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Producing Hydrogen From Seawater Electrolysis

[MIET2133 Final Year Project]

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1. Introduction

1.1 Energy Usage In Australia

The main energy sources for Australia have been petroleum and coal where each contributes 34% and 40% of the energy sources in Australia as stated in the Energy In Australia 2009 report by the Australian Bureau of Agricultural and Resource Economics, ABARE. (ABARE, 2009 p12) Natural gas and renewable sources make up 20% and 5% respectively of the energy source in the country. During 2006-2007, 1695 PJ is consumed to generate electricity, 1369 PJ for manufacturing and 1359 PJ for transportation needs. (ABARE 2009 p16) These are the main usage of the energy resources in Australia, with the increasing trend of energy demand and usage every year.

Transportation sector is one or the largest energy users, specifically road transport. During 2006 to 2007, a sum of 1013.9 PJ is used for the road transport, meaning 74.6% of the energy needs of the transportation sector. The fuels include liquefied petroleum gas, diesel, natural gas and unleaded auto-gasoline. (ABARE 2009 p69) These are all sourced from fossil fuels where depletion is predictable in the future and the prices are anticipated to rise significantly. Apart from that, the fossil fuels are one of the main contributors of the greenhouse gas emission to the atmosphere.

Greenhouse gases

The greenhouse effect is defined as the 'natural increase in the temperature of the earth, due to the existence of greenhouse gases'. (Hopwood&Cohen 1998) However, due to the uncontrolled emissions of greenhouse gases, the earth today is exposed to global warming, the increment of the temperature of the earth which is leaving a bad impact to the earth and its living.

Greenhouse gases include carbon dioxide, nitrous oxide, methane and fluorocarbons, to name a few. However, carbon dioxide represents the largest share of the greenhouse gas emitted to the atmosphere, which is about 76%, as depicted in Figure 1.0, the graph of the distribution of greenhouse gases below. (Hopwood&Cohen 1998) Carbon dioxide emission is mainly due to the burning of fossil fuels such as coal and petroleum, both major energy sources of Australia. Coal is used to generate electricity at power stations such as Hazelwood, Loy Yang and Yallourn in the Latrobe Valley of Victoria, while petroleum is the main transportation fuel that is used widely in the country up to the present days.

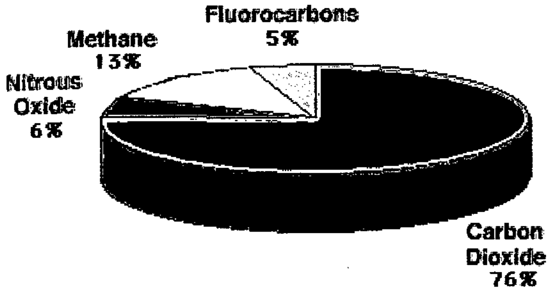

Figure 1.0: The distribution of greenhouse gases in the earth's atmosphere. (Hopwood&Cohen 1998)

There are alternatives to fossil fuels that would lead to the reduction of toxic greenhouse gas emissions. This would minimize the dependency on the fossil fuels and secondary energy such as electricity production based on them. These include the currently emerging energy carrier that is hydrogen, gas to liquid fuels that are mainly derived via Fischer Tropsch processes and biofuels from crops and food feed stocks. Electricity generations based on renewable energy sources are to substitute current coal-based electricity generators in thermal power stations across the country.

Hydrogen as alternatives to fossil fuels

Among all the alternative fuels, hydrogen seems to have a promising future due to its abundant resources in the world. It could be produced from common resources such as water, natural gas and coal. Just like electricity, 'hydrogen is an energy carrier,that could be produced from a wide range of sources and could be used by a wide range of energy applications in the world'. (Scott 2004) The prospect of hydrogen as a future energy carrier is growing fast today with the development of fuel cells and its application such as the fuel cell vehicle, and hydrogen usage as transportation fuel in the form of a compressed gas.

There are a few paths of hydrogen production for short-term storage, such as 'steam reforming of natural gas, recovery of hydrogen from chemical processes, as well as water electrolysis'. (Ogden 2004) However, in the interest of a long term production of hydrogen together with reduction of greenhouse gas emissions, the hydrogen supply options include 'hydrogen production via electrolysis process using renewable and carbon dioxide-free electricity sources such as solar, wind or wave powered electrolysis, gasification of coal, petroleum coke and biomass with carbon dioxide capture and storage technology, and the splitting of water by thermochemical means such as high temperature nuclear and solar heat'. (Ogden 2004) From these options, hydrogen production via electrolysis of water seems to be the most viable method.

Hydrogen production via electrolysis of seawater

Australia is one of the 'driest continents in the world, with high variability in the climate across the continent, from year to year'.(Bureau of Meteorology, 2010) Threatened with drought and limited fresh water resources, the proposal of utilising fresh water in Australia for the production of hydrogen via the electrolysis process might not be appealing, yet vulnerable. Hence, the future of hydrogen production lies in the ability to electrolyse sea water instead. Sea water is abundant in Australia as well as other parts of the world.

The other concern of producing hydrogen from the electrolysis process is the 'availability, location, abundance and cost of primary energy sources' that would be used for hydrogen production. (Ogden 2004) This includes the possibility of utilising renewable energy to fuel hydrogen production from sea water. The most reasonable option would be to run electrolysers using the electricity generated from wave power, along the coastal line of the country. In previous study into this matter, J. Cavanagh suggested the possibility of utilising wave energy, with the power generator range of approximately 8,000 units of Wave Dragon to about 170,000 units of Aquabuoy, for 80% efficiency wave energy converters, as tabulated in Table 1.0 below. (Cavanagh, 2009) The study was made on the basis of replacing Australia's petrol needs in the transportation field.

Table 1.0: The number of wave energy converters (WECs) needed to produce the hydrogen as an alternative for unleaded petrol in Australia. (Cavanagh, 2009)

Wave Energy Converter	Number of wave-energy converters needed to meet Hydrogen requirement for motive power (rounded up)			
	56% i.e. 72.55 kWh/kg	64.5% i.e. 63.15 kW/kg	73% i.e. 55.79 kWh/kg	80% i.e. 50.91 kWh/kg
Pelamis	120821	104899	92685	84575
Aquabuoy	246117	213683	188802	172282
Wavebob	94931	82421	72824	66452
Anaconda Wave Snake	44301	38463	33984	31011
Wave Dragon	11322	9830	8685	7926

In determining the driving force of the technology of sea water electrolysis, the main two factors that are the supplied voltage or power and the costs, are the most dominant. Hence, the optimum electrolysis conditions would be needed to ensure that minimum amount of energy is needed to produce hydrogen from the electrolysis of sea water.

At the moment, seawater is electrolysed to produce hypochlorite from the chlorine gas that is evolved at the anode of the electrolyser. Hydrogen is generated as a by-product of the commercial seawater electrolyser, while chlorine, the main product of the electrolyser is used in wastewater treatment plants and at coastal power stations where it is used to prevent fouling due to growth of microorganisms. (Bennett 1980) The hydrogen produced as a by-product in such processes is usually released to the atmosphere. (Bennett 1980)

This report is an investigation into the methods of producing hydrogen from the electrolysis of seawater, which utilises the conditions and parameters of the electrolysis process such as the materials of the electrodes used and other reaction conditions.

1.2 Objectives

The objectives of this project were:

1. To review the various technical methods for producing hydrogen by electrolysis of sea water in terms of oxygen and hydrogen evolution efficiency, production of chlorine as by product, reaction conditions and electrode materials.
2. To identify a preferred method of hydrogen production for experimental testing and detailed evaluation.
3. To make recommendations for a future research and development program, including both theoretical and experimental work to improve scientific understanding and develop towards implementation the preferred method in hydrogen production from seawater.

1.3 Research Questions

The project is a study to answer these research questions:

1. What are the methods of producing hydrogen from seawater electrolysis?
2. Which materials are the best to be used as electrodes to produce hydrogen via the seawater electrolysis process?
3. Can we totally eliminate chlorine production from the electrolysis of seawater?

1.4 Scope

The study would focus on direct electrolysis of seawater that is producing hydrogen from seawater electrolysis without the seawater being pre-treated in a desalination plant or by other means of processing to remove salt content of the seawater.

Electrolysis of seawater would usually produce chlorine, as a by-product. The method of electrolysis to be selected is ensured to be able to reduce or possibly eliminate chlorine production. Therefore, this study would focus on the two methods of electrolysis of seawater that are to allow higher voltage in electrolysis where chlorine would be produced and dealt with, and to employ electrode materials that are able to suppress chlorine production.

This study would look at the impact of chlorine to the ecosystem as well as humans and other living organisms.

The electricity that would be needed for the electrolysis process is assumed to be obtained from sustainable resources such as wave energy. The outcome of the study on the feasibility of producing electricity from wave energy in Victoria is mentioned in Cavanagh's work 'Using Marine Energy to Generate Hydrogen Using Seawater Electrolysis: A Preliminary Investigation'.

1.5 Planned Outcomes

The planned outcomes would be the ability to produce hydrogen on a laboratory scale electrolysis setup, to reduce and if possible, to be able to eliminate chlorine production from the direct electrolysis of seawater and to be able to determine the impacts of chlorine to the ecosystem if it is released directly into the sea, as well as the impact of chlorine to other living organisms.

1.6 Guide To Thesis

This report is a documentation of the project activities and its outcomes which are divided into a few chapters.

Chapter 2 *outlines the methods that were used in completing this project* which includes the literature search, laboratory work and analysis of results. This section lists down the main activities conducted which include the study of basic electrochemistry, literature review, laboratory work, data analysis and calculations.

Chapter 3 is the introduction to the report, which is focusing on the seawater electrolysis, its basic chemistry and the challenges to the electrolysis process, which were obtained from earlier studies. Chapter 3 outlines the challenges that are to be developed in the next chapters in this report.

Chapter 4 explores the main methods of producing hydrogen from seawater that include direct and indirect electrolysis of seawater. This chapter elaborates more on the scope focused in this project that is the optimization of electrode materials.

Chapter 5 is a documentation of detailed experimental work on a chosen method of producing hydrogen from seawater. The procedures of the experiments conducted are laid in this chapter.

Chapter 6 and 7 are the results and discussions of the project. This report is then ended with a conclusion and recommendations for future work, in Chapter 8 and 9 respectively.

The detailed experimental work, raw data and calculations are attached to this report as appendices.

2. Method

In completing this project, the methods used were:

1. Literature review from journals of past work on electrolysis of seawater.
2. Laboratory scale experimental work
3. Analysis of experimental results via calculations

The literature reviewed started from the journals from the year of 1980 until the latest journals published, covering the areas of electrode preparations, the electrolysis process and reaction conditions, results from electrolysis including the efficiency of product gas evolution and the quantitative methods to determine the production of by-products.

The data and information gathered were then used to construct a basic electrolysis cell. Focus was given unto the materials used for the electrodes and the reaction conditions during the electrolysis process.

The main activities in this project include:

1. The study of basic electrochemistry concepts
2. Literature review from online journals of past work on electrolysis of seawater to produce hydrogen
3. Basic laboratory scale experimental work to observe and prove viability of hydrogen production from direct seawater electrolysis
4. The usage of data from literature search for comparison to key data obtained from the experimental work done
5. Analysis of the viability of the method chosen via calculations

The Report

3. Seawater Electrolysis

3.1 Basic Electrochemistry

Electrolysis is a process of decomposing a molecule by passing electric current through an electrolyte, a solution which conducts electricity. The electrolysis setup consists of 'a pair of electrodes immersed in a conducting electrolyte dissolved in water'. (Casper 1978 p111) Certain electrolysis cells do have diaphragm or membranes that separate anodic and cathodic products. (Grotheer et al, 2006) Electrolysis of water is a process of decomposing water with electric current supplied, to produce the basic elements of water that is hydrogen at the cathode of the electrolysis cell, and oxygen at the anode as presented in Figure 3.1 below.

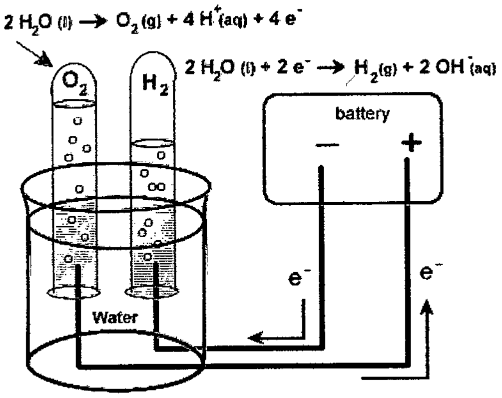

Figure 3.1: A simple set of electrolysis of seawater (Saskatchewan Schools, 2006)

In seawater electrolysis, the seawater itself is sufficient to function as an electrolyte to conduct electricity. The presence of more than 70 elements of dissolved salts in sea water, in the form of ions, mainly sodium (Na^+), chloride (Cl^-), sulphate (SO_4^{2-}), magnesium (Mg^{2+}), calcium (Ca^{2+}) and potassium (K^+) make sea water an excellent conductor. (Badea et al 2007)

The *main reactions that occur at the cathode and* the anode of the cell during the process of seawater electrolysis are:

Cathode:

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Anode:

$6H_2O \rightarrow O_2 + 4H_3O^+ + 4e^-$

And/or

$2Cl^- \rightarrow Cl_2 + 2e^-$

(Badea et al 2007)

Seawater could be electrolysed to produce hydrogen at the cathode and either chlorine or oxygen at the anode, depending on a few factors such as the electrode materials and reaction conditions. According to Badea et al, 2007, the electrolysis of seawater could take on three main routes that are:

1. Electrolysis to produce hydrogen, oxygen and alkalis
2. Electrolysis to produce hydrogen, oxygen, chlorine and alkalis
3. Electrolysis to produce hydrogen and sodium hypochlorite (NaOCl)

However, the 2nd route seems to be the most dominant route of the hydrogen production process. (Badea et al,2007)

3.2 Challenges

There are a few challenges that would need to be dealt with in order to produce hydrogen via the electrolysis of seawater. They are the production of toxic chlorine gas and corrosion at the anode of the cell, precipitation at the cathode, and impact to the environment as other chemical processes.

Chlorine production at the anode

The biggest concern of seawater electrolysis would be at the anode side of the electrolysis cell where either chlorine or oxygen is produced, as the equations below.

$6H_2O \rightarrow O_2 + 4H_3O^+ + 4e^-$

And/or

$2Cl^- \rightarrow Cl_2 + 2e^-$

(Badea et al 2007)

At present, electrolysis of seawater to produce chlorine has been established via commercial applications such as producing hypochlorite that is used as sterilizing agent for used water in secondary recovery of oil fields and as an anti-fouling agent in process cooling water. Chlorine is also widely produced at chloro-alkali plant in Australia, such as Orica. A chloro-alkali plant is one of the most large electricity users in Victoria. A ruthenium-titanium dioxide/titanium anode is used in chlorine production in chloro-alkali industries. (Balaji et al 2009) The manufacturing process of chlorine is similar to electrolysis of seawater to produce hydrogen. Although chlorine is generally toxic, its major applications include disinfection of water supply, treatment of used water such as process cooling water, swimming pool, industrial effluent as well as in the sewage treatment. (Orica, 2010)

Previous studies show that the equilibrium potential for oxygen evolution is lower than chlorine, and oxygen production is actually a thermodynamically favoured anodic reaction.(Abdel-Aal et al 1993) However, due to a 'simpler' reaction of chlorine evolution, chlorine is evolved instead of oxygen, at the anode. (Abdel Ghany 2002) Abdel-Aal et al, in the study of the theoretical background of chlorine evolution, selectivity and determination, addresses two factors of chlorine evolution instead of oxygen at the anode of the cell, which are the pH independency of chlorine evolution and overpotential at practical current density which prohibits oxygen evolution. (Abdel-Aal et al, 1993)

The impact of pH independency of chlorine production which then promotes chlorine evolution at the anode, instead of cathode was also mentioned by Bennet in his study in the development of an oxygen-selective electrode. (Bennett 1980) Bennett claimed that in 'unbuffered solution' that is seawater, both oxygen and chlorine evolution reaction causes the solution adjacent to the electrode to become more acidic, according to these reactions (Bennett 1980):

Oxygen evolution:

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

Chlorine evolution:

$2Cl^- \rightarrow Cl_2 + 2e^-$

Immediate hydrolysis of chlorine:

$Cl_2 + H_2O \leftrightarrow HClO + Cl^- + H^+$

$HClO \leftrightarrow ClO^- + H^+$

From the reactions above, it could be concluded that chlorine production, being independent of pH, would be the most dominant reaction at the anode. Hence, the electrode material should be tailored to produce oxygen instead of chlorine at the anode of the electrolyser cell. The appropriate electrode material would allow the electrolysis process to run at a suitable range of current density, and hence, prevent from overpotential occurrence at the anode of the electrolyser.

Chlorine is produced at a current density range from 1 to 1000mA/cm^2 as mentioned by Bennett in the study of producing hydrogen and oxygen from seawater. (Bennett 1980) Therefore, in present study, electrode materials and reaction conditions would be altered to allow only oxygen to be produced at the anode of the electrolysis cell. In other words, chlorine is suppressed from being produced by altering the electrode materials and reaction conditions such as the current density.

In order to produce oxygen instead of chlorine, the current density would need to be either less than 1mA/cm^2 or more than 1000mA/cm^2 at anode potentials of 1.38 to 1.55 V versus normal hydrogen electrode, NHE, as could be analysed from the Tafel slopes in Figure 3.2 below. (Bennett 1980)

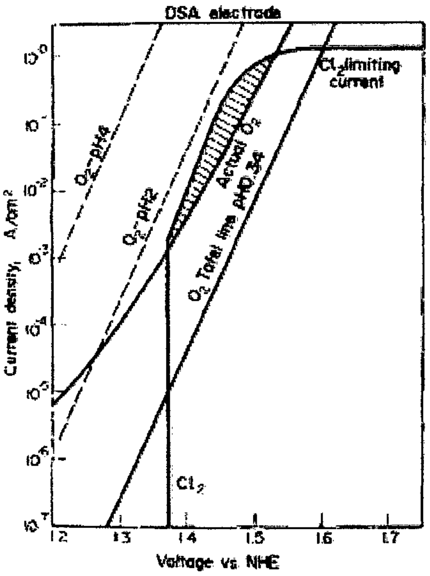

Figure 3.2: The log of current density versus voltage for chlorine and oxygen production in seawater. (Bennett, 1980)

However, generally, the practical current density range of electrolysis processes is between 100 to 1000mA/cm^2 where chlorine is usually produced at standard conditions. (Bennett 1980) This is due to the fact that to operate electrolysis cell below $1mA/cm^2$ would mean that a large area of electrode is needed, which made the electrolysis process impractical, and running the cell at a current density higher than $1000mA/cm^2$ would resort to excessive heating at the electrodes. Higher energy input to the cell is also required, which causes the method of hydrogen production to be more expensive.

However, in producing hydrogen from seawater, one of the aim is to reduce and if possible, to be able to eliminate chlorine production at the anode of the cell. Chlorine in a gaseous form is toxic and harmful to both human and other organisms. In liquid form, chlorine is known as hypochlorite, which would be discharged from the electrolysis cell together with the brine that is the electrolysed seawater that has salinity slightly higher than normal salinity range of seawater.

Hypochlorite production is much more preferable than chlorine. Eventhough chlorine is produced, it could be returned into the environment in its safest form, by converting into hypochlorite, an antibacterial product widely produced commercially and used as a disinfection agent for drinking and waste waters. If hypochlorite is not needed as a product, process could be altered. Hypochlorite could be treated by thermal decomposition into NaCl and O2, thus returning chlorite in into the environment as a non-toxic compound. (Temeev 2006)

At the desalination plant proposed in Burrup Peninsular, the discharge of chlorine in the form of hypochlorite together with the brine is treated with the addition of sodium metabisulphite, which then produces ions that are present naturally in seawater. (EPA, 2001) The concentration of chlorine in seawater would be ensured to be less than detectable limits of 0.1 mg/L. (EPA,2001)

Although toxicity of chlorine to the environment varies depending on the exposure and concentration of the chlorine gas produced, it was concluded that chlorine shall not be released to the environment without pre-treatment. The impact of chlorine gas to the health of human and animals could ranges from acute effects, from as low as 0.014 parts per million (ppm) that causes mild uneasiness to as high as 46ppm which causes toxic pneumonitis and pulmonary edema. (EPA 2007)

Hence, a few solutions were suggested by El-Bassuoni et al, in the study of 'hydrogen and fresh water production from sea water' to deal with chlorine. (El-Bassuoni et al, 1982) They include electrolysis of seawater at sufficient depths that hydrogen would be produced at 100atm and stored, while chlorine produced is reacted with alkali hydroxides that was formed and then released into the sea, or to collect the chlorine produced at the surface of the sea and reacting that with water at 650°C (El-Bassuoni et al, 1982)

Hence, this report would focus more on the electrode materials that would be able to suppress chlorine production, so that only oxygen is evolved at the anode. This could be done by either choosing electrodes with coating elements that limits chlorine production or by using a layer of selective permeable membranes to prevent chloride ions from reaching the electrode, hence, not being converted into chlorine gas.

Precipitation at the cathode

Hydrogen is the only product that is evolved at the cathode of the cell. However, the challenge of seawater electrolysis is to deal with the insoluble precipitation that occurs on the surface of the cathode. As electrolysis proceeds, the solution within the anodic cell gets more alkaline, as hydrogen is produced from the equation below:

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Previous studies showed that magnesium hydroxide precipitate formation at the cathode of a seawater electrolysis cell occurs at pH value greater than 9 (Kirk 1982) and 10.7 to 11.0 (Bennett 1980). In a study by Abdel-Aal, it was shown that magnesium hydroxide precipitate is formed at a higher pH than calcium hydroxide and in the long run clogged the electrode gap. (Abdel-Aal&Hussein 1993) The precipitation on the electrode at anode of the cell could not be entirely eliminated, but it could be reduced by increasing turbulence of seawater within the electrolysis cell, improving electrode materials and running the electrolysis at an optimum current density. (Abdel-Aal&Hussein 1993)

The occurrence of insoluble precipitate at the electrode causes fouling, lowers the active surface area of the electrode, causing overpotential of hydrogen production and hence, results in the additional power needed for the electrolysis process. (Yalcin 1997) Due to the fouling, the cathode of the electrolysis cell would need to be cleaned periodically to ensure efficiency of hydrogen production is at an acceptable level.

Corrosion at the anode

Most electrode combinations for an electrolysis cell would be exposed to the corrosion, due to the contact of the electrode with water or aqueous solution, in this case, seawater. The Faraday's law on corrosion would be:

Weight of metal reacting = kIt

Where k is the electrochemical equivalent constant, I is the current in amperes (A) and t is time in seconds. (Revie 2008) It could be expected, from the equation above that, corrosion increases linearly with the current supplied to the electrodes. Corrosion usually occurs at the anode of the cell, where oxidation occurs. Corrosion in electrolysis of seawater does not only mean rusting of the anode of the cell, but it develops failure in the electrode for a long run, such as cracks and loss in strength of the electrode. (Revie 2008)

There are a few types of corrosion such as the general corrosion or known as the 'uniform attack', pitting, dealloying, intergranular corrosion and cracking. (Revie 2008) However, the most occurrences in seawater electrolysis process would be the general corrosion. As an example, Badea et al used 18Cr-10Ni stainless steel as a cathode, instead of anode, to avoid corrosion in seawater electrolysis. The stainless steel succeeded in being stable as it became 'spontaneous passive' in open circuit, as was electrochemically protected as a cathode. (Badea et al 2007)

Environmental impacts

Based on a desalination project proposal in Burrup Peninsula of Western Australia, the electrolysis plant using seawater as its electrolyte would have similar environmental concerns, such as the impact to the flora and fauna at the proximity of the plant. This include the impact unto the terrestrial flora such as clearing of lands for the construction of the electrolysis plant, which would be situated near the coastal line to reduce the total length of the piping needed to get access to the seawater, marine flora and fauna which would be affected by subsea channel construction and brine discharge, as well as visual impact of the pipelines and the plant itself. (EPA 2001)

4. Main Methods For Seawater Electrolysis

4.1 Introduction

There are a few methods of producing hydrogen from seawater electrolysis that are as summarized by Paul in the 'literature review on seawater electrolysis' (Paul 2010):

1. Desalination of seawater to produce fresh water to input to a standard electrolyser
2. Direct electrolysis of seawater:
    a. Voltage supplied below the threshold of potential chlorine evolution, hence, only oxygen is evolved at the anode of the electrolyser
    b. Voltage supplied is higher than the potential chlorine evolution, which means chlorine is the product at the anode. The chlorine produced is then;
        i. Redissolved into the sea, or
        ii. Collected to be used as a commercial product.
3. Optimisation of electrode materials to suppress chlorine production at the anode

The first method of producing hydrogen from seawater is indirect electrolysis of seawater that is to desalinate seawater before using the water for the electrolysis process, which would be able to eliminate chlorine gas production during the electrolysis process. However, this method requires additional capital cost to operate, as it would need a desalination process prior to the electrolysis process. (Abdel-Aal et al, 2010) The advantage of indirect electrolysis of seawater is to be able to use the readily developed technology of fresh water electrolysis, and hence, no chlorine produced at the anode of the cell during the electrolysis process. (Abdel-Aal et al, 2010)

The second method that is the direct electrolysis of seawater would have two distinguished outcomes, depending on the voltage supplied to the cell.

One of the earliest studies on the direct electrolysis of seawater has shown that hydrogen is evolved at high current efficiency at the cathode of the electrolysis cell, while chlorine is produced in the form of sodium hypochlorite (NaOCl) in large quantities at the anode. (Bennett 1980)

According to Temeev et al, the two oxidation reactions occurring at the anode of the cell are as follows (Temeev et al 2000):

i) Oxygen production

$2OH^- - 2e \rightarrow \frac{1}{2} O_2 + H_2O$ $E = 0.401$ V

ii) Chlorine production

$2Cl^- - 2e \rightarrow Cl_2$ $E = 1.359$ V

During the electrolysis of seawater, chlorine formed is then converted to sodium hypochlorite by the following reaction:

$Cl_2 + 2NaOH \rightarrow NaCl + NaOCl + H_2O$

By applying a voltage lower than the chlorine evolution potential, 1.359 volts; it would enable the production of oxygen instead of chlorine at the anode of the cell. However, it requires a large electrode area so that low current density is produced to run the electrolyser.

Alternatively, higher voltage applied would cause internal heating at the electrodes and result in high power consumption for the electrolysis process. (Balaji et al 2009) Chlorine would be produced at the anode, and the options to deal with the chlorine produced include releasing chlorine into the sea after treatment was made, or to collect them for the production of various commercial products in chemicals and pharmaceuticals industry. These include alkalis, sodium hypochlorite, magnesium hydroxide, calsium hydroxide and primary acids such as hydrochloric and sulphuric acids, apart from chlorine gas. (Ture 2009)

The third option would be to implement electrode materials that are able to suppress chlorine production at the anode of the electrolysis cell. As mentioned previously, the large amount of chlorine produced should not be released to the atmosphere or the sea without being treated. Therefore, to be able to run electrolysis of seawater but not to produce chlorine at the anode of the cell would be both financially attractive and beneficial to the environment.

Hence, this project would focus on producing hydrogen directly from seawater by optimising the electrode materials, such that it would be able to reduce and if possible, eliminate chlorine from being produced at the anode of the electrolyser.

4.2 Electrode materials

The study by Bennett et al suggests that, the usage of conventional electrodes such as platinum and stainless steel at practical electrolysis condition that is between 100 to 1000mA/cm^2 would produce chlorine in the form of sodium hypochlorite. (Bennett 1980) Therefore, the preparation of the electrodes was optimised and anode coating was introduced to enhance oxygen evolution instead of chlorine.

The preparation of the electrodes for seawater electrolysis includes three sections that are the substrate preparation, anodic deposition and the testing electrode performance in an electrolysis cell. These three sections of electrode preparation need to be optimised.

To further analyse the structure of the electrode, it is then characterized by x-ray diffraction method such as using the x-ray photoelectron spectroscopy (XPS) to analyse the thin layer of oxide coating on the electrodes, as well as using the Electron Probe Micro Analyzer to analyse the composition and surface morphology of the electrode. (Abdel Ghany et al 2002)

1. Substrate preparation

The substrate preparation is the initial step to produce an electrode for the electrolysis process, where materials of the electrode are chosen.

One of the earlier studies in the preparation of electrodes for seawater electrolysis was done by Bennett et al, where comparison was made between dimensionally stable anode (DSA), platinised titanium, lead oxide and graphite electrode. (Bennett 1980) The type of DSA that was used in the study is TiO_2/RuO_2 electrode, which is usually used in commercial seawater electrolysers that produces chlorine commercially. (Bennett 1980) The DSA was used at the early stages of the study of seawater electrolysis due to its 'long-term stability and reversibility of chlorine overvoltage' attributes. (Bennett 1980) Figure 4.2.1 shows the current efficiency of the different electrodes with respect to the amount of chlorine in the seawater.

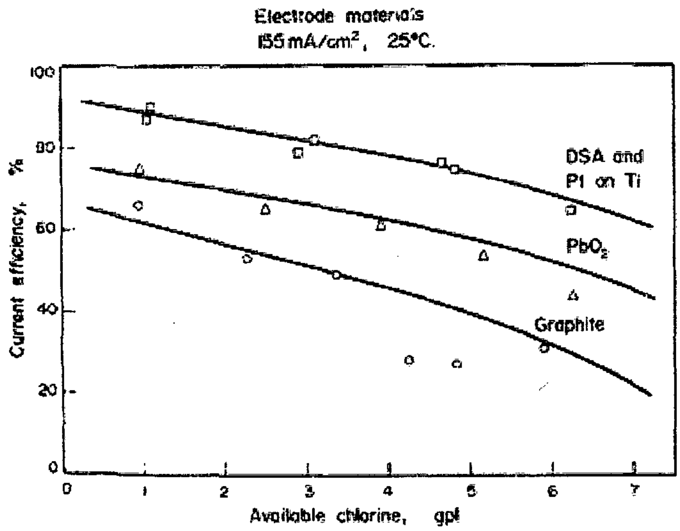

Figure 4.2.1: Current efficiency versus chlorine concentration in seawater. (Bennett 1980)

From the graph above, the most efficient electrode material is the DSA and platinised titanium. Therefore, another common electrode material that was used in the study of electrolysis of seawater, after the TiO_2/RuO_2 DSA is titanium coated with IrO_2 layer (IrO_2/ Ti). Titanium is used as a base metal and the IrO_2 layer is applied to prevent the formation of the insulating layer of titanium oxide that would coat the electrode at long duration of electrolysis with the application of high current densities (Abdel Ghany et al 2002)

The IrO_2 coating was carried out by applying 0.1M chloroiridic acid butanol solution unto the substrate, and drying at 80°C before it undergoes a 450°C treatment for 10 minutes at each step. (Abdel Ghany et al 2002) The detailed procedure of preparing the IrO_2 coating is mentioned in the works by Abdel Ghany et al.

2. Anodic deposition

The anodic deposition is a method of depositing hydrogen-selective metal oxides, unto the electrode, which utilizes electrolysis as a method of deposition. The electrolysis was run in the solution that contains the cation needed to coat the electrode, known as substrate. In a study by Bennett, an oxygen-selective coating that is manganese oxide, is applied to the DSA electrode during the electrolysis of seawater, or in a few experiments, the electrolysis using dilute sodium chloride as the electrolyte, with a current density value of $150mA/cm^2$. (Bennett 1980)

Abdel Ghany utilises electrolysis process at an acidic pH range that is between 0 and 0.4, carried at a temperature of 90°C, with constant stirring, with the application of current density of $600A/m^2$ for about 20 to 60 minutes to coat the IrO_2/ Ti electrode. (Abdel Ghany et al 2002) Abdel Ghany et al in the previous work added that a repetition of anodic deposition for a shorter duration such as 20 minutes intervals, using fresh electrolyte does improve the adhesiveness of the deposits unto the substrate. (Abdel Ghany et al 2002) This method is used by most of the previous studies in seawater electrolysis, such as by Izumiya et al and Fujimura et al. (Izumiya et al 1998, Fujimura 1999)

Apart from the various metal introduced as the oxygen-selective coating, the parameters of the process of anodic deposition of the electrodes were optimised. These include pH and temperature of electrolyte used in the deposition, duration of the anodic deposition process as well as the thickness of the oxide coatings.

Izumiya et al found that the decrease of pH of deposition electrolyte assists increment of tungsten content of the oxide formed, and hence, increases the oxygen evolution efficiency. (Izumiya et al 1998) Fujimura introduced manganese-molybdenum oxide with high oxygen evolution efficiencies. (Fujimura 1999) However, an opposite trend was found for the deposition of molybdenum unto the electrode substrate such that the molybdenum content in the oxide increases as pH of the deposition electrolyte is increased. (Fujimura 1999)

Anodic deposition method was further optimised to ensure that the oxide coatings are more stable and durable such that exfoliation and electrochemical dissolution is hindered. Fujimura suggest that anodic deposition should be run at higher temperature with lower pH electrolyte, together with higher current density during the oxygen-selective oxide deposition of the anode. (Fujimura 2000)