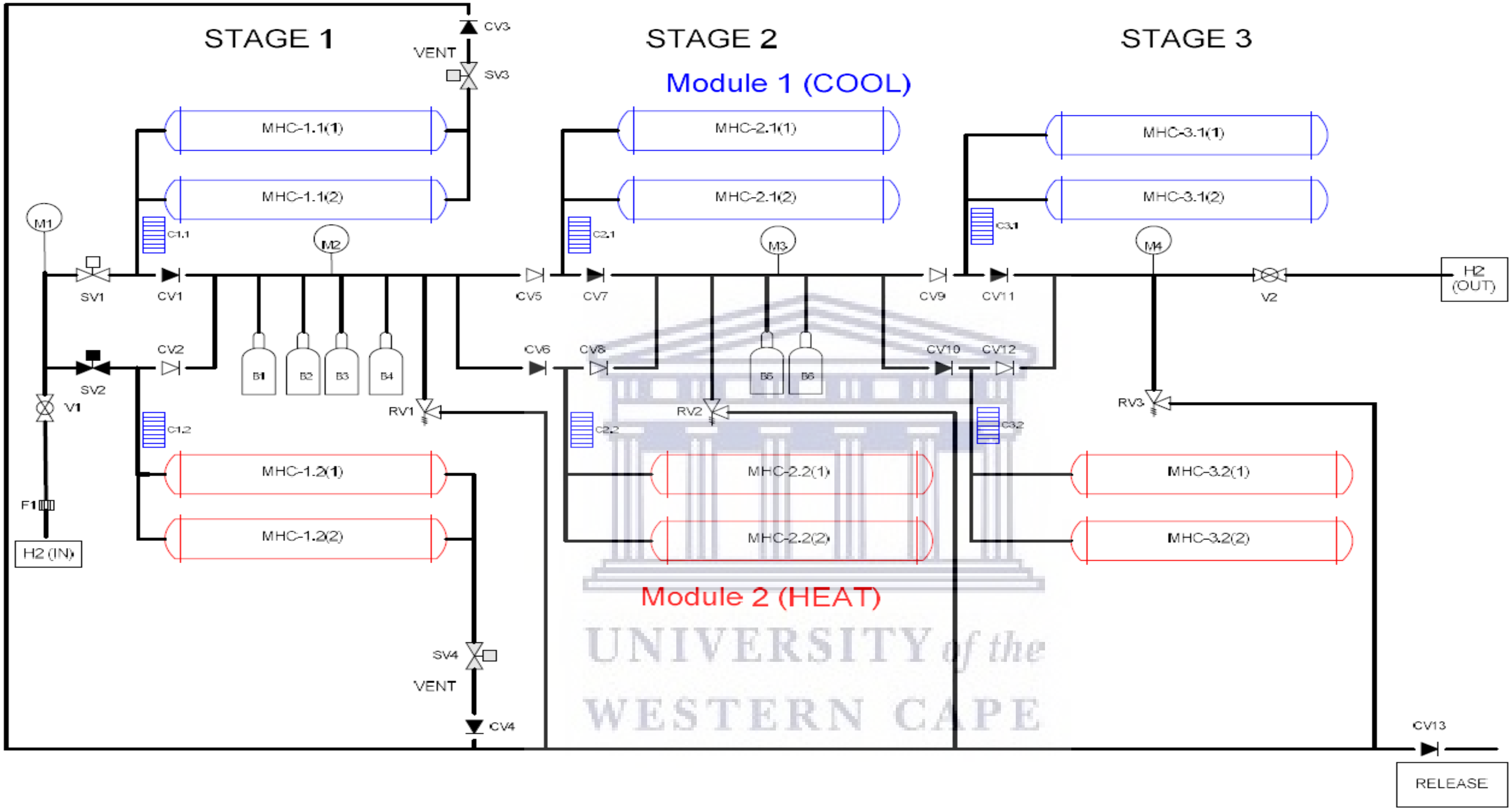


Figure 40: MH Heating and Cooling circuit

The MH compressor layout is presented in Figure 39 and the process and instrumentation diagram of the MH compressor is presented in Figure 40. The operation of the MH compressor and other system components results in the pressurising of hydrogen at the high pressure and a high flow rate. In addition, the compressor uses steam (up to 10 bar / 180 °C) for the heating.

The MH compressor uses metal hydrides on the basis of AB_5- and AB_2 -type inter-metallide ranging in hydrogen storage capacity from 130 to 180 NL H_2 per 1 kg of the material. MH material efficiency and performance in systems has been investigated in our work and presented in a publication entitled Metal hydride systems for hydrogen storage and supply for stationery and automotive low temperature PEM fuel cell power modules (Mykhaylo, et al., 2015).

The operation of the MH compressor contains a potential risk of an accident which can cause injuries to the operator, or damage of the expensive balance of plant equipment and accessories. A detailed system risk assessment document has been drafted and it addresses the following:

- Safety precautions;
- Start-up procedure
- Operating procedure;
- Shut down procedure;
- Emergency shut down procedure

Hydrogen from the electrolyser (see Figure 39) is supplied to the input (suction) pipeline of the compressor (H2IN) via shut-off valves (V1, V2), buffer cylinders (B1..4), reducer (R1) equipped with low- (LP) and high-pressure (HP) manometers, and mass flow meter (MFM). The compressed H_2 from the output (discharge) pipeline of the compressor (H2OUT) equipped with a pressure sensor (PS), via shut-off valve (V3), check valve (CV1) and shut-off valve (V4), is supplied to hydrogen cylinder pack (CP) and, further, via shut-off valve (V5), to high-pressure hydrogen manifold of SAIAMC gas supply system. The cooling is provided by a cooling tower (CT) connected to water supply and drain lines of the compressor via shut-off valves V6 and V7, respectively. The heating steam, from steam generator (SG) equipped with manometer (SP) and safety relief valve (RV1) is connected, via shut-off valve (V8), to steam supply line of the compressor. Switching of the steam and water flows is carried out automatically by solenoid valves in the compressor (MHC) while switching gas flows is provided by a check valve arrangement in the compressor.

SAFETY PRECAUTIONS FOR MH COMPRESSOR

To provide safe operation, the operator and all other personnel must obey the following rules:

1. At the site, smoking, using open fire and tools that can cause sparks is **STRICTLY PROHIBITED**.
2. The operation and service of the testing facility must be done **ONLY** by the authorised personnel who passed the test followed by the authorisation. **UNAUTHORISED OPERATION IS STRICTLY PROHIBITED**.
3. The operation must be done by the operator at the presence of at least one more person.
4. **In the case of a leak, or any other hazardous situation, the operation of MH compressor must be interrupted immediately** according to emergency shutdown procedure.
5. After service and repair work, all gas lines and connections must be carefully leak tested; the leak tests must be repeated after reaching high H_2 pressure (above 100 bar) in high-pressure systems of the compressor after the start of its operation.
6. During routine operation of the system, the leak tests must be done periodically (2–3 times during the shift) when the compressor is operating.
7. For the leak tests, it is recommended to use a Combustible Gas Leak Detector with H_2 detection range 0-1000ppm

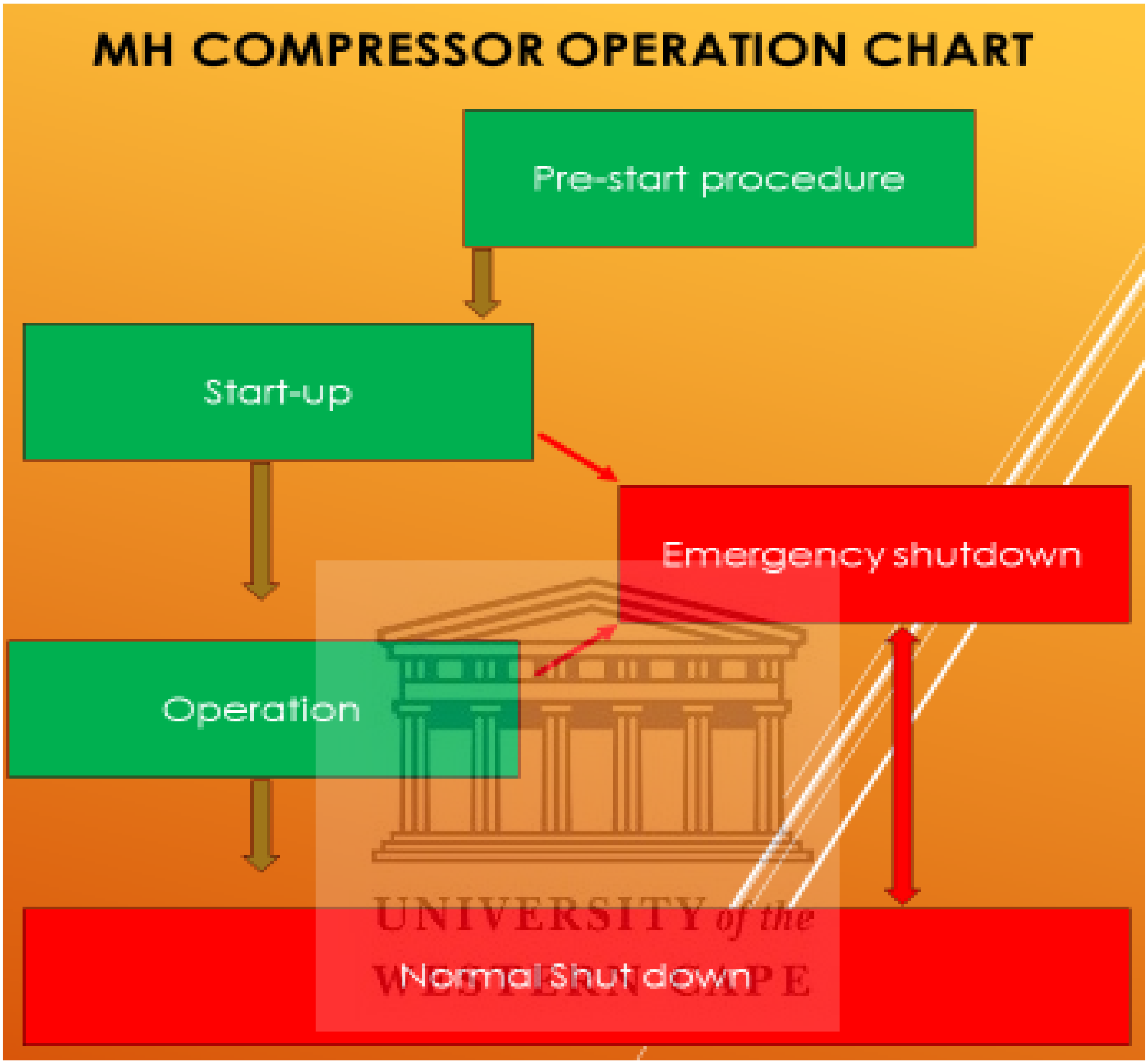


Figure 41: Summary MH Compressor operation chart

3.6 HYDROGEN SUPPLY, COMPRESSION AND DISTRIBUTION

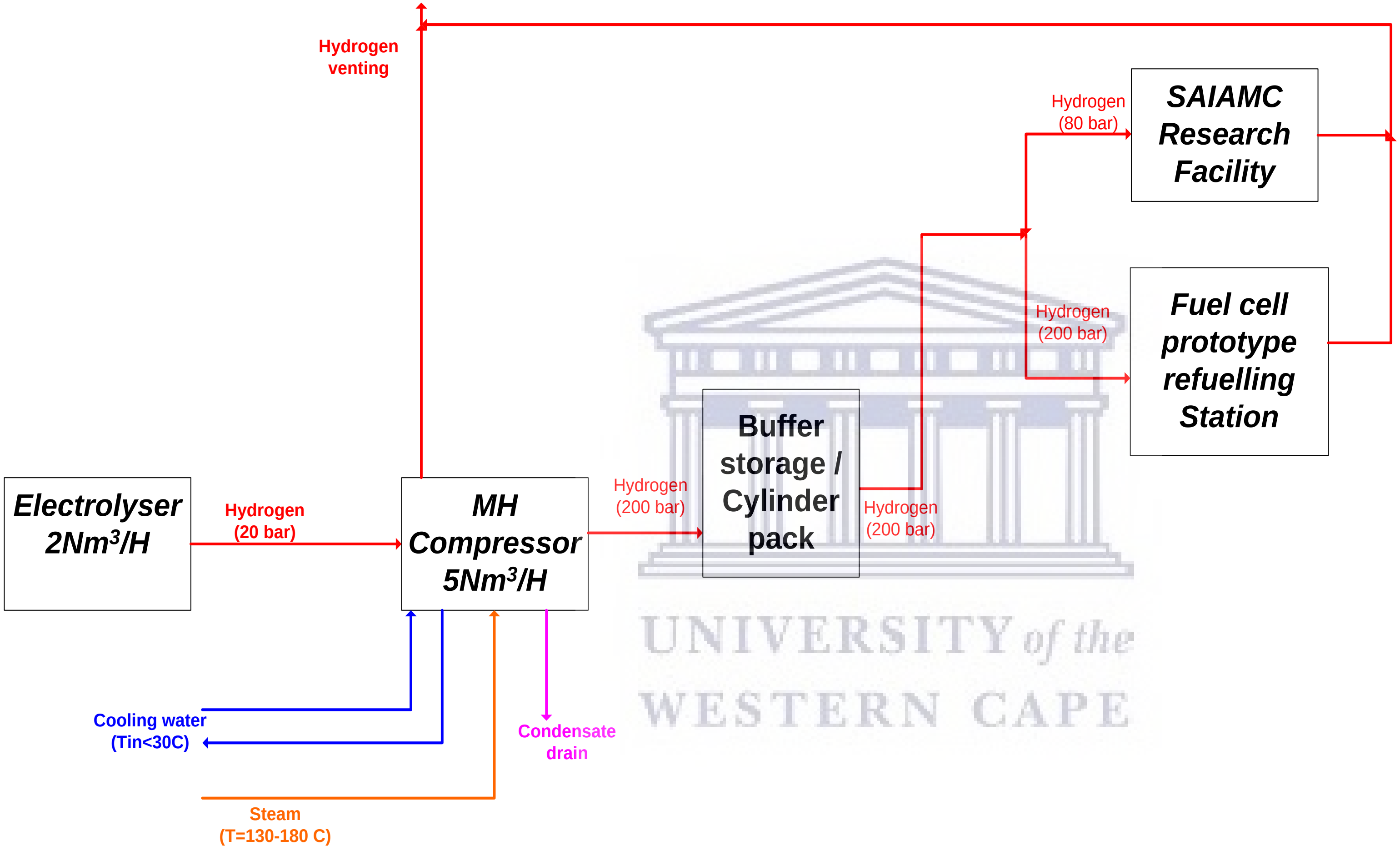


Figure 42: Schematic for complete H2 supply, compression and supply

Figure 42 show the schematic of the complete system showing H_2 production from the 2Nm^3/h PEM electrolyser, the produced hydrogen is supplied through a manifold to the 5 Nm^3/h MH compressor. The MH compressor compresses the hydrogen up to 200 bar into a buffer storage/ cylinder pack. Hydrogen is consumed from the buffer supplied to either SAIAMC research facility or hydrogen refuelling of fuel cell prototypes.

The operation and control of the whole system is segmented into:

- PEM Electrolyser system,
- MH Compressor and
- Hydrogen distribution.

The hydrogen distribution goes either to the refuelling of fuel cell prototypes or to SAIAMC research facility for consumption. Each subsystem has a comprehensive safe and efficient engineering control system that allows for full mode functionality independently. Hydrogen production from PEM electrolyser initiates the production process. The produced hydrogen is feed into the MH compressor and the MH compressor feeds hydrogen into the buffer/cylinder pack which then distributes the hydrogen.

CHAPTER 4 – RESULTS

INTRODUCTION

This chapter presents the data generated from HySA Systems prototype PEM electrolyser system that is system operation, polarisation curves, performance, and system efficiency. Hydrogen compression data with a 5Nm^3/h metal hydride compressor is also presented in this chapter.

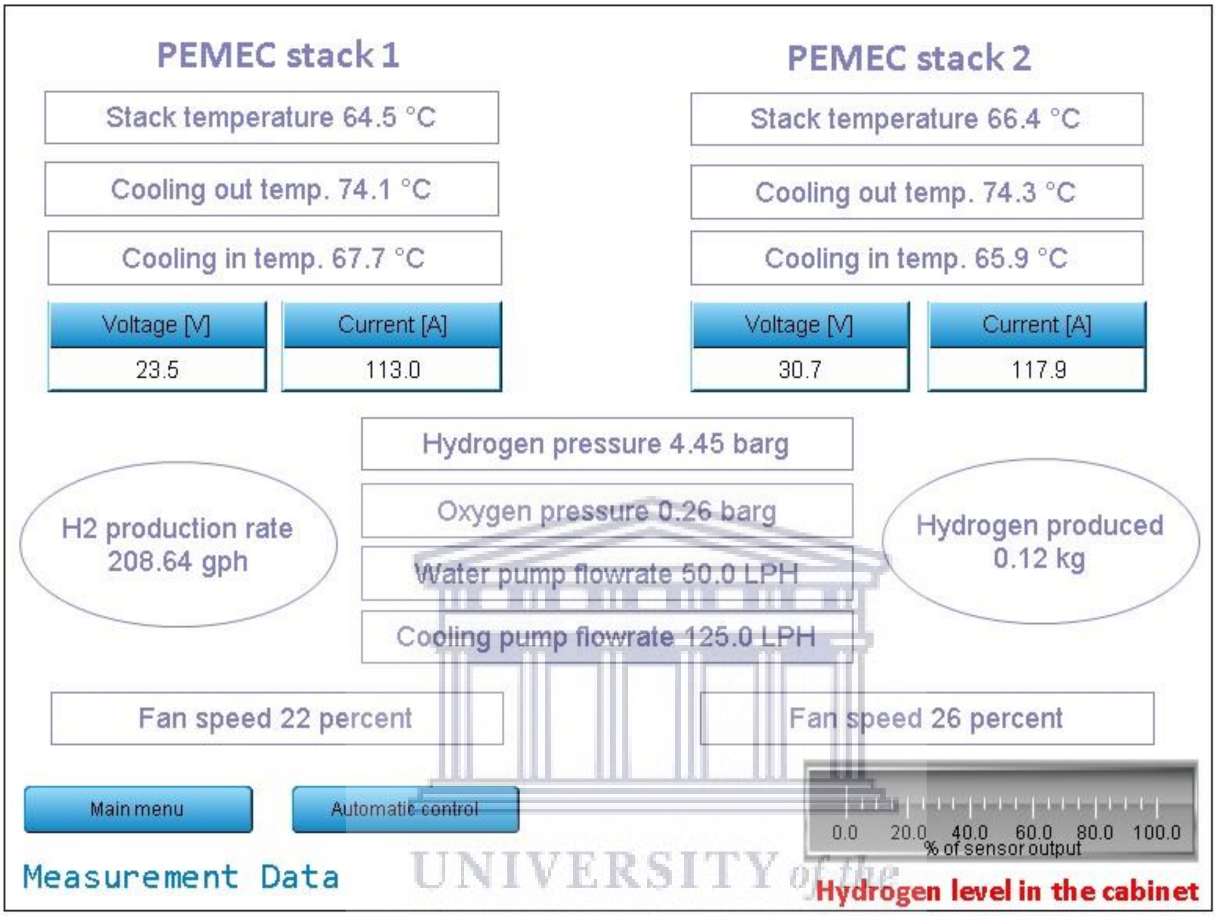
PROTOTYPE PEM WATER ELECTROLYSIS SYSTEM SPECIFICATION

Designed hydrogen production system uses two proton exchange membrane electrolysis cell stacks (PEMECs). Each stack contains 24 cells capable to conduct up to 150 A of electrical current. The stacks operate in parallel utilizing independent balance-of-plant components. The technical specifications of the stack are in Table 12:

No	Parameter	Data	Unit
1	Type	PEMEC	-
2	No of stacks	2	-
3	H_2 production rate	2.0	Nm^3/h
4	O_2 production rate	1.0	Nm^3/h
5	Max H_2 pressure	20	bar
6	Nominal power	9.9	kW
7	Efficiency, HHV	70	%
8	Feed water quality	<1.5	µS/cm
9	Water consumption	0.03	lpm
10	Stack Dimensions (HxWxD)	300 x 154 x 154	mm

Table 12: Technical; parameters of 2.0 Nm^3/h hydrogen production system

The operation window displayed in the HMI screen shown in Figure 43 displays process parameters such as temperature, current, voltage, cathode & anode pressures, hydrogen production rate and cooling system. The data shown in Figure 43 is sent to a data logger, which collects all the process parameters and saves them in a CSV file. The hydrogen sensor gives a real time hydrogen monitoring when the system is in operation.



PEMEC stack 1

Stack temperature 64.5 °C

Cooling out temp. 74.1 °C

Cooling in temp. 67.7 °C

Voltage [V] 23.5

Current [A] 113.0

PEMEC stack 2

Stack temperature 66.4 °C

Cooling out temp. 74.3 °C

Cooling in temp. 65.9 °C

Voltage [V] 30.7

Current [A] 117.9

Hydrogen pressure 4.45 barg

Oxygen pressure 0.26 barg

Water pump flowrate 50.0 LPH

Cooling pump flowrate 125.0 LPH

H2 production rate 208.64 gph

Hydrogen produced 0.12 kg

Fan speed 22 percent

Fan speed 26 percent

Measurement Data

Hydrogen level in the cabinet

Figure 43: PEMWE operation mode

I. HYDROGEN PRODUCTION

PEM water electrolyser produces hydrogen of very high purity, 99.999%. Water supplied on the anode loop is oxidised into hydrogen and oxygen ions. The ultra-pure water is oxidised at the anode to produce hydrogen ions as shown in equation 27. The hydrogen ions passes through the PEM to the cathode were the reduction reaction occurs to produce hydrogen gas as shown in equation 28. The overall reaction inside a PEM electrolyser is shown in equation 29.The amount of hydrogen produced by the electrolyser can be calculated or measured.

Anode reaction

$$2H_2O = O_2 + 4H^+ + 4e^- \qquad 27$$

Cathode reaction

$$4H^+ + 4e^- = 2H_2 \qquad 28$$

Overall reaction

$$H_2O = H_2 + \frac{1}{2}O_2 \qquad 29$$

The amount of hydrogen produced in a PEM electrolyser is calculated using the Faradays law. The Faradays law states that the electrolysis process is closely linked with two laws formulated by Faraday (Millet & Grigoriev, 2013). Equation (30) presents Faraday's first law of electrolysis. According to this law, the mass of ions generated at the electrode is proportional to the total charge that flows through the electrolyte.

$$J = \frac{i}{n * F} \qquad 30$$

Where:

F—Faraday constant value, F= 96485.3365 C/mol;

n - Amount of electrons involved in the reaction;

i - Current in Ampere;

M – Molar mass of hydrogen, M_H = 1.008

Equation (31) shows Faraday's second law of electrolysis, which determines the charge q needed to separate the mass of substance m.

$$m_{H2} = M * J * k \qquad 31$$

Where:

J- Amount of hydrogen flow kg/h

n - Amount of ions involved in the reaction;

k- Number of cells in a stack, k = 24

m_{H2} – Amount of hydrogen produced kg/h

Substituting equation (30) into equation (31), the relationship with the electrochemical equivalent described by equation (31) is as shown in equation 32.

$$m_{H2} = \frac{i * n}{F} \qquad 32$$

The amount of hydrogen produced by the HySA PEM Electrolyser prototype was calculated using the Faraday's law as shown in Figure 44.

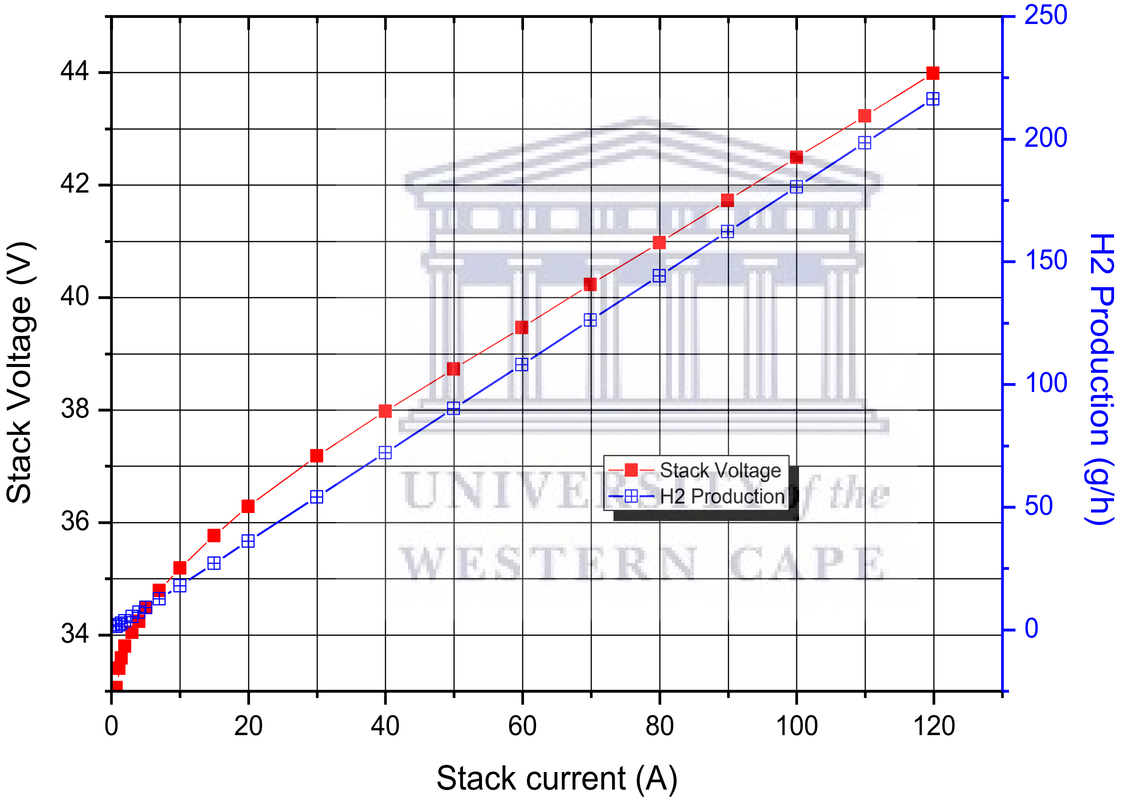


Figure 44: Mass of hydrogen produced

The mass of hydrogen increased exponentially from start up until it reached the maximum stack potential optimum temperature of 78 °C. The mass of hydrogen produced at 2Nm^3/h became constant at stack optimum conditions that is at maximum cell voltage of 2.4V.

II. ELECTROLYSIS SYSTEM EVALUATION AND PERFORMANCE

Constructed water electrolysis system consists of 2 Nm^3/h PEM electrolyser stacks. Table 12 shows the system parameters. For the illustration of hydrogen production process in terms of efficiency and performance, particular parameters calculated for three different voltage points i.e. 1.4, 1.6 and 1.8 V as shown in Table 13.

Electrolysis process starts at approx. 1.4 V per cell at which low hydrogen production rate occurs. At this voltage, the efficiency of the stack is high due to slow rate of electrochemical reactions as well as low current density. System efficiency is low as most of the power consumed internally by balance of plant (BoP) components. Once the voltage scaled up by 200 mV, the rate of hydrogen production increased significantly to 41 and 82 g/h for single stack and the system, respectively. It is an optimal point in terms of system efficiency (77%) as activation losses of the stack are only predominant. At maximum power point (11kW), the highest long-term performance obtained (99 and 197.8 g/h of hydrogen production).

The efficiency for both the stack and the system is decreased - Ohmic and mass transport losses become significant. The system efficiency is also affected by electrical losses occurring at stack power supplies that generate high amount of thermal energy. The heat removed from the system by forced circulation of air through the radiators as well as increased flow rate of cooling water.

This also generates additional parasitic energy consumed by BoP components. Assuming a long life-time of the system, it is advisable to operate at either low or nominal power point (4.2 or 9.9 kW). The operation of the system at maximum performance will quickly lead to creation of additional losses due to ageing process of the electrolysis stack. The power required for nominal hydrogen production at BoL and EoL (beginning and end of life) for the stack is 4.2 and 5.8 kW respectively.

Parameter		Average cell voltage [V]		
		1.4	1.6	1.8
Stack	Power [kW]	0.049	1.75	4.73
	Efficiency, LHV [%]	89.0	78.4	70.0
	H_2 production [g/h]	1.3	41.1	99.0
System	Power [kW]	0.37	4.23	11.01
	Efficiency, HHV [%]	28.7	76.7	70.9
	H_2 production [g/h]	2.7	82.2	197.8

Table 13: The comparison of parameters recorded and calculated at different cell's voltage for single electrolysis stack and whole electrolysis system consisting of 2 stacks

The characterisation of electrolysis stack is crucial from the system design point of view. In Figure 45 there is stack power and efficiency depicted as a function of stack current. The nominal power point (at BoL) for the stack is at the voltage of 42 V and current of 100 A. At this point the efficiency calculated for the lower heating value of hydrogen (LHV, 33.4 kWh/kg) is around 86%.

This allows on the generation of low amount of thermal energy in the consequence of small electrochemical losses and changes of entropy for given reactants and products of hydrogen and oxygen evolution reactions. The maximum power point is achieved at the point of 44 V, 120 A (5.3 kW). Lifetime of the PEM electrolysers was taken into consideration during development process of the system, as at EoL the power requirement of the stack might exceed the available resources.

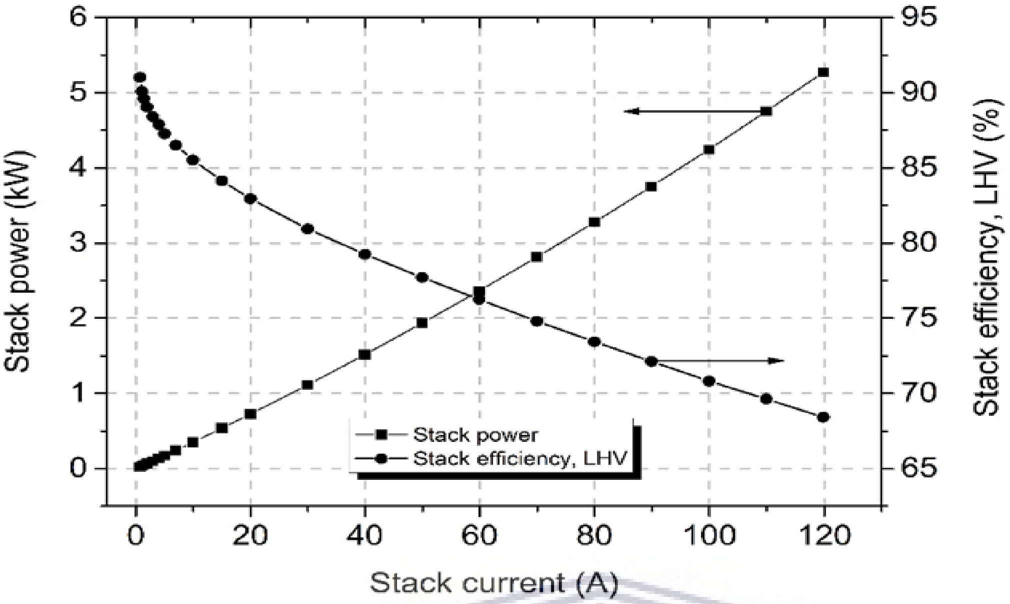


Figure 45 Electrical characterization of the 1.0 Nm^3*/hr PEMWE stack; lower heating value of hydrogen taken for calculation of efficiency*

Total energy consumption of the electrolysis system is an aggregation of the utilization by two stacks and BoP components. The latter includes high power supplies, water and cooling pumps, cabinet and cooling fans and PLC controller with its dedicated hardware (programmable voltage sources, input/output terminals, etc.). Calculation of total energy utilization includes all internal consumption in order to obtain reliable dependency of system efficiency.

Figure 46 describes the system performance as a function of total power. At slow hydrogen production rate (less than 12 g/h), the system efficiency is low due to BoP requirements. Increasing the production rate increases also the efficiency maximally up to 77% (3.7 kW).

It is an optimal point of operation for the system at which the ratio of hydrogen energy produced to the total energy consumed has the highest value. Above this point, the efficiency is still high (around 70%) however, it is linearly decreasing.

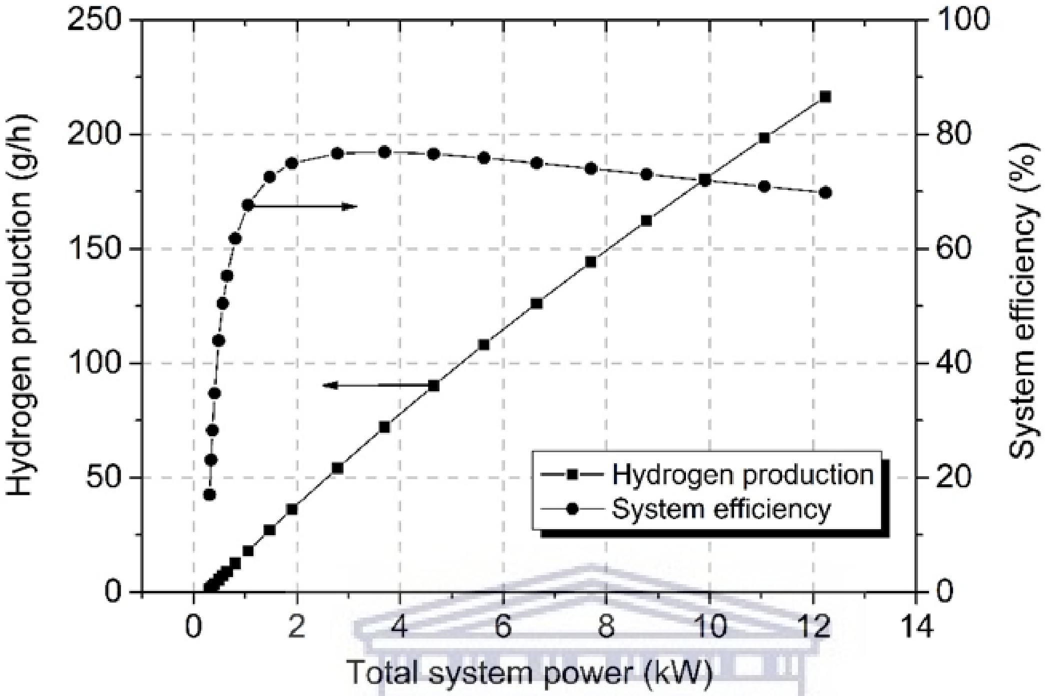


Figure 46: Electrolysis system performance, including Balance of Plant and two stacks under operation

Taking into account the higher heating value of hydrogen (39.49 kWh/kg) and recording the energy utilization for electrolysis system, the energy input/output dependency was obtained.

In Figure 47, chemical energy of produced hydrogen is shown as a function of total energy consumption. The amount of hydrogen generated in electrolysis process calculated based on Faraday's law assuming there were not any electrochemical losses nor internal currents. Hydrogen mass (m_{H2}) calculated from the following equation 33:

$$m_{H_2} = \frac{M_{H_2} \cdot I \cdot N_o}{nF} \qquad 33$$

Where MH_2 is molecular mass of H_2,

I – electrical current,

N_0 – number of cells in the stack,

n – Number of electrons per hydrogen molecule,

F – Faraday’s constant.

Hydrogen production method via the electrolysis is an energy-consuming process. For the designed system, at least 30% of energy has to be lost. The system can operate the most effectively at the efficiency of 77%, which means a constant utilization of 3.7 kWh of electricity corresponding to 2.85 kWh of hydrogen produced (HHV). However, it is relatively slow production rate. At the nominal point of operation, this relation is 9.9 vs. 7.1 kWh, while at maximum power point 12.2 vs. 8.5 kWh.

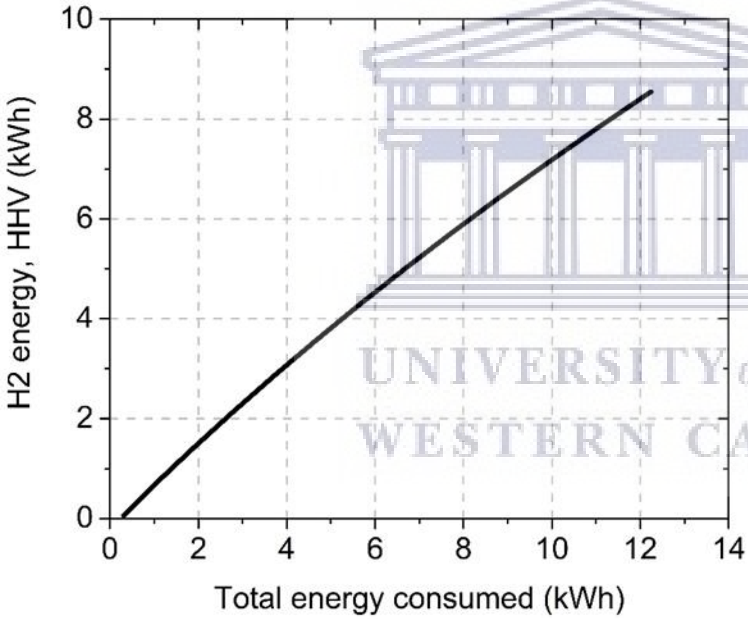


Figure 47: Performance of the system in terms of capability to produce chemical energy of hydrogen, Calculated based on the higher heating value of this fuel (39.49 kWh/kg)

III. EFFICIENCY

A PEM electrolyser system for hydrogen production is established and the corresponding efficiency is derived. Based on semi-empirical equations, thermodynamic-electrochemical modelling of water splitting reaction is systematically carried out. It is confirmed that the Joule heat resulting from the irreversibility inside the PEM electrolyser is larger than that needed in the water splitting process in the whole region of the electric current density. Some alternative configurations are designed to improve the overall performance of the system and the corresponding expressions of the efficiency are derived (Zhang, Su, Lin, & Chen, 2012).

The efficiency of an electrolyser is inversely proportional to the cell potential, which in turn is determined by the current density, which in turn directly corresponds to the rate of hydrogen production per unit of electrode active area. A higher voltage would result in more hydrogen production, but at a lower efficiency. Typically, cell voltage is selected at about 2V, but a lower nominal voltage (as low as 1.6V) may be selected, if the efficiency is more important than the size (and capital cost) of the electrolyser (Kwaka, Chaeb, & Kanga, 2014).

Another ‘‘source’’ of inefficiency is hydrogen permeation (loss) through the polymer membrane. This is typically insignificant at low operating pressures, but it may significantly affect the overall efficiency at very high pressures (>100bar).In addition, there are power losses in voltage regulation and some power is required for the auxiliary equipment (pumps, fans, solenoid valves, instrumentation and controls). Typical industrial electrolysers have electricity consumption between 4.5 and 6.0kWh/Nm^3, corresponding to the efficiency of 65–80% (Zhang, Su, Lin, & Chen, 2012).

PEM electrolyser efficiency calculation using some electrochemical calculations based on the hydrogen Higher Heating Value (HHV) of H_2 was applied in this study. Electrolyser efficiency using HHV of H_2 in equation 34:

$$\eta_{PEMWE} = \frac{W_{H2}}{W_{el}} \qquad 34$$

Where:

η_{PEMWE} – Efficiency of PEMWE

HHV_{H2} – High Heating Value of hydrogen

W_{el} – Electric energy used to produce hydrogen (kWh)

Hydrogen energy is calculated by the equation 35:

$$W_{H2} = HHV_{H2} \cdot N_{H2} \; \left[\frac{J}{s}\right] \qquad 35$$

Where, HHV – higher heating value of hydrogen,$HHV_{H2} = -286.02 \; \left[\frac{kJ}{mol}\right]$

N_{H2} – the amount of hydrogen produced [mol/s].

Based on Faraday's law:

$$N_{H2} = \frac{I}{nF} \qquad 36$$

Where N_{H2} – Molecular mass of hydrogen

F – Faradays law

And n – number of Hydydgen ions = 2

Hydrogen energy can be calculated from:

$$W_{H2} = HHV_{H2} \cdot \frac{I}{nF} \qquad 37$$

Energy utilized to produce hydrogen:

$$W_{el} = I \cdot V \; \left[\frac{J}{s}\right] \qquad 38$$

Combining the equations 34, 35, 36 and 37, the thermodynamic efficiency of electrolysis can be described by equation (39) written as:

$$\eta_{PEMWE} = \frac{W_{H2}}{W_{el}} = \frac{HHV_{H2} \cdot \frac{I}{nF}}{I \cdot V} = \frac{HHV_{H2}}{nFV}$$

$$\eta_{PEMWE} = \frac{286.02 \cdot 10^3}{2 \cdot 96485.33} \cdot \frac{1}{V}$$

$$\eta_{PEMWE} = \frac{1.482}{V} \qquad 39$$

The system efficiency is affected also by electrical losses occurring at stack power supplies that generate high amount of thermal energy. The heat is removed from the system by forced circulation of air through the radiators as well as increased flow rate of cooling water. This also generates additional parasitic energy that is consumed by BoP components.

Assuming long life time of the system, it is advisable to operate at either low or nominal power point (4.2 or 9.9 kW). The operation of the system at maximum performance will quickly lead to creation of additional losses due to ageing process of the electrolysis stack. The power required for nominal hydrogen production at BoL and EoL (beginning and end of life) for the stack is 4.2 and 5.8 kW respectively.

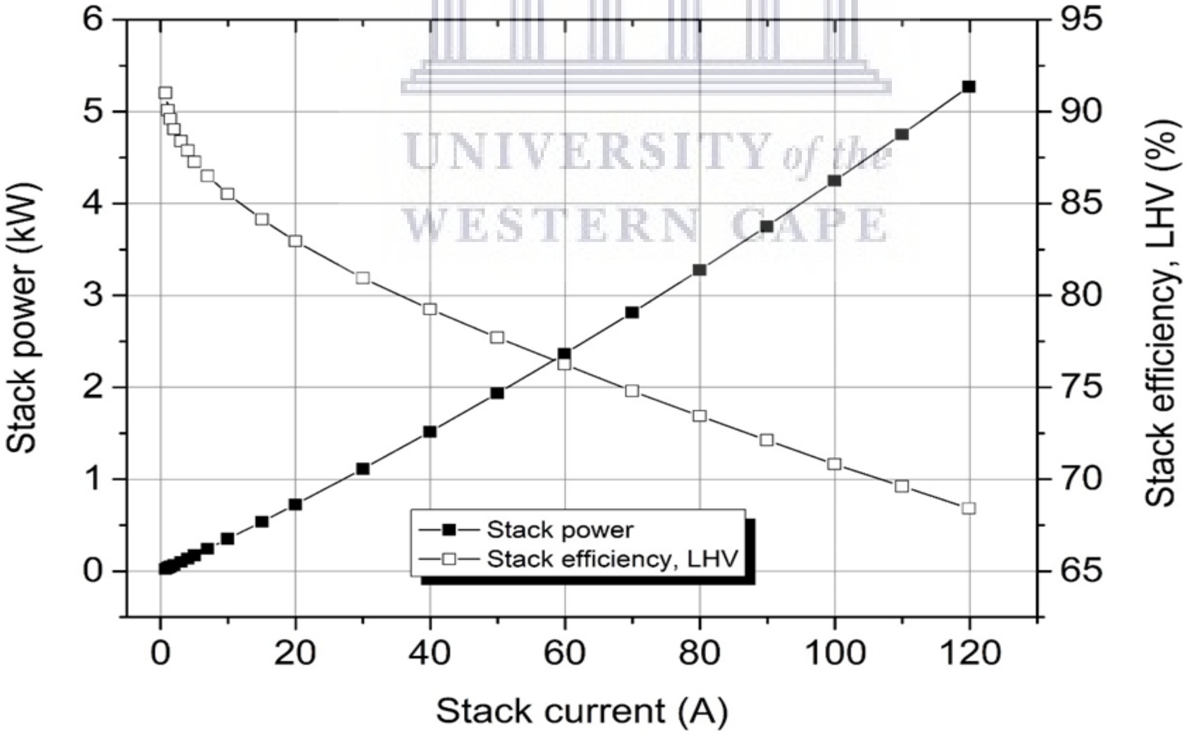


Figure 48: System Stack power and Efficiency

The characterisation of electrolysis stack is crucial from the system design point of view. In Figure 48 there is stack power and efficiency depicted as a function of stack current. The nominal power point (at BoL) for the stack is at the voltage of 42 V and current of 100 A. At this point the efficiency calculated for the lower heating value of hydrogen (LHV, 33.4 kWh/kg) is around 86%.

This allows on the generation of low amount of thermal energy in the consequence of small electrochemical losses and changes of entropy for given reactants and products of hydrogen and oxygen evolution reactions. The maximum power point is achieved at the point of 44 V, 120 A (5.3 kW). Lifetime of the PEM electrolysers was taken into consideration during development process of the system, as at EoL the power requirement of the stack might exceed the available resources.

Total energy consumption of the electrolysis system is an aggregation of the utilization by two stacks and BoP components. The latter includes high power supplies, water and cooling pumps, cabinet and cooling fans and PLC controller with its dedicated hardware (programmable voltage sources, input/output terminals, etc.). Calculation of total energy utilization includes all internal consumption in order to obtain reliable dependency of system efficiency.

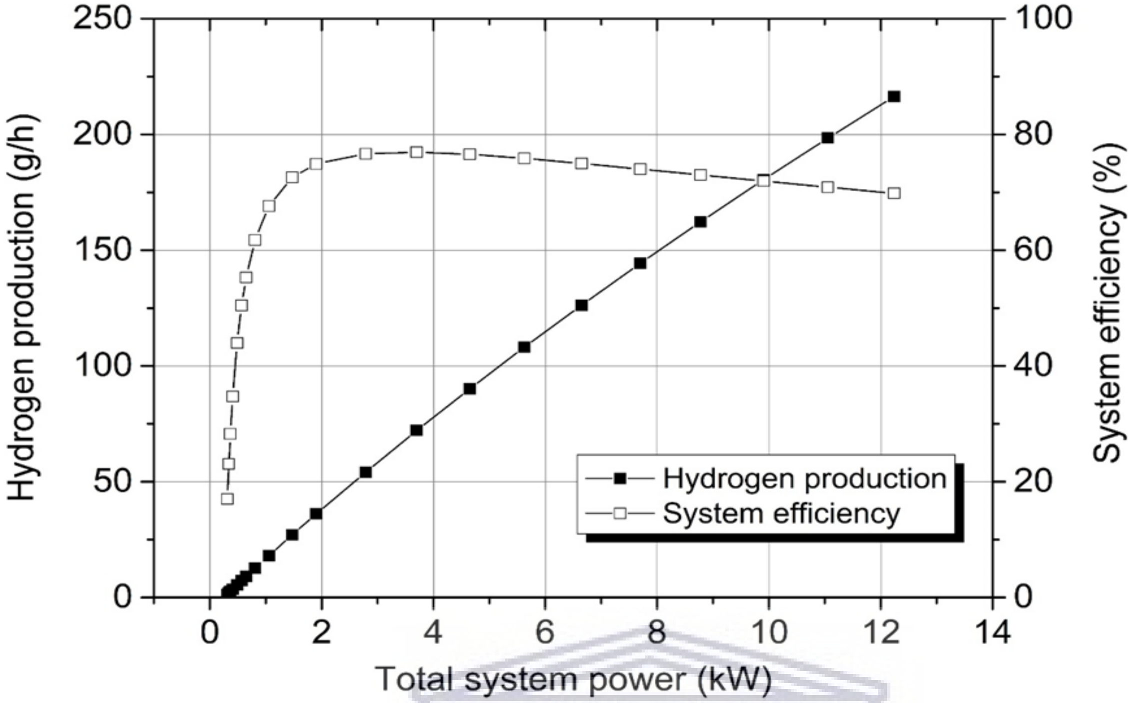


Figure 49: Hydrogen production versus System Efficiency

Figure 49 describes the system performance as a function of total power. At slow hydrogen production rate (less than 12 g/h) the system efficiency is low due to BoP requirements. Increasing the production rate increases also the efficiency maximally up to 77% (3.7 kW). It is an optimal point of operation for the system at which the ratio of hydrogen energy produced to the total energy consumed has the highest value. Above this point, the efficiency is still high (around 70%) however it is linearly decreasing.

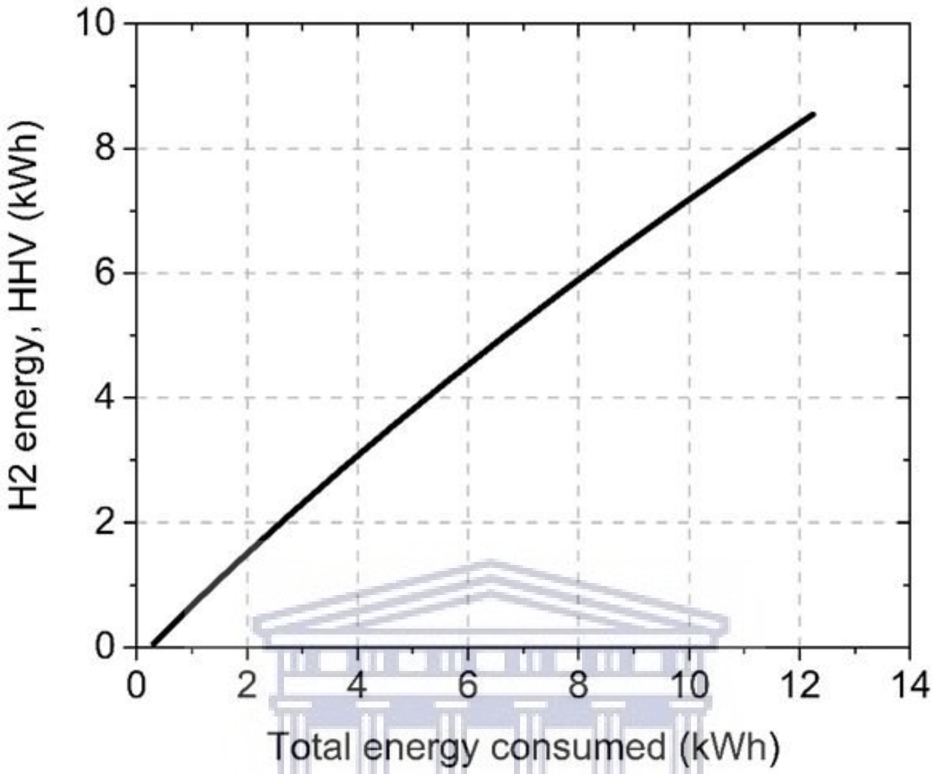


Figure 50: Performance of the system in terms of capability to produce chemical energy of hydrogen, calculated based on the higher heating value of this fuel (39.49 kWh/kg)

In Figure 50, chemical energy of produced hydrogen is shown as a function of total energy consumption. The amount of hydrogen generated in electrolysis process calculated based on Faraday's law assuming there were not any electrochemical losses nor internal currents. Hydrogen mass (m_{H2}) calculated from the following equation

$$m_{H2} = \frac{M_{H2} .I .N_O}{nF} \qquad 35$$

Where M_{H2} is molecular mass of H_2,

I – electrical current,

N_0 – number of cells in the stack,

n – Number of electrons per hydrogen molecule, F – Faraday constant.

Hydrogen production method via the electrolysis is an energy-consuming process. For the designed system, at least 30% of energy has to be lost. The system can operate the most effectively at the efficiency of 77%, which means a constant utilization of 3.7 kWh of electricity corresponding to 2.85 kWh of hydrogen produced (HHV). However, it is relatively slow production rate. At the nominal point of operation, this relation is 9.9 vs. 7.1 kWh, while at maximum power point 12.2 vs. 8.5 kWh.

IV. POLARISATION CURVES

A polarisation curve is a plot of cell voltage against current density, it is a standard electrochemical technique used to characterise the performance of electrochemical cells (Baniasadi, Dincer, & Naterer, 2012). Current- voltage polarisation curve for HySA PEMWE prototype in Figure 51 is a commercial stack operated at stack temperature 78 ^{o}C, process feed water flow 60 LPH; anode pressure 2 bars and cathode pressure two bars:

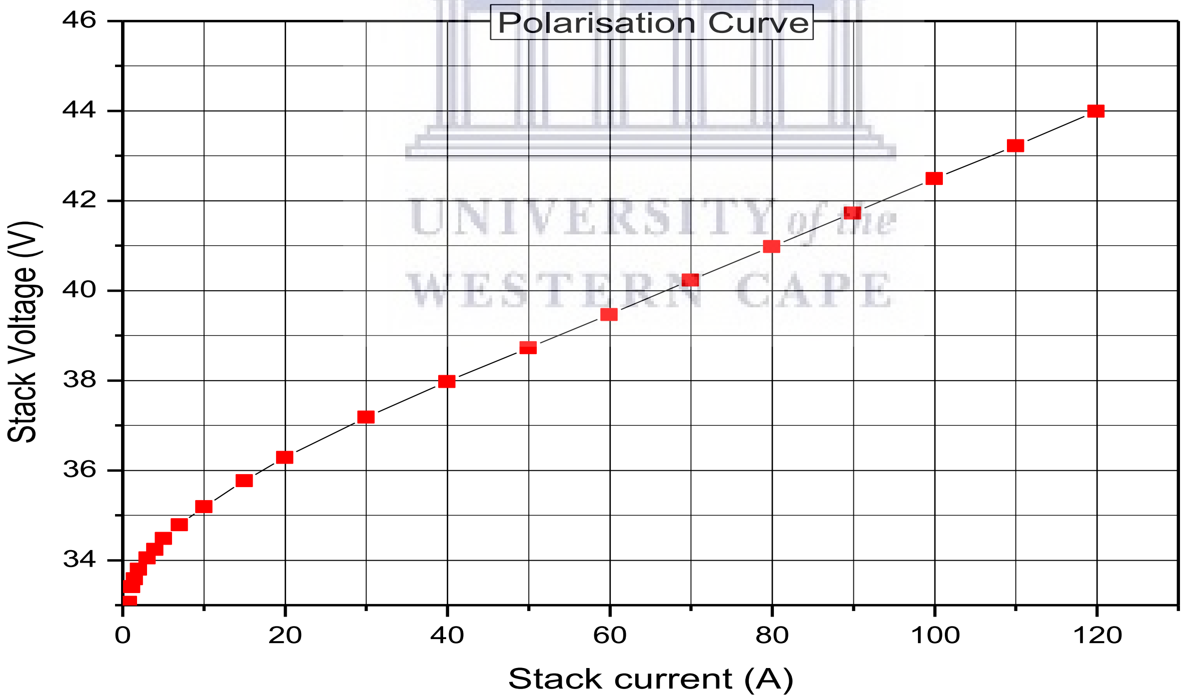
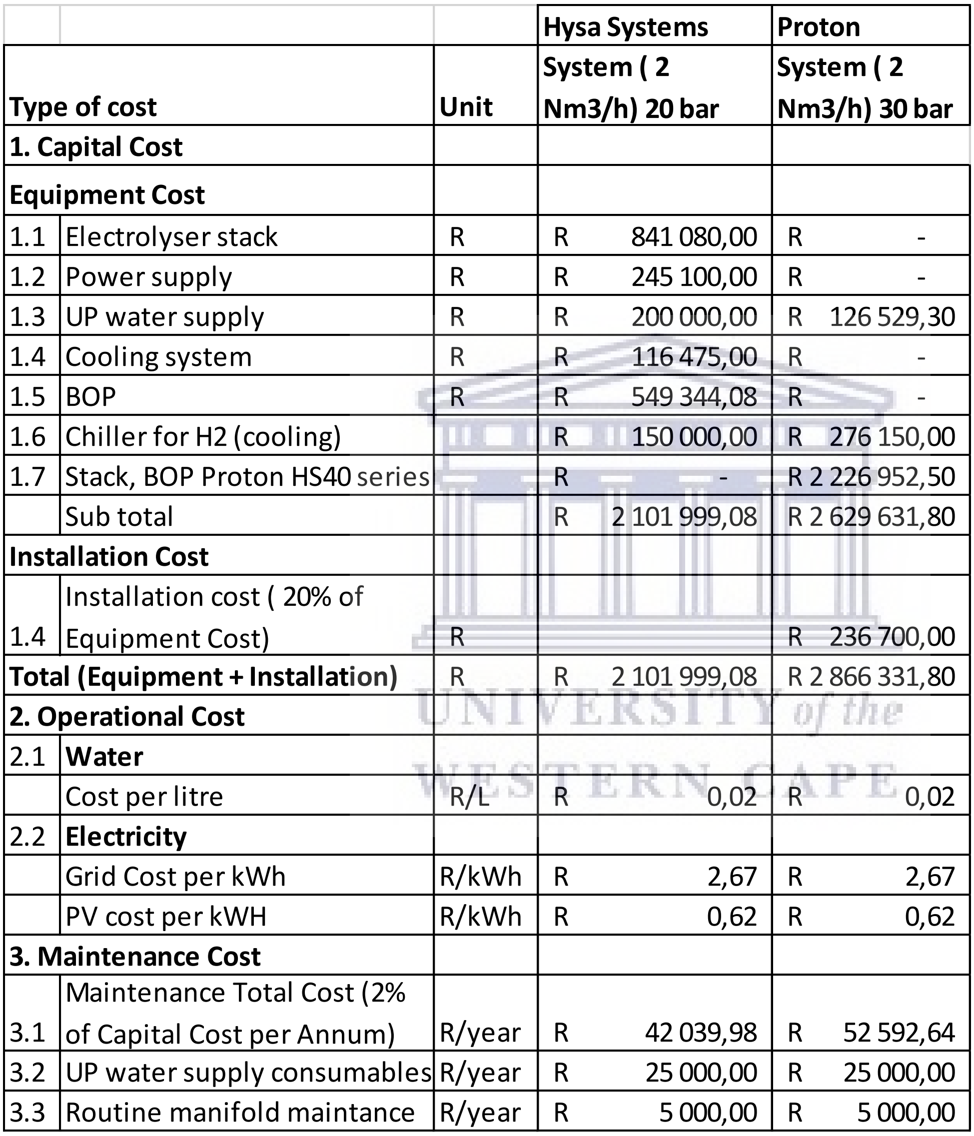


Figure 51: Voltage-current characteristics (Polarisation Curve)

V. PEM COST ANALYSIS

The cost analysis of the produced prototype PEM electrolyser system compared to a commercially produced system from one commercial supplier called Proton. Both systems have the same hydrogen productivity of 2 Nm^3/h. Table 14 show the capital, installation and maintenance costs of both systems.



Type of cost		Unit	Hysa Systems System (2 Nm3/h) 20 bar	Proton System (2 Nm3/h) 30 bar
1. Capital Cost				
Equipment Cost				
1.1	Electrolyser stack	R	R 841 080,00	R -
1.2	Power supply	R	R 245 100,00	R -
1.3	UP water supply	R	R 200 000,00	R 126 529,30
1.4	Cooling system	R	R 116 475,00	R -
1.5	BOP	R	R 549 344,08	R -
1.6	Chiller for H2 (cooling)		R 150 000,00	R 276 150,00
1.7	Stack, BOP Proton HS40 series		R -	R 2 226 952,50
	Sub total		R 2 101 999,08	R 2 629 631,80
Installation Cost				
1.4	Installation cost (20% of Equipment Cost)	R		R 236 700,00
Total (Equipment + Installation)		R	R 2 101 999,08	R 2 866 331,80
2. Operational Cost				
2.1	**Water**			
	Cost per litre	R/L	R 0,02	R 0,02
2.2	**Electricity**			
	Grid Cost per kWh	R/kWh	R 2,67	R 2,67
	PV cost per kWH	R/kWh	R 0,62	R 0,62
3. Maintenance Cost				
3.1	Maintenance Total Cost (2% of Capital Cost per Annum)	R/year	R 42 039,98	R 52 592,64
3.2	UP water supply consumables	R/year	R 25 000,00	R 25 000,00
3.3	Routine manifold maintance	R/year	R 5 000,00	R 5 000,00

Table 14: System Capital, Installation and Maintenance Costs

Operational costs

Description	Capacity	Unit	Capacity	Unit	Yearly 1 Stack	Yearly 2 Stacks
Production capacity	2	Nm3/h	3,970378	kg/d	1449	2898
Production capacity	82,1	mol H2/h	1969,433		718843,22	1437686,45
Water requirement	1477,1	g/h	35,45		12939,18	25878,36
Sufficient capacity for purifier	0,9	l/h	21,6		7884,00	15768
Water cost(Schools & Sport Bill)	50	R/kL			473,04	946,08
Power consumption BoT	206,4	kWh/day				
Power consumption BoT	227,04	kWh/day				
Power consumption EoT	247,68	kWh/day				
Grid power Cost	2,67	R/kwh	606,1968		221261,832	442523,664
PV power Cost	0,62	R/kwh	14,88		5431,2	10862,4
Ave Electrical cost	2,242916667	R/kwh	509,2318		185869,607	371739,214

Table 15: System Operation Costs

Table 17 shows the standard operational cost involved in operating the systems during the 2 year life span of the Stack. The Stack life span determines the amount of hydrogen that can be produced before the stack can be refurbished and given another new life span. Table 16 shows the standard International units used in the calculation of the total cost of hydrogen produced.

Hydrogen Production	Unit	Value
Faraday Constant	C/mol	96485,34
Number of H2 ions (n)		2
Current (i)	A	100
Number of cells in a stack (k)		24
Amount of H2 flow (J)	mol/s	0,000518213
Molecular mass of H2 (M)	g	2,016
Amount of H2 produced (mh2)	g/h	90,26366078
Amount of H2 produced/ day	kg/day	2,166327859
Total H2 produced by 2 stacks	kg/day	4,332655717

Table 16: System units and standards

Total Cost of H2

	Hysa Systems	**Proton**
Equipment(E) + Installation	R 2 101 999,08	R 2 866 331,80
Interest	R 210 199,91	R 286 633,18
Maintenance (M)	R 42 039,98	R 52 592,64
Water cost (W)	R 946,08	R 946,08
Electrical	R 371 739,21	R 371 739,21
E+Inst+Interest + M+W	**R** 2 726 924,26	**R** 3 578 242,91
Utilization factor	**1**	**1**
Total Cost of H2 per Kg	**R 940,85**	**R 1 234,57**

Table 17: Total Cost of H2 per Kg

PEM hydrogen production is still expensive mainly because of the cost of the electrolyser stack. In Table 17 prototype PEM electrolyser system is found to be cheaper than the PEM electrolyser system from the commercial supplier when comparing the cost of hydrogen per kg. The cost of hydrogen per kg compared to fossil fuel is still expensive, considerable work need to be done in renewable energy technology development to bring comparative cost to the existing fossil fuel market.

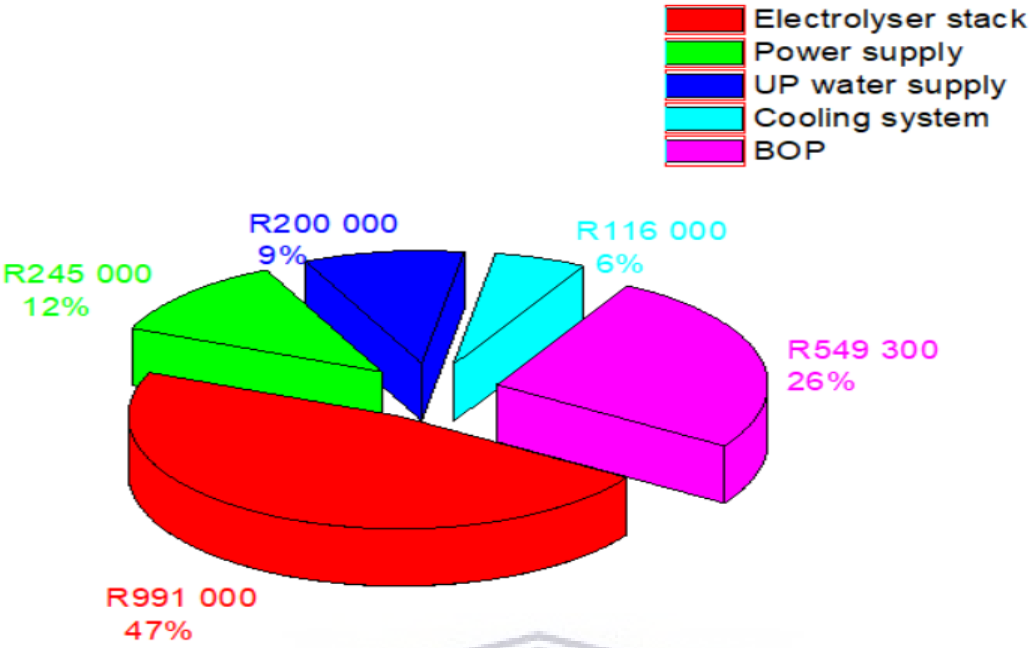


Figure 52: Breakdown of the incurred cost for the integration and commissioning of Prototype PEM water Electrolyser (Cost in South African Rand 2016-2019)

Figure 52 show the cost breakdown for the complete prototype system. Considerable cost of up to 47% went for the PEM electrolyser stack procurement. Extensive research still needs to be explored in order to bring down the cost for the Electrolyser stack if the hydrogen economy is to take centre stage in the global market compared to fossil fuels. Government and private equity funding is key to the success of hydrogen economy.

VI. HYDROGEN COMPRESSION AND SUPPLY

The produced hydrogen form the prototype PEMWE was supplied to a 5 Nm^3/H Metal Hydride (MH) compressor. The industrial scale metal hydride hydrogen compressor was developed at South Africa Institute of Advanced Material Chemistry that we published in (Lototskyy, et al., 2018) was used for hydrogen compression.

The three-stage compressor supplied with hydrogen form the electrolyser at 20 bar (further reduced to 3–5 bar to minimise influence of the operation of the compressor on performance of the electrolyser) and compressed to 180–200 bar. The commercial refuelling fuel cell station and SAIAMC research facility had hydrogen supplied at 180–200 bar from the MH compressor.

They made use of high-pressure regulators to step down the pressure to their optimum operational pressure.

Hydrogen compression is carried out by the periodic heating (T_H=130 °C) and cooling (T_L=25 °C) of metal hydride materials disposed in metal hydride containers for hydrogen compression. The compression is carried out in three stages using:

- AB_5 material ($LaNi_{4.9}Sn_{0.1}$) for stage 1,
- AB_5 material ($La_{0.8}Ce_{0.2}Ni_5$) for stage 2 and
- AB_2-type material ($C14\text{-}Ti_{0.65}Zr_{0.35}(Mn,Cr,Fe,Ni)_{2+x}$) for stage 3.

In Figure 54, hydrogen is absorbed in the cooled MH container of stage 1 at 3-5 bar, desorbed from the heated MH container of stage 1 to the cooled container of stage 2 at 15-20 bar, then desorbed from the heated MH container of stage 2 to the cooled container of stage 3 at 50-80 bar.

When MH container of stage 3 is heated, it desorbs hydrogen to a receiver (cylinder pack) at a pressure up to 200 bar. The amount of hydrogen compressed per unit weight of the MH (Δ C) depends on both the operating temperatures and pressures and varies between 100 and 145 NL H_2 per 1 kg of the MH material.

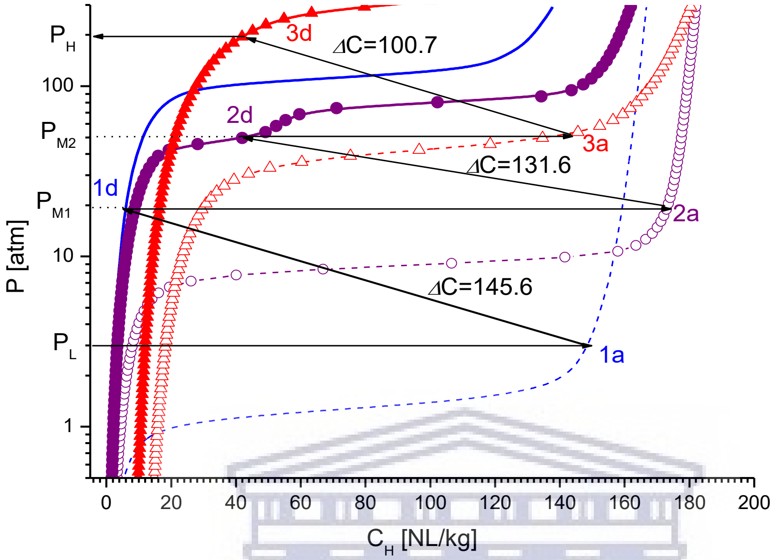


Figure 53: Pressure – composition isotherms for H absorption at T_L=298 K (a) and H desorption at T_H=403 K (d) for MH H_2 compression alloys: $LaNi_{4.9}Sn_{0.1}$ (1), $La_{0.8}Ce_{0.2}Ni_5$ (2) and C14-$Ti_{0.65}Zr_{0.35}$ (Mn, Cr, Fe, Ni)$_{2+x}$ (3).

From Figure 53 it can be seen that hydrogen compression by a MH material takes place when the H_2 suction pressure is higher than the plateau pressure for hydrogen absorption in the MH at T=T_L and the discharge pressure is lower than the plateau pressure for hydrogen desorption from the MH at T=T_H. The amount of hydrogen compressed per unit weight of the MH (C) depends on both the operating temperatures and pressures and can be estimated as the difference of hydrogen concentrations, C_H (P, T).

The MH materials are loaded in MH containers each able to absorb and desorb up to 2 Nm^3 H_2. The containers belonging to stages 1, 2 and 3 have the same design differing only by the length when the MH container belonging to the next compression stage is 10% shorter than the container of the previous compression stage. The operation and performance of the MH compressor has been presented in our paper entitled industrial scale metal hydride compressors developed at the South African Institute of Advance Material Chemistry (Lototskyy, et al., 2018).

A typical cyclogram of the compressor operation is presented in figure 55. Periodic heating and cooling of two compression modules in the opposite phase (T1, T2) results in the increase of H_2 pressure from 3–5 bar in the suction line (P (in)) to 20–30 bar between stages 1 and 2 (P1–2), 40–80 bar between stages 2 and 3 (P2–3) and higher, up to 200 bar at the output of the compressor (P (out)).

In doing so, the H_2 flow rate at the input of the compressor periodically changes between 0 and 3–4 Nm^3/h. The values of H_2 flow rate (up to 6 Nm^3/h) and the average compressor productivity (1–4 Nm^3/h) depend on the duration of the heating / cooling cycle (20–35 minutes), steam temperature (120–150 °C) and, in the lesser extent, the suction (above 3 bar) and discharge (up to 200 bar) H_2 pressures.

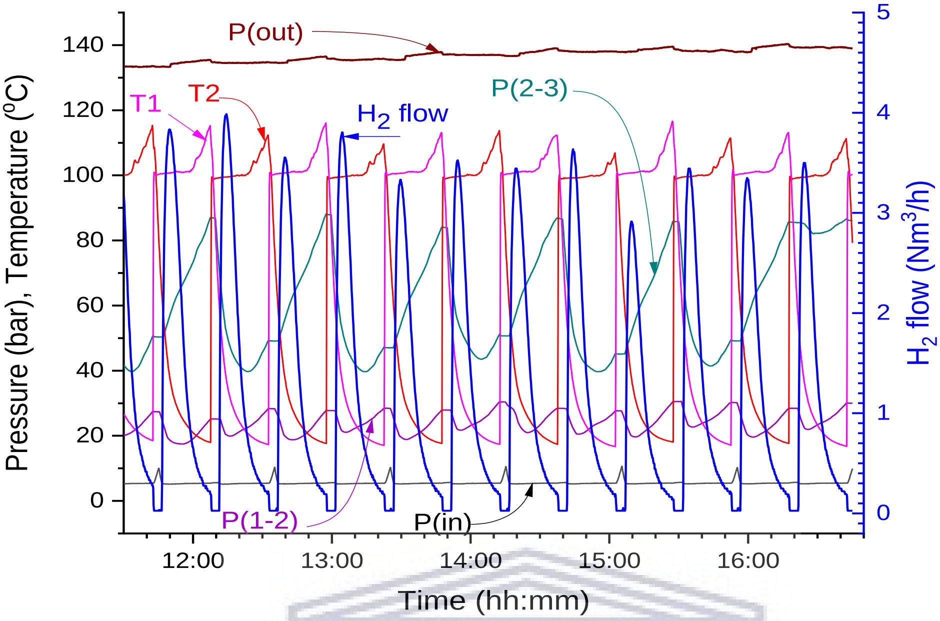


Figure 54: Typical operation of MH compressor at SAIAMC; heating / cooling time 25 minutes, average productivity 1.2 Nm^3/h. Left Y-axis: T1, T2 – temperatures in the first and the second compression modules, respectively; P(in) – H_2 suction pressure; P(out) – H_2 discharge pressure; P(1-2) – H_2 pressure between stages 1 and 2; P(2-3) – H_2 pressure between stages 2 and 3. Right Y-axis: H_2 flow in the suction line of the compressor.

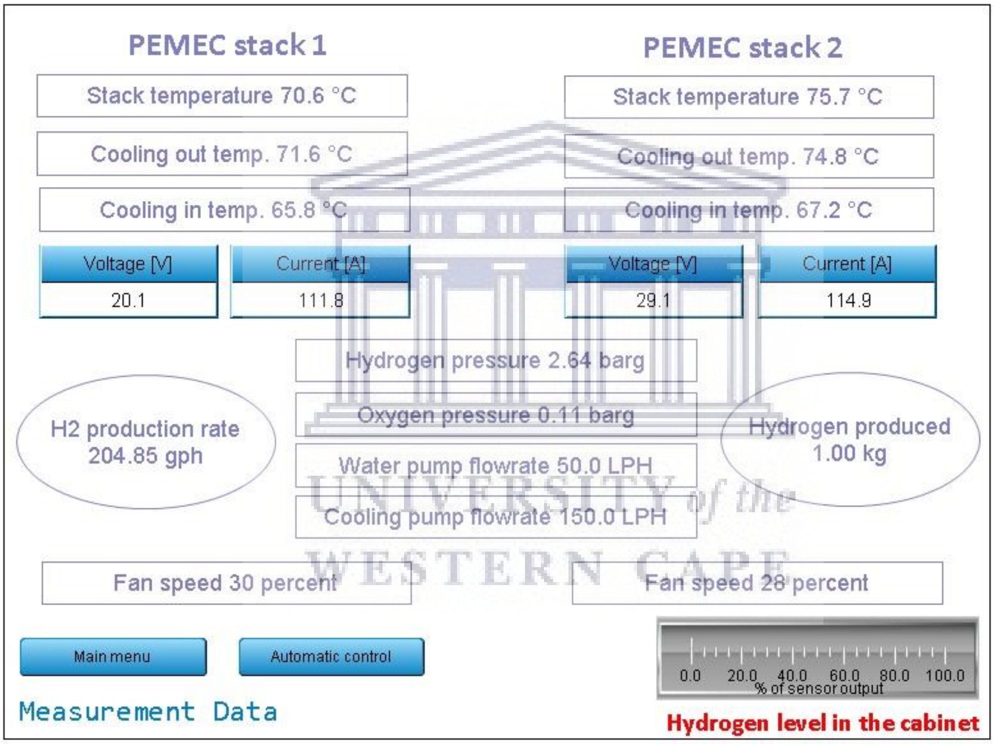
The compressed hydrogen is supplied to either SAIAMC Research facility for consumption, or for refuelling fuel cell vehicle prototypes.

VII. PEM STACK FAILURE

During the system operation, as seen in the screen shot (Figure 56), it was discovered that both our stacks had low voltage. Individual cell voltages for each stack were tested and it was discovered that all the cells had low voltage of an average of 0.7V/ cell except two cells, which had 2.2V/cell in each stack and current less than 10A (measured separately). Therefore, it was concluded that most of the cells were broken or damaged.

The possible reasons for the damage were:

- Possibly some corrosion in the cooling loop which might have filtered some ions to the stack
- The metal profile that was used to support the PEM stacks to stand in upright position might have had a contact with the current collectors that might have resulted in a short circuit that might have damaged the PEM stacks.


PEMEC stack 1

Stack temperature 70.6 °C

Cooling out temp. 71.6 °C

Cooling in temp. 65.8 °C

Voltage [V] 20.1

Current [A] 111.8

PEMEC stack 2

Stack temperature 75.7 °C

Cooling out temp. 74.8 °C

Cooling in temp. 67.2 °C

Voltage [V] 29.1

Current [A] 114.9

Hydrogen pressure 2.64 barg

Oxygen pressure 0.11 barg

Water pump flowrate 50.0 LPH

Cooling pump flowrate 150.0 LPH

H2 production rate 204.85 gph

Hydrogen produced 1.00 kg

Fan speed 30 percent

Fan speed 28 percent

Measurement Data

Hydrogen level in the cabinet

Figure 55: PEMWE readings indicating failure of the stacks

The most possible reason as to why both electrolyser stacks failed at the same time due to metal bar which physically "switched off" some of the cells in the stack. The graph in Figure 56 indicated of one of the stack when the failure happened. The data for second electrolyser are very relevant. At that time metal bars were not isolated as is visible in the picture. Once we put isolation and started the electrolysers these cells that were covered and "protected" by metal bar were also destroyed due to over-voltage (as some of the cells were already damaged). It was interesting that two cells in each stack survived and were working, however their maximum current (measured independently) is just around 10 A @ 2.4 V.

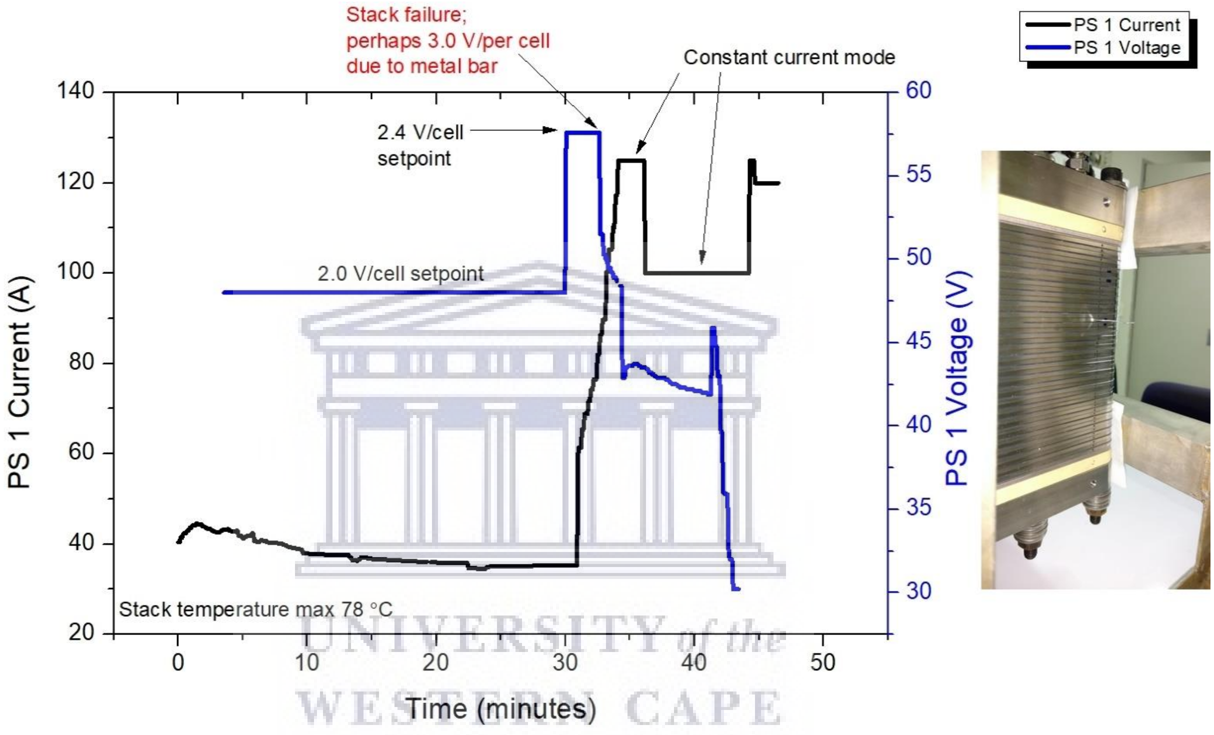


Figure 56: Stack Current/ Voltage when failure occurred

a) ANALYSIS OF DEFECTIVE STACKS

The following activities were carried out to ascertain the defective stacks:

I. STACK HYDROSTATIC TEST,

The hydrostatic test revealed that both stacks were leaking internally: with the anode and cathode header capped off on one side, a pressurised water flow (~2 bar), resulted in a water discharge at the cathode header indicating a “macro leak” across the membranes/MEAs;

II. STACK DISASSEMBLY AND INSPECTION OF COMPONENTS

Both stacks were disassembled and all the components have been inspected. It immediately became clear that the MEAs were severely damaged. Figure 57 shows typical damaged MEA out of the stack. Furthermore, unfortunately the ‘flow fields’ were also damaged (see Figure 58). One current collector was bent; perhaps this happened when dismounting the stack out of the system. All other stack components were approved to be usable.

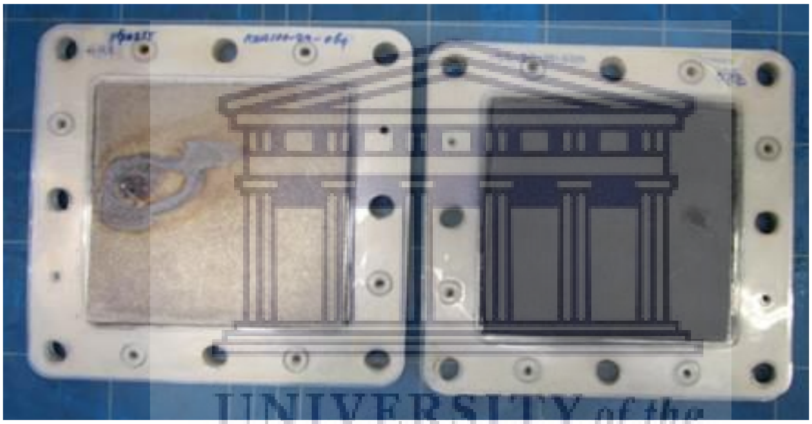


Figure 57: Damaged MEAs

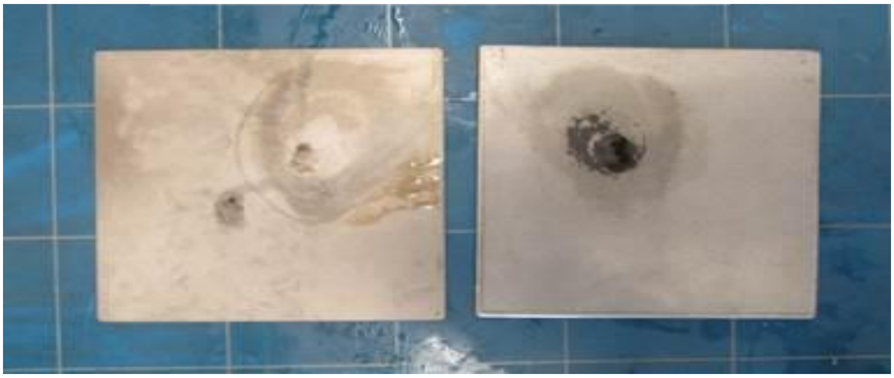


Figure 58: Damaged Flow Fields

b) PLAN FOR REFURBISHMENT

The good news are that the cell plates and compression assembly can be cleaned and re-used. The MEAs, flow fields and sealing have to be renewed or refurbished. The plan for refurbishment of both stacks is quite extensive and account for over 50% of the total stack cost: ~€24.000 for the two 1Nm^3/h PEM stacks. The refurbishment cost funding will be co-funded by HySA systems and a private company, Isondo Precious Metals.

VIII. QUANTITATIVE RISK ASSESSMENT

The prototype PEMWE system has been equipped with hydrogen sensors and cathode exhaust line connected to a flame arrestor. The oxygen from the anode loop connected to an exhaust line that takes produced oxygen outside the building into the environment in order to avoid high concentration of oxygen inside the location of the electrolyser. Safety procedures were implemented to protect the stacks following sound engineering practice. BoP, cooling system and power supply units were integrated with the PLC to protect the entire prototype system.

Modelling of the facility housing prototype PEMWE was carried out using Hydrogen Risk Assessment Model. The HyRAM toolkit is the first-ever software toolkit that integrates deterministic and probabilistic models for quantifying accident scenarios, predicting physical effects, and characterizing hydrogen hazards’ impact on people and structures.

HyRAM incorporates generic probabilities for equipment failures and probabilistic models for heat-flux impact on humans and structures, with computationally and experimentally validated models of hydrogen release and flame physics.

Modelling of the facility housing prototype PEMWE was modelled using HyRAM and the following was obtained:

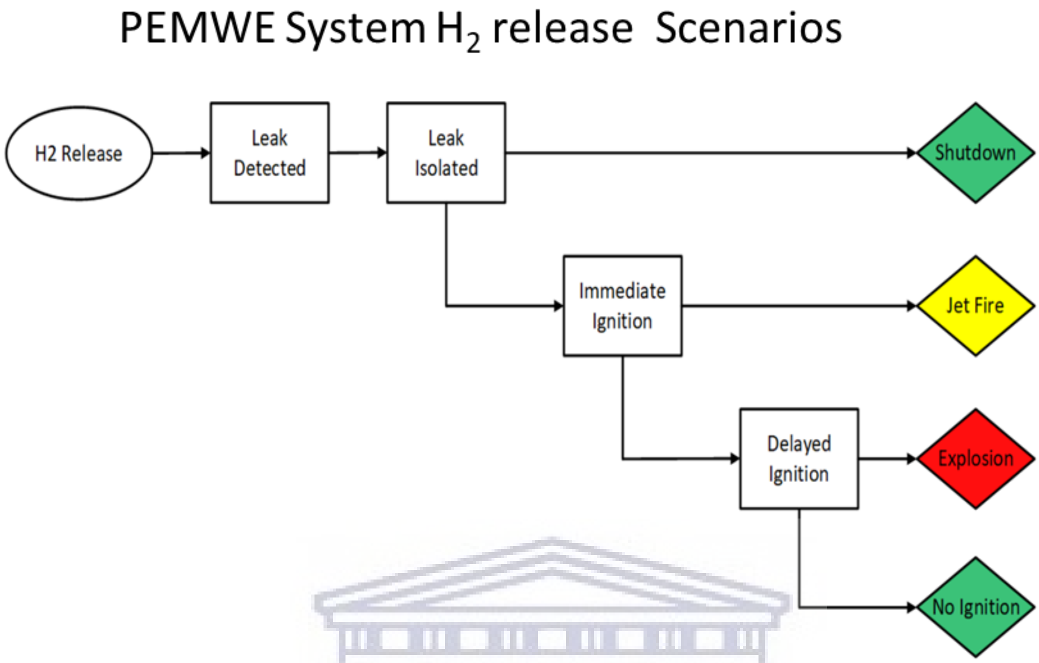


Figure 59: PEMWE System H_2 release scenarios

Application of HyRAM modelling software on the facility housing the PEMWE system revealed the hazard scenarios in Figure 59. Hydrogen leak triggers complete system shutdown and no ignition. In cases of hydrogen ignition it will result in either a jet fire or explosion in worst case scenario. Dedicated engineering controls embedded in the PLC mitigate hydrogen fires risks.

IX. HYDROGEN PRODUCTION, COMPRESSION AND SUPPLY TO SAIAMC FACILITY & FUEL CELL PROTOTYPE REFUELLING

The testing has been done in separate subsystems (results presented above) namely:

- Hydrogen production – 2Nm^3/h HySA Systems Prototype PEM Electrolyser system
- Hydrogen compression – 5 Nm^3/h Metal hydride compressor

Though the detailed testing of the complete system was not done due to the PEM stack failure, this study (including the collected experimental data) allowed to show technical feasibility of the system and to develop detailed safety protocols presented above.

Note that after the stack failure the incomplete system including MH compressor, dispensing station and H_2 distribution between refuelling and SAIAMC research facilities (Figure 14) continued to operate. The operation was provided by the connection of hydrogen cylinder packs from H_2 suppliers to the input of the MH compressor instead of the output collectors of the electrolyser (Figure 41). It allowed to maintain the pressure in the high pressure buffer (CP in Figure 39) above 180 bar thus providing the operation of both fuel cell prototype refuelling station (required H_2 pressure 180–200 bar) and SAIAMC research facility (required H_2 pressure 80 bar; see Figure 42). At the same time, the pressure in the source cylinder pack could drop down to 5–10 bar without interruption of the main operations requiring the higher H_2 pressures. In doing so, the hydrogen compression part of developed system allowed to utilise most of the delivered hydrogen resulting in significant costs savings.

CHAPTER 5 – CONCLUSIONS AND RECOMMENDATIONS

INTRODUCTION

This study aimed at the integration of hydrogen production and storage technologies into one large project, demonstrating South African competencies in the renewable energy space and technological development towards the growing hydrogen economy. This study developed a safe, green hydrogen production, compression and distribution system for fuel cell applications and general hydrogen consumption in SAIAMC research facility.

GENERAL CONCLUSIONS

Hydrogen economy has become a necessary action for our civilization due to environmental issues such as global warming effect, air pollution, and depletion of fossil fuels. During this study, the renewable hydrogen production autonomous system was developed including its engineering, testing and analysis. The produced hydrogen was fed to a prototype 5 Nm^3/h Metal Hydride compressor. Hydrogen safety was also taken into consideration as one of the most important issue arising when it comes to development of practical hydrogen production and compression systems.

Public acceptance of hydrogen as a clean reliable energy source is still a challenge mainly because of previously publicized hydrogen accidents like the Hindenburg disaster of 1937. Public awareness of the clean energy hydrogen is a key to the success of hydrogen economy. This may imply that there is a need to the establishment of a new hydrogen safety culture in the society, development of innovative safety strategies and breakthrough engineering solutions that mitigate hydrogen accidents or incidents.

PEM electrolysis is a commercially viable hydrogen production method that has potential to produce green energy of high purity (99.999%). PEM Electrolyzer has a low gas crossover rate that result in yielding hydrogen of high purity. PEM Electrolyzer have the ability to operate with a wide range of power input like the grid, wind and solar. This is due to the fact that the proton transport across the membrane responds quickly to the power input. PEM electrolysis covers practically the full nominal power density range (10 -100%).

PEM electrolysis system efficiency, performance and cell degradation are keys to the development of clean hydrogen production. The concern related to high cost of catalysts used has opened research for alternative catalyst loading or substituting the expensive noble metals like platinum and iridium. The promising alternatives are core-shell catalysts, bulk metallic glasses and nanostructured thin films.

Hydrogen compression technology using MH compressors is a mature technology that has been published in many publications. MH compressors have been developed that can compress hydrogen to pressure >700 bars safely.

GAPS FROM THE LITERATURE RELATED TO THE CURRENT STUDY

Water electrolysis is a mature technology, and it is being used for hydrogen production capacities ranging from few cm^3/min to thousands m^3/h today. It is relatively efficient (>70%), but because it needs high quality energy (electricity) hydrogen produced by water-electrolysis is expensive. There is a potential to generate relatively inexpensive hydrogen from hydropower and nuclear plants during off-peak hours.

Hydrogen could be economically produced from large PV power plants if the cost of PVs could be brought to US$0.2 to US$0.4/Watts Peak. PEM electrolysers produce hydrogen with very high purity (up to 99.999), which may be used in a fuel cell directly without purification process.

Voltage increase is steeper in the first couple of thousands of hours of operation, 20–50lV/h, but then it levels off (<3lV/h), mainly because of electrolyser initial conditioning and equilibration of the complete system. The reasons for voltage increase are equilibration of water content in the membrane, and oxidation of catalyst and other metallic components. With good design and careful selection of materials, this performance degradation may be minimized.

The efficiency of an Electrolyser is inversely proportional to the cell potential, which in turn is determined by the current density, which in turn directly corresponds to the rate of hydrogen production per unit of electrode active area of the cell. A higher voltage would result in more hydrogen production, but at a lower efficiency. Typically, cell voltage is selected at about 2V, but a lower nominal voltage (as low as 1.6V) may be selected, if the efficiency is more important than the size (and capital cost) of the electrolyser system.

In addition there are power losses in voltage regulation and some power is needed for the auxiliary equipment (pumps, fans, solenoid valves, instrumentation and controls). Typical industrial electrolysers systems/ units have electricity consumption between 4.5 and 6.0kWh/Nm^3, corresponding to the efficiency of 65–80%.

Metal Hydride (MH) hydrogen compression utilises a reversible heat-driven interaction of a hydride-forming metal, alloy or intermetallic compound with hydrogen gas to form MH and is considered as a promising application for hydrogen energy systems.

The advantages of MH compression include simplicity in design and operation, absence of moving parts, compactness, safety and reliability, and the possibility to consume waste industrial heat instead of electricity.

The major factor affecting hydrogen compression efficiency of the MH materials is the plateau slope. Hydrogen compression performances of the real MH systems are significantly affected by hysteresis, as the values of plateau pressures for hydrogen absorption/hydrogenation are higher than the ones for hydrogen desorption/ dehydrogenation. Efficient metal hydride compression process requires a high compression ratio, high productivity and efficiency, long and reliable operation.

FINDINGS OF THIS STUDY

Designed prototype had a productivity of 2 Nm^3/h. PEM Electrolyzer system had a power rating of 8.6 kW PEM stacks managed by Beckhoff PLC controller. The Electrolyzer had a discharge output pressure of 20 bars. The prototype system was capable of working with the efficiency of 77% at optimal conditions. Its efficiency depended on selected power point therefore this value can vary significantly. Hydrogen production method, electrolysis is an energy-consuming process.

For the designed system, at least 23% of energy has been lost as a heat and due to internal consumption. Thermal energy generated due to stack electrochemical losses and BoP electrical losses accounts for approximately 33% increase of energy consumed. The PLC controller operated in a closed infinite loop, this enabled system safety that protected the whole system and ensured reliable operation.

PEM electrolysis cells characteristically operate between about 1.4 V at zero current and 1.9 V at full current. The lower voltage defines the energy required for electrochemical hydrogen conversion whilst voltages greater than that may be associated with internal resistive cell losses and consequent heat dissipation. These characteristics suggest a design configuration of 24 cells operating in series at 100 A, with a peak dissipation of 3.8 kW to achieve an efficiency of approximately 80%, with a 38 V total stack voltage.

Prototype PEMWE electrolysis process started at approximately 1.4 V per cell at which low hydrogen production rate occurs. At this voltage, the efficiency of the stack is high due to slow rate of electrochemical reactions as well as low current density. System efficiency is low as most of the power is consumed internally by balance of plant (BoP) components.

Once the voltage is scaled up by 200 mV, the rate of hydrogen production increases significantly to 41 and 82 g/h for single stack and the whole system, respectively. It is an optimal point in terms of system efficiency (77%) as activation losses of the stack are predominant. At maximum power point (11kW), the highest performance is obtained (99 and 197.8 g/h of hydrogen production). The efficiency for both the stack and the system is decreased - Ohmic and mass transport losses become significant.

Parameter		Average cell voltage [V]		
		1.4	1.6	1.8
Stack	Power [kW]	0.049	1.75	4.73
	Efficiency, LHV [%]	89.0	78.4	70.0
	H_2 production [g/h]	1.3	41.1	99.0
System	Power [kW]	0.37	4.23	11.01
	Efficiency, HHV [%]	28.7	76.7	70.9
	H_2 production [g/h]	2.7	82.2	197.8

Table 18: The comparison of parameters recorded and calculated at different cell's voltage for single electrolysis stack and whole electrolysis system consisting of 2 stacks

The system efficiency is decreased by electrical losses occurring at power supplies that generate high amount of thermal energy. The heat is removed from the system by forced circulation of air through the radiators as well as increased flow rate of cooling water. This also generates additional parasitic energy consumed by BoP components. For long lifespan of the system, it is advisable to operate at either low or nominal power point (4.2 or 9.9 kW).

The operation of the system at maximum performance will quickly lead to creation of additional losses due to ageing process of the electrolysis stack. The power required for nominal hydrogen production at BoL (Beginning of Life) and EoL (End of life) for the stack is 4.2 and 5.8 kW respectively.

In this work, we reported the hydrogen production autonomous system including its engineering, safety, testing and analysis. Designed electrolysis system operated based on an 8.6 kW PEM stack managed by safely integrated PLC controller. The system achieved an efficiency (HHV) of 82% at optimal conditions. Its efficiency depends on selected power point therefore this value can vary significantly in operation.

The calculations based on system lifespan indicate high productivity and efficiency at BoL 8.6kW and decreased production and efficiency at EoL 11.6kW. The power requirement of the stack might exceed the available resources hence trigger system decommissioning or stack refurbishment.

The system has multiple levels of built-in operator and stack safety redundancy. Control and safety systems monitor all flows, levels and temperatures of significance. All fault conditions are failsafe and are duplicated, triggering latching relays which shut the system down. Process indicators monitor several key variables and allow operating limits to be easily adjusted in response to experience of system performance gained in the field.

The prototype PEM electrolyser operated from a power supply with a capability of up to 100 A and up to 38 V corresponding to a power input of 8.6 kW at full load. The system has an extensive monitoring, control and safety system which encompasses all process values relevant to its safe operation. These include pressures, temperatures, flow rates and water levels at various locations, stack voltage and stack current, and hydrogen gas leakage detection.

The system is highly configurable but the usual consequence of detecting any abnormal value or fault is to remove power and shut down the system. Design details of the electrolysis stack itself was not considered in this study, it was a commercial stack supplied by Hydron Energy.

The design, integration and commissioning of the prototype PEMWE system was a critical part of this study. System testing and operation of the prototype PEMWE was an integral part of the study.

To facilitate comprehensive monitoring and control, the Beckhoff Twin CAT software, windows based with a multi-PLC system with on board data logging was employed on the prototype PEMWE. The prototype PEMWE was housed, in an equipment cabinet of modest size, the balance-of-plant incorporated a relatively sophisticated control and monitoring system providing emphasis on flexible operation and high levels of system safety and redundancy.

An attempt was made to achieve a compact package at this stage, resulting in a cabinet of generous size which was straightforward to assemble and is easy to service. Considerable size reduction would be possible for similar future designs.

PEM Water Electrolyser prototype system was subjected to a quantitative risk assessment method called Hazard Operability Study (HAZOP). The purpose of the HAZOP study was to investigate the complete prototype system, identify potential hazards and operability challenges. Appropriate remedial measures were highlighted, mitigated and integrated in the prototype system. Pre-start-up, start-up, shut-down and emergency procedures were formulated.

The production of hydrogen by electrolysis is an initiative aimed at reducing global warming by reducing toxic gas emissions which is a key to the establishment of clean environment. The waste product of electrolysis is oxygen. Oxygen is an environmentally friendly gas. This is in support of the South Africa's economy, a drive to reduce carbon footprint through initiatives like the White Paper on Renewable Energy of 2003 released by the department of energy.

Application of Hydrogen Risk Assessment Model modelling software on the facility housing the PEMWE system on H_2 release revealed some hazard scenarios. Hydrogen leak can either triggers complete system shutdown with no ignition or can result in a jet fire or explosion in worst case scenario. Dedicated engineering controls embedded in the PLC mitigate hydrogen fires risks.

The hydrogen produced by PEM electrolyser was feed to a 5 Nm^3/h 3-stage MH compressor. Hydrogen was compressed from 3 bar to 200 bars. The compressor fed the compressed hydrogen to a buffer - 12 cylinder pack (supplied by Air Products). Extensive work on the industrial MH compressors has been done and published as part of this project. Also the author has been able to demonstrate metal hydride compression technology, its performance, reliability, productivity and efficiency in other related publications.

SAIAMC research facility and HySA systems commercial fuel cell refuelling station were supplied with hydrogen from the buffer cylinder pack at high pressure of 200 bars. The refuelling infrastructure is a commercial refuelling equipment that is intrinsically safe and the hydrogen distribution infrastructure is certified and maintained by certified gas installers.

The project demonstrated South Africa's capabilities in hydrogen production and compression technologies embracing the emerging Hydrogen economy. This renewable energy technology initiative reduces the carbon footprint and addresses global warming challenges facing the world today.

Hydrogen production, compression and dispensing technology developed during this study can be used extensively in emerging Hydrogen economy in South Africa, creating employment opportunities to talented scientists and engineers. Application of hydrogen safety and sound engineering practise mitigated all safety related issues resulting in an intrinsically safe operating system.

This thesis was focused on proof of concept of the integrated hydrogen production, compression, storage and dispensing system, by the development of a prototype system and its trial operation at SAIAMC with a special focus on the establishment on design and operation protocols around hydrogen safety. The system modelling is indeed critical for the system optimisation and upscaling, but it is a subject of a separate study presently commenced with the participation of the candidate on the basis of the research outputs from his PhD thesis.

It has to be noted that though the modelling was not a part of this study, some results including detailed consideration of the operation of the PEM electrolyser (pages 133-139 and 147-152), as well as experimental study of the operation of the metal hydride compressor (pages 144-147) provide important starting data for the future modelling activities

RECOMMENDATIONS

Further investigations are highly recommended as a follow up to the research and results obtained in this PhD study:

- Integration & Testing of a locally (HySA Systems) produced 1Nm^{3}h PEM stack into the Prototype HySA PEM electrolyser system.
- Automation of all manual valves and the Ultra-Pure water supply system.
- Integration of prototype HySA PEM electrolyser system with a 5.2kW Photovoltaic supply (This objective was not achieved due to lack of funding for the purchase of a 5.2 kW photovoltaic supply system).
- Testing of the complete integrated subsystems, PEM electrolyser and 5 Nm^3/h Metal hydride compressor
- Design of a centralised PLC that controls and monitors all subsystems that is the hydrogen production (PEM Electrolyser), hydrogen compression (MH Compressor) and hydrogen distribution system.
- Mathematical modelling and simulation of complete system- hydrogen production, compression and dispensing

CHAPTER 6 – REFERNCES AND APPENDIX

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2. APPENDIX 1

PEM ELECTROLYSER OPERATION MANUAL

SYSTEM OPERATION

I. PRE-START UP PROCEDURE

After the stack is properly installed in the test set up / system and all the process lines are connected and inspected, the operator should check the following items prior to operation:

- Check if the stack is properly assembled and leak tight by turning on the process water pump (P- 101). No water should be leaking to the outside of the stack. Furthermore check if water is flowing in the anode loop (it should be safeguarded that a water flow is present when operating the stack e.g. by visual inspection of transparent tubing).

- Check if the stack is properly assembled and leak tight by turning on the thermal management subsystem. No heat transfer fluid should be leaking to the outside of the stack. Furthermore check if heat transfer fluid is flowing in the thermal management loop.

- Make sure the power supply sensing probes are connected to the designated cell plates (the cell plates that are next to the current collectors).

II. STARTUP CHECK LIST

- Is the extraction / ventilation switched on in the test bench / electrolysis system?

- Is the hydrogen sensor (HS-203) online and calibrated?

- Are all process connections and fittings properly tightened?

- ❖ Are the power cables and power supply probes properly connected? Are the 'live parts' not touching other components and/or frames?
- ❖ Are there no tears and/or ruptures visible in the installed piping (hoses of rigid piping)?
- ❖ Is the process water in R-301 clean? No dirt/particles in the water observed?
- ❖ Is the water quality of the process water below 1, 5 µS/cm?
- ❖ Is the temperature of the process water below 50 ˚C?
- ❖ Is the temperature of the EL100 stack below 50 ˚C?
- ❖ Is there no water on the surface on which the stack is installed indicating a leakage in stack, process piping and/or appendages?

- ❖ Is there any water in D-102 (as indicated by level sensor EIZA-104)?
- ❖ Is the temperature sensor of the stack (TIZA-403) properly fitted in the bore of the middle cell of the EL100 stack?
- ❖ Check all hoses and cables of the system. Check the stack. Is everything looking OK?

III. ELECTROLYSIS SYSTEM START UP SEQUENCE AND OPERATION

1. Switch on magna power supply 1 and 2. They must be in standby mode.
2. Switch on the PLC.
   - ➢ From the desktop click the icon Green Hydrogen system
   - ➢ From the main menu of Green Hydrogen system:

- Click manual control, open system P&ID
- Switch on cabinet fans
- Check the water level sensor for D-102A and D-102B
- Switch on water pump P-101A and P-101B,
- Circulate water in stack 1 and 2 for 2 minutes at 30 LPH
- Check water

3. Start pumps P-101A and P-101B from the PLC. Make sure the flow is between 50 ml/min and 2000 ml/min.

4. Check the water temperature entering the stack (sensor TS-403A and TS-403B). The value should be between 5 and 60 ˚C.

5. Check the water temperature exiting the stack (TS-401A and TS-401B). This should be between 5 and 70 ˚C.

6. Turn on the power supply (PS-501). Set the voltage level to 1, 5 V/cell (calculate the specific set voltage by the number of cells in the stack) (24 x 1.5) = 36V. Set the current to 100 A. Turn on the output of the power supply: the power supply is now operating in a constant voltage modus.

7. The stack is now performing the water electrolysis process: hydrogen and oxygen is now being produced (when transparent hoses are utilized bubble formation can be detected).

8. After 5 minutes raise the stack potential to 2 V/cell (calculate the specific set voltage by the number of cells in the stack) (24 x2) = 48V. The current set point is still 100 A.

9. The drawn current starts to increase as the stack heats up. When a current of 100 A is achieved, the stack voltage starts to decrease and stabilizes when the stack temperature (TS-403A and TS- 403B) of max 80˚C is reached.

10. Monitor the following process parameters:

    - Stack temperature (TS-403A and TS-403B),
    - The stack voltage Stack 1 and Stack 2 from PLC and magna power source 1 & 2,
    - Stack current Stack 1 and Stack 2 from PLC and magna power source 1 & 2,
    - Anode pressure (PS- 103),
    - Cathode pressure (PSH – 202),
    - Process water temperature entering the stack (TS-101A and TS-101B)
    - Process water exiting the stack (TIZA-102),
    - Coolant temperature entering the stack (TS-402A and TS-402B),
    - Coolant exiting the stack (TS-401A and TS-401B),
    - Proton water temperature (TIZA-201),
    - Process water conductivity (EIZA-105),
    - Hydrogen concentration in cabinet (HS-203),
    - Water level in D-102 (LS-104A and LS-104B).

11. Make sure that the following maximum threshold (trip) values are observed for:

    a. Stack temperature (TS-403A and TS-403B): 80˚C

   b. Stack voltage PLC electrical parameters: maximum individual cell voltage of 2,4V/cell times the number of cells in the stack
   c. Stack current PLC Stack 1 and 2 electrical parameters: 120 A
   d. Anode (oxygen/process water) pressure (PS-103): 5 bar
   e. Cathode (hydrogen) pressure (PSH-202): 20 bars
   f. Process water temperature exiting the stack (TIZA-102): 80˚C
   g. Coolant temperature exiting the stack (TS-401A and TS-401B): 80˚C
   h. Proton water temperature (TIZA-201): 70˚C
   i. Process water conductivity (EIZA-105): <1,5 µS/cm
   j. Hydrogen concentration in cabinet (HS-203): 75% of LEL (lower explosive limit : 4% H_2 in air)
   k. water level in D-102 (LS-104A and LS-104B): low water level in separator (D-102)

12. Adjust the set points for the actuators (e.g. the flow rate of pump P-101 and/or P-404 or the stack current and/or potential (E-501) when an alarm value (defined as a percentage of the threshold trip value) is reached.
13. The electrolysis process utilizes process water as a reactant. Make sure the process water reservoir (R-301) contains enough water at all time, the process water loop is replenished according to the process water utilization and the process water is continuously circulated through the stack according to the specified flow set point at a rated current. Note that adding cold process water to the reservoir R-301 will influence the stack performance.

14. As described in chapter 4, the proton water can be recirculated back to the process water loop (please provide means for recirculation) in order to decrease the process water consumption of the process.
15. EMERGENCY SHUT DOWN: WHEN A THE THRESHOLD OF A TRIP VALUE IS REACHED THE POWER SUPPLY TO THE STACK MUST BE TURNED OFF INSTANTENOUSLY BY MEANS OF OPENING THE ELECTRICAL LOOP E.G. BY MEANS OF A RELAY/CONTACTOR (R-504). TURNING OFF THE POWER OF THE ELECTROLYSIS PROCESS WILL STOP THE PRODUCTION OF GASSES.

IV. SYSTEM SHUT DOWN

When the system needs to be shut down (after operation or in case of emergency shutdown) the following sequence need to be initiated:

1. Open electrical parameters

Set Voltage and current on both power supply 1 and 2 to zero and click stop

2. Turn off the power supply into standby mode
3. Increase the cooling pumps P-404A and P-404B to 200 LPH and the fan speed to 100
4. Monitor the decreasing pressure in the cathode compartment with sensor PSH-202.
5. Monitor the decreasing pressure in the anode compartment with sensor PS-103.
6. Allow pump P-101A and P-101B to pump at a minimum flow rate of 150 ml/min for approximately 5 min.

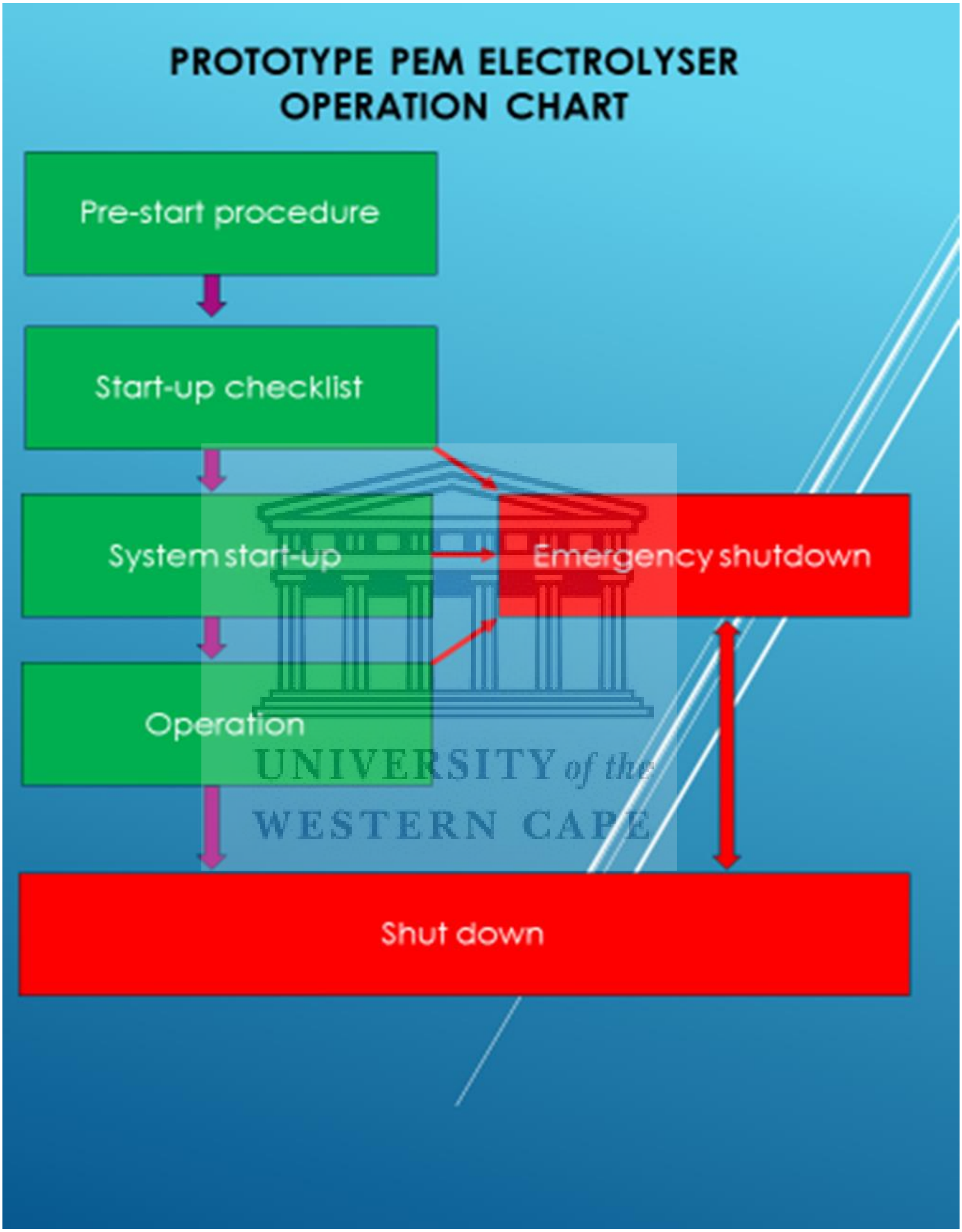
7. Turn off the pump P-404A and P-404B when the stack 1 & 2 temperature is between 25-30 °C
8. As the power to the stack is off and the water pump is no longer operational, the electrolysis process is fully stopped.
9. Please note that a potential is still present at the poles/current collectors of the stack.
10. Open Nitrogen, 2 bar through the cathode compartment of the stack to flush the system. This process will enable the inertisation of electrochemical reactions within the stack by replacing residual hydrogen by nitrogen.

DO NOT TOUCH OR IN ANY OTHER MEANS SHORT CIRCUIT THE POLES AS DANGEROUS CURRENTS CAN BE DRAWN.

V. CHECKLIST AFTER OPERATION

The following checklist need to be followed before operation:

- Is there enough process water present in the anode loop?
- Is the water clean? No particles in the water observed?
- Is there no water on the surface where the stack is placed upon indicating a leakage in stack, process piping and/or appendages?
- Check all hoses and cables of the system. Is everything looking OK and not detached



PROTOTYPE PEM ELECTROLYSER OPERATION CHART

Pre-start procedure

Start-up checklist

System start-up

Emergency shutdown

Operation

Shut down

Figure 60: Summary of Prototype PEM Electrolyser operation chart