Design, Scale-Up, and Integration of an Ammonia Electrolytic Cell with a Proton Exchange Membrane (PEM) Fuel Cell

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This thesis titled
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Abstract

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Design, Scale-Up, and Integration of an Ammonia Electrolytic Cell with a Proton Exchange Membrane (PEM) Fuel Cell (75 pp.)

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The design and performance of an alkaline ammonia electrolyzer for hydrogen production and its feasibility for fuel cell applications is presented. Pt based C-paper electrodes were used in the ammonia electrolytic cell (AEC). The separator electrode assembly design (SEA) for the AEC comprised of end plates, end electrode plates, separator plates, the Pt-Ir electrodes, gaskets, and the membrane/separator. The operating procedure for the designed electrolyzer was established. The electrochemical performance of the 9-cell AEC was evaluated at 25°C and 55°C. A Faradaic efficiency of 97.55 ± 0.04 % was obtained on the hydrogen gas produced from the designed electrolyzer. Including the prevailing ohmic losses, a net energy of 4.10 ± 0.97 W h g⁻¹H₂ and 6.10 ± 0.97 W h g⁻¹H₂ with an energy conversion efficiency of 23.62 ± 0.36 % and 39.71 ± 0.69 % at 25°C and 55°C respectively were achieved from the AEC-PEM fuel cell integration. The results prove the scalability and potential of ammonia electrolysis as a novel and alternative hydrogen production process for PEM fuel cell applications, which would help realize the goal of green hydrogen economy in true sense.

Approved: _____________________________________________________________

Gerardine G. Botte

Associate Professor of Chemical and Biomolecular Engineering
To my parents, Dr. Balwant Biradar, Dr. C. S. Patil, and my brother Nitesh.
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CHAPTER 1: INTRODUCTION

1.1 Project Overview

Since its evolution, mankind has been continuously trying to find different sources of power or energy for its survival. Today in 21st century, we can see that the entire human race depends completely on different forms of energy, and one such prominent example is the automobile. During the last few years the dependence on automobiles has increased tremendously. By now everyone has started to realize that the reserves of petroleum which drive the automobiles are not going to last for a very long time. This led to the development of fuel cells, which are a promising source of power in the near future. Fuel cells have emerged as a promising solution to the apparent future energy related problems. Amongst all the known fuel cells, Proton Exchange Membrane (PEM) fuel cells or low temperature fuel cells have a well developed technology. They also have a technically sound infrastructure for their necessary implementation. Hydrogen is the primary fuel for the PEM fuel cells and is thus going to play an important role in the economy of the nation. Taking this in account, hydrogen research is gaining considerable importance.

Fuel cells generate energy in the form of electricity using the chemical energy of gases such as hydrogen and oxygen while clean water is the only by-product of this process. The complete dependence on the petroleum products like gasoline can thus be minimized. Hydrogen as a fuel moreover, does not cause any environmental hazard and is also very proficient. Thus, hydrogen is being considered as the “Fuel of the Future.”
As a result, the search for various sources of hydrogen has gained a remarkable importance since last few years.

The overall objective of the research presented here is to develop a clean and economical technology to generate hydrogen by electrolysis of ammonia, which can be used as fuel in fuel cells. Botte [2] has identified ammonia as a promising source of hydrogen and has proposed the mechanism for hydrogen production. The ammonia powered fuel cells can be used in a wide range of stationary applications where energy or power is required. Other important application as stated above will be for the automobile industry, which is one of the largest power consuming fields. Besides the mobile applications it can be further extended for space applications too.

In this regard, this research work will involve the following specific objectives:

1) Design a prototype multi-stack, continuous ammonia electrolyzer; 2) Scale up the prototype design stated in objective (1) to power a 2.5 W PEM fuel cell; and 3) Establish the operating conditions, parameters for the electrolyzer which will be the hydrogen generation unit and determine the feasibility of the integration of the Ammonia Electrolytic Cell (AEC) with a PEM fuel cell.

The significance of this research is very well proven from the fact that it will provide a novel technology in hydrogen production process which has an upper hand over the other existing technologies with respect to different factors like hazards, economics, need of complicated infrastructure etc. This in turn will have a positive effect on different fields apart from automobile power technology such as environment, security, and economy of a nation.
1.2 Statement of Objectives

Since quite a few years for now, fuel cells have been proven to be a promising source of power. The application of PEM fuel cells for automobile purposes has been demonstrated by major automobile companies like GM, Ford, Toyota, Honda, etc. As explained before, since the fuel required for the fuel cells is hydrogen, it is extremely imperative to look out for reliable sources of hydrogen. There has been a significant amount of research going on in this regard. Some of the technologies for hydrogen generation are water electrolysis [3], natural gas [4], catalytic reforming process [5] etc. Recently, a new technology has been developed for hydrogen generation from ammonia by its electrolysis [6]. This is a clean technology compared to other ones mentioned above because this low temperature process produces pure hydrogen on demand which solves the crucial problem for hydrogen storage. The only other product of this process is nitrogen, which can be safely released in the atmosphere or even captured, bottled, and sold commercially once the technology is developed.

Till date, different noble elements have been used as a catalyst for ammonia electrolysis with an objective to improve the kinetics of the process. Continuous efforts are being made to improve the process and more information is still needed for this process to be scaled up for bulk scale production of hydrogen required by the proton exchange membrane fuel cells. The design of an AEC, which will demonstrate the potential of the technology, is a crucial objective. Once a successful design is developed, crucial factors like the operating temperature, reactant concentration, etc. need to be known. The flow rate of hydrogen production with respect to the established operating
parameters needs to be determined. Other important aspect to be known is appropriate scale up of the electrodes used in the electrolysis. This would be based on the electrochemical performance of the electrodes.

This research in long term will help in solving the energy crisis by providing an alternate energy source. It will minimize the dependence on non-renewable sources of energy. It may bring a revolutionary change in the automobile power technology in regard to the use of gasoline and other petroleum products. The specific objectives of this research includes the scale-up and preparation of electrodes, design and construction of the AEC, preparing and assembling the separator electrode assembly (SEA) for the electrolyzer, testing the electrochemical performance of the AEC, establishing the operating parameters for the set-up, and study the feasibility of integration of the AEC with a commercial PEM fuel cell for automotive applications.

To achieve the specific objectives a specific methodology will be followed which will involve considerable experimental work on a bench scale set up for ammonia electrolysis. This will determine the important parameters to be studied during the design of the scaled up setup.

1.3 Significance of the Research

The research is extremely significant since it will have a profound influence in diverse fields; the automobile power technology might be one of the major and the most important one too. Other areas which this research will impact positively will be the environment, the army, the navy, and also the economy of a nation. Today, everyone has realized that the future of tomorrow is going to be hydrogen-driven economy. The
hydrogen economy as defined by John Turner [7] is the large scale production, storage, transfer, and use of hydrogen as an energy carrier. Thus, a reliable and an efficient source of hydrogen is a prime need and in this aspect electrolysis of ammonia for hydrogen production can be a path breaking technology.

The major sources of hydrogen currently known are non-renewable namely, natural gas, petroleum, coal, water by electrolysis, biomass etc. Most of the technologies involve the high temperature process of combustion making the process inefficient. Moreover, the hydrogen produced has to be processed and purified since the end product is often a mixture of different gases. Some of the other technologies have a large energy requirement thus making the process cost ineffective. The other biggest problem all these technologies have is the storage of hydrogen. Though, advanced carbon fiber tanks have been developed to store hydrogen under safe conditions up to 750 bars, 10% of the hydrogen energy is lost during the compression cycle [7]. Currently there is no single, effective hydrogen storage facility established. Taking into account all these problems, the proposed technology of ammonia electrolysis for hydrogen manufacture stands apart.

The ammonia electrolysis is an on-demand hydrogen production process which resolves the major problem of hydrogen storage. In this process, pure hydrogen is produced at one electrode, thus elimination the need of any downstream separation and/or purification methods for hydrogen production. At the other electrode, only pure nitrogen is obtained proving that the process does not cause any environmental hazard. This is very important in the automobile sector because currently the vehicles, which use gasoline as a fuel produce huge amount of pollutants such as NO\textsubscript{x}, SO\textsubscript{x} etc. and
greenhouse gases like CO₂ leading to the serious problem of global warming. Another important aspect of this process is that the electrolytic cell producing the hydrogen operates in a *low temperature* range (50°C-60°C). This low operating temperature makes it simpler to be adapted into an automobile setting along with a low temperature fuel cell which is the PEM fuel cells. This conformance makes the integrated setup extremely energy efficient.

As stated earlier, because of the low temperature process and there are no separation costs associated, the technology is very cost effective. In the future, it can also be viewed that once the technology is commercially proven, the raw material i.e. ammonia can be used from the agricultural wastes, waste water runoff, fertilizer industries etc. can be used. This will make the technology cheaper and the cost savings one can say will be incalculable. Considering the scope of this project the cost discussions will be limited to automobile applications. For example, assuming the current average price of gasoline as $3 per gallon, the fuel cost for a car will be $0.1/mile (assuming the car mileage is 30 mpg). On the other hand, considering the highest cost of ammonia in last decade i.e. $500 per ton, the cost of ammonia as a fuel will be just $0.04. *This shows 250% cost savings when ammonia is used as a fuel in the automobile.* It is projected that an ammonia car can achieve a fuel consumption of 60 mpg as compared to the standard 30 mpg of the vehicle using gasoline as their fuel.

This research project in short, will lay the foundation for a *novel technology* for hydrogen production for a large number of applications involving the use of fuel cells. It will also give us an idea about the economical aspects associated with the technology.
CHAPTER 2: LITERATURE REVIEW

As explained in the previous section, hydrogen is going to play a very important role in the U.S. economy. It is thus important to know some background information about the various current hydrogen production technologies available and some aspects of well developed electrolysers that aid current hydrogen generation processes. This section will give an insight into the previous work done in this regard with respect to the technological analysis of these processes, their comparison with the proposed ammonia electrolysis technology for hydrogen production, and the role of electrolysers in the current hydrogen economy. Hydrogen research is gaining a substantial importance. As an example, the expenditure on fuel cells and hydrogen economy worldwide through government organizations was $1.5 billion in 2004 [8]. The study on the market profile, according to the report [8], also indicates that the sales of fuel cells globally in 2005 generated revenue of approximately $400 and it predicts that in the next decade the annual revenue that will be generated through the fuel cell and related market will be at least around $18.4 billion. If we take a look at status of commercialization of the hydrogen technology, PEM fuel cell applications in transportation is leading the path. The first fuel cell bus in the world was constructed by Ballard Power Systems, Vancouver, Canada in the year 1993. Since then, many programs for the building of fuel cell buses have been implemented in various states in the U.S. like Illinois, California etc. [9]. The significance of this research is thus self explanatory.
2.1 Hydrogen Production by Reforming Process

A significant amount of research is being done in the area of use of reforming process to produce hydrogen for fuel cell applications [10]. Methane, gasoline, methanol could be used to obtain hydrogen. Steam methane reforming process is a well known process. Uribe et al. [10] also identify auto-thermal reforming (ATR) and partial oxidation (POX) as other reforming processes to obtain hydrogen from methane and other hydrocarbons. Similarly, Choudhary and Goodman [11] have reviewed other processes like catalytic decomposition of hydrocarbons, stepwise reforming of hydrocarbons, preferential oxidation of CO, catalytic decomposition of ammonia etc.

Ammonia has always been identified as a promising carrier of hydrogen. Metkemeijer and Achard [12] proved that ammonia as a fuel has more benefits than methanol for an indirect type of a fuel cell. They did a detailed research on the use of ammonia as a feedstock for hydrogen fuel cell. One of their most notable findings includes the energy density study, where they showed that the specific energy density of an ammonia-fuel cell system (346 W h g⁻¹) was better than a direct hydrogen type fuel cell system (125 W h g⁻¹). The use of an ammonia cracker for hydrogen production was described. The results of the performance obtained from an alkaline fuel cell in combination with the ammonia cracker were explained. The process proposed however, involved the use of high temperature reforming process carried out at about 600°C. The ammonia used was in the form of a compressed liquid, which was stored under a pressure of 8 bars and atmospheric temperature. Also, the reactor i.e. the reformer unit had tubes, catalyst, insulation system etc. The diameter of the tube was 40 mm and the length was
750 mm. The mass and the volume of the reactor were 15 Kg and 80 L respectively. It can be seen that the set-up of the reformer was quite dense and thus makes the overall hydrogen production system complex. On the contrary, the current proposed research, i.e. the generation of hydrogen from ammonia electrolysis, is done at a low temperature ranging from 50°C-60°C. The ammonia electrolytic cell designed and constructed is much simpler than the reformer unit. If we consider the ammonia decomposition technology proposed in the discussed paper, economics shows that this process is promising for alkaline fuel cells [12]. However, the only fuel cell which has a sound infrastructure to support the transportation industry is the PEM. The PEM fuel cells dominate the hybrid fuel cell vehicle technology. Therefore, the electrolysis of ammonia comes in handy for PEM applications.

The performance of a fuel cell deteriorates if the fuel has traces of CO, CO₂ etc. As described earlier, Choudhary and Goodman [11] enlisted the different methods through which CO-free hydrogen fuel could be obtained. The common characteristics associated with all the above mentioned processes was again the high temperature and the complexity of the reactors, reformers similar to the one described by Metkemeijer and Achard [12], they required large volumes of reactors, specific requirements of the catalysts etc. In addition to this, they still imply the use of non-renewable sources for the hydrogen production. The major sources of hydrogen currently known are non-renewable namely, natural gas, petroleum, coal, biomass etc. Most of the reforming technologies involve the high temperature process of combustion making the process inefficient. Moreover, the hydrogen produced has to be processed and purified since the end product
is often a mixture of different gases. Reforming processes were reported to have at least 150 ppm of ammonia in the exit hydrogen gas stream [13]. This finding is important from the point of view that recently, researchers [10, 14, 15] identified the deteriorating effect of ammonia in the hydrogen gas inlet to PEM fuel cells. The study reveals that ammonia concentration of as low as 1 ppm significantly affected the fuel cell performance for prolonged operation though the loss in performance was reversible. The reforming studies did not address this crucial issue in their findings. Some of the other technologies have a large energy requirement thus making the process cost ineffective. The other biggest problem all these technologies have is the storage of hydrogen. As explained in the earlier section, in current hydrogen storage processes 10% of the hydrogen energy is lost during the compression cycle [7]. Currently there is no single, effective hydrogen storage facility established. Taking into account all these problems, the proposed technology of ammonia electrolysis for hydrogen manufacture stands apart.

2.2 Hydrogen by Ammonia Electrolysis

Electrolysis in crude terms is a process in which electricity is used to generate gases or it can be described as a process in which electrical energy is converted to chemical energy of gases. This process is exactly the reverse of that occurring in the fuel cell. The process of electrolysis can be categorized into the following types: namely, the alkaline electrolysis, PEM electrolysis, and the high temperature electrolysis. Ammonia electrolysis is the alkaline type of electrolysis while the water electrolysis falls in the category of PEM technology. The following reactions describes the ammonia electrolysis process [6];
At Anode: Oxidation of Ammonia

\[ 2NH_3(g) + 6OH^- (aq) \rightarrow N_2(g) + 6H_2O(l) + 6e^- \quad E^0 = -0.77 \text{ V vs SHE} \]

At Cathode: Reduction of Water

\[ 6H_2O(l) + 6e^- \rightarrow 3H_2(g) + 6OH^- (aq) \quad E^0 = -0.82 \text{ V vs SHE} \]

Overall Reaction:

\[ 2NH_3(l) \rightarrow N_2(g) + 3H_2(g) \quad E^0 = -0.059 \text{ V} \]

From the above standard potentials, we see that thermodynamically ammonia electrolysis occurs at a meager voltage of 0.06 V as compared to 1.23 V for water electrolysis, which is a commercialized process widely used today for hydrogen production employing electrolysis technology. This indicates that the power requirement for ammonia electrolysis is almost 95% less as compared to the water electrolysis process. The ammonia electrolysis surely has the potential to be the technology of the future if parameters are carefully studied and optimized.

Past studies for only the ammonia electro oxidation reaction have shown that Pt and Ir as catalyst give better performance than other noble metals [15]. A comprehensive study on the development of an appropriate catalyst for novel ammonia electrolysis technology, purity of the hydrogen produced in the process, enhancement of the cell efficiency and process stability of ammonia electrolysis has been done by Vitse et al. [6]. They conclude that the Pt-Ir electrode showed the highest activity for ammonia electrolysis. The conversion of ammonia to hydrogen is 100% which is in conformance with the faraday’s law. These findings by Vitse et al. [6] are valuable from the point of view that they lay the foundation for the further enhancement, development and possible
commercialization of the ammonia electrolysis. The Pt catalyst loses its activity at higher current densities [17-19]. For this reason, the current density for the AEC operation in this project was limited to 500 mA cell\(^{-1}\). In order to improve the kinetics of the ammonia electrolysis process, which is the limiting factor; new materials and methods are being continuously tried, tested and optimized as electrodes for this novel process at the EERL.

2.3 Electrolyzers for Hydrogen Production: A Comparative Study

As mentioned above in section 2.2, the electrolysis processes vary based on the type of the electrolyte used. There are different types of electrolyzers available or developed on similar lines. This section will highlight the progress done in the past in regard to the different electrolyzers built and used to produce hydrogen. The design, scale up and building of the ammonia electrolytic cell being the main objective of this research, it was essential to study the already available commercial electrolyzers which gave an insight into the design aspects to be taken care of for the large scale design of the AEC. Today, water electrolysis technology is one of the most important sources of hydrogen for fuel cell applications. This process has been in use since a long time and thus is commercialized. As explained earlier, thermodynamics proves that ammonia electrolysis is an energy effective process for hydrogen production as compared to water electrolysis.

A detailed comparison of different electrolyzers for large applications was made [20]. The authors in their study reported that the installation of large scale electrolyzers has been very limited. Further, the general aspects of an electrolyzer design and performance was also discussed [3]. The technology of the traditional water electrolysis along with a modern alkaline electrolyzer was discussed. Even they described the
advantage of use of alkaline electrolysis over water electrolysis on an industrial scale with respect to the economy of the material of construction required and better control over the corrosion as compared to the water electrolysis. It is also known that alkaline electrolyzers that operate at pressures of 25 bars are in use and have had a noteworthy record of operation in the industry. The currently used design for the alkaline electrolyzer, which has several cells arranged as a stack was described [21]. The ammonia electrolysis differs in different ways; the major difference being the fuel used is ammonia as compared to water, which has to be purified. Whereas, ammonia can be obtained in plenty from agricultural runoff water, fertilizer industry, effluents from petroleum and other industries [22]. Secondly, there is need of only one separator as compared to two separators needed in alkaline water electrolysis. The last but the most important difference is the safety, because the ammonia electrolysis produces pure nitrogen and pure hydrogen, while oxygen and hydrogen as formed in alkaline water electrolysis which cause a danger of explosion. Also, the technology of alkaline electrolysis is much qualified as compared to PEM electrolysis. The important parameters for the ammonia electrolysis process thus need to be determined and optimized for the appropriate implementation of this technology.

A project for design, integration and building of a hydrogen fueling station has been planned [23]. This vehicle fueling station under construction in the campus of the University of British Columbia, Canada is managed by BOC Canada Ltd. and National Research Council Canada (NRC). Meticulous design considerations were done for the large scale alkaline electrolyzer to be used in the project. The big problem in this process
being developed is the need of hydrogen storage and compression. The projected compression and hydrogen storage involves the pressures ranging from 250 bars to 450 bars, which are extremely dangerous and unsafe. This need of high pressures would be eliminated if on demand hydrogen production technology is developed, which is the biggest advantage of the ammonia electrolytic process in consideration.

For the scale up of the AEC, various factors were needed to be taken care of. As electrolysis and fuel cells both operate electrochemically, their design is more or less the same. Such a design of both a PEM fuel cell and an electrolyzer for a remote control car was completed [24]. In the design an acetal plastic known as Derlin was used as the gas diffuser for both the PEM and the electrolyzer. Solar electric panel was used as the power source. The membrane used was the commercially known Nafion. The power rating of the PEM constructed was 130 W which consisted of 12 cells in series with an output of 7.2 V and two such stacks in parallel. Based on preliminary data the electrolyzer was designed for 8 cells operating at 2 V per cell. The water electrolysis technology was put into use here for hydrogen production. The testing of the fuel cell was carried out. The electrolyzer however had some problems during the testing procedures. The electrolyzer as a complete unit after some time stopped electrolyzing the water which was not the problem when single cell was tested. It was discovered that the anode of the electrolyzer if layered with Pt, allows the continuity of the electrolysis process. Finally, the stack was re constructed using a 20% Pt black on C compound and liquid Nafion. The efficiency of the designed cell was reported as 50%. Their concluded that if 85-90% efficiency for the electrolytic cells are achieved, the combined efficiency of the electrolyzer-PEM fuel cell
could reach as high as 60%. This is higher than the current efficiencies of fuel extracted from fossils etc. thus electrolysis can be looked upon as a promising source of energy in the future. Though the fuel used here was water instead of ammonia which is the fuel in the research here, the design aspects are important for the building of the AEC. From the above study we can observe that for a successful design of the electrolytic cell, favorable parameters for the operation of the electrolyzer, the membrane used, and choice of the other material of construction etc. play a very important role.

The membrane used in the process of electrolysis is another important aspect to be considered during the design of the scaled up version of the AEC. Newer materials as membranes for the water electrolysis were tested and investigated [25]. The research was aimed at finding new materials for the replacement of asbestos diaphragm used in water electrolysis. The materials were analyzed at 100 °C and corrosive conditions of KOH (~28-30 wt.%). The findings showed that because of the good wettable nature and high porosity asbestos is the best material moreover, the conductivity of the asbestos increases with the thickness. Other materials used were polytetrafluoroethylene (PTFE) in the woven and the filter forms, polyphenyl sulfide (PPS), and polysulfone (PSF) etc. the woven form of the PPS and Teflon showed a performance similar to the asbestos in the conditions mentioned above. Actually, the PSF was considered to be better as compared to asbestos. In the PTFE class, the woven form was supposed to be better because of the porosity and less resistant. These findings are important because the alkaline conditions of KOH are involved in the ammonia electrolysis too. The appropriate selection of
materials as membrane or separator needs to be done. Similar materials were used for the current technology as a starting point and better materials can be used later.

From the literature review we have some important findings. It is now absolutely clear that ammonia is a better and a promising source of hydrogen as compared to the other reforming, combustion, and water electrolysis processes. Other important findings include some of the design aspects of electrolyzers and PEM fuel cells which will form the design basis for the AEC. The basic information on operating and testing a PEM fuel cell could be obtained from the Mark 9 SSL fuel cell stack series (from Ballard Power Systems Inc., Canada) specification sheet [26] used as a reference. To date, in the area of the catalytic development for the improvement of kinetics of the ammonia electrolysis reaction, Pt-Ir electrocatalyst on carbon paper electrodes has proven to be the best. In the lab, an improvement for the same is being researched extensively. For bulk production of hydrogen from large scale electrolyzers, many electrodes are required. The geometric area and the optimum catalyst loading are required to reduce the number of electrodes. Some important parameters that were determined through this research project will be discussed in the later sections. These include hydrogen flow rate generated, operating temperature, and concentration of the reactants for the AEC. Besides, the electrochemical performance and a standard operating procedure for the AEC were established.
CHAPTER 3: EXPERIMENTAL METHODOLOGY

3.1 Electrode Preparation

A standard methodology for the electrode preparation and electroplating was followed throughout this project. This procedure is described in detail in the next chapter.

3.2 Electrochemical Testing

The preliminary testing procedure for the electrodes is described in the next chapter.

3.3 Equations Used

Faraday’s law was used to calculate the theoretical amount of hydrogen produced from the AEC at a particular current. The equation is described below,

\[ m = \frac{s \times M \times I \times t}{n \times F} \]  
(Equation 3.1)

Where,

\[ m = \text{mass of hydrogen produced (g)} \]
\[ s = \text{stoichiometric factor} = 3 \text{ mol} \]
\[ M = \text{molecular weight of hydrogen gas} = 2 \text{ g} \]
\[ I = \text{applied current (A)} \]
\[ t = \text{time (h)} \]
\[ n = \text{equivalent mole} = 6 \text{ eq} \]
\[ F = \text{Faraday’s constant} = 26.8 \text{ A-h-eq}^{-1} \]

The values of \( s \) and \( n \) in the above equation are for the ammonia electrolysis process described before.

The power consumption for an electrolyzer or a fuel cell is given by,
\[ P = N \times V \times I \]  
(Equation 3.2)

Where, 

P = Power consumed/produced (W)  
N = number of cells in the electrochemical cell  
V = voltage  
I = current/load 

The Faradaic efficiency was calculated using, 

\[ \eta = \frac{Actual_{H_2}}{Theoretical_{H_2}} \times 100 \]  
(Equation 3.3)

Where, 

\( \eta \) = Faradaic efficiency of the hydrogen gas produced from the AEC  
Actual \( H_2 \) = amount of hydrogen gas experimentally collected/measured from the AEC  
Theoretical \( H_2 \) = amount of hydrogen gas predicted by faraday’s law at the operating conditions for the AEC.
CHAPTER 4: DESIGN, SCALE-UP, AND INTEGRATION OF AN AMMONIA ELECTROLYTIC CELL WITH A PROTON EXCHANGE MEMBRANE (MEA) FUEL CELL

This chapter appears as a manuscript for a paper that intends to be submitted for publication to the Journal of Power Sources by Mahesh Biradar, Madhivanan Muthuvel, and Gerardine Botte [27].

4.1 Introduction

Fuel cells have emerged as a promising solution to the apparent future energy related problems. A fuel cell is an electrochemical device that converts the chemical energy of hydrogen to electrical energy. The only by-product of this process is clean and pure water along with heat. The air (oxygen) serves as the oxidant in the above process. Fuel cells have several advantages compared to other traditional fuels. It is a clean energy conversion process without the emission of any environmental hazards. The high efficiencies of fuel cells are an added advantage. Amongst all the known fuel cells, Proton Exchange Membrane (PEM) fuel cells or low temperature fuel cells have a well developed technology. They also have a technically sound infrastructure for their necessary implementation. Hydrogen is the primary fuel for the PEM fuel cells. A reliable source of hydrogen, hydrogen storage, and high cost for catalyst and materials are the key limitations for the commercialization of fuel cells. Current major sources for hydrogen production are methane, methanol and other alcohols, gasoline and other hydrocarbons, coal etc., and processes for hydrogen production include reforming for
example stem methane reforming (SMR), auto-thermal reforming, partial oxidation etc. [10]. These sources and technologies pose several limitations such as high operating temperature, complexity of the process, purity of the gas produced etc. posing additional restrictions on the possible commercialization of fuel cell technology.

A novel technology for hydrogen production by the electrolysis of ammonia has been recently developed [2]. This novel, patent pending technology will provide a breakthrough in the hydrogen production industry. A detailed comparison of different currently developed electrolyzers for large scale applications has been studied [20].

4.1.1 Hydrogen production from Ammonia: Background

There has been an increasing amount of research being done in the area of use of ammonia as a source of hydrogen. It has been proved that ammonia as a fuel has more benefits than methanol for an indirect type of a fuel cell. In addition it has also been shown that the specific energy density of such ammonia-fuel cell system is better than a direct hydrogen type fuel cell system [12]. The process proposed however, involves the use high temperature reforming process carried out at about 600°C. The ammonia used is in the form of a compressed liquid which is a pressure of 8 bars and atmospheric temperature. Also, the reactor i.e. the reformer unit which has tubes, catalyst, insulation system etc. makes the set-up and thus the process complicated which is undesired. In this regard, the current proposed research i.e. the generation of hydrogen from ammonia electrolysis is done at a low temperature ranging from 50°C - 60°C.

The performance of a fuel cell deteriorates if the fuel has traces of CO, CO₂ etc. thus researchers are trying to process the fuel obtained by various methods using
technologies like catalytic decomposition of hydrocarbon’s, step wise reforming of hydrocarbon’s, preferential oxidation of CO, catalytic decomposition of ammonia [11]. The common problem again encountered with all the above mentioned processes is again the high temperature and the complexity. If we consider the ammonia decomposition, economics show that this process is promising for alkaline fuel cells [12]. However, the only fuel cell which has a sound infrastructure to support the transportation or vehicle application is the PEM. The PEM technology dominates the most of the prototype fuel cell vehicles. Therefore, it the electrolysis of ammonia comes in handy for PEM applications.

Recent study by researchers in Turkey has shown that 97% ammonia from human urine can be recovered using traditional chemical engineering processes of stripping and absorption. The human urine is reported to have almost 2 g L\(^{-1}\) ammonia [28]. This study is very important because it shows that in the future energy in the form of hydrogen can be obtained from sheer human waste. In addition to this, ammonia is available in plenty in the industrial effluents, fertilizer industry, petrochemical refineries etc.

4.1.2 The Ammonia Electrolysis Technology

The following reactions for the ammonia electrolysis technology have been proposed by Vitse et al. [6].

At Anode: Oxidation of Ammonia

\[
2NH_3(g) + 6OH^-_{(aq)} \rightarrow N_2(g) + 6H_2O(l) + 6e^- \quad E^0 = -0.77 \text{ V vs SHE}
\]

At Cathode: Reduction of Water

\[
6H_2O(l) + 6e^- \rightarrow 3H_2(g) + 6OH^-_{(aq)} \quad E^0 = -0.82 \text{ V vs SHE}
\]
Overall Reaction:

\[ 2NH_3(l) \rightarrow N_2(g) + 3H_2(g) \quad E^0 = -0.059 \text{ V} \]

We see that the ammonia electrolysis occurs at a meager voltage of 0.06 V as compared to the theoretical value of 1.23 V for water electrolysis which is a commercialized process indicating that the power requirement for the process is extremely small as compared to the water electrolysis process. The ammonia electrolysis surely has the potential to be the technology of the future if parameters are carefully studied and optimized.

Past studies for only the ammonia electro oxidation reaction have shown that Pt and Ir as catalyst give better performance than other noble metals [16]. A comprehensive study on the development of an appropriate catalyst for novel ammonia electrolysis technology, purity of the hydrogen produced in the process, enhancement of the cell efficiency and process stability of ammonia electrolysis has been done by Vitse et al. [6]. They conclude that the Pt-Ir electrode showed the highest activity for ammonia electrolysis. The conversion of ammonia to hydrogen is 100% which is in conformance with the faraday’s law. These findings by Vitse et al. [6] are valuable from the point of view that they lay the foundation for the further enhancement, development and possible commercialization of the ammonia electrolysis technology. In order to improve the kinetics of the ammonia electrolysis process, which is the limiting factor; new materials and methods are being continuously tried, tested and optimized as electrodes for this novel process at the EERL.
4.2 Research Objectives

The overall general objective of the research presented here was to scale up the ammonia electrolysis process to power PEM fuel cells up to 2.5 W. This paper has three specific objectives. Each specific objective has its related in-built specific tasks:

1. Design a prototype, continuous, multi-stack ammonia electrolyzer. To accomplish this objective, first the required number of electrodes to produce enough hydrogen to power a 2.5 W fuel cell was built. The electrodes were scaled-up, designed and prepared based on the electrode preparation methodology available at the EERL. The carbon paper Pt-Ir electroplated electrodes were then tested galvanostatically in open cell batch mode condition. The electrodes were then assembled in a prototype 2-cell (4-electrodes) stack designed to establish the performance of the continuous closed cell system. Finally, the operating conditions and operating parameters were established for the prototype designed ammonia electrolytic cell (AEC).

2. Scale-up of the prototype design to power a 2.5 W fuel cell. This specific objective was based on the results and insights obtained from the above mentioned tasks. The 2-cell design was scaled-up or extended to a 4-cell, 5-cell and then finally to a 9-cell stack. This involved design, preparation and assembly of the membrane electrode assembly for the AEC.

3. Establish the operating parameters and conditions for the electrolyzer (AEC) for fuel cell applications. The operating procedure for the electrolyzer stack was established. The electrochemical performance of the stack was studied at different
temperatures. The actual amount of hydrogen gas produced from the stack, the faradaic efficiency, the amount of ammonia carried with the hydrogen gas stream was evaluated. The feasibility of integrating the 9-cell AEC with a 2.5 W PEM fuel cell was studied.

4.3 Experimental Conditions and Methodology

To accomplish the research objectives a specific methodology was followed for all the experiments. The detailed methodology for the preparation and electroplating for the electrodes used for the research project is described by Boggs and Botte [1].

An ARBIN cycler BT2000 equipment was used during all the electrochemical testing. All the experiments involved galvanostatic testing for which the current-voltage data was recorded by a computer using the MITS Pro (Multiple Integrated Testing Software) software provided with the arbin instrument. The testing solutions mentioned above were obtained from Fisher Scientific. The plates and all the fittings required to construct the AEC were purchased from McMaster-Carr. The Masterflex tubing, pumps (model 07553 80) and speed controllers were obtained from Cole-Parmer. A factorial design of experiments was always used for the electrochemical testing of the electrodes and the AEC. For the open cell (batch mode) testing of the electrodes 1 M NH₄OH + 5 M KOH solutions were used. This concentration was established and used by previous research for similar testing [6]. However, for closed cell testing in the AEC a concentration of 1 M NH₄OH + 1 M KOH on the anode and 1M KOH on the cathode were found to be suitable based on the testing results for the prototype 2-cell AEC design. Custom made Erlenmeyer flasks were from Specialty Glass Inc. were used for holding
the reactants for the AEC testing. The measurement of ammonia concentration in the hydrogen gas stream was aided with ammonia ion selective electrode (ISE). A standard operating procedure explained in the next section was established and followed for the AEC testing based on the prototype testing. Throughout the project, the performance criterion for the electrochemical testing was the voltage response at a current of 500 mA cell\(^{-1}\) to avoid high anodic over potentials [17-19] thus, the current in the scale-up design was limited to the above mentioned value.

4.4 Scale-Up Design for the Electrodes

4.4.1 Calculation of the Number of Electrodes Required

The calculation of the number of electrodes required for this project has been described in Appendix A. A total of 18 electrodes (9-AEC) were required to power at least a 2.5 W fuel cell at standard ambient conditions and assuming a fuel cell efficiency of 50%.

4.4.2 Electrode Preparation

Based on the research carried being done at the Electrochemical Engineering Laboratory (EERL) at the Ohio University, the Pt-Ir electrodes have proven to be better than the other noble metal catalysts tested [6]. The working electrodes used for the ammonia electrolysis in this project were the carbon paper based Pt-Ir. The procedure for the preparation of carbon paper electrodes has been developed by Boggs and Botte [1]. The TORAY carbon paper was used for the electrode preparation. The paper is supported on a titanium gauze support. Based on the experiments performed in the laboratory, the scale-up geometric dimensions selected for the gauze used for preparing electrodes in this
project were 4cm × 5cm. The gauze served as the current collector. Boggs and Botte [1] have described the detailed procedure for the electrode preparation and subsequent electroplating. The schematic representation for the electrode preparation could be represented as shown in Figure 4.1 [1]. The electrode once prepared using this procedure was then electroplated with Pt-Ir. The plating solutions were comprised of Pt and Ir salts namely dihydrogen hexachloroplatinate (H₂PtCl₆(H₂O)₆) and Iridium Chloride (IrCl₃) respectively in the stoichiometric quantities in 1M HCl solution. The working electrode in the plating process was the anode i.e. the carbon paper electrode prepared as described above and the counter electrode was the Pt electrode i.e. a Pt foil. The researchers at the EERL have been trying to optimize the electrode recipe for the ammonia electro-oxidation process. Different compositions and loadings of Pt-Ir catalyst are currently and continuously being tested on different geometrical areas for electrodes. Following were the plating conditions used for building the electrodes for this project:

Electrode Material: TORAY Carbon paper

Plating Temperature: 78°C (with stirring)

Plating solution: 1M HCl

Plating current: 500 mA-600 mA

Plating Voltage: 1.1 V-1.2 V

Total average electrode loading: ~8.5 mg/cm² Pt-Ir
The TORAY carbon paper was electro plated with Pt-Ir as the electrocatalyst. Ti was used as the support metal for the electrode.

### 4.4.3 Electrochemical testing

The electrodes prepared using the above methodology were first tested galvanostatically in an open cell or in a batch cell condition as represented in Figure 4.2. Galvanostatic testing involves the application of constant current in steps and measuring the voltage response or potential of the electrode pair. For this project, the maximum testing current was decided as 500 mA cell⁻¹. One cell includes a pair of electrodes i.e. the anode and the cathode. Thus the performance criterion for the electrochemical testing of the electrodes was the total cell voltage at 500 mA. Based on the past work done at
EERL, the testing solutions for open/batch cell condition consisted of 1 M NH$_4$OH + 5 M KOH.

![Diagram of an open/batch cell testing setup](image)

**Figure 4.2: Galvanostatic Open/Batch Cell testing of the Carbon Paper based Pt-Ir Electrodes.** The testing solution used was 5M KOH+1M NH$_4$OH and no gas separation or collection was done.

Similarly, the closed, continuous, multi-cell ammonia electrolyzer designed for this project was tested galvanostatically at the above mentioned testing current. The equipment used for the above testing was the standard ARBIN Cycler BT2000 also called as a potentiostat. Based on the extensive preliminary testing on a prototype 2-cell, closed AEC, the testing solution concentrations established for the closed cell ammonia electrolyzer were 1 M NH$_4$OH + 1 M KOH on the anode and 1M KOH on the cathode.
Thus, the above reactant concentrations were used throughout the testing of the AEC designed for the project.

4.5 Design of the Continuous, Multi-Stack, Ammonia Electrolytic Cell (AEC)

A schematic representation of the ammonia electrolytic cell is shown in Figure 4.3. The figure shows the arrangement of different components for a 2-cell (4-electrode) stack. The typical closed stack configuration was used to construct the AEC.

Figure 4.3: Exploded view of the Separator Electrode Assembly (SEA) of the prototype 2-Cell AEC. The SEA is similar to the Membrane Electrode Assembly (MEA) of the fuel cells.
Multiple components will be arranged in a fashion similar to shown in the above figure for the final 9-cell stack. The components constituting the cell are end plates, end electrode plates, gaskets, and separator plates. The separator electrode assembly (SEA) consists of the anode and the cathode electrode separated by a proprietary Teflon membrane obtained from a commercial manufacture (W.L. Gore Associates). The end plates were made from stainless steel, the end electrode plates and the separator plates were each constructed from chlorinated poly-vinyl chloride (CPVC) while the gaskets were made from polytetrafluoroethylene (PTFE). The material selection for the above components was based on the machinability and the chemical compatibility of each of them with respect to ammonium hydroxide (NH₄OH), potassium hydroxide (KOH) and high temperature (55°C) operation. Figures 4.4 represent the assembled 3-D view of the 9-cell stack.
Figure 4.4: A 3-D view of the assembled 9-Cell AEC Stack. The stack was electrochemically tested and a standard operating procedure was established. This stack could power a 2.5 W PEM fuel cell.

The Figures 4.5, 4.6, 4.7, and 4.8 represent the detail dimensions of each of the plates comprising the AEC. All the dimensions are in inches.
Figure 4.5: Front view of the Stainless Steel End Plate. A thickness of 0.354 inches was used for the 2 end plates.
Figure 4.6: Front view of the CPVC End Electrode Plate. A thickness of 0.354 inches was used for the 2 end electrode plates.
Figure 4.7: Front view of the CPVC Separator Plate. A thickness of 0.177 inches was used for a total of 8 separator plates.
4.5.1 Flow of the Reactants inside the Ammonia Electrolytic Cell

The design of the AEC and the arrangement of its components were done in a particular way so that the anode electrodes face only the ammonium hydroxide (NH₄OH) solution and the potassium hydroxide (KOH) solution reaches only the cathode.
electrodes, which is in conformity with the reactions explained in section 1.2. Figure 4.9 gives an idea of the internal stack design through the mesh view of the 9-cell stack.

Figure 4.9: A 3-D Mesh view of the assembled 9-Cell AEC. This view gives an idea of the stack internals and a better understanding of the flow of the reactants across the AEC.
The ammonium hydroxide enters the AEC through the Teflon barbed fitting attached to the first end electrode plate placed near the end stainless steel plate. Similarly, the potassium hydroxide solution enters from the other end of the stack. The ammonium hydroxide solution flows through all the CPVC plates where the anode electrodes are placed. The solution fills the 2 mm slot cut in the electrode plates from bottom-right corner to the top-left corner of each plate. On the other hand the potassium hydroxide solution in a similar fashion fills the 2 mm slots cut out but on the cathode electrode plates. This way, the ammonium hydroxide solution along with the hydrogen gas produced comes out of the stack from the top left corner of the last end electrode plate on the other side of the stack, which also serves as the inlet for the potassium hydroxide solution to the stack as explained before. The potassium hydroxide solution and the nitrogen gas produced exits from the top left corner of the first cell end electrode plate, which also serves as the inlet of the ammonium hydroxide solution to the stack. This way the solutions reach only their respective electrodes. The experimental set-up for this research project is represented in Figure 4.10
Figure 4.10: Experimental Set-up for the 9-Cell AEC. The clean nitrogen gas was let to the atmosphere, while the hydrogen gas was fed to a PEM fuel cell.

4.6 Results and Discussion

4.6.1 Open/Batch Cell Galvanostatic Testing

After the electrodes were prepared as explained in Section 4.4.3, the electrodes were tested galvanostatically and arranged in the ascending order of voltage performance at a current of 500 mA through an electrode pair (1-cell). Preliminary experiments in the lab have proved that the best performance of the Pt-Ir electrodes was obtained at an operating temperature of 55°C. The results of the open cell conditions at 25°C and 55°C are given below in Table 4.1.
Table 4.1: Galvanostatic performance of the Pt-Ir Electrodes in Open cell conditions

<table>
<thead>
<tr>
<th>Electrode Pair</th>
<th>V (±0.0001) Response at (500±0.1 mA)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T = 25°C</td>
</tr>
<tr>
<td>1</td>
<td>0.4642</td>
</tr>
<tr>
<td>2</td>
<td>0.4674</td>
</tr>
<tr>
<td>3</td>
<td>0.4791</td>
</tr>
<tr>
<td>4</td>
<td>0.4804</td>
</tr>
<tr>
<td>5</td>
<td>0.4813</td>
</tr>
<tr>
<td>6</td>
<td>0.4838</td>
</tr>
<tr>
<td>7</td>
<td>0.4841</td>
</tr>
<tr>
<td>8</td>
<td>0.4868</td>
</tr>
<tr>
<td>9</td>
<td>0.4873</td>
</tr>
</tbody>
</table>

Thus from Table 4.1 we see that a better performance is obtained at 55°C. The average voltage response obtained at 25°C and 55°C was 0.48 V and 0.38 V respectively. In open cell testing though, there was no gas separation achieved. This testing helped in comparing with the closed cell AEC testing implying the use of the same electrodes.

4.6.2 Standard Operating Procedure (SOP) for the AEC

A standard operating procedure for the operation of the 9-cell AEC stack was established. This procedure was always followed during all the electrochemical testing of the electrolyzer. The major steps involved in the operating procedure are listed below,

1. 500 mL of 1M NH₄OH + 1 M KOH and 1M KOH was added to the Erlenmeyer flaks at the anode and the cathode respectively and the pumps were started.
2. The speed controllers on both the pumps were adjusted so that the flow rates of the reactants to the AEC were ~145 mL/min. This flow rate was selected based on the extensive testing of the stack. At this flow rate the solutions in the Erlenmeyer flaks were properly circulated through the AEC.

3. The solution was let run through the AEC for 15 minutes.

4. The anode and cathode leads of the AEC were connected to the ARBIN potentiostat.

5. After the 15 minutes, the current was supplied through the potentiostat to the AEC in the form of a current staircase from 0.45 A to 4.5 A. Each stair was held for at least 15 minutes.

6. Once the test was completed, the current supply to the AEC was disconnected.

7. The AEC was always operated with the pumps on for at least 5-10 minutes after the test was completed to make sure that any accumulated H₂/N₂ gas in the AEC was pushed out and not create any air-gap in the AEC, which is not good for the electrodes. The flow of the reactants to the AEC was stopped.

8. The AEC was stored in the same solutions described above, which were used on the respective sides for the testing.

4.6.3 Electrochemical Testing of the 5-Cell and the 9-Cell AEC

The design for the prototype 2-cell AEC was extended in a stepwise manner to a 4- cell, 5-cell, and then finally to the 9-cell electrolyzer stack. Though the 9-cell stack is of primary interest here, a comparison of the electrochemical testing of the 5-cell and 9-
cell stack is presented. As explained before, the stack testing was carried out at two operating temperatures viz. 25°C and 55°C.

![Graph showing temperature effect on the 5-Cell AEC.](image)

**Figure 4.11: Temperature effect on the 5-Cell AEC.** A maximum current of 2.5 A was applied through the 5-cell stack (500 mA cell⁻¹).

From Figure 4.11, it can be clearly seen that the electrochemical performance for the 5-cell AEC is better at 55°C (0.450 V) as compared to at 25°C (0.533 V). Secondly, it should be noted that the voltage response for the 5-cell stack increased from 0.480 V at 25°C in open cell condition to 0.533 V and from 0.38 V to 0.45 V at 55°C. Thus, the
increases in the potential losses observed in the scale-up from batch cell to 5-cell stack were 53 mV and 70 mV at 25°C and 55°C respectively.

![Graph showing temperature effect on the 9-Cell AEC.](image)

**Figure 4.12: Temperature effect on the 9-Cell AEC.** A maximum current of 4.5 A was applied through the 9-cell stack (500 mA cell⁻¹).

From Figure 4.12, it can be again clearly seen that the electrochemical performance for the 9-cell AEC is better at 55°C (0.560 V) as compared to at 25°C (0.633 V). Quantifying the potential drop in this case, it should be noted that the voltage response for the 9-cell stack increased from 0.480 V at 25°C in open cell condition to
0.633 V and from 0.38 V to 0.560 V at 55°C. Thus, the potential losses observed in the scale-up from batch cell to 9-cell stack were 153 mV and 180 mV at 25°C and 55°C respectively. This increase in the voltage is explained below. A lower voltage response from the AEC implies lower power requirement for the ammonia electrolysis. The comparison of the above performance of the closed cell, continuous AEC with the open cell or batch cell operation at temperatures of 25°C and 55°C is described in Table 4.2 and Table 4.3 respectively.

Table 4.2: Electrochemical Performance Comparison for the 5-Cell and the 9-Cell AEC Stack Operation with the Open/Batch mode Operation at 25°C

<table>
<thead>
<tr>
<th>Electrode Pair</th>
<th>Voltage (±0.0001V) Response at (500±1 mA/cell)</th>
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<tbody>
<tr>
<td></td>
<td>Batch Cell Operation</td>
</tr>
<tr>
<td></td>
<td>5 Cell Stack</td>
</tr>
<tr>
<td>1</td>
<td>0.4642</td>
</tr>
<tr>
<td>2</td>
<td>0.4674</td>
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<tr>
<td>3</td>
<td>0.4791</td>
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<td>4</td>
<td>0.4804</td>
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<td>0.4868</td>
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<td>9</td>
<td>0.4873</td>
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</table>
Table 4.3: Electrochemical Performance Comparison for the 5-Cell and the 9-Cell AEC Stack Operation with the Open/Batch mode Operation at 55°C

<table>
<thead>
<tr>
<th>Electrode Pair</th>
<th>Voltage (±0.0001V) Response at (500±1 mA/cell)</th>
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<tbody>
<tr>
<td></td>
<td>Batch Cell Operation</td>
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<tr>
<td></td>
<td>5 Cell Stack</td>
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<tr>
<td>1</td>
<td>0.3642</td>
</tr>
<tr>
<td>2</td>
<td>0.3674</td>
</tr>
<tr>
<td>3</td>
<td>0.3791</td>
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<tr>
<td>4</td>
<td>0.3804</td>
</tr>
<tr>
<td>5</td>
<td>0.3813</td>
</tr>
<tr>
<td>6</td>
<td>0.3838</td>
</tr>
<tr>
<td>7</td>
<td>0.3841</td>
</tr>
<tr>
<td>8</td>
<td>0.3868</td>
</tr>
<tr>
<td>9</td>
<td>0.3873</td>
</tr>
</tbody>
</table>

It could be observed from Tables 4.2 and 4.3 that, the voltage performance of the closed, multi cell, AEC operation is higher than that observed in the open cell operation. There are two major reasons for this. First and the most significant reason is the potential or the ohmic losses caused in the stack operation due to the electrical connections in the AEC. There is a huge resistance built-up across the stack. Secondly, in the open cell operation, the gases produced after electrolysis directly escapes into the atmosphere, while in the closed AEC, the gas produced travels through the channels in the plates along with the fluid throughout the stack. There is a strong possibility that the gas is accumulated, obstructed within the plates comprising the AEC. This increases the resistance for the gases to come out and increasing the overall voltage response from the
AEC. These losses increase with the number of cells assembled in the stack. However, unlike the open cell operation, the closed cell design achieves the separation of the gases i.e. N$_2$ on the anode and H$_2$ on the cathode. This makes the design extremely feasible for commercial fuel cell applications. Apart from this, it could be very well observed that the performance of the stack is significantly better at a higher temperature of 25°C, which was expected based on the preliminary results obtained.

Another important test was performed on the 9-cell stack to prove that the use of pumps in this set-up is merely for experimental purposes and in actual real time applications the pumps will not be required. The solutions that flow in the AEC were set at a height of 30 cm from the ground. This test was thus called as the hydrostatic test, since the reactant liquids were at rest. At this height, the reactant solutions were observed to fill the AEC for the electrochemical reactions to occur. A galvanostatic test was completed on the stack at 25°C without the use of pumps and the voltage response was measured. The Figure 4.13 shows the performance obtained in this test.
Comparing the voltage observed in the hydrostatic testing above in Figure 4.13 with the voltage obtained on the galvanostatic testing with pumps in Figure 4.12 it could be observed that the performance is almost the same. The voltage for the 9-cell stack in the hydrostatic testing was merely 27 mV higher. The reason for this small over potential could be attributed to the fact that the use of pumps facilitates the ease of hydrogen
evolution from the AEC and also helps replenish the surface of the electrodes with the reactant solutions. It can be thus proved that for future work, the use of pumps could be avoided considering the peristaltic losses that might occur in the pumps and moreover since the above test proves that the effect of using pumps on the voltage response of the 9-cell AEC is negligible.

4.6.4 Gas Collection and Analysis from the 9-Cell AEC

After establishing the standard procedure for the AEC and achieving a reproducible electrochemical performance, the gases were collected and the gas collection efficiency for the designed 9-cell stack was obtained. The gas collection was done at both 25°C and 55°C to confirm with Faraday’s law prediction. A standard water displacement procedure was used to collect and measure the gas flow rate. The results for this test are shown in Table 4.4.

Table 4.4: Faradaic Gas Collection Efficiency (%) for the 9-Cell AEC

<table>
<thead>
<tr>
<th>Temperature</th>
<th>H₂ Gas Produced g/hr (±0.006)</th>
<th>Gas Collection Efficiency (±0.04%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Faraday's Law</td>
<td>Experimental</td>
</tr>
<tr>
<td>25°C</td>
<td>0.168</td>
<td>0.164</td>
</tr>
<tr>
<td>55°C</td>
<td>0.168</td>
<td>0.164</td>
</tr>
</tbody>
</table>

According to Faraday’s law, the gas produced is independent of the operating temperature. This was proved as represented in Table 4.4. The gas produced at both 25°C
and 55°C was the same (0.164 ± 0.006 g/h). An efficiency of 97.55 ± 0.04% was achieved on the AEC. There might be some gas obstructed in the channels of the AEC plates as explained before.

Vitse et al. [6] have already established that there was no CO$_x$, NO$_x$, etc. observed in the analyzed gas stream of nitrogen and hydrogen from the electrolysis of ammonia. They also carried out a test to confirm the concentration of ammonia carried with the hydrogen gas stream. A similar test was performed at both 25°C and 55°C to determine the ammonia carried over with the hydrogen gas stream evolved from the AEC. The hydrogen gas was passed into HPLC water until all the ammonia was electrolyzed (~7 hours). The pH and the ammonia concentration (ppm) were determined over the entire period. The ammonia concentrations were measured using an ammonia ion selective electrode (ISE). The pH was plotted as a function of time as shown in Figure 4.14.
Figure 4.14: pH of HPLC Water as a function of time bubbled with the stream of Hydrogen gas produced from the 9-Cell AEC. A pH glass electrode was used to monitor the pH. The monitoring was done at a regular time interval of 30 minutes at 25°C and every 60 minutes at 55°C.

A similar trend was observed as explained by Vitse et al. [6]. Initially, a sharp rise in the pH of the hydrogen bubbled water was observed but then a steady value was observed as seen in the Figure 4.14. The final pH for operation at 25°C observed was 8.61, and 9.20 at 55°C. The higher pH value could be explained based on the fact that ammonia has a vapor-liquid equilibrium with water. The amount of ammonia present in
the gas stream was calculated assuming the existence of a vapor-liquid equilibrium between and bubbling water and the gas stream as explained by Vitse et al. [6] The concentrations of ammonia found using thermodynamic co-relation for Henry’s law was found to be far less than 1 ppm at both 25°C and 55°C. Thus, the hydrogen gas produced from ammonia electrolysis could be directly used in fuel cells without the need for any downstream scrubbing process. This makes the technology more feasible for pure hydrogen production for fuel cell applications, which was also the important finding by Vitse et al. [6].

4.6.5 Energy Balance for the AEC-PEMFC Integration

The 9-cell stack could power a 2.5 W PEM fuel cell. The power consumption (W) and the energy consumption (W-h) per gram of hydrogen produced are shown in Table 4.5 at the operating temperatures of 25°C and 55°C.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Power and Energy consumption for the 9-Cell AEC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Power (W)</td>
</tr>
<tr>
<td>25°C</td>
<td>2.8463 ± 0.0008</td>
</tr>
<tr>
<td>55°C</td>
<td>2.5182 ± 0.0007</td>
</tr>
</tbody>
</table>

Table 4.5: Power and Energy consumption comparison at 25°C and 55°C for the 9-Cell AEC
It was observed that the energy required per gram of hydrogen at 55°C is approximately 12% less than that at 25°C. The reasons for better performance at higher temperatures could be attributed to increased reaction rate due to better ionic conduction at 55°C, and improved catalytic activity. Secondly, the ease of gas evolution at higher temperature is better because at higher temperature the density of the hydrogen gas decreases.

In addition to this, a test was done to determine the time constant for the hydrogen gas production from the AEC as shown in Table 4.6. It is a well known fact that electrolysis process for hydrogen production has some time lag. This study is thus important in the view that it will help design better integrated set-up in the future work for fuel cell applications. The time constant studies will indicate the time lag or frequency for hydrogen production from the AEC designed, which in turn would signify the minimum amount of hydrogen to be made available for the fuel cell since fuel cells need a continuous uninterrupted hydrogen gas supply.

Table 4.6: Time Constant (τ) for the gas produced from the 9-Cell AEC

<table>
<thead>
<tr>
<th>Gas</th>
<th>τ (±1sec)</th>
<th>Gas Collected/Produced (±1 ml) in one time constant (τ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>28</td>
<td>14.0</td>
</tr>
<tr>
<td>N₂</td>
<td>51</td>
<td>8.0</td>
</tr>
</tbody>
</table>
The time constant (τ) for hydrogen gas produced from the 9-cell AEC was observed to be 28 sec. and the amount of gas produced in one time constant (τ) was 14.0 ml (0.162 ± 0.006 g hr⁻¹). This is in consistent with the values for hydrogen gas produced represented in table 4.4. Similar results were obtained for the time constant study at 55°C.

Based on the results obtained from the design of the ammonia electrolytic cell, and the hydrogen gas production obtained from the AEC, it was established that the electrolyzer stacks could be designed and assembled accordingly to power PEM fuel cells ranging from 1 W to at least 2.5 W. At atmospheric conditions, assuming a fuel cell efficiency of 50% and the operating current of 500 mA cell⁻¹ for the AEC, the number of AEC stacks required to power the fuel cells is tabulated below in Table 4.7.

Table 4.7: Number of AEC Stacks required, powering Fuel Cells ranging from 1 W to 2.5 W

<table>
<thead>
<tr>
<th>PEM Fuel Cell (W)</th>
<th>Hydrogen Requirement (g·hr⁻¹)</th>
<th>Number of AEC Stacks required</th>
<th>Hydrogen Production rate from equivalent number of Stacks (g·hr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>0.061</td>
<td>4</td>
<td>0.073</td>
</tr>
<tr>
<td>1.50</td>
<td>0.091</td>
<td>5</td>
<td>0.091</td>
</tr>
<tr>
<td>2.00</td>
<td>0.121</td>
<td>7</td>
<td>0.127</td>
</tr>
<tr>
<td>2.50</td>
<td>0.152</td>
<td>9</td>
<td>0.164</td>
</tr>
</tbody>
</table>
To demonstrate the feasibility of the integration of the AEC with PEM fuel cells a 5-cell (4 W) PEM fuel cell stack from Parker Energy Systems Parker Hannifin Corporation was used. A bench scale, 1-cell AEC integration study with the same fuel cell at the EERL has proved that the average energy efficiency of the fuel cell is 65% [1]. Based on this efficiency of the fuel cell and the fact that 1 g of H₂ has 33 Wh of energy, the energy conversion efficiencies were established and compared with the existing commercial hydrogen production technologies. The energy conversion efficiency is calculated as the net useful energy available from the integration over the total energy consumed by the AEC stack for ammonia electrolysis. In this regard, two scenarios are presented. As explained previously that the potential losses across the stack increased with the number of cells in the stack. Table 4.8 represents the current scenario where there is significant ohmic resistance built across AEC stack, while Table 4.9 presents the second case where the voltage losses are not accounted for since the future work will be dedicated to minimize the current losses in the AEC design. The 9-cell stack currently has external potential loss of 153 mV and 180 mV at 25°C and 55°C respectively. Once these losses in the future are decreased so that voltages corresponding to the open/batch cell conditions are obtained in the stack the integration will show increased energy conversion efficiency as represented in Table 4.9.
Table 4.8: Energy Conversion Efficiency for the 9-Cell AEC-PEMFC Integration.
This includes the Ohmic losses observed in the Stack. *Based on the Fuel Cell efficiency of 65% obtained on a 1-cell AEC Bench scale set-up [1]

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Energy Consumed by AEC (W-hr-g(^{-1}) H(_2))</th>
<th>Average Energy Generated by PEMFC (W-hr-g(^{-1}) H(_2))</th>
<th>Net Energy available from the Integration (W-hr-g(^{-1}) H(_2))</th>
<th>Energy Conversion Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C</td>
<td>17.36 ± 0.64</td>
<td>21.45 ± 0.90*</td>
<td>4.10 ± 0.97</td>
<td>23.62 ± 0.36</td>
</tr>
<tr>
<td>55°C</td>
<td>15.36 ± 0.56</td>
<td>21.45 ± 0.90*</td>
<td>6.10 ± 0.97</td>
<td>39.71 ± 0.69</td>
</tr>
</tbody>
</table>

Table 4.9: Energy Conversion Efficiency for the 9-Cell AEC-PEMFC Integration.
This does not include the Ohmic losses observed across the Stack. *Based on the Fuel Cell efficiency of 65% obtained on a 1-cell AEC Bench scale set-up [1]

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Energy Consumed by AEC (W-hr-g(^{-1}) H(_2))</th>
<th>Average Energy Generated by PEMFC (W-hr-g(^{-1}) H(_2))</th>
<th>Net Energy available from the Integration (W-hr-g(^{-1}) H(_2))</th>
<th>Energy Conversion Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C</td>
<td>13.17 ± 0.64</td>
<td>21.45 ± 0.90*</td>
<td>8.28 ± 0.97</td>
<td>62.87 ± 0.95</td>
</tr>
<tr>
<td>55°C</td>
<td>10.98 ± 0.56</td>
<td>21.45 ± 0.90*</td>
<td>10.47 ± 0.97</td>
<td>95.36 ± 1.65</td>
</tr>
</tbody>
</table>
The values shown in Tables 4.8 and 4.9 prove that energy conversion efficiencies of 23.62% and 39.71% were obtained at 25°C and 55°C respectively on the currently designed electrolyzer. Secondly it should be also noted that ohmic losses in the design account to energy losses of about 4.18 W h g⁻¹ H₂ at 25°C and 4.37 W h g⁻¹ H₂ at 55°C. In the future once a better design is achieved, energy conversion efficiencies as high as 62.87% and 95.36% could be achieved. This once again proves the feasibility of ammonia electrolysis technology for PEM fuel cell applications.

The current commercial hydrogen production technologies are required to store the gas. A detailed study for the economic analysis for different hydrogen production technologies was done [29]. Using photovoltaic solar cells for renewable hydrogen production, the solar-to-hydrogen conversion efficiency reported was just 18%, while the same study also confirms that at 25°C, the energy efficiency reported for alkaline water electrolysis was 21%. A study on a methanol fuel processor integrated with a PEM fuel for portable power applications was carried out at the Pacific Northwest National Laboratory. It has been shown that the system has an energy efficiency obtained was 22% [30]. A study on the system integration for natural gas reforming and a PEM fuel cell for residential applications has shown an energy efficiency of 28% [31]. An energy efficiency of 35% was obtained with an integrated methane fired low temperature fuel cell plant [32]. An energy conversion efficiency of just 37% was obtained on a methanol fuel processor integrated with a PEM fuel cell [33]. The researchers have also proved that huge exergy losses occur across various constituent devices such as the fuel cell, the vaporizer, the burner, and the reformer. Similarly, a gross energy efficiency of 38% has
been predicted for a natural gas steam reforming process integrated with a 50 kW PEM fuel cell by the DOE [34]. For a biogas reforming plant integrated with a PEMFC a gross energy efficiency of 40% was obtained [35].

Thus from the above numbers it could be seen that the current AEC-PEMFC integration has already achieved higher energy efficiencies than the currently available or existing process for hydrogen production like water electrolysis, traditional methanol, natural gas and other hydrocarbon reforming, etc. Moreover, these processes are highly cost intensive and complex considering the components required and the rigorous operating conditions. It also has been proven that the electrolysis of ammonia has tremendous potential to offer higher energy conversion efficiencies once more advancements and improvements are achieved for the electrodes and the AEC design.
CHAPTER 5: CONCLUSIONS

Through this research, the overall objective to design and scale-up the ammonia electrolysis process was successfully achieved. A multi-stack, continuous flow, closed cell 9-cell ammonia electrolyzer (AEC) was designed and built to test the feasibility of hydrogen generation for fuel cell applications. The membrane electrode assembly (MEA) comprised of end plates, end electrode plates, separator plates, the Pt-Ir electrodes, gaskets, and the membrane/separator. The initial design for a 2-cell prototype was extended in a stepwise manner to a 4-cell, 5-cell and finally to the 9-cell AEC. The operating parameters and conditions for the 9-cell electrolyzer stack were established, which involved establishing the standard operating procedure (SOP). Extensive electrochemical testing of the stack was performed.

It was observed that reactant concentrations of 1 M NH₄OH + 1 M KOH at the anode and 1M KOH at the cathode were suitable for the electrolyzer operation. The most notable finding of the research is the net energy available from the AEC-PEMFC system integration. This is based on the 65% energy efficiency obtained with a PEMFC on a bench scale 1-cell AEC [1]. Thus, on the 9-cell electrolyzer stack, a net energy of 4.10 ± 0.97 Whg⁻¹H₂ at 25°C and 6.10 ± 0.97 Whg⁻¹H₂ at 55°C was obtained. The power consumption for the 9-cell stack at 55°C (15.36 ± 0.56 Whg⁻¹H₂) was less than that at 25°C (17.36 ± 0.64 Whg⁻¹H₂). A Faradaic efficiency of 97.55 ± 0.04 % was achieved on the designed 9-cell electrolyzer stack. The AEC design achieved energy conversion efficiencies of 23.62 ± 0.36 % and 39.71 ± 0.69 % at 25°C and 55°C respectively. The other important conclusion was the ohmic or potential losses observed in the current
stack. This was based on the difference in the voltage response of the electrodes in the open cell operation and the closed cell operation. These losses are predominantly due to the electrical connections of the electrodes from the AEC, and the conductivity of the base metal titanium used for preparing the Pt-Ir electrodes. The 9-cell stack currently has voltage loss of 153 mV and 180 mV at 25°C and 55°C respectively. These losses in the design account to energy losses of about 4.18 W h g⁻¹ H₂ at 25°C and 4.37 W h g⁻¹ H₂ at 55°C. Thus, once these losses are minimized with improved electrode and cell design, energy conversion efficiencies as high as 62.87 ± 0.95 % and 95.36 ± 1.65 % could be achieved. The same energy conversion efficiencies for the currently developed and commercially available integrated hydrogen production – fuel cell systems are about 21% for water electrolysis, 38% for natural gas and other hydrocarbon reforming. It can thus be conclude that current AEC-PEMFC integration involving the ammonia electrolysis technology for hydrogen production has already achieved comparable and far better energy efficiencies than the currently demonstrated integrated systems. It has also showed that even higher energy efficiencies in the order of 63% and 95% could be obtained in the future.

Another important finding from the hydrostatic testing is that the AEC-PEMFC integration does not need any pumps. The effect of pumps on the performance of the AEC was negligible. A meager decrease of 27 mV was observed with the pumps. The use of pumps was just for experimental purposes and need not to be used in real life applications in the future. The time constant/lag tests indicate that a time lag of 28 seconds is involved for the hydrogen gas evolution. This study is important for the future
integration of the AEC with a PEM fuel cell. Finally, the ammonia concentration in the hydrogen gas stream was found to be far less than 1 ppm at both the operating temperatures indicating that the hydrogen produced is pure and can be directly used in PEM fuel cells. The research indicates that the novel path breaking technology of ammonia electrolysis process will play an imperative role in the future hydrogen economy of the nation. The success of the currently designed will help realize the goal of 'green hydrogen economy' in true sense in the coming years.
CHAPTER 6: FUTURE WORK

It has been already proved by previous researchers that the ammonia electrolysis process is limited by kinetics [6]. Continuous efforts in this regard to improve the electrodes in this regard are being carried out continuously at the EERL. New and improved electro-catalyst, catalyst loadings, and electrode dimensions are being tested. The new electrodes should be designed and selected so as to be able to operate at higher current densities. Secondly, the significant potential losses in the electrical connections should be decreased. This could be achieved by using better electrical connections for the AEC or employing the use of bipolar plates, which are used in fuel cells. The bipolar plates offer easier flow of reactants and better electrical connections. However, the compatibility of the use of the prospective bipolar plates should be taken in to account considering that the electrolysis of ammonia is done in an alkaline medium. Based on the improved electrode design, different plate design and dimensions in the MEA could be tried to test the electrochemical performance of the AEC. An increased hole diameter for the gas outlet might decrease the amount of gas that might be accumulated or obstructed in the AEC. These recommendations will help decrease the volume and the weight of the electrolyzer. The AEC modeling for the flow of the reactants and the gas evolution from the stack could give a better understanding for the future design improvements. A detailed optimization could be performed on the currently designed AEC stack. These studies will also aid in future design for the electrolyzer.

The fuel cells require continuous hydrogen supply. In this regard, based on the hydrogen requirement of the fuel cell a buffer gas chamber should be designed since the
hydrogen production from the electrolysis process has an inherent time lag. The design for the buffer gas collection device will be based on the power rating of the fuel cell and the rate of hydrogen produced from the AEC.
REFERENCES


APPENDIX A: CALCULATION FOR THE NUMBER OF ELECTRODES REQUIRED

Energy from a gram of hydrogen (E) = 33 W h
Maximum Output of fuel cell = 2.5 W
Fuel cell efficiency (\(\eta\)) = 50%

Hydrogen Mass Flowrate Required = \(\frac{P}{\eta \times E}\)

\[= \frac{2.5}{0.5 \times 33}\]

= 0.152 g hr

Scale-Up of the AEC

Proposed Electrode Area (\(A_e\)) = 40 cm²
Current selected for AEC operation (One Cell) (\(I_{AEC}\)) = 0.5 A
Hydrogen Production from the AEC (applying Faraday's Law)

Molecular weight for \(H_2\) (\(M_{H_2}\)) = 2 \(\frac{g}{mol}\)
Number of electron transfer (\(n\)) = 2

Faraday Constant (\(F\)) = 26.8 A hr\(\frac{mol}{mol}\)

Mass flow rate (One Cell) = \(\frac{I_{AEC} \times M_{H_2}}{n \times F}\)

\[= \frac{0.5 \times 2}{2 \times 26.8}\]

= 0.0187 g hr

Number of AEC's Required = \(\frac{0.152}{0.0187}\) = 8.13 \(\sim\) 9

Number of Electrodes Required = \(2 \times \) Number of AEC's

= 18 Electrodes