CHAPTER 1

INTRODUCTION

This introductory chapter is divided into five sections. Section 1.1 entails the background and rationale behind this research project, Section 1.2 covers the production of energy in South Africa, Section 1.3 consists of ways for producing hydrogen, Section 1.4 outlines the SO_2 electro-oxidation within the Hybrid Sulphur (HyS) cycle and Section 1.5 addresses the problem statement and research objectives.

1.1 Background and rationale

The gradual depletion of and dependence on fossil fuels, air pollution and global warming have accelerated the development of alternative energy systems which use hydrogen as an energy carrier [1]. If we are going to wait until fossil fuels are even more scarce and expensive, the opportunity to benefit from the growing renewable energy sector will be lost [67]. Challenges presented by the earth's diminishing energy supply include developing new sources of energy, improving efficiency and energy conservation [153]. Since 1900, the use of energy has almost doubled every 20 years. Causes of this growth include: the population increase, growth of the labour force, increased wealth, products that use large amounts of energy to be manufactured and nonfuel uses of fossil fuels.

In 1977, Brecher *et al.* [1] stated that within the next few decades, alternative forms of transportable energy must be made available to counter environmental pollution from economically unstable fossil fuels. Moreover, the work already invested in hydrogen means that it is a strong candidate as a successor to the petrochemical age [153].

1.1.1 Problems

The use of energy creates serious problems. They include (1) depletion of fuel reserves (2) political and economic effects and (3) environmental pollution.

1.1.1.1 Depletion of fuel reserves

The global community have rapidly used available sources of energy that had accumulated for millions of years. The rapid growth of energy use threatens to exhaust the world's energy supply. Petroleum may become the first fuel to run out (growing scarce in the early 2000's). Coal, the most plentiful fossil fuel, will last more than 200 years. Eventually, people will have to find different sources of energy altogether [153].

1.1.1.2 Political and economic effects

About two-thirds of the world's oil reserves are situated in the Middle East and North Africa. Many industrialised nations rely on oil from Arab countries to fuel their economies. The continuous political instability in Arab nations has led to high oil prices and can exert severe political pressure with the institution of oil embargo [153].

1.1.1.3 Environmental pollution

The production, transportation and the use of fossil fuels all create environmental problems. Oil spills pollute the oceans, damage beaches and kill sea life. Strip mining of coal exposes land to erosion. Even the cleanest fossil fuel produces carbon dioxide when it burns. Carbon dioxide is a harmless gas but a build-up of this gas in the atmosphere may cause a phenomenon known as the greenhouse effect. Carbon dioxide, like glass in a greenhouse, allows sunlight to warm the earth but prevents heat from escaping back into space. The greenhouse effect could permanently raise temperatures on the earth, partially melting the polar icecaps resulting in global flooding [153].

1.1.2 South Africa's greenhouse gas emissions

In this era of climate change, South Africa needs to take more urgent measures to reduce energy usage than in the past. It is hoped that the Energy Efficiency Strategy will provide a blueprint for this venture [68].South Africa is the 13th largest emitting country based on 2007 fossil fuel CO_2 emissions, annually emitting 7 tonnes of carbon dioxide per capita, due to the energy intensive economy and high dependence on coal for primary energy requirements and is by far the largest emitter of greenhouse gases in Africa [64].

South Africa's greenhouse gas emissions contributed about 1.2% to the global increase in 1988[106]. With the domestic economy powered by coal, South Africa has experienced a seven-fold increase in fossil-fuel CO_2 emissions since 1950, with 80-90% of the emissions originating from coal [64]. For 2007, 85% of South Africa's fossil-fuel CO_2 emissions of 118 million metric tons were from coal, another 11.5% were from oil consumption, and the remainder was from cement manufacture, natural gas and coke-oven gas consumption. The oil price problems so evident in other countries appear to have had only a minor impact on South African fossil-fuel CO_2 emissions [68].

The South African Department of Science and Technology (DST) has identified hydrogen and fuel cell technologies as one of its *Frontier Science and Technology* initiatives and its recently approved National Hydrogen and Fuel Cell Strategy (2007) advises that local cost-competitive hydrogen generation solutions be developed by building on existing knowledge in high temperature gas-cooled nuclear reactors and coal gasification Fischer-Tropsch (F-T) technology [107].

1.2 Energy in South Africa

South Africa is a developing nation with significant heavy industry, which is by its nature energy intensive. South Africa is endowed with rich deposits of minerals and fossil fuel in the form of coal. It is no surprise, therefore, that the economic development of our country has historically been built upon the extraction and processing of these resources. Coal has inevitably emerged as the major source of primary energy (shown in Figure 1.1) to meet the demands of industry and the country as a whole. In 2000 the total primary energy supply to the nation was 4,300 petajoules, of which 79% was attributable to coal [68].

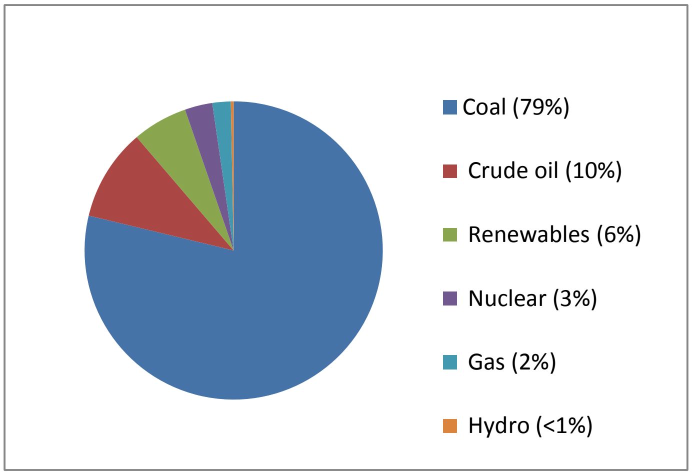

Figure 1.1 Primary energy supply in South Africa in the year 2000[70]

The existing energy policy of South Africa is captured within the White Paper on Energy Policy (1998). The policy aims to provide the nation with wider access to energy services, by various means, whilst ensuring that the environmental impacts of energy conversion and use are minimised as far as possible. This is of relevance to Africa as a whole as South Africa uses 40% of the total electricity consumed on the continent [68].

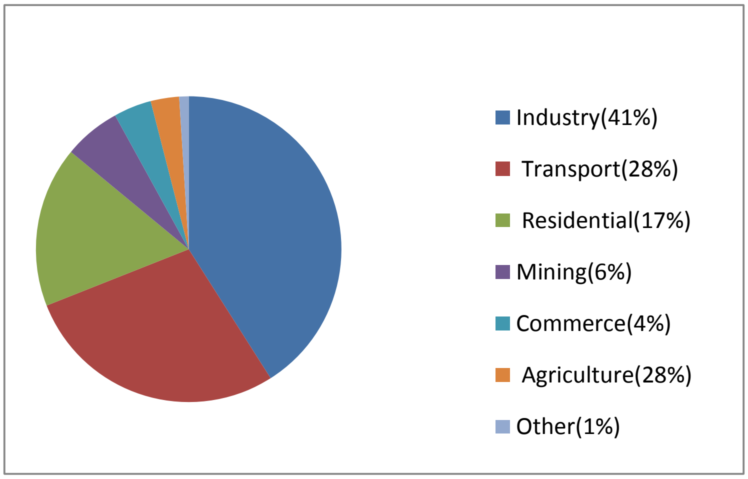

Figure 1.2 South African final energy uses by sector in the year 2000[70]

1.3 Hydrogen as an energy carrier

Hydrogen is the lightest element in the periodic table and it is the most abundant element in the universe. It is not a primary energy source but an energy carrier [70, 72].

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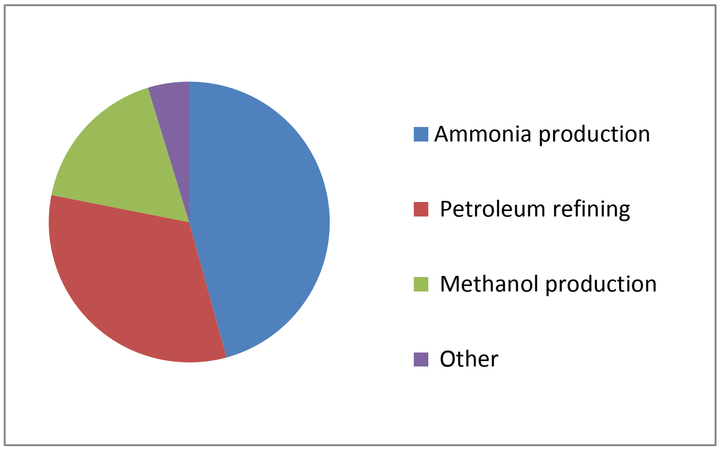

Figure 1.3 Representation of global hydrogen use [70]

Hydrogen is an important industrial chemical, particularly when used in systems for converting coal into synthetic gas and oil and it is projected as a fuel for the future [1]. Hydrogen has a high heat of combustion, which results in benign by-products and if produced using renewable/clean energy systems hydrogen production will not be dependent on decreasing reserves of oil and coal [38].

As shown in Figure 1.3, the breakdown of hydrogen used globally shows that approximately 60% of hydrogen is used as feedstock for ammonia production, 23% is used in oil refining, whilst 9% is used to manufacture methanol and the remaining 8% is used for chemical, metallurgical and space purposes [70]. This goes to show that hydrogen is not employed at present to replace the current primary energy supplies.

The vast majority (Approximately 95%) of hydrogen is produced from fossil fuel and only a small percentage of hydrogen is produced using water electrolysis since it is less efficient and more expensive (shown in Figure 1.4) [70]. Current hydrogen production technologies include steam methane reforming, partial oxidation, auto thermal reforming and gasification of coal or other organic fuels and small scale water electrolysis [70, 68].

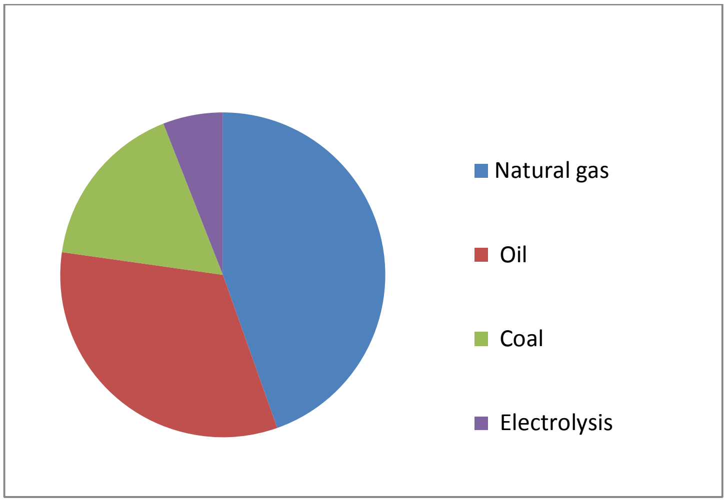

Figure 1.4 Different systems used for the global hydrogen production [70]

Hydrogen has the advantage that it can be stored until required, unlike electricity; this enables the elimination of costly backup systems which are maintenance intensive. The renewed investigation into nuclear energy as primary input energy of a future hydrogen economy resulted in interest in the hybrid sulphur process [14,27,65,70,75]. Hydrogen is a promising renewable fuel for transportation and domestic applications. Hence, in both the near term and long term, hydrogen demand is expected to increase significantly [70]. However, hydrogen is only present on earth in compounds and separating hydrogen from these compounds is energy intensive [72]. There are numerous of ways in which hydrogen can be produced, which is discussed below:

1.3.1 Hydrogen produced by coal

Coal is the most abundant fossil fuel on earth and is expected to continue to be an important source of energy over the next several hundred years. Coal deposits are widely distributed on earth and only a few areas do not have reasonable access to coal. Currently, about 23% of the world's primary energy comes from coal and the International Energy Agency expects consumption of coal to continue to increase in the future. For example, about 7.5 billion tons of coal is projected to be used in 2025. This amount, which includes coal used for production of hydrogen, will be nearly twice the amount consumed in 2004[67].

1.3.2 Hydrogen produced by hydrocarbons

With the transition to environmentally sustainable energy systems based on hydrogen and electricity as two major energy carriers of the future, it is forecasted that the demand for hydrogen would explode over the next decade or two. Given the advantages inherent in hydrocarbon fuels, such as their availability, cost competitiveness and convenience of storage and distribution, they are likely to continue to play a major role in hydrogen production for the near to medium-term future [67].All the existing processes for hydrogen production from hydrocarbon feedstocks are classified into two major categories: oxidative and non-oxidative processes.

Oxidative processing of hydrocarbons to hydrogen occurs in the presence of oxidants such as steam, oxygen (air), CO_2, or a combination thereof. Generally, the processes related to oxidative conversion of hydrocarbons to hydrogen are well established technologies and most of the industrial hydrogen production processes (such as steam methane reforming, partial oxidation of hydrocarbons, auto thermal reforming) belong to this category. Non-oxidative conversion of hydrocarbons to hydrogen occurs by splitting of C-H bonds in hydrocarbons in response to an energy input (heat, plasma, radiation) and it does not require the presence of an oxidising agent. These technologies produce minimal CO_2 emissions, which is certainly a great advantage over the oxidative processes that produce a great deal of CO_2 emissions [67].

1.3.3 Hydrogen produced by nuclear energy

The nuclear power industry is not an acceptable alternative because the problem of radioactive waste remains unsolved. The fuel most widely used by nuclear plants for nuclear fission is uranium, which is non-renewable. Nuclear power accounts for about 20 percent of the total electricity generated in the United States and like all industrial processes, nuclear power generation has by-product wastes; i.e. radioactive waste and heat [67].Radioactive waste is the main environmental concern. The waste is supposed to be stored in specially designed pools like large swimming pools or dry storage containers so that they will not come in contact with the outside environment [67].

1.3.4 Hydrogen produced by renewable sources

A thermochemical cycle combines heat sources (thermo) with chemical reactions to split water into its hydrogen and oxygen components. The term cycle is used because the chemical components used in these processes are continuously recycled. If work is partially used as an input, then the resulting thermochemical cycle is a hybrid one [141].

Since water rather than hydrocarbons are used as the source of hydrogen, no carbon dioxide emissions are produced and the hydrogen produced is highly pure [1, 15]. The ideal thermochemical cycle for water decomposition should accomplish two goals [1]:

1. Minimize product cost by achieving high thermal efficiencies in a process with low capital and operating costs.
2. Maintain the efficiency over a range of heat source temperatures, thereby permitting maximum flexibility in the choice of energy sources and heat exchanger materials.

1.4 The Hybrid Sulphur (HyS) cycle

The HyS cycle (also known as the Westinghouse sulphur cycle) was first proposed by Brecher and Wu at Westinghouse electric Corporation, where it was developed in the 1970s and 1980s in order to produce hydrogen from water. The HyS cycle is one of a number of thermochemical schemes proposed and was placed first of the 115 thermochemical hydrogen production cycles identified by the office of nuclear energy at the USA Department of Energy [1, 27]. The schematic diagram of the HyS is shown in Figure 1.5.

1.4.1 Process description

Sulphuric acid is decomposed to sulphur dioxide, water and oxygen using thermal energy from a high temperature (>800˚C) heat source according to the following thermochemical reaction.

$$H_2SO_4 \rightarrow H_2O + SO_2 + ½O_2 \qquad 1.1$$

Sulphur dioxide (SO_2) resulting from the decomposition reactor is combined with recycled sulphuric acid (H_2SO_4) and make-up water (H_2O) and is fed to the anode of the electrolyser where it is oxidised to H_2SO_4 and protons (H^+) at a low temperature (100˚C). This electrochemical oxidation process has a standard reduction potential (E) of 0.158V vs. SHE (standard hydrogen electrode).

The protons subsequently diffuse through the proton exchange membrane (PEM) of the electrolyser to the cathode where they are reduced into hydrogen (H_2).The net electrochemical cell reaction is the sum of a cathodic reaction for producing hydrogen and an anodic reaction for the oxidation of sulphur dioxide to form sulphuric acid [2, 19].

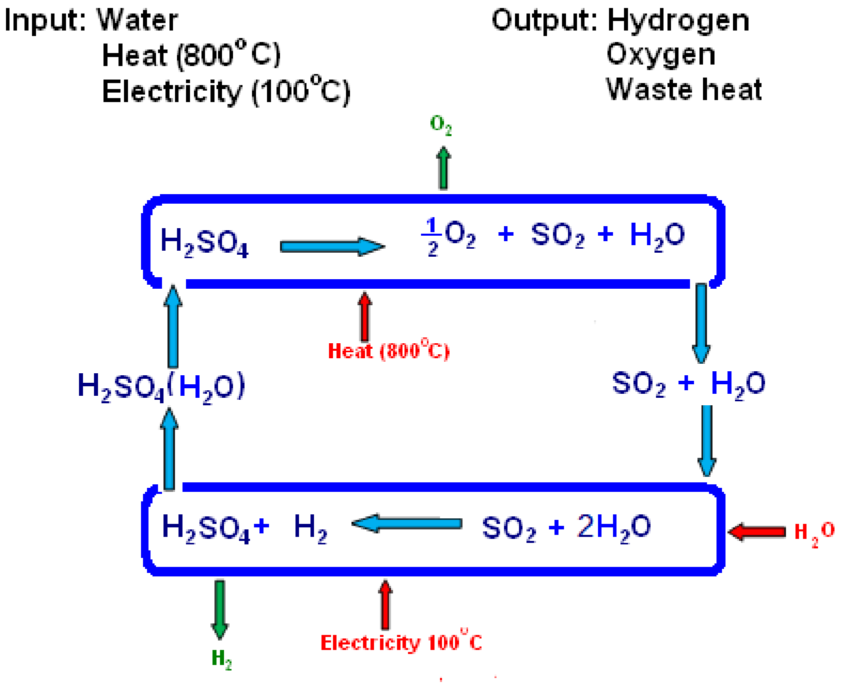

Figure 1.5 Hybrid sulphur (HyS) cycle

$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H^+ + 2e^-$ E˚ = 0.158V 1.2

$2H^+ + 2e^- \longrightarrow H_2$ E˚ = 0.00V 1.3

Net electrochemical reaction:

$SO_2 + 2H_2O \longrightarrow H_2SO_4 + H_2$ E˚ = 0.158V 1.4

The HyS cycle is advantageous and attractive for the following reasons:

The SO_2-depolarized electrolyser (SDE) will consume much less electricity per mole of H_2 produced than regular water electrolysis. In reality normal water electrolysers operate at cell potentials of 1.7V to 2.0V when economically reasonable current densities are maintained [1, 27], whilst the theoretical voltage to decompose pure water is 1.23V at 25˚C. The potential (V) for SO_2-depolarized electrolyser (SDE) is less than 15% of the voltage required in commercial water electrolysers, which makes the HyS cycle an obvious H_2 production alternative [27, 30, 31].

$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$ E˚ =1.23V 1.5

$2H^+(aq) + 2e^- \longrightarrow H_2(g)$ E˚ = 0.00V 1.6

$2H_2O(l) \longrightarrow 2H_2(g) + O_2(g)$ E˚ =1.23V 1.7

The hybrid sulphur cycle requires minimal chemical feedstocks because oxides of sulphur serve as recycled intermediates within the system and sulphur is the only element in the cycle other than H_2 and oxygen. The HyS cycle is recognised to have high thermal efficiencies and low hydrogen production costs when combined with an advanced nuclear or solar reactor [1, 13]. When a sensitivity analysis was carried out by Graf *et al.* [36] for three different cost scenarios, hydrogen production costs ranging from €3.9-5.6/kg for the HyS cycle, €3.5-12.8/kg for the metal oxide based cycle and €2.1-6.8/kg for electrolysis were obtained.

Given the current state of the art, the current hydrogen production cost employing the hybrid sulphur cycle was assessed at €6.6/kg for the first-of-a-kind plant. This estimate is based on quite optimistic assumptions as many uncertainties are attached to this evaluation, in particular regarding the electrolyser; e.g. what will the final technology to be implemented be? What will the resulting price be? Is the 0.6V applied potential realistic? How often will the electrolysers have to be replaced? Experiments are then needed to acquire data concerning the electrolyser performances and durability. Comparing hydrogen production costs of diverse processes is tricky as uncertainties are numerous and different [35].

Improvements to the HyS system design have resulted in higher expectations for system efficiency and lower expected hydrogen production costs. The projected HyS hydrogen cost with these assumptions could be in the range of $2.00-3.00/kg. These results are only indicative as to what could be achieved if a number of technology development challenges are successfully addressed [32].

It was reported by Jeong *et al.* [30] that the SDE is the main source of the HyS cycle inefficiency and that a 3% reduction of the cell potential will result in a 1% increase of the overall cycle efficiency [150]. Lu *et al.* [151] predicted that cell potentials of -0.45 to -0.75V could be obtained at current densities of 0.1-0.4A.cm^{-2} for properly designed and optimised SDEs. Savannah River National Laboratories (SRNL) are of the conviction (given their PEM SDE development experience) that cell potentials of 0.6V should be attainable at economically reasonable current densities with (a) higher operating temperatures (>100˚C) and (b) higher operating pressures (≥10bar).

According to Gorensek and Summers [27] of SRNL, their target is a cell potential of 0.6V at a current density of 0.5A.cm^{-2}. A phenomenological model of the electrolyser (SDE) operation has been characterised using development performance targets i.e. the SDE is assumed to operate at a fixed cell potential of 0.6V with a SO_2 conversion of 40% at a 50wt% H_2SO_4 product composition. If these targets cannot be met, the efficiency advantage of HyS over water electrolysis will be diminished. The conversion target should be easiest to achieve, while the cell potential will likely be the hardest.

Although the thermodynamics of the SDE is more favourable than that for normal water electrolysis, a major challenge is the development of an efficient and cost effective electrochemical reactor (SDE). Supported by the US DOE, SRNL have been leading efforts, together with Giner Electrochemical Systems, to develop an SDE. The main challenges with regard to component development are the following: (a) electrocatalysts, (b) membranes, (c) MEAs, and (d) operating conditions such as temperature, pressures and different electrolytes.

(a) Electrocatalysts are aimed at lowering the operating potential and/or increasing the current density. It would seem that the slow rate of oxidation of SO_2 at the anode is a major contributor (~70%) towards the overpotential. The largest source of improvement in SDE performance will arise from the identification of a means to increase electrode kinetics. This can be achieved by the development of a superior electrocatalyst (in conjunction with increased operating temperatures, which may require a superior membrane).

(b) Three membranes that are currently being investigated due to having shown promise from preliminary studies include (1) modified Nafion® (2) polybenzimidazole (PBI) and (3) Sulfonated Diels Alder Polyphenylene (SDAPP). One of the biggest challenges is the prevention of SO_2 diffusion from the anode through the membrane to the cathode where it is reduced to elemental sulphur and deposited onto the cathode, thereby poisoning the cathode catalyst.

(c) MEA is made up of electrocatalysts (on the cathode and anode) and the proton exchange membrane.

(d) Electrolytes are tested for proton conductivity, an obvious hurdle to overcome due to the corrosive nature of sulphuric acid and SO_2 transport. Pressure and temperature are tested for SO_2 solubility.

1.4.2 Description of the SO_2 Depolarised Electrode

The most important attribute of the SDE is lowering of the overall theoretical potential from 1.23V to 0.158V vs. SHE [19]. This could make for the more efficient production of hydrogen having lower power input compared to regular water electrolysis [2]. The original electrolyser design concept consisted of two compartments separated by a membrane. More modern electrolyser designs, shown in Figure 1.6, include the use of a membrane electrode assembly (MEA), which results in a reduced overall cell potential [108].

Two types of catalysts will be needed for the SDE, one for the anode and one for the cathode. The electrochemical reaction at the cathode occurs at higher rates than the reaction that occurs at the anode. Compared to the cathode, the kinetics of the electrochemical oxidation of SO_2 at the anode are very slow [2, 19, 15]. Consequently, most of the inefficiencies of the electrolyser arise from the slow kinetics of the reaction at the anode [113].Furthermore, this anode catalyst is subject to a harsher chemical environment (concentrated H_2SO_4 solutions) compared to the cathode.

The reaction medium affects the catalyst and can change its chemical composition, surface area and even catalytic properties [113]. As already mentioned the SO_2 depolarized electrolyser (SDE) used in the HyS process, oxidises sulphur dioxide to form sulphuric acid, protons and electrons at the anode [2, 19, 15] as shown in Figure 1.6. The SO_2 and H_2O are combined with make-up H_2O (and recycled H_2SO_4) and fed to the anode of an electrolyser, where the oxidation of SO_2 takes place. In the electrolysis process, sulphur dioxide is reoxidised to hexavalent sulphur as H_2SO_4. The reoxidised species is recycled back to the decomposition reactor [18-21].

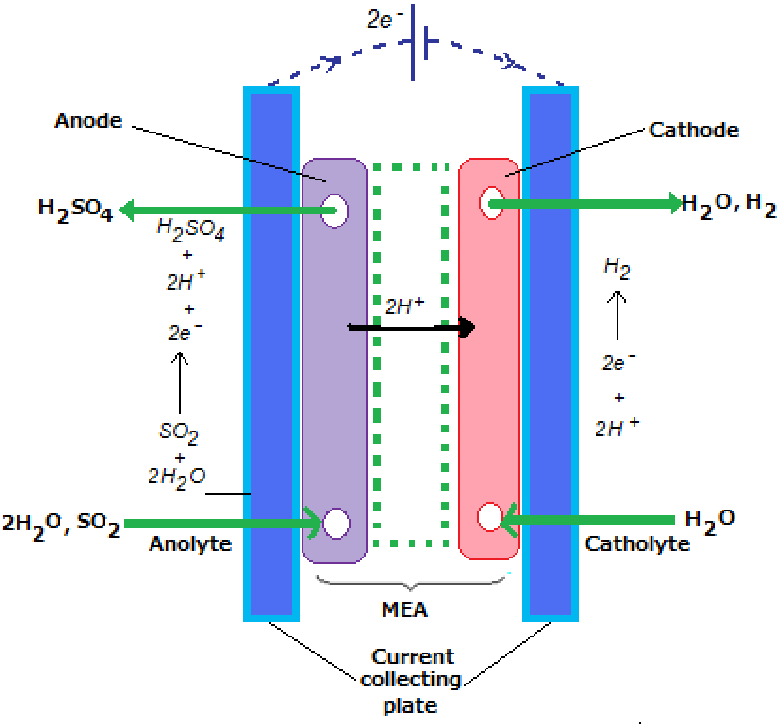

Figure 1.6 SO_2-depolarised electrolyser for hydrogen production[108]

According to Gorensek *et al.* [26] several papers [1,5-9] incorrectly report the standard reduction potential for the SO_2 oxidation to be 0.17V vs SHE. It is obtained from the original proposal of the HyS cycle, in which the inventors used a well-known relationship between Gibbs free energy and equilibrium cell potential to calculate E˚. The reason for the discrepancy is that Brecher and Wu only had access to older thermodynamic data which have since been rendered obsolete. Gorensek *et.al* [26] further stated that, if the standard reduction potential for the SO_2 oxidation reaction is recalculated using currently accepted standard Gibbs free energies of formation for the species involved, a value of E˚=0.158V vs. SHE is obtained. This then, is the cell voltage value of the standard reduction potential for the reaction that will be used henceforth. The advantages of the HyS design concept include high electrochemical efficiency and a small footprint, both of which are crucial for successful implementation on a commercial scale. The smaller footprint is a major benefit in scaling the electrolyser to the size that will be required for the commercial production of H_2 [14]. O'Brien *et al.* [20] states that the current density a cell is capable of producing at a specified voltage is dependent on several factors including the composition and concentration of the anolyte and catholyte, as well as the applied temperature and pressure.

According to Jomard *et al.* [28] the SDE operating conditions (potential and current density) are strongly dependent on concentration, temperature and pressure with the lowering of the sulphuric acid concentration resulting in the decrease of cell potential. On the other hand, the heat requirement increases due to the water amount to be processed. Current targets are that the SDE will operate at the following conditions: a potential of 0.6V, a current density of $0.2A.cm^{-2}$ with SO_2 dissolved to saturation at 10bar and 80˚C (353K) in 50wt% sulphuric acid.$0.2A.cm^{-2}$ was reportedly achieved by Westinghouse in early development of the electrolyser and a performance goal of $0.5A.cm^{-2}$ was specified. An improvement of this magnitude will result in a 60% decrease in the required electrolyser area and significantly reduce electrolyser capital cost [20, 30].

The target for optimal electrolyser performance proposed by Gorensek and Summers involved a current density of $0.5A.cm^{-2}$ at an applied voltage of 0.6V [27]. This performance was reportedly achieved by Staser *et al.* for a gaseous sulphur dioxide feed[7], although best performance with dissolved sulphur dioxide has not exceeded the original target of $0.2A.cm^{-2}$ at an applied potential of 0.6V[14]. If all of the SO_2 is delivered to the SDE and consumed to produce H_2, this is equivalent to 328.6kJ/mol H_2. Since this number is significantly less than 450kJ/mol H_2, the HyS cycle using a SDE operating at a cell potential of 0.6V, coupled to a bayonet decomposition reactor heated by an advanced nuclear heat source, have the potential to outperform normal water electrolysis[27]. SDE operating parameters are provided in Table 1.1.

Major challenges facing SDE are

- Good stability in concentrated sulphuric acid media
- Prevention of SO_2 migration into the cathodic compartment H_2 migration the anodic compartment, allowing H^+ to move through the membrane to maintain a low resistivity,
- The choice of the separator is important to optimise the performance of the electrolyser
- Optimisation of catalysts for the anodic and cathodic reaction (low overpotential) [17, 14, 13].

Originally Westinghouse designed a SDE known as the ‘Parallel Plate Design’ (Figure 1.7) this design however suffered from high overpotentials (η) resulting in high cell potentials. This is the direct result of large electrolyte volumes, poor electrolyte electrode contact, poor electrochemical conversion, loss of SO_2 and H^+ and poor current density.

Table 1.1 SDE operation parameters within HyS cycle[26]

Property	Value	Units
Single cell size (active area)	1	m^2
No. of cells per module	200	
Avg. Voltage per module	600	mV
Current density	500	mA/cm^2
Cell operating temperature (outlet)	100	℃
Cell operating pressure	20	bar
SO_2 utilisation	40	%
Anode H_2SO_4 concentration (outlet)	50	wt%
Anolyte flow rate (inlet)	322.3	kg/hr
Catholyte water flow rate (inlet)	56	kg/hr
Module voltage	120	V(DC)
Module current	5000	A
DC power input	600	kW
Hydrogen output (flow rate)	37.62	kg/hr
Hydrogen output (HHV)	1.5	MW_{th}

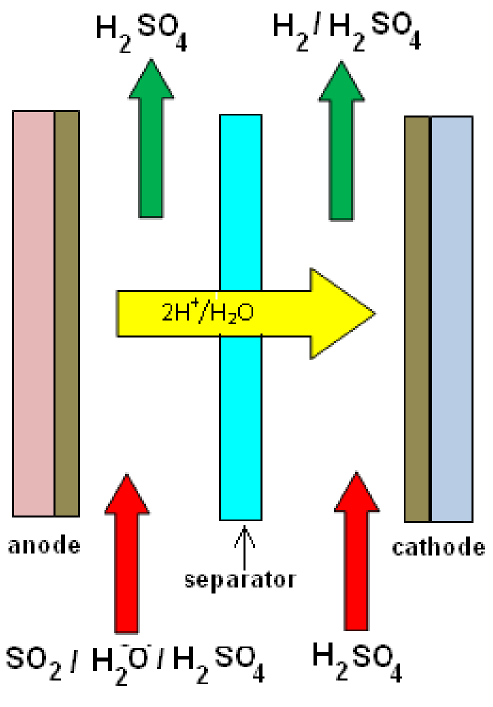

Figure 1.7 Westinghouse's design for a parallel plate SDE[18]

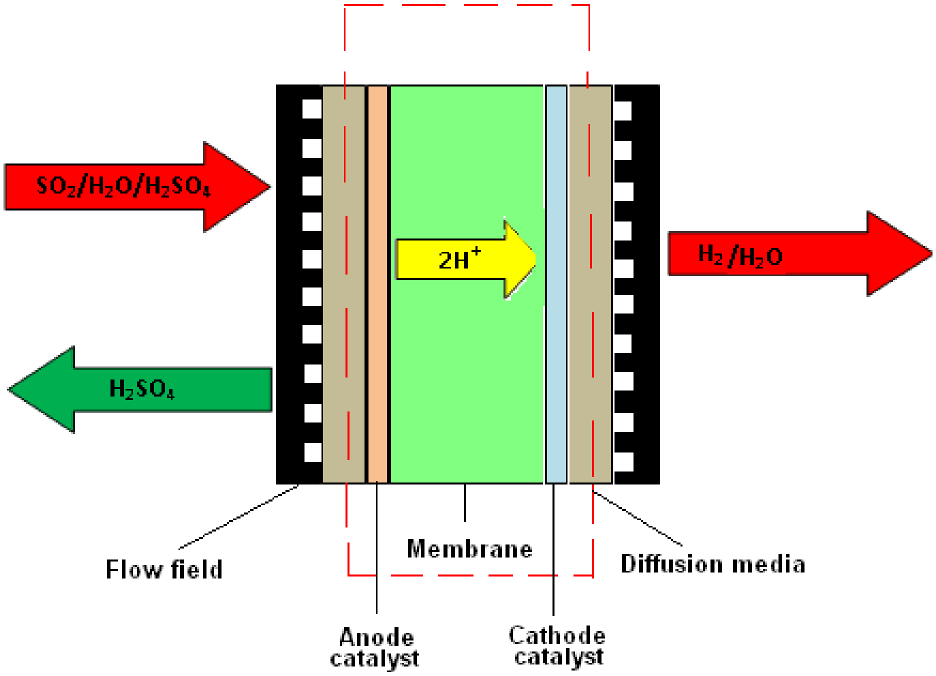

Figure 1.8 A PEM (proton exchange membrane) fuel cell electrolyser design [18]

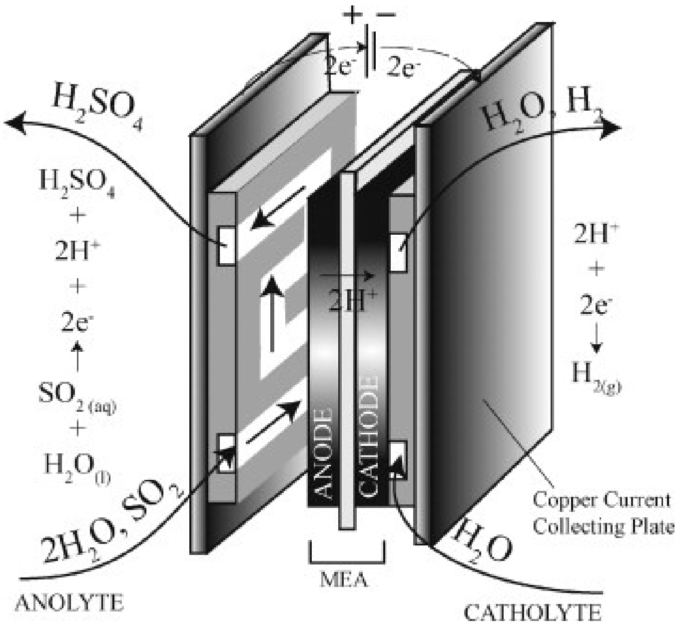

Figure 1.9 Electrolyser set up (MEA) [108]

An improved SDE design, shown in Figure 1.8, was subsequently borrowed from the fuel cell industry and based on a PEM (proton exchange membrane) fuel cell. This brought about smaller electrolyte volumes, improved electrolyte electrode contact, improved electrochemical conversion, improved usage of SO_2 and H^+ , improved current density and resulted in lower overpotentials (η) and lower cell potentials

Research institutions such as Savannah River National Laboratory and the University of South Carolina are highly involved in these aspects with focus on mass transfer issues and sulphur dioxide cross-over. Sulphur dioxide cross-over relates to the problematic diffusion of sulphur dioxide through the membrane to the cathode compartment where it is subsequently reduced to sulphur. The most recent SDE is shown in Figure 1.9.

At present, the acid electrolyser within the cycle is thermodynamically inefficient, exhibiting significant and (yet) unexplainable overpotential. This loss can mainly be attributed to the high anodic onset potential for the oxidation of sulphur dioxide to sulphuric acid and poor reaction kinetics [152].

1.4.3 The effect of sulphuric acid on SO_2 oxidation

Anhydrous H_2SO_4 is a very polar liquid, having a dielectric constant of around 100 and high electrical conductivity. Conductivity is defined as the ability of a solution to pass electric current, with the conductivity of a solution depending on the concentration of ions, the mobility of ions and the temperature of the solution [29].

Darling *et al.* [46] conducted experiments to determine the conductivity of sulphuric acid over a concentration range of 0.5 to 99wt% in a temperature range of -33.13 to 46.42℃. The results showed that the conductivity of the acid increased with increasing temperature, whilst conductivity decreased (at acid concentration of 40wt% and above). This is due to the hydrogen ion concentration in diluted sulphuric acid concentration, but at higher concentrations it decreases again. The ions resulting from the dissociation of H_2SO_4 in water are responsible for passing the electric current. Maximum conductivity is achieved for sulphuric acid between 20-40wt%. In spite of the viscosity of the acid, the effective conductivities of the $H_3SO_4^+$ and HSO_4^- ions are high due to an intra-molecular proton switch mechanism, making sulphuric acid a good conductor. It is also an excellent solvent for many reactions.

SO_2 oxidises and produce H_2SO_4 as product according to the following reaction:

$$SO_2(aq) + 2H_2O(l) \rightarrow H_2SO_4(aq) + 2H^+(aq) + 2e^- \qquad 1.2$$

Considering the Nernst equation for this oxidation reaction it is clear that with increased sulphuric acid concentration E_{cell} will increase negatively as E° equals 0.158V. The overpotential therefore increases and we move further away from the standard condition where $E_{cell} = E^\circ$

$$E_{cell} = E^o - \frac{RT}{nF} ln \frac{[H_2SO_4][H^+]^2}{[SO_2]} \qquad 1.8$$

Colon-Mercado and Hobbs [21] confirmed that the onset of SO_2 oxidation occurred at increased open circuit potentials (OCP) as the sulphuric acid concentration was increased, with OCP being the potential at which no current flows, i.e. the oxidation and reduction reactions balance out. Struck *et al.* [9] found that current density decreased from 25 to 0mA.cm^{-2} with an increase in sulphuric acid concentration from 5 to 80wt% at 0.7V. The concentration of H_2SO_4 produced by the oxidation of SO_2 is crucial in determining the overall operating efficiency of the HyS cycle. The rate of H_2SO_4 production is determined by Faraday's law because the current density is the same at every point on the electrode, the water flux and hence, the concentration of sulphuric acid is uniform throughout the electrolyzer. The less the amount of water (higher H_2SO_4 concentration) sent to the decomposition reactor the less the energy needed to vaporise this stream [8].

Scott *et al.* [12] studied the effects of sulphuric acid concentration on the oxidation of SO_2. The activity of H^+ ions and relative concentrations of sulphoxy species (SO_2, HSO_3^-, and SO_2^-) change. Current efficiency also decreased with increasing electrolyte concentration, whereas energy consumption increased slightly and the mass transfer coefficient decreased with increasing H^+ ion concentration due to the reduction in activity of dissolved sulphoxy species [12].

Not only does increasing the sulphuric acid concentration decrease the solubility of SO_2, which may lead to mass transport limitations at the anode, but it also increases the operating cell potential. The net result is higher energy consumption by the SDE at higher acid concentrations. Clearly, less concentrated sulphuric acid is desirable for efficient SDE operation. However, more concentrated sulphuric acid is better for the high-temperature decomposition reaction that regenerates SO_2 [26]. Gorensek *et al.* [26] found that at a temperature of 80˚C and pressure of 6.00 bar, the reversible potential grows from 0.206V at a sulphuric acid concentration of 30wt% to 0.347V at a sulphuric acid concentration of 60wt%. This result indicates that sulphuric acid concentration has a major impact on electrolyser operation.

Therefore, optimising the efficiency of the HyS cycle requires a trade-off between the electrolyser and the decomposition reactor energy requirements. Sulphuric acid could be decreased as well by increasing water transport to the anode. While this would result in a lower reversible cell potential and higher SO_2 solubility at all current densities, less concentrated sulphuric acid would be detrimental to the efficiency of the downstream decomposition step. The activation barrier for SO_2 oxidation is also large, suggesting that reductions in cell voltage could be obtained with more active catalysts [8, 26]. Clearly, a trade-off exists between sulphuric acid decomposition and electrolyzer performance [26].

However, the decomposition reactor is not a crucial necessity for the SDE. Gaseous SO_2 can be fed directly into the SDE. Capturing SO_2 (emitted as a pollutant) for this purpose has a huge environmental benefit. Jung *et al.* [149] proposed the Once-through Hybrid sulphur (Ot-HyS) process which produces hydrogen using the same sulphur dioxide depolarised water electrolysis (SDE) process found in the original Hybrid

Sulphur cycle (HyS). In this process the sulphuric acid decomposition (SAD) process in the HyS process is replaced with the well-established sulphur combustion process as shown in Figure 1.10

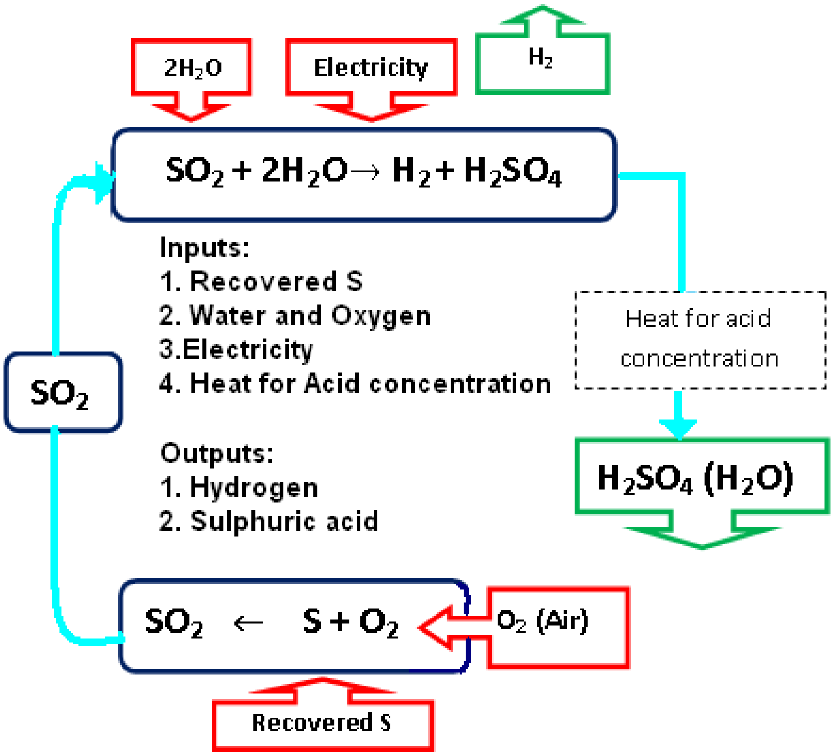

Figure 1.10 Reaction steps of Once-through Hybrid sulphur cycle[149]

Table 2.2 Net thermal efficiency benchmarking[149]

Benchmark (Based on 1kmol/s-H_2)	Ot-HyS	SRNL's PBMR/HyS
Heat requirement [MW_{th}]	112.5	417.1
Electricity requirement [MW_e]	142.4	120.9
Thermal-to-electric conversion efficiency of NPP	33.33%	42%
Equivalent heat requirement [MW_{th}]	401.4	287.9
Total heat requirement [MW_{th}]	513.9	705.0
Net thermal efficiency (LHV basis)	47.09%	34.33%
Net thermal efficiency (HHV basis)	55.65%	40.57%

The Ot-HyS process could play an important role in securing a bridge to the sustainable energy future during the short-term transitional period because of its competitive advantages such as a higher net thermal efficiency, less technical challenge and favourable sulphur statistics (shown in Table 2.2) [149].

1.4.4 Solubility of sulphur dioxide

Water, sulphur dioxide and oxygen can never be at true equilibrium in the liquid phase since oxygen reacts with ions formed by dissolved sulphur dioxide in a reaction that is strongly dependent on pH and dissolved impurities. Shaw *et al.* [16] has observed that if sulphur dioxide was added to water at a fixed temperature, both the concentration and pressure became correspondingly greater. When the solution reached its saturation concentration a second liquid phase separated out, which was determined to be water dissolved sulphur dioxide [16].

Further additions of sulphur dioxide resulted in the readjustment of the relative amounts of the two phases to a new equilibrium but the percentage composition of both phases remained unaltered. It was determined that the vapour pressures of the two phase system were consistently lower than the vapour pressure of pure sulphur dioxide [16].

Although thermally-activated processes are known to be enhanced by temperature, a strong negative effect of this parameter on the SO_2 oxidation current is observed by Charton *et al.* [25]. Sulphur dioxide solubility and its concentration in the laboratory cell actually decreases with temperature and could be responsible for this behaviour. Indeed, at atmospheric pressure the SO_2 solubility in water decreases with temperature according to Equation 1.9.

$$C_{SO_2} = 3.146 \times e^{-0.0364T} \qquad 1.9$$

In aqueous concentrated sulphuric acid solutions, SO_2 exists in molecular and ionic forms. In high sulphuric acid concentrations, SO_2 dissolves mostly in its molecular form rather than its ionic form. Govindarao *et al.* [135] further showed that the ionisation of SO_2 becomes negligible at sulphuric acid concentrations >22wt%. The concentration of dissolved molecular SO_2 is taken to be equal to the solubility of SO_2 in concentrated sulphuric acid. Increasing the sulphuric acid concentration will decrease the solubility of SO_2, which may lead to mass transport limitations at the anode [135].

Lu *et al.* [109] developed the following empirical equation (Equation 1.10) to predict the solubility of SO_2 gas in g/100g sulphuric acid solution at 1atm

$$C_{SO_2} = 8.1 \times 10^{-4} \exp\left(\frac{2800}{T} - 1.3X_{soln}\right) \tag{1.10}$$

Where X is the weight percentage (wt %) of H_2SO_4 and T is the temperature in Kelvin [109].

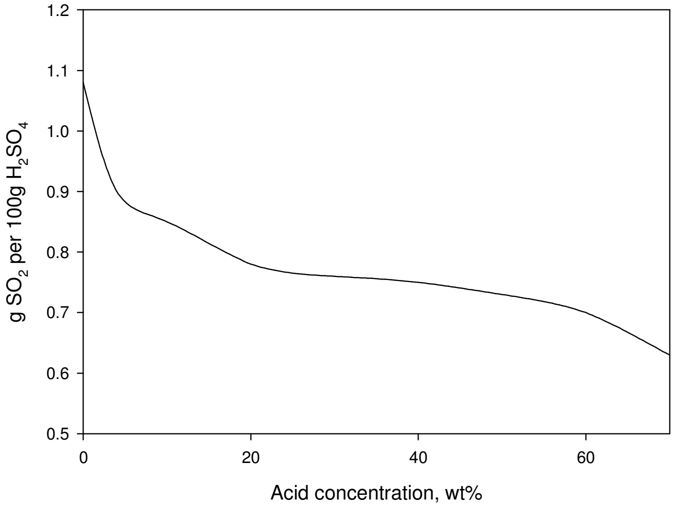

Figure 1.11 SO_2 solubility in sulphuric acid as a function of acid concentration. The system temperature is 80˚C and the pressure is 1bar[26]

The OLI MSE (mixed solvent electrolyte) model predicts that SO_2 solubility decreases as the sulphuric acid concentration increases. For example, the solubility of SO_2 decreases from 7.54g to 5.49g per 100g of sulphuric acid at 80˚C and 60bar system pressure when the acid concentration is raised from 30 to 60wt%. Indeed, at atmospheric pressure the SO_2 solubility in water decreases with temperature [26]. SO_2 solubility in the H_2SO_4 solutions as a function of acid concentration at 80˚C with pressure of 1bar is shown in Figure 1.11.

In sulphuric acid solutions ranging from 50 to 80wt%, where the solubility is lower than in water (i.e. 1.0mol.L^{-1} at 20˚C versus 1.5mol.L^{-1} in water), it is only 0.1mol.L^{-1} at 90˚C. The kinetic model described below is therefore valid only under atmospheric pressure conditions.

Above 40wt% the favourable effects of a temperature rise on both water activity and thermally activated process kinetics competed with its unfavourable effect on SO_2 solubility in the H_2SO_4 solutions [111].

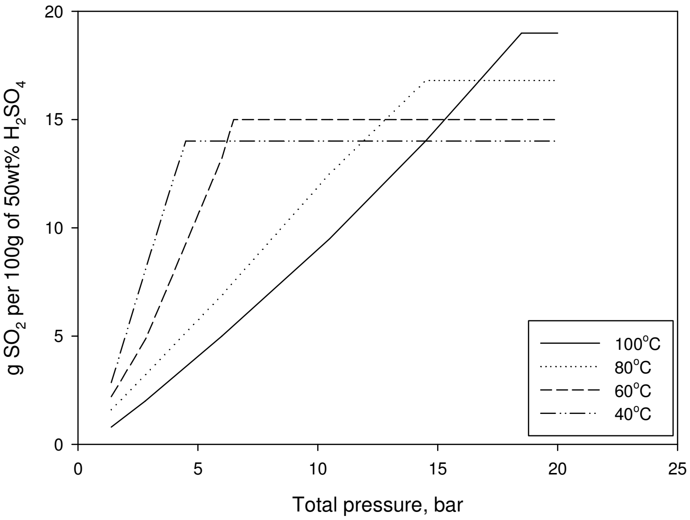

Figure 1.12 SO_2 solubility in sulphuric acid as a function of system pressure. The concentration of sulphuric acid is 50wt%[26]

Without a pressurised cell, the achievable improvement in the performance of an SO_2 depolarised electrolyser is limited by decreasing SO_2 solubility in 10wt% H_2SO_4 and increasing temperature [110]. SO_2 solubility in the H_2SO_4 solutions as a function of system pressure at different temperatures in 50wt% H_2SO_4 is shown in Figure 1.12.

Staser *et al.*[7] showed higher efficiency than Westinghouse's liquid SO_2 cell. That is, Staser *et al* achieved 0.4A.cm^{-2} at 0.76V compared to Westinghouse's 1.05V at this current. At the potential of 1.05V a current density of 0.66A.cm-^{2} was achieved. The large increase in voltage for the liquid-phase SO_2 electrolyzer between 0.050 and 0.4A.cm^{-2} is due to the relatively poor conductivity of the diaphragm separator. The liquid-phase electrolyzer is limited to a maximum current density of 0.4A.cm^{-2} due to mass-transfer limitations resulting from the solubility of SO_2 in water. The gas-phase electrolyzer does not face these solubility limitations. Instead, the increase in voltage for the gas-phase electrolyser beyond 0.6A.cm^{-2} is due to the limited rate at which water can diffuse through the PEM.

Work done by Appleby *et al.* [11] has shown that the solubility of SO_2 in H_2SO_4 is relatively independent of acid concentration in the range of 50-80wt%H_2SO_4 but it falls tenfold in the temperature ranges between 20-95℃. SO_2 evaporates at and below 40bar at room temperature and becomes liquid above 40bar. Hayduk *et al.* [61] reported a decrease in SO_2 solubility for very low acid concentrations than in water. As the acid concentration is increased above about 40-50wt% H_2SO_4, a steady increase of SO_2 solubility is observed with increasing acid concentration.

The electrolysis cell utilises dissolved sulphur dioxide as the electroactive species for oxidation at the anode. Unfortunately, however, sulphur dioxide is sparingly soluble in sulphuric acid. Consequently, there is a limited ability of the solvent to carry the electroactive species to the electrode, which in turn results in low limiting current. One technique that has been used to mitigate this problem has been to increase the pressure of the gaseous species in the supporting electrolyte. The sulphur dioxide is typically introduced at high pressure such as 20 bars. However the introduction of sulphur dioxide at such high pressures requires the electrolyser to be engineered to contain gas safely at such high pressures. This presents safety and cost limitations and measures to mitigate this shortcoming are not commercially viable at this point in time [51].

1.5 Research problem and objectives

A critical step in the HyS cycle is the electrochemical oxidation of sulphur dioxide to sulphuric acid in a sulphur dioxide anode depolarized electrolyser as this results in the production of hydrogen at the cathode. The overpotential or cell potential needs to be reduced whilst the current density or the electrode kinetics needs to be increased. This is a direct result of the slow rate of SO_2 oxidation at the anode, which contributes approximately 70% towards the overpotential and the largest source of improvement in SDE performance will arise from the identification of a means to increase electrode kinetics i.e. the rate of oxidation of SO_2 at the anode, resulting in increased current density.

This can be accomplished by the development of a superior electrocatalyst. A better understanding of the oxidation mechanism may allow optimisation of electrode materials and a lowering of the electrode overpotential [39]. Over the last thirty years a number of papers [1-51] have been published dealing with the electrochemical behaviour of dissolved sulphur dioxide using carbon platinum as the electrode material. Most of these papers suggest that a platinum-only catalyst is susceptible to sulphur poisoning and has unstable long-term performance characteristics in sulphuric acid at high temperatures [13, 16, 18, 19, 21].This research project aims to investigate platinum metal combined with oxides of zirconium, tantalum and niobium acting as catalyst support, along with carbon black, for the electrocatalytic oxidation of SO_2. Currently the carbon support used for the platinum (Pt) catalyst result in a loss of Pt (thus reduced current density) due to the corrosion of the support (C). The oxides of zirconium, tantalum and niobium were selected as potential supports due to their high corrosion resistivity and having been used for fuel cell applications.

The difference between the theoretical (0.158V) and the experimental electrode potential (~0.5V) shows that there is room for efficiency enhancement through developing advanced electrolysis methods. A reduced electrode potential (70% of original experimental value) by an advanced technology is predicted to achieve 57% cycle efficiency [31]. Based on current available experimental data for the electrode potential, 47% (Lower Heating Value) appears to be the best cycle efficiency (and is attained at 10bar, 926.85˚C and 60mol% of H_2SO_4 for decomposer, 70wt% of H_2SO_4 for electrolyser). There is much room for further efficiency enhancement by reducing the electrode potential, since the theoretical value is only 15% of the experimental value [31].

The objectives of this study are therefore:

- To review literature that will serve as a guideline for the experimental work to be conducted and obtain understanding on the electro-oxidation of SO_2.

- To study the surface morphology of all the prepared carbon-metal oxides supported Pt using transmission electron microscopy (TEM), scanning electron microscopy (SEM) and X-ray diffraction (XRD).

- To prepare a catalyst with small particle size to obtain high surface area, increased active sites and therefore attain low overpotential. And hence integrate and compare the addition of niobium, zirconium and tantalum oxides on the catalytic activity of carbon supported platinum as electrocatalysts for the oxidation of SO_2.

- To evaluate the limitations of the electrocatalysts in the harsh electrochemical conditions using linear polarization and cyclic voltammetry.

1.6 Research methodology

The methodology for conducting this project can be divided into two sections, i.e. a literature review and experimental section.

1.6.1 Literature review

A literature review will be conducted so as to identify the different catalyst preparation methods and catalyst materials that have already been investigated with regard to their ability to electro-oxidise SO_2 in the sulphuric acid with various concentration and temperature. The study will also consist of the catalysts which were used for fuel cell application.

1.6.2 Experimental section

The experimental section is divided into four segments and there are as follows:

(a) Selection of catalysts and catalyst preparation method

Resulting from the literature review a selection will be made of the different catalyst preparation methods and catalyst materials that will be investigated with regard to their ability to electro-oxidise SO_2.

(b) Characterisation

Characterisation is used to magnify and study the internal structure of the materials that are investigated. Then determine the distribution and compositions of elements and their interactions. The correlation of physical and chemical properties with structural characteristics is crucial for the preparation of catalysts and the optimization of existing catalysts. The techniques that will be used to conduct material characterisation will be selected depending on the availability of instruments in the North-West University (Potchefstroom).

(c) Electrochemical investigation

Employing a potentiostat equipped with a rotating disc working electrode (manufactured with the specific metal to be investigated). A cyclic voltammetry and linear polarisation scan will be conducted across a predetermined potential range. The cyclic voltammetry and linear polarisation scan, i.e. current-flow versus potential, conveys the kinetics of the electro-oxidation process as it measures the current-flow (A) at a specific applied potential (V).

(d) Dissolution experiments

Linear polarisation will be conducted then the inductively coupled plasma (ICP) optical emission spectrometer will be used to determine the amount of the catalyst material is dissolved in the electrolyte.

1.6.3 Dissertation outline

In the chapters that follow the concept, findings, as well as the recommendations and conclusions of this research project are presented.

Chapter two deals with the literature review focusing on the electrocatalysts used for SO_2 oxidation, methods for preparation of catalysts, electrochemical measurements and the physical characterisation of the prepared catalysts. Literature sources are from electrochemistry and hydrogen energy journals and reports, reliable printed articles (from internet sources) and chemistry handbooks.

Chapter three entails a discussion of the methods used in the collection of data. The experimental section will consist of catalyst preparation, characterisation, electrochemical investigations and dissolution experiments.

Chapter four will focus on the analyses results and discussion of the outcomes of this experimental investigation. This will cover characterisation using TEM and XRD and the electrochemical measurements using cyclic voltammetry and linear polarisation.

Chapter five concludes the research work and makes a few recommendations.

Appendices consist of Figures and Tables to support all the conclusions found in this experimental investigation.