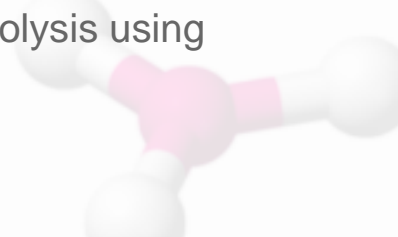
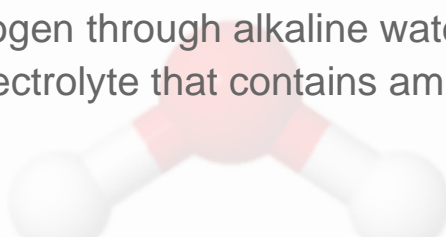
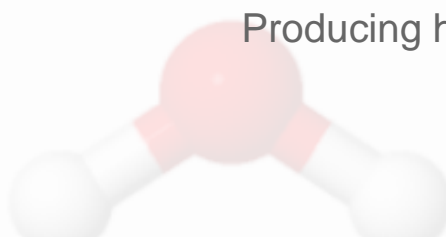




Recycling steam condensate for hydrogen production



Producing hydrogen through alkaline water electrolysis using
electrolyte that contains ammonia



Master thesis
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Abstract

Producing green hydrogen can be done using alkaline water electrolysis. Recycling water might help to fulfil the large water demand of hydrogen production facilities. In fertiliser production, steam condensate could be a recyclable water source for hydrogen production. This condensate is relatively clean as its main contaminant is a small concentration of ammonia. This report researches the effect of adding ammonia to the electrolyte of an alkaline water electrolysis cell.

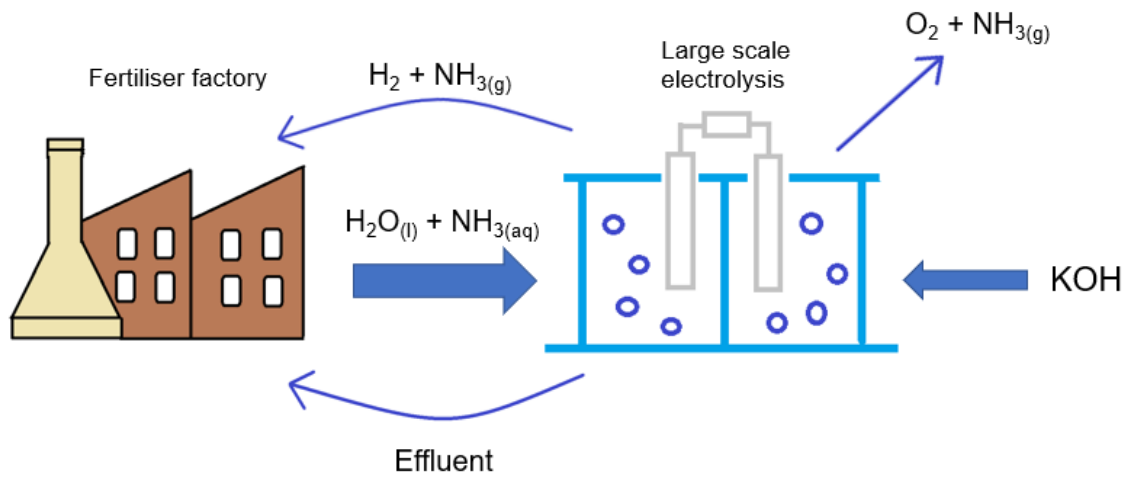
When steam condensate is used instead of ultra-pure water, it is important to find out what happens to the added ammonia and if it affects the production rate and the production efficiency, or if it degrades the equipment. The experiments in this report used three different ammonia concentrations and the electrolyte was made using potassium hydroxide. The electrolysis cell used nickel mesh electrodes and a Selemion™ anion exchange membrane. Each of the experiments were carried out at 2.15 Volts for a duration of 50 minutes.

It was found that adding 1 mmol/L ammonia to the electrolyte decreased the current density of the cell. Doubling the ammonia concentration led to an even larger decrease in current density of up to 19%. A significant effect on the Faraday efficiency was not measured. During the experiments, the ammonia was partially stripped from the electrolyte due to its high alkalinity. Another part was oxidised to produce nitrogen gas and nitrate. Some of the ammonia had not reacted after the 50-minute experiment and could be measured in the spent electrolyte. After all the experiments were carried out, the cell was disassembled. The cathode showed significant signs of degradation. However, the many starts and stops between experiments could be the primary reason for this degradation. The ammonia could have accelerated the degradation, but this was not proven.

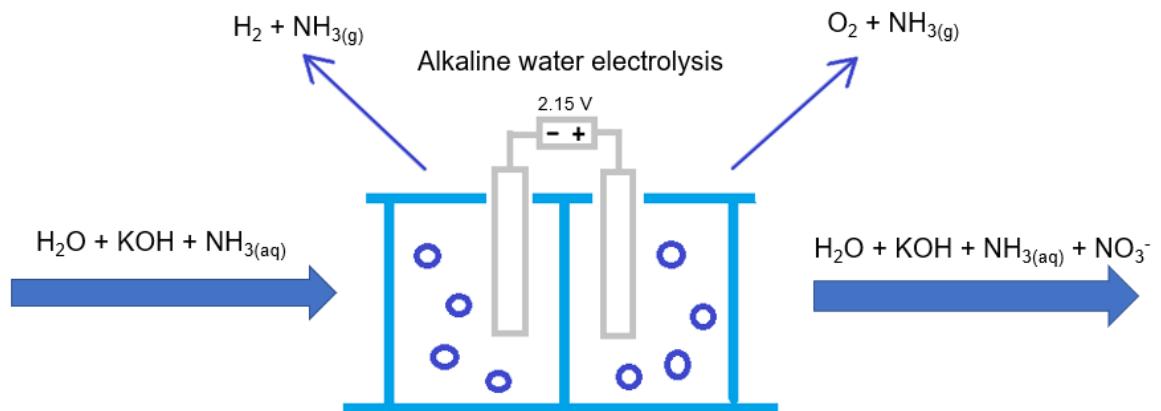
Overall, the benefits of using steam condensate do not seem to outweigh the drawbacks. The ammonia caused a significant decrease in current density. On the long term, ammonia might cause electrode poisoning which would further lower the current density. The experiments also found nitrate in the spent electrolyte. Having additional pollutants in both the spent electrolyte and the produced gasses might introduce additional disadvantages to using an ammonia containing electrolyte. If steam condensate is used as a water source, a treatment step is advised. Aeration could be used to strip the ammonia from the electrolyte. To get a more accurate insight into the effects of ammonia on alkaline water electrolysis, additional research is necessary. In future research, the effects of ammonia should be measured more accurately, and the long-term effects should be researched.

Visual abstract

Application



Experiment



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1. Literature review

1.1 Water source for alkaline water electrolysis

Alkaline water electrolysis is a widely researched topic. Emphasis in this research is usually put on the electrodes or the gas separator. These components are researched to make the process more efficient and more resistant to degradation. The electrolyte in research is generally described as an electrolyte containing a high concentration of potassium hydroxide which is used to increase the pH and to reach an optimal conductivity (Chi & Yu 2018) (Brauns & Turek 2020). The water used for the electrolyte is usually ultra-pure water. The reason for this is that there exist many impurities that can lower the electrolysis performance due to deposition on the catalyst surface or in the gas separation membrane. Blockage is mostly caused by divalent cations like calcium, magnesium, and zinc (Barwe et al. 2018) (Zeng & Zhang 2010). Other ions can lead to unwanted side-reactions that lower the efficiency. Some can even be corrosive to the electrodes (Zeng & Zhang 2010).

Governments worldwide are aiming to reach a total water electrolysis capacity of 134-720 GW (IEA 2023). At this scale, the ultra-pure water consumption will be significant. A water requirement calculation was made for this report and can be found in appendix chapter 10.2. This calculation showed that a 1 GW plant consumes 3800 m³ of water per day. Large volumes of ultra-pure water are not abundant. Instead of producing more ultra-pure water, more widely available water source might have to be considered to fulfil the thirst of the future water electrolysis industry.

Some research about alkaline water electrolysis has been done that focusses on using wastewater. The research on wastewater often focusses on the oxidation of certain compounds. For example, the oxidation of ammonia (Shu et al. 2016), the oxidation of urea (Zhang et al. 2020), the oxidation of sulfide (Ntagia et al. 2019), or the oxidation of phenols (Comninellis et al. 1995). While these experiments often give great results, they are not focussed on production of hydrogen. Alkaline water electrolysis requires a high pH, and to produce hydrogen efficiently, a high conductivity. This is achieved by adding 25-30% in weight of potassium hydroxide (Brauns & Turek 2020). Therefore, combining wastewater treatment and efficient hydrogen production through alkaline water electrolysis is very difficult. When the focus does lie on hydrogen production, results are mixed. Using domestic wastewater for alkaline water electrolysis shows a decrease in production rates and more anodic corrosion but had the benefit that the produced oxygen could be used for the activated sludge process (Chauhan & Ahn 2023). Further research is rare. Recently, NASA has done research on the topic. During missions, NASA aims to mine water which could then be used to produce hydrogen (Burke 2023). However, that research proposed a less conventional setup that focussed on a small scale and niche application.

Seawater has also been proposed as a water source for alkaline water electrolysis. Seawater faces the problem that it has a high concentration of many ions. Especially chloride can be problematic. Chloride is a competitor in the process of water oxidation, at an overpotential of 480 mV hypochlorite is formed (Zhou et al. 2022). Furthermore, the calcium and magnesium in the seawater form insoluble precipitates that cause blockage of the catalytic surface and

membrane (Lu et al. 2018). While development of new catalysts and membranes can solve many problems, there might be less problematic water sources available.

Using an alternative water source can lead to significant degradation of the equipment depending on the impurities that are introduced. Even when ultrapure water is used, degradation of equipment takes place during the electrolysis process. Electrode degradation is an important factor in alkaline water electrolysis. For large scale applications, degradation must be minimized to guarantee a long lifetime of the equipment. Cathode degradation occurs when the electrolyser cell voltage drops below a minimum value of approximately 0.25 V (Ursúa et al. 2016) (Bard et al. 2022). This means that each time the electrolysis process is stopped, the cathode degrades slightly.

Anodic degradation mechanisms can also decrease the lifetime of a cell. There are multiple mechanisms that degrade the anode. Firstly, metal oxide corrosion can take place. This happens when metal-metal bonds are weakened by electron transfers from the metal surface to reaction intermediates (ul Haq, et al. 2023). Secondly, catalyst surface blockage can develop. This means unwanted species such as adsorbed intermediates or reaction products can accumulate on the catalyst surface. The more accumulation occurs, the less active sites are available for the reaction. This can eventually lead to complete deactivation of the catalyst (Hu et al. 2019). By using water that contains some impurities, additional product might accelerate metal oxide corrosion and catalyst surface blockage.

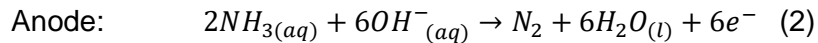
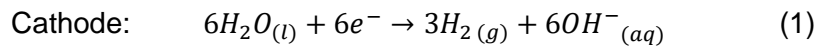
1.2 Steam condensate

If possible, recycling water or using seawater for alkaline electrolysis would be great for the environment. However, recycled water is unlikely to be used if using it causes a lower energy efficiency or increases the already high capital costs. Wastewaters have different compositions. For alkaline water electrolysis, a relatively clean water source would be ideal. In this report, a fertiliser production plant is considered. During fertiliser production, steam condensate is produced. To make this steam condensate less aggressive, approximately 1 ppm ammonia is added. Theoretically, the factory could use the condensate to produce hydrogen. Research into the effects of using such a water source on the alkaline water electrolysis process is absent in literature. If steam condensate is to be used as a water source, its effect on the process is essential knowledge. In the case of the steam condensate, the effect of ammonia must be researched. A lot of research into ammonia electro-oxidation has been done. The next chapter gives an introduction to ammonia electro-oxidation and discusses how it might impact the alkaline water electrolysis process.

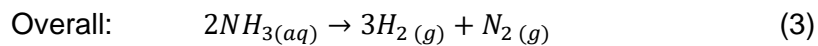
1.3 Ammonia electro-oxidation

Hydrogen has a few key problems that make it hard for our society to implement it on a large scale. The main problems are that there is very little infrastructure available for the transport and storage of hydrogen. Some propose that instead of producing hydrogen using renewable energy sources, it would be better to produce ammonia instead (MacFarlane et al. 2020). Transporting and storing ammonia is less problematic. This ammonia can then be used to produce hydrogen for industrial processes that require it. In this process, instead of an Oxygen Evolution Reaction (OER), there will be an Ammonia electro-Oxidation Reaction (AOR) (Adli et al. 2018).

One of the methods that is used to produce hydrogen from ammonia uses aqueous alkaline electrolyte. This process is in some ways very similar to alkaline water electrolysis. A big difference is that very little energy input is required because ammonia already carries so much energy. The minimum cell voltage is only 0.06 V and is thermodynamically favourable at standard conditions (Adli et al. 2018). This difference is attributed to the ammonia oxidation potential being so low and is further explained by the half reactions 1 and 2. The reactions have standard potentials of -0.83 V vs Standard Hydrogen Electrode (SHE) and -0.77 V vs SHE respectively (Vitse et al. 2005).



Combining both half-reactions gives equation 3 below:



Ideally, for every two ammonia molecules, one nitrogen gas molecule would be produced. However, additional reaction mechanisms exist. One of these mechanisms can create an adsorbed nitrogen atom N_{ads} (Adli et al. 2018). This adsorption should be minimised as much as possible since this poisons the electrode resulting in a slower reaction. The pathways of ammonia oxidation in an electrolysis cell are visualised in figure 1 below.

The horizontal reaction shows a single ammonia molecule being adsorbed and reacting with a hydroxide ion three times. This leaves a strongly chemisorbed nitrogen atom which poisons the anode. The vertical steps show the reaction that takes place when two ammonia molecules react to produce an adsorbate containing two nitrogen atoms. The vertical pathway leads to the formation of dinitrogen which can desorb as nitrogen gas. The oxidation of the intermediate products is quite easy while the production of the adsorbed nitrogen atoms is very slow (Gerischer & Mauerer 1970).

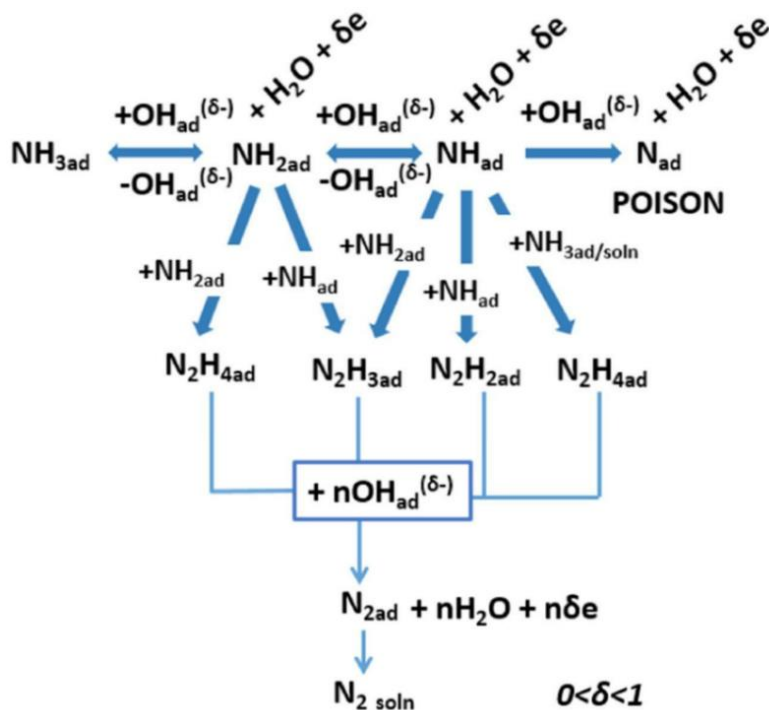


Figure 1: Anodic reaction pathways of ammonia oxidation. From: Gerischer & Mauerer (1970) and translated by Adli et al. (2018)

The catalyst that is used has a big influence on the reaction rate. For water splitting, nickel is a great catalyst. However, this does not mean that nickel also acts as a good catalyst for the oxidation of ammonia. The Sabatier principle predicts an optimum bond strength that defines the best catalytic material (Medford et al. 2015). If the bond is too strong, the oxidation reaction is limited by the desorption of the product. But if the bond is too weak, the reaction is limited by the activation of the reagent.

Because of the Sabatier principle, finding a single material that is a catalyst of multiple oxidation reactions can be difficult if the optimal bond strengths of the oxidation reactions vary greatly. While nickel is a good catalyst for alkaline water electrolysis, nickel electrodes show little activity to catalyse ammonia electro-oxidation (Kapařka et al. 2010). However, this does not make nickel useless. By treating a nickel electrode using potential cycling, a Ni/Ni(OH)₂ electrode can be produced. This electrode did show the capability to oxidise ammonia without deactivation of the electrode (Kapařka et al. 2010). Furthermore, a nanocomposite of Ni/Ni(OH)₂ is a great catalyst for alkaline water electrolysis (Lim et al. 2020). These results show that nickel could potentially be used in an electrode that can function as a catalyst for hydrogen production from both water and ammonia in one. Important to note is although Ni/Ni(OH)₂ might be a good catalyst, its stability might not be as good. For ammonia oxidation the electrolyte solution turned grey after a runtime of just 12 hours indicating significant corrosion (Kapařka et al. 2010). In any large-scale application this would not be acceptable.

It is important to realise that side reactions might occur during the ammonia oxidation process. Mainly, nitrate can be formed when oxygen is present. At voltages above 0.75 V, nitrate predominantly and other nitrogen oxides are produced as a by-product of ammonia oxidation (Shih et al. 2018). This fraction of by-product can be quite large. An experiment by Kapařka et al. (2010) shows that 11% of the ammonia can be converted to nitrate. Nitrite was measured as well but did not reach the detection limit of the measurement equipment. Having nitrate in

the electrolyte does not only lead to an additional chemical in the spent electrolyte, but also lowers the overall voltage efficiency (see Appendix 10.1) of the process due to the low minimum cell voltage of the ammonia electro-oxidation reaction. It is important to note that the electrode used might have an influence on the formation of these by-products. As discussed in the previous paragraph, Ni/Ni(OH)₂ is a lot more effective at oxidising ammonia. Other electrodes might form nitrate at different rates. The produced gas could also be altered. Instead of pure N₂, a mixture of volatile N-species (N₂, N₂O, NO) might be produced (Kapařka et al. 2010).

2. Introduction

As society is trying to drastically cut carbon emissions, hydrogen poses many obstacles but also many possibilities. While it can be difficult to produce and store green hydrogen at a low cost, the potential role that hydrogen can play in the society of the future is enormous. This report focusses on producing green hydrogen through electrolysis with an electrolyte that contains a low concentration of ammonia. Currently, a lot of hydrogen is used in chemical processes. Companies that try to move to a green source of hydrogen face a multitude of problems. It would be advantageous to produce hydrogen onsite since storage and transport of hydrogen are still quite inefficient (Lahnaoui et al. 2021). To produce hydrogen onsite, water is needed. Chemical processes often create wastewater which could potentially be reused in the electrolysis process.

The water source in this report focuses on steam condensate from fertiliser production. The main contaminant of interest in this water is ammonia. The steam condensate could either be used directly as a water source for electrolysis, or a treatment step could be implemented. If steam condensate is used without prior treatment, it is important to find out if it causes a significant increase in corrosion or a decrease in the efficiency of the electrolyser? Literature shows that depending on the contaminant, using impure water to make the electrolyte, can reduce the lifetime of an electrolysis stack and can lead to a decrease in overall efficiency (Kötz & Stucki 1987) (Abdel-Aal & Hussein 1993) (Wei et al. 2010).

Future large scale electrolysis operations are likely to use ultra-pure water obtained by using reverse osmosis. However, reverse osmosis does not guarantee the purity of water. Ions could still pass through the membrane due to membrane failure (Glater et al. 1994) or wear and tear of equipment (Hajeer 2019). If steam condensate is used for reverse osmosis, a low ammonia concentration might remain in the water that is used as electrolyte. It is important to find out if traces of ammonia breaching the membrane can cause a significant increase in corrosion or decrease in efficiency of the electrolyser.

On one hand, ammonia in the electrolyte might not play a significant role since it is expected that it will mostly be oxidised to nitrogen and hydrogen (Candido & Gomes 2011). On the other hand, before oxidation occurs, ammonia can still be very corrosive for nickel electrodes and could lead to poisoning of the catalyst surface (Kapařka et al. 2010). Ammonia also competes for catalyst surface since the nickel electrode will catalyse two oxidation reactions at the same time (Adli et al. 2018). It is important to understand the additional reactions that take place due to the presence of ammonia. Furthermore, additional reaction products might contaminate the electrolyte or the produced gasses.

Current research mainly focuses on using pure water as a base for the electrolyte. Alternatively, when ammonia is considered, anhydrous ammonia is considered since this mitigates the production of unwanted oxygenated nitrogen products and due to its non-corrosive nature (Adli et al. 2018). Other research considers treating ammonia containing wastewater. In this treatment, oxidising the ammonia is the main purpose of the electrolysis. No research was found on the effects of having a low ammonia concentration in the electrolyte for an alkaline electrolysis system that was designed for the electrolysis of water. The difference in this paper is that ammonia is seen as a contaminant even though it also produces

hydrogen. An important problem that arises from having ammonia in the electrolyte is that regular nickel electrodes are not a good catalyst to oxidise ammonia due to the layer of oxide on the catalyst that forms under alkaline conditions (Yao & Cheng 2008). This effect can be negated by using a Ni/Ni(OH)₂ electrode but there will still be significant corrosion due to the ammonia (Kapałka et al. 2010). Also, using Ni/Ni(OH)₂ electrodes could affect the efficiency of the electrolysis of the water molecules. In this report, a nickel foam electrode was used which was not treated to become a Ni/Ni(OH)₂ electrode. How much corrosion occurs might heavily depend on the ammonia concentration. The reaction rate at which the nickel corrodes the electrodes might be way lower than the reaction rate at which ammonia oxidises in which case there might not be much corrosion at all.

3. Objective

Main research question: What are the effects of having ammonia in the electrolyte for alkaline water electrolysis?

Main hypotheses:

- Ammonia competes for catalyst surface on a small scale and contributes to electrode degradation.
- Adding ammonia to the electrolyte decreases the current density and thus the total hydrogen production.
- The ammonia does not oxidise quickly because the nickel electrodes are a poor catalyst.

Sub-questions:

- Does standard electrolyte with added ammonia for hydrogen production cause a significant increase in corrosion or decrease in efficiency of the electrolyser?
- Is the hydrogen evolution rate affected by the addition of ammonia?
- What contaminants does the spent electrolyte contain and is treatment required?
- How does the addition of ammonia to the electrolyte affect the quality of the gas produced at both the anode and the cathode?

4. Methodology

To test the first hypothesis, the first question to answer was: Does standard electrolyte with added ammonia for hydrogen production cause a significant increase in corrosion or decrease in efficiency of the electrolyser? To answer this question, an experiment was carried out in which ammonia was added to standard electrolyte. Another experiment used standard electrolyte without any ammonia added. By comparing these experiments, the effect of adding ammonia was analysed. Since the electrolyte should be alkaline, 20-30 wt% of KOH is generally added to produce electrolyte (Ito et al. 2018). However, for safety reasons, a maximum KOH concentration of 1 M KOH, which corresponds to 5 wt%, was used.

The second and third hypotheses were tested by accurately measuring the concentration of ammonium in the spent electrolyte. In addition, the concentration of nitrate in the spent electrolyte was measured. Quantifying electrode degradation was not possible since its effects develops over hundreds or even thousands of hours. Running the experiments for very long periods of time was not deemed safe. After performing the experiments, the electrodes should also be compared to a control experiment which was not possible. Alternatively, electrode degradation can be detected visually but this will not give a quantitative answer. After all the experiments were performed, the cell was opened. Looking at the electrodes could then give an indication of any potential electrode degradation. Current density and production rates of experiments can be compared to get an insight into electrode degradation or blockage of the catalyst surface as well.

Table 1: Main experiment sets that were performed. Comparison between set 1 and 2 explains the effect of ammonia on electrolysis.

Experiment sets	
1	Demi water + KOH
2	Demi water + KOH + ammonia
Additional experiments	Different ammonia concentrations, different KOH concentrations

4.1 Safety

Safety measures are very important since hydrogen can be explosive. Creating a good setup with the right measurement devices is challenging. Furthermore, the fact that hydrogen molecules are so small means that every compartment of the experimental setup must be very well assembled. Ventilation must be in place to prevent unexpected build-up of hydrogen. While the experiments were carried out, the hydrogen and oxygen were separately stored in two accumulators. The concentration of the hydrogen gas in any workspace should be kept below 4% to prevent the potential for combustion or an explosion. Additionally, by keeping the amount of hydrogen produced per experiment low, any risks were minimized. Also, by performing the experiments in a fume hood, the risk of even small amounts of hydrogen building up becomes very low.

Another safety risk could be electrocution from the current that was used to drive the electrolysis reaction. This sounds like a big risk but is very unlikely to occur. This is because

the distance between the electrodes was small. Sometimes, electrocution can occur when people get into contact with water that carries current. But when the live wire and the neutral wire are close to each other, the current will stay in that circuit rather than going through someone's body towards the floor. Even when a finger would be put between the electrode plates, which would be impossible since the cell is a closed off system, the resistance would be greater through the finger than through the water. This and the fact that the current is very low made electrocution a non-existent threat. When skin would have touched the electrolyte, the high pH would have been a way greater threat to human health.

The main safety concern was the use of concentrated potassium hydroxide solution as the electrolyte. This solution has a very high pH. According to the safety data sheet, contact with skin or eyes should be avoided completely since it causes severe irritation and potentially even blindness (Potassium hydroxide solution K017). To prevent health hazards, protective equipment was worn at all times. This includes gloves, a lab coat, and safety glasses. Also, if aerosols could form, respiratory protection should also be worn.

4.2 Experimental setup

The experimental setup should meet certain requirements. Apart from the electrolysis cell itself, which is discussed in more detail later, there are many parts around the cell that have important functions. Because the gasses should be kept separate, two storage compartments for electrolyte were used. In one storage the hydrogen was separated from the electrolyte while the other storage separated the oxygen. The separate gasses were then led through a storage compartment which contained a citric acid solution. The ammonia in the electrolyte was prone to stripping due to the high pH. This citric acid solution should have dissolved any ammonia gas that escapes the electrolyte. Measuring the ammonia concentration in the acid would have quantified how much ammonia escapes the electrolyte. The remaining gas was then stored in an upside-down cylinder submerged in water. The schematic visualisation of the setup and its gas and liquid flows is visualised in figure 2. The actual setup can be found in chapter 10.3.

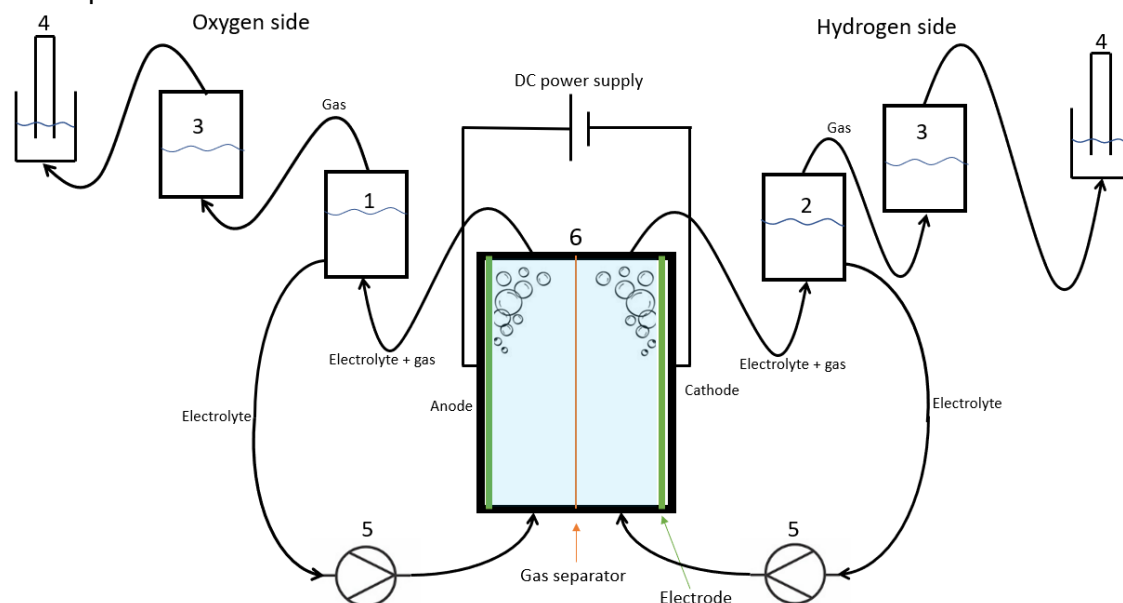


Figure 2: Experimental setup. Inspired by the setup from Bhatia (2023). Components are numbered as follows: 1) Electrolyte-oxygen separator and electrolyte storage, 2) Electrolyte-hydrogen separator and electrolyte storage, 3) Acid traps, 4) Gas collectors, 5) Circulation pumps, 6) Electrolysis cell.

4.3 Materials

In this chapter, the materials used in the experimental setup are explained in more depth. Starting with the main component, the electrolysis cell itself. The cell consisted of a number of components which are seen in figure 3. The electrodes used in the experiments was a nickel foam electrode for both the anode and the cathode. The area of each of these electrodes was 86 cm². The Membrane used was a selemon anion exchange membrane. For this experiment, the membrane did not have to be state-of-the-art or high end. Having a thinner diaphragm can decrease the ohmic resistance which in turn increases the efficiency especially at a higher current density (Brauns et al. 2021). However, the focus of this experiment was not to increase efficiency and therefore a simple reliable diaphragm sufficed.

The current collector is a metal sheet which was separated from the casing by a rubber layer. The casing has four holes on each side for the current wires to be attached to the current collector. Of course, figure 3 only shows half of the cell. In reality, the cell is mirrored at the membrane to form a full cell. Between the current collector is approximately 6 mm of distance. It is hard to say if this distance was optimal. The optimal electrode distance depends on multiple variables and is even harder to establish when porous electrodes are used (Amores et al. 2014). Most experiments use higher operating temperatures and different electrolyte concentrations which influences the optimal electrode distance. Nevertheless, since the nickel foam itself also has a thickness, the electrode distance used in the experiment will have been quite close to the optimum.

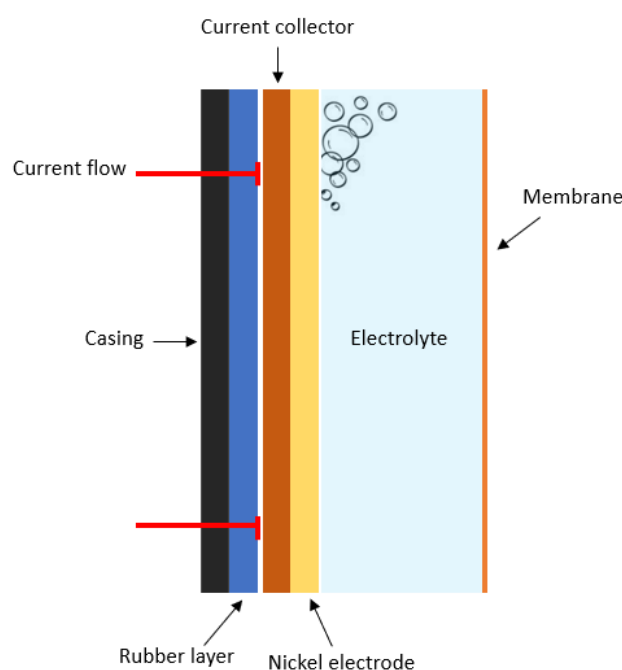


Figure 3: Schematic overview of the components in the left half of the electrolysis cell as seen from the side.

For the gas-electrolyte separators and the acid traps, glass containers were used. The components were connected using a tubing with an inner diameter of 2 mm. Where possible, Teflon tape was used to prevent gas from leaking out. The gas collectors were made using 800 mL beakers and 250 mL graduated cylinders. Each cylinder was suspended in a beaker upside-down with a tube that led to the bottom of the cylinder. The beaker was then filled with demi-water. The air in the cylinder was extracted using a syringe. When an experiment ran, the gas was captured in the cylinder. This way, it was possible to measure the volume of gas produced in a certain amount of time.

Peristaltic pumps were used to pump the electrolyte around. This is done at a rate of about 100 mL/min. This rate is more than sufficient to flush the gas bubbles out of the electrolysis cell and to keep the electrolyte well mixed. Specifics about the pumps and the DC current can be found in chapter 10.3 in the appendix.

4.4 Chemicals

For the electrolyte, pure water with potassium hydroxide (KOH) was used. In general, 20-30 wt% of KOH is added to produce electrolyte (Ito et al. 2018). This is not only to increase pH. KOH is also added to increase the conductivity. In the experiments, a concentration of up to 1 M is used. Although this electrolyte has a lower conductivity, it is safer to handle. The pH was >14 due to the added KOH. Therefore, the pH change from the addition of ammonia was negligible.

Although the purity of a chemical is usually displayed on its label, the exact composition of the impurities is not always known. Potassium hydroxide was used in great quantities in the experiments. The solution was bought from the chemical company ROTH. According to the company, the concentration was $1 \text{ M} \pm 0.2\%$. When a lower concentration was required, demi water was added. Demi water has negligible concentrations of ions. While demi water can still have some organic pollutants, these are not expected to have influenced the electrolysis process much at such low concentrations.

The ammonia used also had a concentration of 1 M. It was produced by the company Sigma-Aldrich. It had a purity of at least 99.99%. The actual ammonia concentration in the electrolyte was much lower than 1 M. This means that the impurities from the ammonia were negligible for the experiments.

4.5 Measurements

There are six parameters that were measured during and after the experiments. These parameters are listed below:

- 1) Voltage
- 2) Amperage
- 3) Ammonia and nitrate concentrations
- 4) Time
- 5) Temperature/pressure
- 6) Hydrogen production

Voltage and amperage are interconnected. Using the power supply, either of them can be stabilised. For the experiments, a constant voltage was used. The power supply therefore balanced out the amperage to keep this voltage constant. Choosing the right voltage is difficult. There is no perfect voltage for alkaline water electrolysis. If a low voltage is chosen, the setup will have a very high efficiency but a low hydrogen evolution. But if a high voltage is chosen, the efficiency might be too low, and equipment might deteriorate. For this reason, a small test was performed. A first experiment was performed using electrolyte with a moderately low concentration. At the start of the experiment, the voltage was set very low. The voltage was then slowly increased until bubbles started to appear. Significant bubbles started to form at approximately 1.8 V, but at a very slow pace. Therefore, the voltage was increased further. At 2.15 V, a steady flow of bubbles was observed and so the voltage for the experiments was chosen. All the performed experiments were potentiostatic.

Measuring ammonia was done using ion chromatography (IC). The ammonia can be measured in both the spent electrolyte and in the acid trap. IC can easily measure concentrations as low as 1 ppm ammonium. This is helpful since the concentration of the spent

electrolyte might not have been high after an experiment. Before the measurement was done, samples were diluted with acid. By bringing down the pH, the ammonia reacted with protons to make ammonium. This is the ion that was measured in the IC and relates directly to the ammonia concentration in the samples. To measure nitrate, a HACH kit was used. This kit uses the dimethylphenol method but has most of the chemicals pre-mixed in vials making it very user friendly. The measurement was done in a spectrophotometer which autonomously makes 10 measurements, rejects outliers, and gives the average result all automatically.

Time and temperature are both parameters that were easy to measure. Time is important since experiments should all have the same runtime to make them comparable. Also, the hydrogen production was measured at a set time during the experiment. The temperature and pressure were not measured constantly. The pressure was assumed to be atmospheric and was not measured at all. The temperature of the electrolyte was measured before and after the experiment. It was expected that the temperature of the electrolyte would increase slightly due to some of the energy being converted to heat. Varying temperature has an impact on the reaction rates in the electrolysis cell. The temperature of the electrolyte at the start of each experiment should therefore be similar.

Measuring hydrogen evolution can be done by measuring how much hydrogen is evolved over a certain amount of time. Oxygen production can be measured in the same way to get an even better insight in the production rates. The gas production was read on the graduated cylinder in which it was captured. The time it took to produce a certain volume of gas was used to calculate production rates.

4.6 Hydrogen production rate estimation

It is important to do a quick calculation of how much hydrogen would be produced during each experiment. In the experiment, only 40 mL of hydrogen was stored. The excess hydrogen was not captured and was released into the fume hood. The density of hydrogen at 25 °C and atmospheric pressure is 0.0813 kg/m³ (Lemmon et al. 2013). This means 40 mL contains just 3.25 mg of hydrogen. For a system that would be 100% efficient, approximately 39 kWh would be required to produce 1 kg of hydrogen. This means 3.25 mg requires 456 J to be produced.

Of course, the efficiency was a lot lower. Since the aim of this research was not to go for the highest efficiency, a quite simple setup was used that reached an overall efficiency of about 50% to 70%. This means the number of joules required was twice as high as the calculated 456 J. It is important to realise that a lot of efficiency is lost due to the overpotential. However, this can be equated out. Increasing the voltage does not directly increase hydrogen production. The reason an increased voltage leads to an increase in gas production is due to the higher current density it causes. Therefore, an equation can be used in which the only variables are current density and time. The steps taken to calculate the time it takes to produce 40 mL of hydrogen at standard conditions are formulated below:

- 1) In theory, the thermoneutral voltage to produce hydrogen through electrolysis is 1.48 V at standard conditions. At this voltage, producing 1 mol of hydrogen requires 286 kJ (Lide 1999).

- 2) 40 mL of hydrogen weighs 3.25 mg at standard conditions. This equates to 1.61 mmol which requires a power input of 456 J to be produced at thermoneutral conditions.
- 3) Joules = Power (W) * seconds (s) = Voltage (V) * Amperage (A) * seconds (s)
- 4) For example, at 1 A it would take 5 minutes and 8 seconds to produce 40 mL of hydrogen.

The only problem this leaves is that the current density had to be estimated. In the experiments, potassium hydroxide concentration and potential both had a large influence on the current density. As these variables increased, the gas production also increased. The calculated time in the example did not take the Faradays efficiency into account. Since the Faraday efficiency was quite high (about 90%), a more realistic production time was expected to be approximately 10% higher than calculated. The estimated 5-6 minutes did seem realistic compared to the experiments from Bhatia (2023) that were observed.

While gas is made, the electrolyte becomes slightly more concentrated. Using the prediction of the time it would take to produce 40 ml of gas, the water loss during the experiments can also be calculated. The 40 mL of gas equates to 3.25 mg of hydrogen. This means 29 mg of water would have been consumed. This means approximately 0.3 mL of water would be consumed during an experiment that takes 50 minutes. If the current is a lot higher than the 1 A that was predicted, more water will be consumed. However, even if the current would be an order of magnitude greater, the electrolyte would not get noticeably more concentrated.

4.7 Experimental procedure

First, the electrolyte was prepared. This was done by mixing 1 molar potassium hydroxide solution with demi water until the desired molarity was achieved. The total volume of electrolyte per experiment was 0.5 L. The conductivity, temperature, and if desired the pH of the sample were all measured. The electrolyte was then pumped into the system to get 250 mL into both storage bottles for the hydrogen side and the oxygen side. By closing the system and turning on the pumps for just a few seconds, the electrolysis cell also filled with electrolyte.

To capture any ammonia that escapes as gas due to stripping, an acid trap was used. A 250 mL trap was used on both sides of the setup. Citric acid powder was used to make a 1 M stock solution. To prepare the traps, 5 mL of 1 molar citric acid was added to 495 mL of demi water. This gave a 10 mmol/L acid trap which should had a more than high enough concentration to trap ammonia throughout the entire experiment. If desired, the pH of the trap could have been measured. After this, the trap is divided over the 250 mL glass bottles.

Adding ammonium and then starting the experiment was done in quick succession to prevent unnecessary aeration. Furthermore, air inflow into the system through the pumps was minimised. This prevented the ammonia from being stripped and escaping as gas without having the chance to oxidise in the electrolysis cell.

For the experiments 1 molar ammonium hydroxide was used. For example, if 1 mmol/L ammonia in the electrolyte was desired, 0.5 mL was pipetted into a beaker. This was then diluted by adding a few millilitres of demi water to help the pumps get it into the system.

Pumping the ammonium into the system only took a few seconds since it was such a small volume. After this, the system was closed quickly, and the current supply was turned on. At this point, the stopwatch was started.

The experiments ran for a total of 50 minutes each. While the experiment ran, the current was recorded down. This was done at a set timepoint. This point was set at 10 minutes of runtime, but if the current did seem to change over time it was noted down as well. Additionally, the gas production should be measured. This was done by setting an additional timer, waiting for 20 mL of gas to be produced, and then noting down the time it took.

After 50 minutes, the experiment finishes, and the current should be turned off. Samples of the spent electrolyte and the acid traps were taken. The remaining electrolyte and acid trap solution were disposed of. For each experiment, a duplicate experiment was performed.

4.8 Experiments

The main set of experiments that was performed used three different potassium hydroxide concentrations and three different ammonia concentrations. This means a total of 9 experiments were performed. Additionally, experiments were done in duplicates resulting in a total of 18 experiments. The electrolyte concentrations and ammonia concentrations were as follows:

KOH concentration: 0.2M, 0.6M, 1.0M.

NH₃ concentration: 0 mM, 1.0 mM, 2.0 mM.

The reason for choosing these electrolyte concentrations is that the usual higher concentrations were not deemed safe. If only a single concentration would have been tested, making a prediction for experiments done using a different electrolyte concentration would not be possible. It was important to find out how electrolyte concentration impacted the oxidation of ammonia. Especially since the electrolyte concentration is so much higher in other research or applications.

For the ammonia concentrations, an experiment with no added ammonia served as a reference for the other experiments. The 1.0 mM concentration was chosen with the steam condensate in mind. To this steam condensate, approximately 1 ppm ammonia is added to make it less corrosive. This would translate to an ammonia concentration of about 0.058 mM. The ammonia concentration in the experiments was a lot higher. A higher concentration was used because it makes the effect of ammonia easier to measure. It was deemed unlikely that the available equipment would be able to measure the effects of 1 ppm ammonia in the electrolyte. By spiking the electrolyte with 1.0 mM ammonia, it was expected that the effect of the ammonia would create significantly different enough outcomes compared to the experiments with no ammonia. Using a higher ammonia concentration also led to smaller relative errors. The last experiments used 2.0 mM ammonia. Another option would have been 0.5 mM ammonia. However, this seemed like a concentration that would have been slightly too low. Carrying out the experiment for three different ammonia concentrations gave a better insight into the effect of ammonia on the hydrogen production process than if only two concentrations were tested.

5. Results and discussion

5.1 Effect of KOH concentration

The concentrations of potassium hydroxide used for the electrolyte in the experiments was 0.2 M, 0.6 M, and 1.0 M. These values were lower than what is commonly used in alkaline water electrolysis experiments. The average values of the conductivity were plotted in figure 4. The plot also includes the conductivity values obtained from the experiments that added ammonia to the electrolyte. Although the conductivity seemed to increase linearly with concentration, this is not the case. At the concentration range used in the experiments, a seemingly linear relationship between conductivity and concentration can be found. But if a larger range is used, the conductivity does not increase linearly (Gilliam et al. 2007). For conductivity of a KOH electrolyte, it is best to compare results to data from empirical results. Unexpectedly, comparing the data from the experiments to empirical data from Gilliam et al. (2007), showed that the electrolyte used in the experiments had a higher conductivity. To compare conductivity to empirical results, the temperature must be taken into account. Temperature greatly influences the conductivity. The electrolyte used in the experiments had a temperature of about 15 °C giving a conductivity of 48 mS/cm and 214 mS/cm at concentrations of 0.2 M and 1.0 M respectively. Empirical data shows that the expected conductivity would be about 42 mS/cm and 188 mS/cm for a concentration of 0.2 M and 1.0 M respectively. Additionally, the conductivity was simulated using the computer program PHREEQC Interactive version 3.7.3. Adding 0.2 M potassium hydroxide to pure water at 15 °C resulted in a conductivity of 40 mS/cm. Adding 1.0 M potassium hydroxide resulted in a conductivity of 173 mS/cm. This means the empirical data and the results from PHREEQC are quite well aligned. However, the solution used for the experiments had a noticeably higher conductivity. This discrepancy was probably caused by either the conductivity meter not being calibrated, or by the KOH solution being contaminated with additional ions. However, since all values were slightly higher, it is not expected to have influenced the results of the experiments negatively.

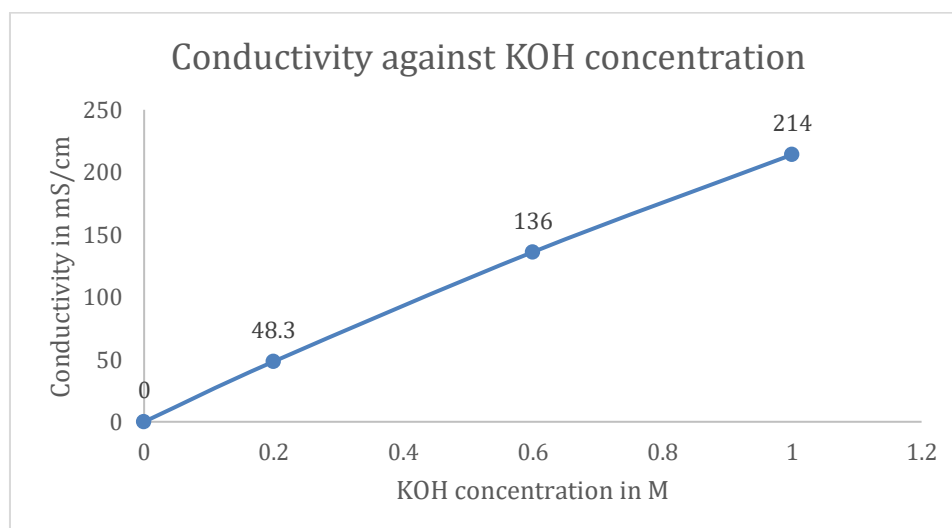


Figure 4: Average conductivity of the electrolyte used for the experiments. Measurements were taken before pumping the electrolyte into the cell.

Important to note about figure 4 is that these measurements were taken before the electrolyte was pumped into the cell. The conductivity was also measured after each experiment. These

values were 3-7% lower even though the temperature of the electrolyte had increased slightly. The reason for this drop in conductivity was that between experiments, demi water was pumped into the system. This was done to clean and remove the previous electrolyte. When drained, some water will have remained inside the cell. This slightly diluted the electrolyte of the next experiment. Figure 22 in the appendix shows the conductivity of the electrolyte after the experiment against the KOH concentration.

Figure 4 shows that a higher KOH concentration led to a higher conductivity. In theory, a higher conductivity also leads to a higher current density. This was confirmed by plotting the current density of the experiments with varying KOH concentrations. Figure 5 shows how the current density increased when a higher KOH concentration was used. The values used are the average of the experiments and therefore includes results obtained with added ammonia as well as results without added ammonia.

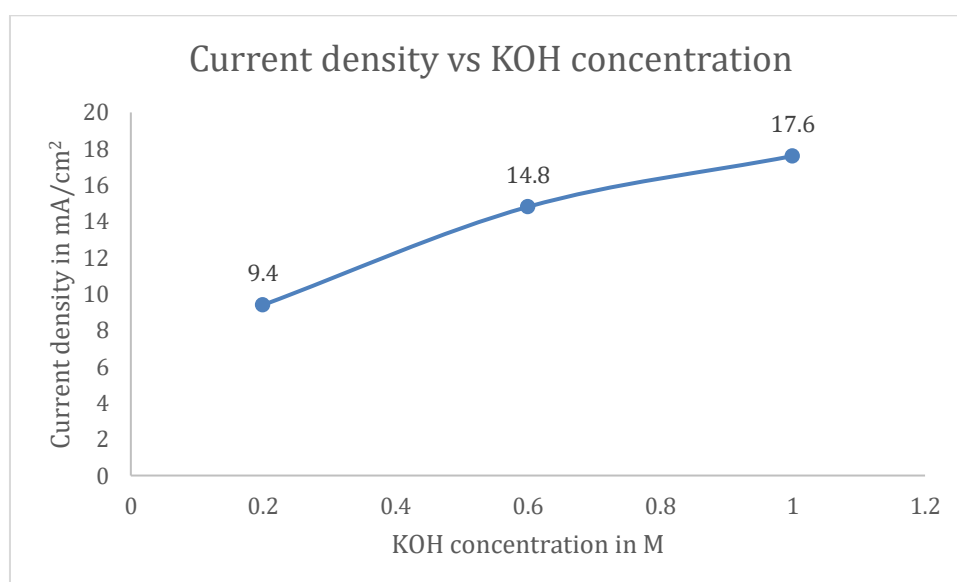


Figure 5: Current density vs KOH concentration. Each point is an average of six experiments with varying amounts of added ammonia.

As mentioned before, conductivity did not increase linearly compared to KOH concentration even though it did approach linearity for the concentrations used in the experiments. Similarly, current density did not increase linearly compared to conductivity. Figure 5 shows both relations because the current density was linked directly to the KOH concentration leaving the conductivity out.

The error margin of the current density observation was quite big. This was partially caused by the electrolysis cell producing gas bubbles which reduced the conductivity. The volume of bubbles in the cell constantly changed with time while experiments ran. This meant that the current also constantly changed to keep the voltage stable. The current supply therefore displayed a current that fluctuated constantly. After observing it for a while, a decent average was estimated. The fluctuation was ± 0.02 A. This resulted in an error margin for the current density calculation of up to $\pm 3\%$. This error margin was decreased by the fact that figure 4 and figure 5 used the average of six experiments for each datapoint.

The current density also related to hydrogen gas production. If there is no drop in efficiency, the hydrogen gas production should double if the current density doubles. This is because

current and hydrogen evolution both have a relation to the energy that is put into the cell. Current relates directly to power when multiplied by the voltage. Hydrogen gas production also directly relates to power since it requires a set number of Joules over a certain amount of time. Plotting the average hydrogen gas production against the potassium hydroxide concentration, as shown in figure 23 in the appendix, gave a plot similar to that in figure 5. However, the error margin was slightly bigger since the gas production was measured in a less accurate way.

5.2 Effect of ammonia on production rates

Ammonia was dosed in three concentrations to test its effect on alkaline water electrolysis. Figure 6 shows the result in a column chart. The experiments were performed using three different KOH concentrations. The current density is expressed in mA/cm² instead of the ten times smaller A/m². Figure 6 shows that the current density decreased slightly when 1 mmol/L ammonia was dosed compared to dosing no ammonia. Adding 2 mmol/L led to an even bigger decline except for the experiment with a KOH concentration of 0.2 M.

At a concentration of 1 M KOH, the decrease in current density was the largest. Between 0 mmol/L and 2 mmol/L ammonia, the current density decreased by almost 19%. This is a very large difference that was also found when comparing the hydrogen production, which showed a decrease of 17%.

At a concentration of 0.6 M KOH, adding 2 mmol/L ammonia only led to a decrease in current density of 7% compared to not adding any ammonia. At a concentration of 0.2 M KOH, adding 1 mmol/L ammonia gave the lowest current density which seems to contradict the other results. This contradiction might be explained by the uncertainty of the measurements which is discussed below.

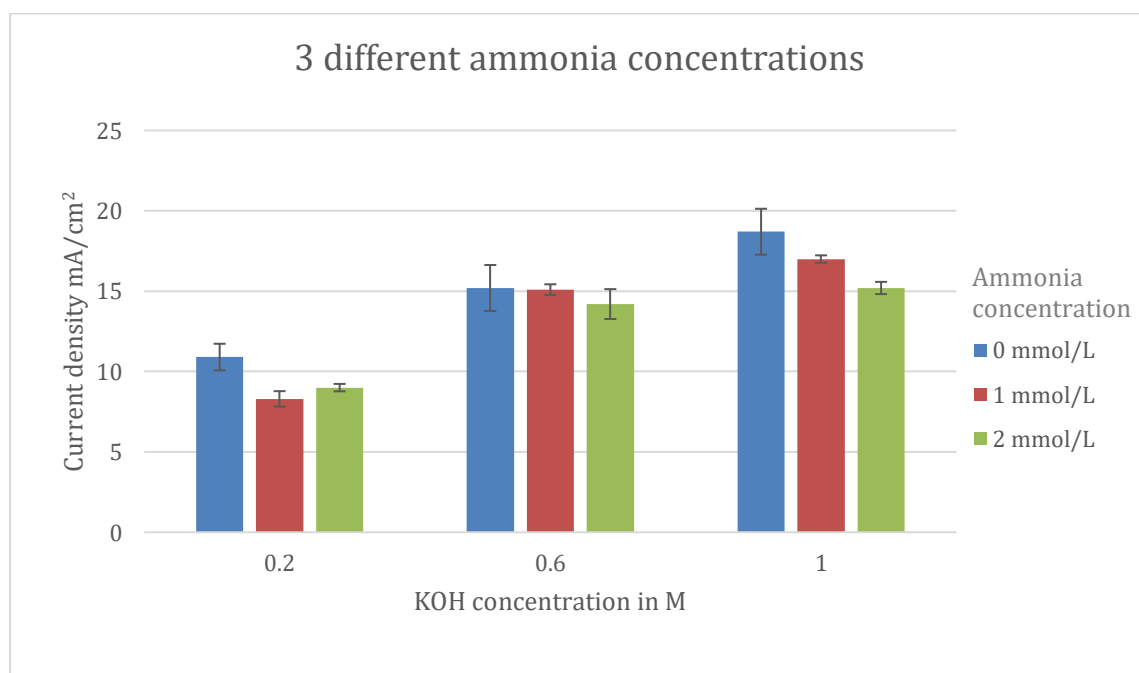


Figure 6: Current density vs KOH concentration for three different ammonia concentrations. Each bar is the average of two experiments. Error bars gives the difference between the two experiments the plus observation error.

The bars in figure 6 show errors that are quite significant. The error bars consist of the deviation from the average of the two experiments to which a small observation error from the current measurement is added. Some experiments showed a significant variance compared to their counterparts. It is not completely clear what caused this variance. To decrease the uncertainty, experiments should have been repeated more than twice. Nevertheless, the experiments with smaller error bars also showed a downward trend in the current density when ammonia is added. Whether the relationship between added ammonia and current decrease was linear or nonlinear cannot be determined with uncertainties this large.

A decrease in current density meant a decrease in gas production. Even though ammonia was oxidised, its oxidation still requires two electrons per hydrogen molecule to be produced. This is the same number of electrons that is required for the splitting of water. This means that the addition of ammonia should be avoided in any large-scale setup. The reason for the decrease in current density could have been due to gas bubble behaviour or a decrease in catalytic performance. Gas bubbles might have behaved differently due to the presence of nitrogen. This different gas composition might have adhered to the electrode for a longer time. This would have increased the gas volume in the cell which increased its resistivity. A decrease in catalytic surface could have been due to competition for its surface. Nickel is not a good catalyst for the oxidation of ammonia. Therefore, any surface of the nickel electrode that oxidised ammonia was doing this inefficiently. Meanwhile the OER competed for the same surface. The more ammonia was being oxidised; the less surface would have been available for the OER. This would have led to a lower current density and thus a lower hydrogen production rate. The decrease in current density could be undone by increasing the voltage. However, this would decrease the overall voltage efficiency of the process.

An argument might be made that gas bubbles and catalytic performance might not have played a role in the decrease of the current density at all. Instead, the order in which experiments were performed might have played a role. As experiments were carried out, the electrodes slowly degraded. Experiments were performed in the order of 0 mmol/L, 1.0 mmol/L, and then 2.0 mmol/L added ammonia. This means that the electrodes had degraded the most when the experiments with higher ammonia concentration were done. However, this would have been visible in the measurements. A comparison between KOH concentrations cannot be made. But for each experiment, a duplicate experiment was performed. This duplicate was not always performed instantly. Sometimes, experiments with a different KOH concentration were performed before the duplicate experiment of another experiment was performed. If degradation of the electrode plays a big role, duplicate experiments should have had a lower current density on average. This was not the case. On average, the current density of the experiments was in fact slightly lower than the current density of the duplicate experiments. Although this difference was so small that measurement errors would have played a bigger role. While degradation of the electrodes does occur, its effect was not measurable in the experiments.

Theoretically, electrode degradation due to ammonia can occur. If a nitrogen gas molecule is not formed, an individual nitrogen atom can be chemisorbed to the electrode surface. This acts as a poison for the electrode and leads to a lower current density. It was not sure if this effect would be measured in these experiments. Since the current density was stable between experiments and its duplicates, chemisorption did not have a measurable effect. However, the experiments were quite short. The total time of all the experiments that use ammonia in the

electrolyte was about 10 hours combined. To get a proper insight in the degradation, it might have been necessary to carry out experiments with a runtime of 100 hours or longer.

5.3 Effect of ammonia on efficiency

In the background information, three definitions of efficiency were defined. The most relevant definition for this chapter is the Faraday efficiency. The Faraday efficiency accounts for diffusion losses, current losses, and losses due to side-reactions. The voltage efficiency was constant during the experiments because the experiments were all performed at the same constant voltage of 2.15 V. Additionally, it was assumed that the thermoneutral voltage stayed constant at 1.48 V. While the voltage efficiency was constant, the Faraday efficiency could have changed between experiments.

The results showed no effect on hydrogen evolution efficiency due to addition of ammonia in the electrolyte. Each experiment showed a Faraday efficiency of about 90%. The error of this efficiency calculation was quite large because it depends on the production measurement. Hydrogen production was measured by observing a graduated cylinder which made it less reliable than if measurements were obtained using equipment designed to measure gas volumes. Figure 7 shows the efficiency of the experiments against KOH concentration in a column chart.

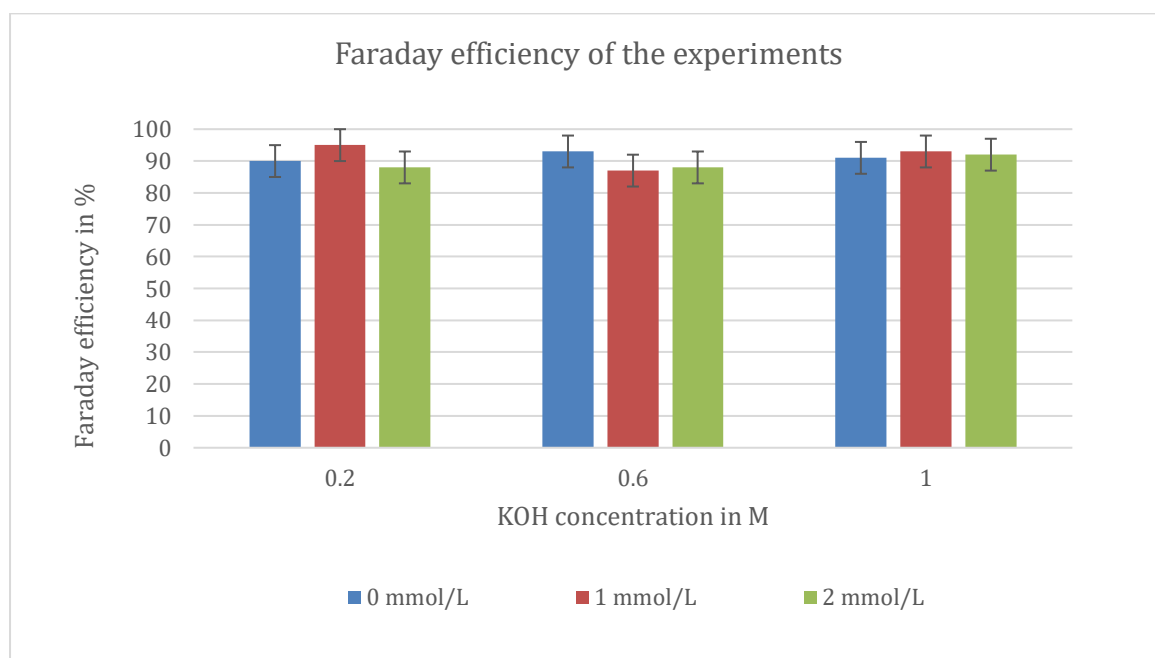


Figure 7: Faraday efficiency of the experiments. Error of 5% in each direction.

Between ammonia concentrations, there was no dependency visible. The KOH concentration also seems to have had no effect on the Faraday efficiency. The error bars are 5% in both directions. Even if a dependency was found, an error this large would have made it difficult to defend it. The error of 5% is so large because it includes the error from the observation of the current, and the error from the hydrogen production measurement. The latter was a visual observation dependent on time. It was estimated that the observation could be off by about six seconds. Each bar is the average of two experiments. The individual Faraday efficiency values of each experiment all fell within the error bars. Even though the error was large, the results did give insight in the effect of ammonia. If its effect were to decrease the Faraday efficiency by a lot, this would have been visible in the results. In these results, neither adding

ammonia, nor increasing the electrolyte concentration showed any effect on the Faraday efficiency.

However, the fact that adding ammonia did not show any effect on the efficiency in the results of the experiments does not mean there was no effect at all. Some additional side-reactions could have started to occur when ammonia was added to the electrolyte. This is even more likely given that nitrate was present in the spent electrolyte. Oxidising ammonia to nitrate involves many possible reaction pathways and is not well understood (Wu et al. 2021). Some steps might be reversible which can lead to a reaction loop. For example, nitrite could be oxidised to nitrate at the anode and then be reduced again at the cathode. This would have led to a small decrease in efficiency but would be difficult to measure.

5.4 Ammonia in acid traps

Originally, acid traps were implemented into the experimental setup to catch the ammonia gas that escaped the electrolyte. The ammonium concentration of the acid solution was then measured using ion chromatography. The results were disappointing. The solution in the traps was tested. However, no ammonium was found in the trap. This led to the conclusion that either, the ammonia was not escaping as gas, the ammonia was oxidised before it could escape, or the escaped ammonia gas was not dissolving into the acid solution. The ammonia in the spent electrolyte was also measured. After the experiment, there was still some ammonia present in the electrolyte. This means the option of ammonia being oxidised before it escaped as gas could be ruled out.

An additional test was performed to find out why there was no ammonium in the acid traps. In this test, electrolyte was aerated while the current supply was off. Aeration was done in the same way the produced gasses would aerate the electrolyte but at a higher rate of about 80 mL/min. This was done for 15 minutes. The ammonia concentration in the electrolyte after aeration was found to be lower than at the start of the experiment. This means ammonia gas did escape the electrolyte but was not being captured by the acid traps.

The electrolyte that was aerated for 15 minutes showed a decrease in ammonia concentration of 50%. Initially the concentration was 2 mmol/L, a similar concentration compared to the other experiments that were performed. Bubbles are led into the bottom of the acid trap where they rise about 10 cm to the surface. The bubbles in the test were mostly ambient air combined with a very small volume of ammonia. The dissolution of ammonia into water or a slightly acidic medium is proven by many examples even in high school experiments. From the aeration test, it appears that the short interaction time in the acid trap and the ammonia gas only making up about 3% of the total volume of produced gas caused the dissolution of ammonia into the acid solution to be negligible.

A final experiment was performed to prove the presence of ammonia in the produced gasses. Gas samples were taken during the experiments. The gas was stored in 30 mL syringes. By adding 5 mL of 0.1 M HCl to the gas and then shaking it, it was hypothesized that most of the ammonia would eventually diffuse into the acid solution. The syringes from the 0.2 M KOH and 2 mmol/L ammonia experiment were used for this experiment because it used the highest ammonia concentration and lowest electrolyte purity. This would have led to the highest ammonia gas concentration in the produced gas. After adding the acid to the syringe, it was

shaken every few minutes for about an hour. The acid was then taken out and added to the next syringe and the shaking process was repeated. This process was repeated once more for the last syringe. A prediction of the expected ammonia concentration in the acid that was used was made. The highest possible concentration was estimated to be 2 ppm ammonia if the acid had captured all of the ammonia gas in the syringes. The sample was measured using the ion chromatograph. There was a minimal concentration of about ammonia present in the sample. However, it fell well below the minimum value that the IC was calibrated for.

5.5 Ammonia in spent electrolyte

The ammonia that did not get oxidised or escape as a gas remained in the electrolyte. This ammonia concentration was measured. The first set of experiments with ammonia that was performed had 1.0 mmol ammonia per litre. The results showed an unexpected outcome. Figure 8 shows the experiments and its duplicates separately. The first experiments were done in the order 0.2 M, 0.6 M and then 1.0 M KOH concentration. After this, the duplicate experiments were performed in the same order.

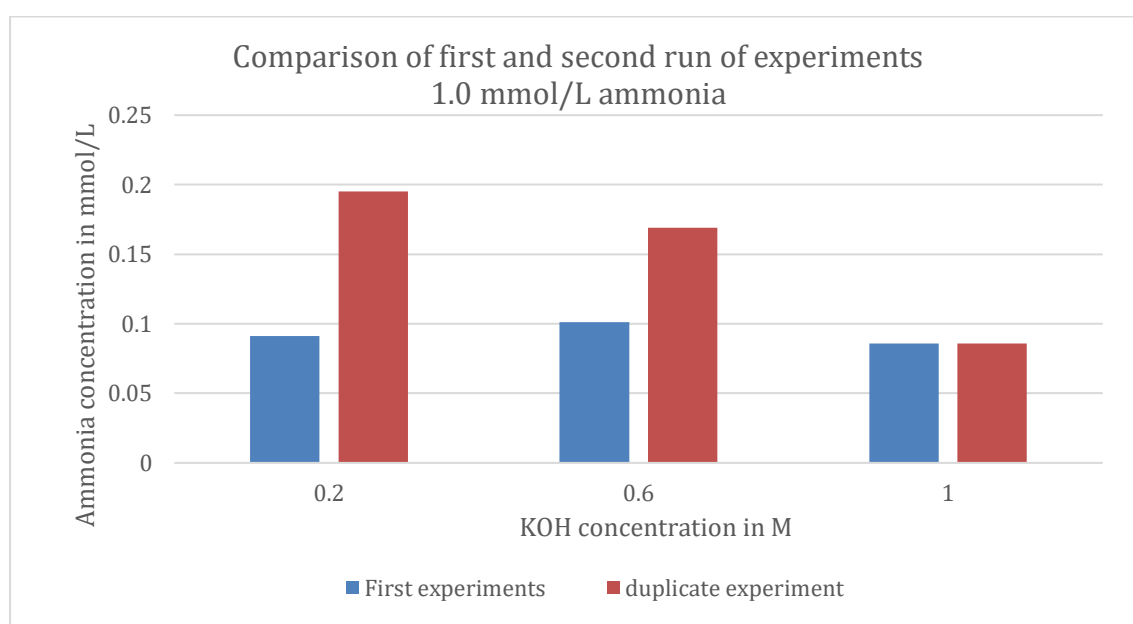


Figure 8: Ammonia concentration of the spent electrolyte for the first set of experiments and the duplicates done with 1.0 mmol/L ammonia as initial concentration.

An interesting trend was observed. While the first set of experiments all gave a similar ammonia measurement, the duplicate set showed a downward trend. There are two things that could have caused this trend. Since each of these bars represents just a single experiment, the error margin could have caused it. However, the difference between the first experiment and its duplicate of the 0.2 M, and 0.6 M KOH concentration were quite substantial. The IC is a very accurate measurement instrument. Also, the sample was diluted and gave a very well-shaped curve where ammonia is expected. Some of the ammonia measurements are shown in appendix chapter 10.3. A bigger error could have been caused by the pipetting of the ammonia, or the pipetting of the electrolyte sample. However, this error would have been just a few percent and could therefore not explain the results in figure 8. A different explanation is that some of the surface of the electrode was more prone to nitrogen chemisorption. In the first two experiments done, these surfaces could still actively oxidise ammonia which led to a lower ammonia concentration in the electrolyte.

The results from the experiments performed with 2.0 mmol/L ammonia added gave a similar result to the results in figure 10. However, the difference between each experiment and its duplicate was much smaller. It also must be noted that the experiments were performed in a different order. First, the 0.2 M and 0.6 M KOH experiments were performed. Then, the duplicates of these experiments were performed in the same order. After this, the 1 M KOH experiment and its duplicate were carried out. The order was altered because of a temporary shortage of KOH solution. The results are shown in figure 9 below.

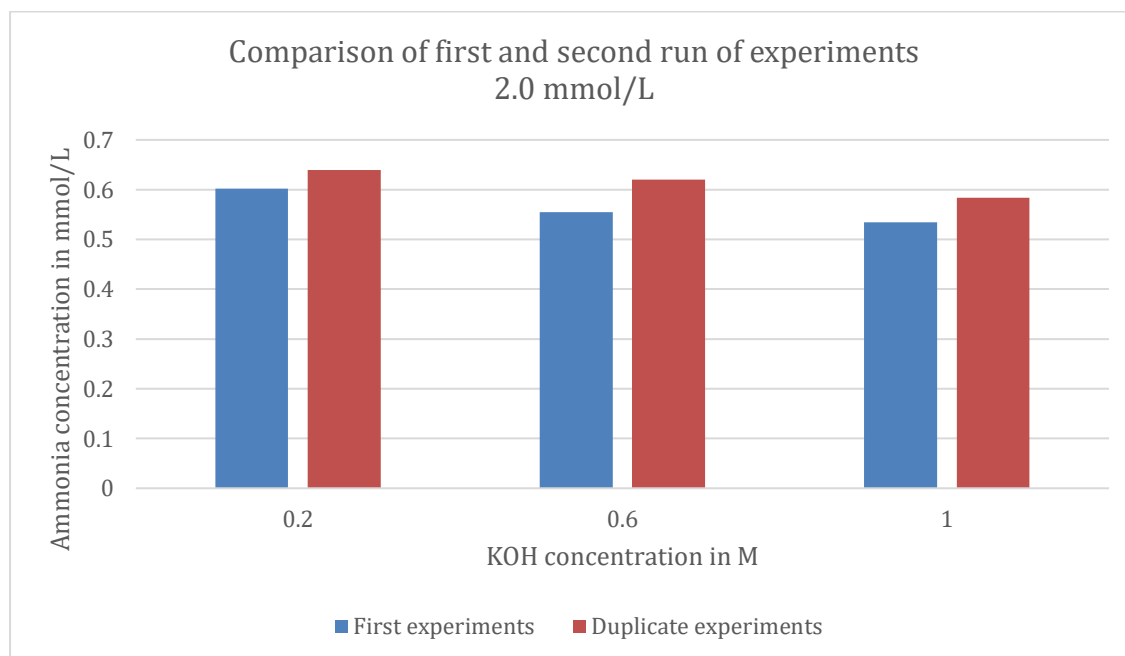


Figure 9: Ammonia concentration of the spent electrolyte for the first set of experiments and the duplicates with an initial ammonia concentration of 2.0 mmol/L.

The ammonia concentration in the spent electrolyte increased between the first and duplicate experiments. This could have been caused by the electrode surface being blocked off by nitrogen over time. Another result that was observed is that the ammonia concentration in the spent electrolyte was higher when the KOH concentration of the electrolyte is lower. This could have been caused by two things. The higher KOH concentration caused a higher current density. This would have led to a higher oxidation rate. Another reason could have been that the higher current density also increased the gas production. More gas was thus pumped into the electrolyte which could have caused more aeration. Therefore, more ammonia gas would have escaped the solution.

There was a large difference in ammonia concentration between the experiments done with 1.0 mmol/L ammonia and 2.0 mmol/L ammonia. When twice as much ammonia was added to the electrolyte, the spent electrolyte had more than twice as much ammonia after the same amount of time. Aeration would have been more efficient the higher the ammonia concentration. However, the oxidation might not have been much more efficient with increasing ammonia concentration. The catalytic surface is likely to have been the limiting factor. This explains why the ammonia reduction of the experiments with 1.0 mmol/L ammonia ranged from 81-92%, while the ammonia reduction of the experiments with 2.0 mmol/L ammonia ranged from 68-74%. This further showed that the nickel foam electrode did not act as a good catalyst for the ammonia oxidation reaction.

5.6 Production of nitrate

The nitrate concentration of the electrolyte samples was measured. This was done using a HACH kit for nitrate. The formation of nitrate occurs in the presence of oxygen. Since this experiment had both water electrolysis and ammonia oxidation occurring at the same time, it is likely that nitrate was formed. The results are shown in figure 10 below. The blue bars are the average of each of the 1.0 mmol/L ammonia experiments and its duplicate. The red bars represent the 2.0 mmol/L ammonia experiments.

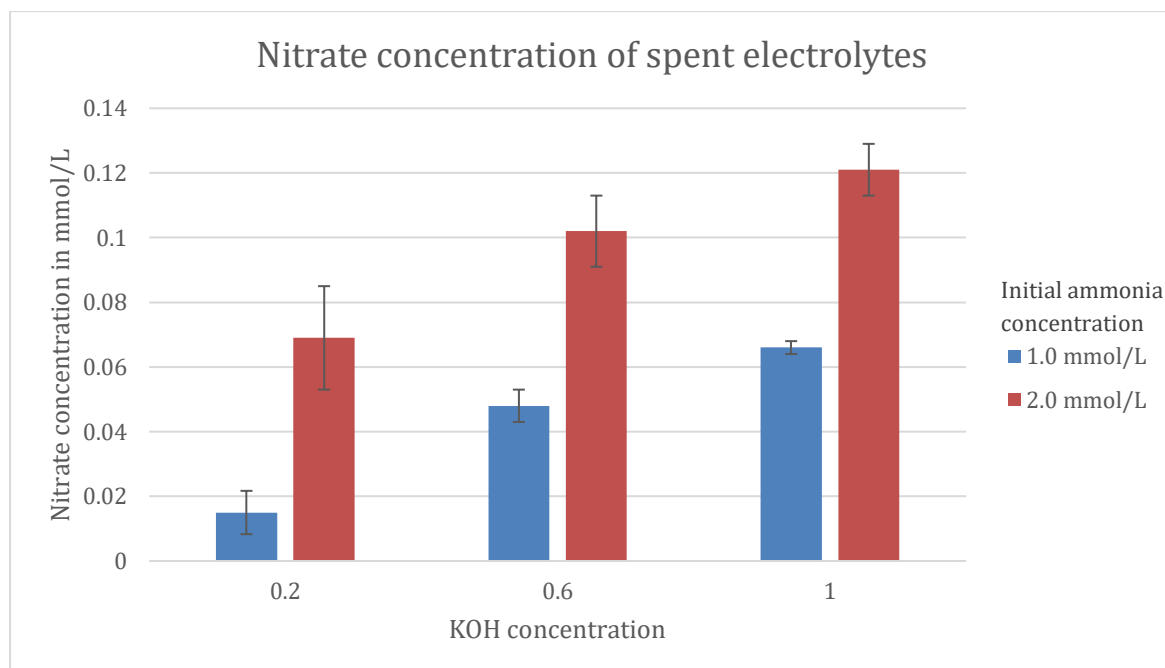


Figure 10: Nitrate concentration in the spent electrolyte of the experiments. Each bar is the average of two experiments. Error bars represent the deviation of the two experiments from the average plus the observational error.

Both ammonia concentrations showed a clear upward trend with increasing KOH concentration. The higher initial ammonia concentration also resulted in a higher nitrate concentration in the spent electrolyte. While the nitrate concentration indicates faster ammonia oxidation when current density was higher, figures 10 and 11 from the previous chapter contradict this. The ammonia concentration in the spent electrolyte was similar for each KOH concentration. However, it might have been the case that the higher current density led to more oxygen being available since the OER had a higher reaction rate. This means there was more oxygen available for the nitrate to form.

The first experiment gave somewhat of an outlier for the nitrate measurements. The first 0.2 M KOH experiment found a nitrate concentration of about 0.01 mmol/L. Its duplicate experiment had a nitrate concentration of about 0.02 mmol/L. This also caused the big error bar for the first bar. The large difference between these measurements is hard to explain.

The uncertainty of the nitrate measurements was quite large. The error bars include the deviation of the two experiments from the average, and the uncertainty of the nitrate measurement. To decrease the uncertainty, the experiments should have been repeated more than once. Each bar in figure 12 represents just two measurements. The HACH kit used also caused the uncertainty to be large. The kit can be used to make measurements for

concentrations of at least 1 mg/L NO_3^- - N. Some nitrate concentrations were below this minimum. A test was done which showed that concentrations of 0.4 mg/L NO_3^- - N could still be reliably measured. Measuring lower concentrations does mean that the error of the measurements can be relatively larger than normal. The first experiment and its duplicate were measured but fell below the limit that would give a reliable result. This could have been the reason that it fell out lower than what would be expected when looking at the other measurements. Additionally, the high KOH concentration could have also influenced the nitrate measurements.

To compare the results between the experiments with different starting ammonia concentrations, an additional chart was made. Figure 11 shows the percentage of the ammonia that was converted to nitrate. Comparing the percentage of ammonia converted to nitrate gave a better insight in the effect of differing initial ammonia concentrations.

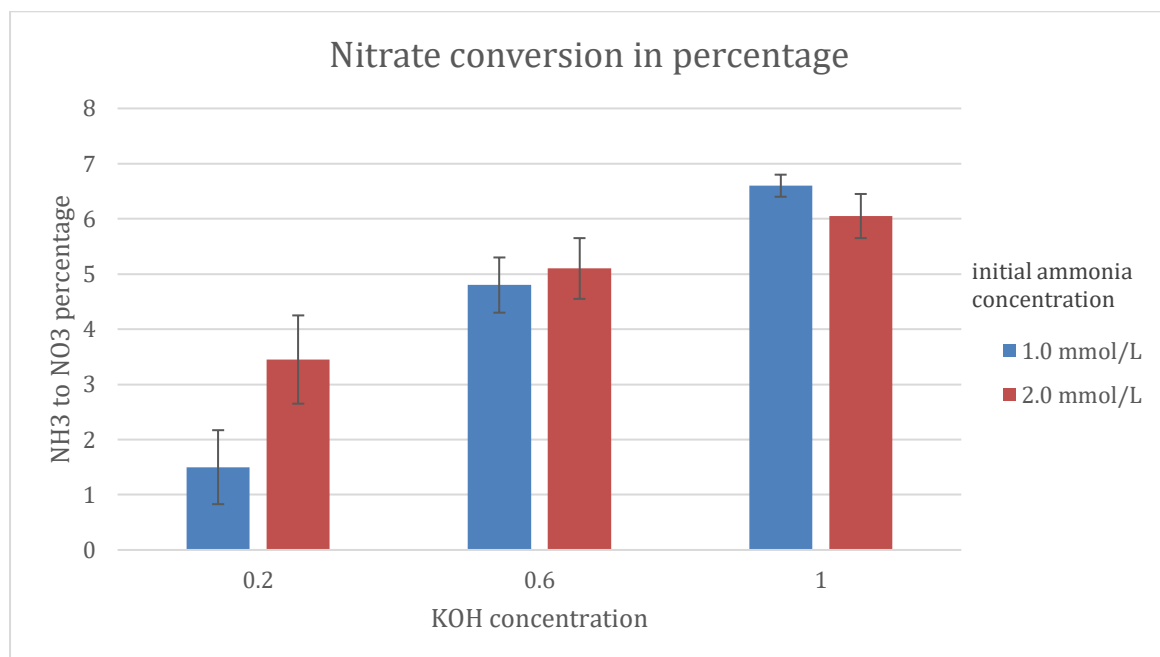


Figure 11: Percentage of ammonia converted to nitrate against KOH concentration. Each bar represents outcomes from two experiments. The conversion is based on the initial ammonia concentration.

Figure 11 shows that the percentage of ammonia converted to nitrate was somewhat equal for differing initial ammonia concentrations. This was different for the results of the 0.2 M KOH experiments with 1.0 mmol/L ammonia. While it seemed plausible that these measurements could have been lower because it included the first experiment with added ammonia that was performed. The large error might simply indicate that it was an outlier.

The results show that approximately 3-6% of the ammonia in the experiments was converted to nitrate. Results from Kapalka et al. (2010), show that approximately 11% of the initial ammonia concentration should be converted to nitrate if there is no aeration. If the assumption is made that this percentage also applied to the experiments done in this report, then the concentration loss due to ammonia stripping can be estimated. The nitrate concentrations of the 1.0 mmol/L and 2.0 mmol/L experiments were almost equal for the 0.6 M and 1.0 M KOH. However, the ammonia left in the electrolyte of the 2.0 mmol/L initial ammonia concentration experiments was a lot higher than the 1.0 mmol/L ammonia experiment. Nevertheless, the

percentage of ammonia stripped from the electrolyte was lower in the 0.6 M experiments. Table 3 below shows the percentage of ammonia that was stripped from the electrolyte due to aeration. The 0.2 M KOH experiments were excluded due to the large errors in the ammonia concentration of the spent electrolyte.

Table 3: Average percentage of ammonia stripped from the electrolyte for four of the experiments. This uses the assumption that 11% of ammonia that is oxidised forms nitrate.

	1.0 mmol/L NH ₃	2.0 mmol/L NH ₃
0.6 M KOH	35%	19%
1.0 M KOH	30%	12%

Table 3 shows that a higher KOH concentration in the electrolyte resulted in less ammonia escaping the electrolyte as gas. This is likely because the aeration and oxidation happened at the same time. A higher KOH concentration led to a higher current density. This resulted in ammonia being oxidised faster. Over time this lowered the ammonia concentration in the electrolyte. A lower ammonia concentration made aeration less efficient which explains the lower percentage.

The difference in ammonia stripping between the 1.0 mmol/L and 2.0 mmol/L ammonia concentration experiments was larger than the difference between the 0.6 M KOH and 1.0 M KOH experiments. Important to keep in mind is that percentages are used. The absolute concentration of ammonia that was stripped was closer between the two different starting concentrations. The experiment with 1.0 M KOH showed less aeration had occurred in the 2.0 mmol/L even when the percentage was accounted for. This is quite a contradicting result. Therefore, it is more likely that the 11% conversion rate used to calculate the percentages in table 3 was not correct in this case. The conversion rate of ammonia to nitrate might have depended on the ratio between oxygen and nitrogen that was available at the catalytic surface. The 1.0 mmol/L ammonia experiments had more oxygen available compared to the 2.0 mmol/L ammonia experiments. This could have resulted in different conversion rates for these experiments. Measuring ammonia gas directly would have benefitted the results. To find out how much ammonia was stripped from the electrolyte, accurate gas measurements should have been made. This is the only way to get an accurate measurement since the acid traps showed very poor results.

5.7 Factorial design

A regression analysis was performed to confirm if variables indeed showed the relations that were observed. This was done by making a Design Of Experiments (DOE) in the computer program miniTAB. The variables that were put in are the KOH concentration, and the ammonia starting concentration. The results of the design uses a certainty cut-off line of 95%. In the results, an increase in the current density was clearly observed for a higher KOH concentration. The results also showed that ammonia was likely to have a negative impact on the current density.

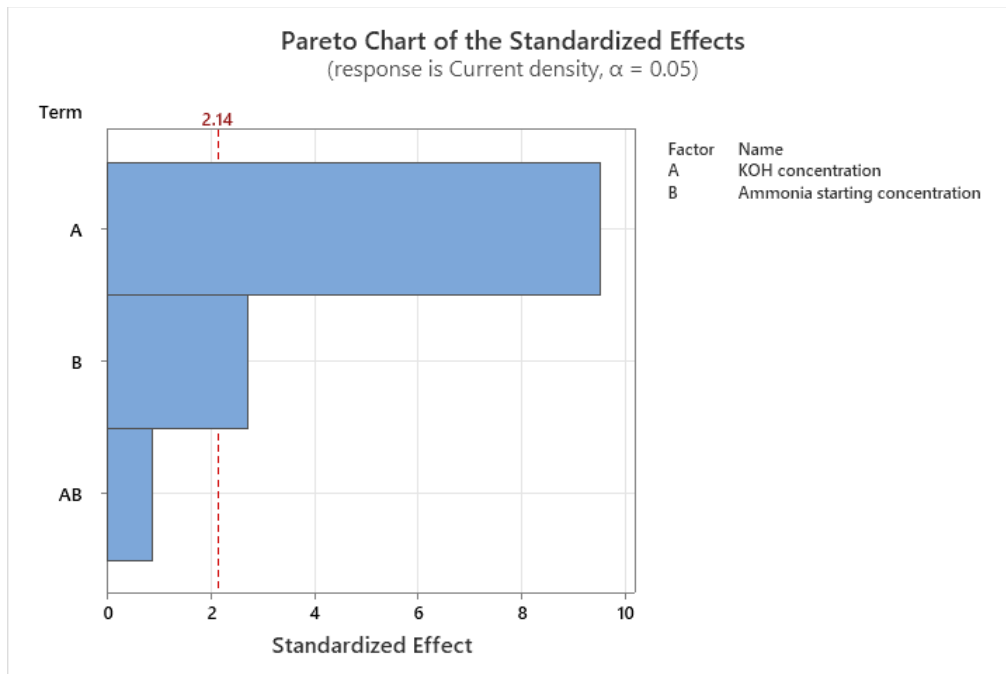


Figure 12: Pareto chart of the standardised effects on current density

The Pareto chart in figure 12 shows that KOH had a clear effect on the current density. Adding ammonia also influenced the current density. The hydrogen production is related to the current density. However, the hydrogen production had a greater uncertainty. A Pareto chart for the effects on hydrogen production was also made. In this chart, the ammonia concentration fell short of the cut-off line. This means it could not be stated with 95% certainty that adding ammonia had an effect on hydrogen production. Nevertheless, since adding ammonia did show a negative effect on current density it is evident that there was also a negative effect on hydrogen production.

The analysis also showed that the Faraday efficiency did not correlate with either KOH concentration or Ammonia starting concentration. These factors fell well below the correlation line. As mentioned in chapter 4.3, this does not mean there was no correlation at all. To find out if ammonia influences the Faraday efficiency, more precise measurements should be made.

To analyse the correlation between the ammonia in the spent electrolyte and the initial parameters and the correlation between nitrate in the spent electrolyte and the initial parameters, a slight alteration was made. The experiments with no added ammonia were

excluded. Of course, these experiments had no ammonia or nitrate in the spent electrolyte. If included, the correlation would have been skewed.

The correlation between nitrate and KOH concentration and ammonia concentrations were as expected. Both parameters gave a strong correlation with nitrate. The results in chapter 5.6 showed that adding more ammonia to the electrolyte resulted in an increase in the nitrate concentration of the spent electrolyte. The factorial design strongly supports this observation.

The Pareto chart of the standardised effects on ammonia concentration in the spent electrolyte is shown in figure 13 below. It shows that the ammonia starting concentration had a large correlation with the ammonia in the spent electrolyte. This was also observed in chapter 5.5. This chapter showed that the difference between dosed ammonia led to a relatively greater difference in the measurements of the spent electrolyte. However, it was also assumed that the KOH concentration had influenced the ammonia measurement. In chapter 4.5, the results showed that an increase in KOH concentration led to a slight decline of the ammonia concentration in the spent electrolyte. However, figure 13 shows that this correlation was not found with 95% confidence. Even though this does not mean that the KOH concentration had no influence on the ammonia concentration in the spent electrolyte, it does indicate that aeration might have had a much larger impact.

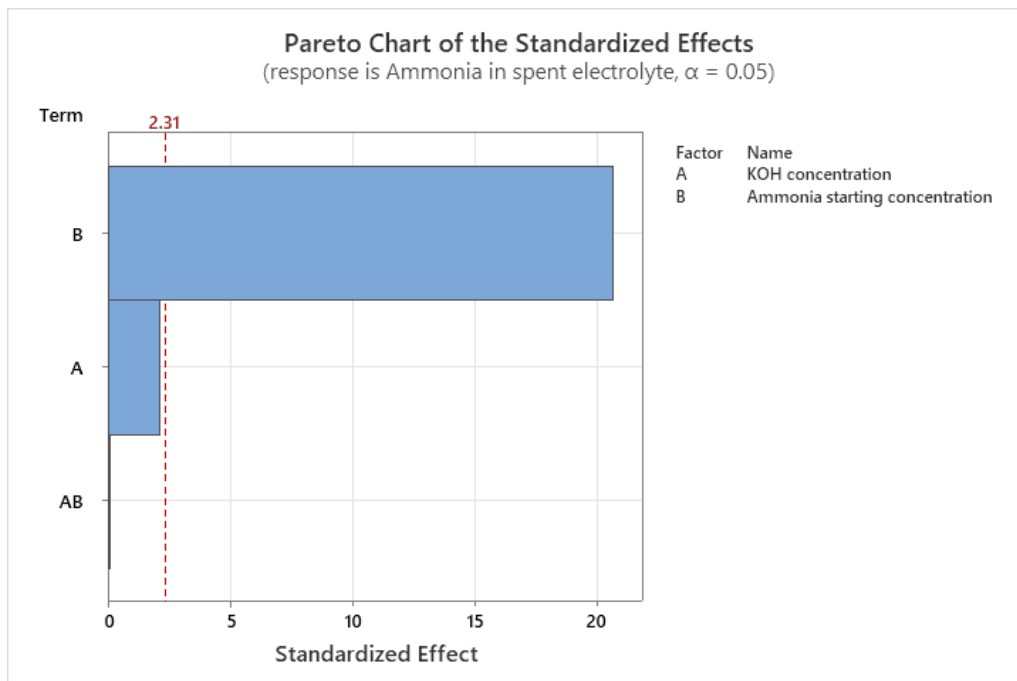


Figure 13: Pareto chart of the standardised effects on ammonia concentration of the spent electrolyte

5.8 Electrode degradation

After all experiments were completed, the electrolysis cell was opened. The gas separation membrane did not show any signs of degradation. However, the electrodes had changed significantly. The cathode changed the most. As seen in figure 14, it turned completely black. This is likely the result of nickel oxidation. The cathode felt quite brittle and fragile. At the edges, it even seemed like some of the material had eroded away. The bottom right of the figure shows the nickel foam material the electrodes were made of. The difference in colour is striking.



Figure 14: Cathode after the experiments were carried out. Original nickel foam material in the bottom right.

The anode also showed signs of degradation. However, its condition looked a lot better than that of the cathode. As seen in figure 15, the anode had a light brown colour with some darker brown spots. The reason for the locally darker brown spots is unknown. It could have been caused by bubbles adhering to certain parts of the electrode for longer. Or it could have been caused by nitrogen poisoning.



Figure 15: Anode after the experiments were carried out. Original nickel foam material in the bottom right.

The degradation of the cathode seemed a lot more severe than the degradation of the anode. A known reason for cathode degradation is repeated starting and stopping of the electrolysis process (Ursúa et al. 2016). It is likely that a lot of the cathode degradation occurred after stopping the electrolysis process when the voltage slowly dropped below 0.25 V. Each experiment had a start and stop. However, the corrosion seems too severe for the low amount of start stop cycles that the experiments caused. The addition of ammonia to the electrolyte might have accelerated the degradation of the cathode although this was not proven in the experiments. The anode showed less degradation. The darker brown spots did indicate that some alteration of the catalytic surface has taken place. This could have been by mechanisms like metal oxide corrosion or catalyst surface blockage. It is likely that nitrogen blocked some of the active sites as predicted. However, similarly to the cathode degradation, the experiments from this report do not provide proof for a specific degradation mechanism. To get better insight into the electrode degradation, additional analyses would have to be performed. If possible, a scanning electron microscope analysis could have given better insight in the electrode degradation.

6. Further discussion

In the previous chapter, the results of the experiments were presented and discussed. The discussion in the previous chapter focussed on explaining the experimental results. The following chapter presents a more general discussion. It tries to answer the question if steam condensate could be used for alkaline water electrolysis, but also looks critically at the experiments that were carried out.

6.1 Current density

The current density of the experiments was quite low. Usually, regular alkaline electrolysis cells operate at a current density of around 200 mA/cm² (Zhao et al. 2020) and zero gap alkaline electrolysis cells even at 400 mA/cm² (Gandia et al. 2013). In the experiments the current density was between 10-20 mA/cm². There are many factors that influence the current density. For example, the conductivity of the electrolyte plays a role. In the experiments, an electrolyte concentration of 0.2 M to 1.0 M KOH was used. In conventional setups, the electrolyte is usually at least a 5 M KOH solution.

The voltage also influences the current density. As the voltage increases, the current density will also increase. The trade-off between higher current density and lower efficiency is important to keep in mind. When the experiments were performed, a voltage of 2.15 V was chosen. A voltage of 2.0 V was needed for bubbles to form in any significant quantity. But due to the efficiency declining, the decision was made to not increase the voltage by too much. Unfortunately, after the experiments, an explanation was found for the low current density. Conventional alkaline electrolysis usually uses an electrolyte which is about 80 °C. The electrolyte in the experiments had a much lower temperature of about 15 °C. The difference in voltage due to the temperature at which the process is carried out can be well over 0.5 V (Amores et al. 2017) which is visualised in figure 16 below. This means the experiments could have been more realistic and accurate if a higher voltage was used.

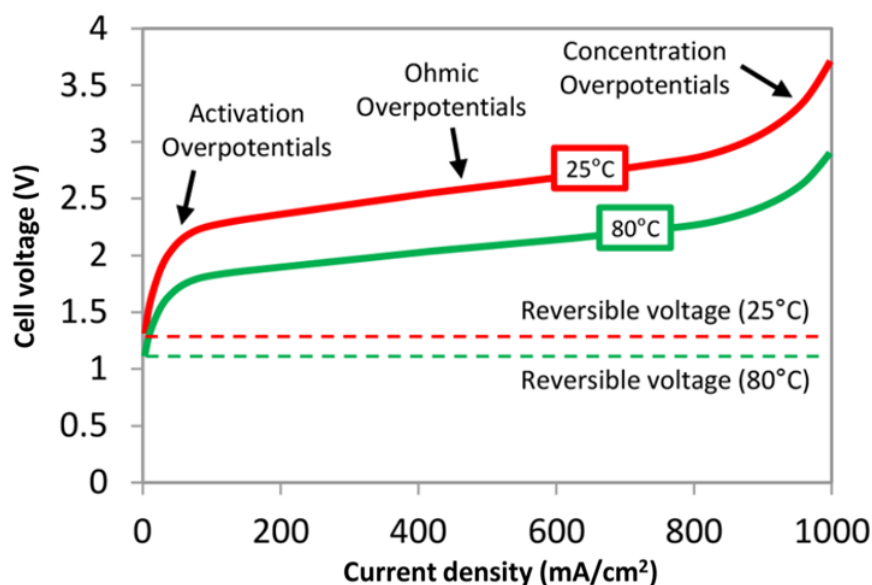


Figure 16: Cell voltage against current density at different temperatures of an alkaline electrolysis cell. From Amores et al. (2017).

6.2 Could untreated steam condensate be used as electrolyte?

The inspiration for the research in this paper came from a discussion between the technical university of Delft and YARA which is a producer of fertiliser. To produce fertiliser, hydrogen can be used. In theory, this producer could build facility that produces hydrogen. To feed this facility, a clean source of water is needed. During fertiliser production, steam condensate is produced. This is a source of water that is quite clean. So clean in fact that about 1 ppm ammonia is added to make the water less aggressive. This water could be used directly for alkaline water electrolysis by simply adding potassium hydroxide. The results in this paper show that adding ammonia did not lead to a measurable decrease in Faraday efficiency. There were some disadvantages though. Adding ammonia led to a decrease in current density. This means less hydrogen can be produced at a given voltage. Furthermore, some pollutants are introduced. Ammonia gas gets captured with the hydrogen lowering its purity. Also, the spent electrolyte of the experiments contained ammonia and nitrate. Another problem that might occur if steam condensate is used directly is that the lifetime of the electrodes could decrease significantly. While this effect was not measured in the experiments, oxidation of ammonia can lead to poisoning of the electrode. This leads to a reduction in catalytic surface which would reduce current density over time.

Purifying the steam condensate using reverse osmosis would resolve these issues. However, reverse osmosis is a costly way to treat water. The best option between treating or not treating the steam condensate for hydrogen production depends on the cost. Steam condensate can only be used directly if the loss in electrode lifetime and current density outweighs the cost of the reverse osmosis process.

There are also ways to treat only the ammonia in the condensate. Ion exchange can be used to treat the ammonia (Jorgensen & Weatherley 2003). This method uses a zeolite that worked in a variety of conditions. While this method to treat ammonia has been proven to be able to treat ammonia in wastewater, treating the steam condensate described in this report should also be possible.

Another alternative could be degassing the ammonia using nitrogen gas before the electrolyte enters the electrolyser. In this process, the KOH is added to the steam condensate. This increases the pH. The higher the pH, the more efficient the degassing process is. Results from Özyonar et al. (2012) show multiple degassing methods that had a removal rate close to 100% at a pH of 12. Depending on how long the solution must be aerated, this method might use a lot less energy and capital than reverse osmosis. One condition that applies is that the steam condensate does not have other contaminants that influence the electrolysis negatively. If removal is not perfect or if this treatment process malfunctions temporarily, a small concentration of ammonia might still end up in the electrolyte. This is not expected to have any large long-term effects on the electrolysis cell.

6.3 Impact of ammonia on gas quality

The ammonia gas in the hydrogen causes a lower purity. Depending on the application, this decrease in hydrogen gas purity might be very damaging. For example, vehicles that use a full cell require hydrogen gas with a high purity. In this case, the maximum total non-hydrogen gasses concentration should not exceed 300 $\mu\text{mol} / \text{mol}$ (ISO 2019). However, applications like combustion do not require a very pure hydrogen gas (Hy4Heat 2019). The maximum total

non-hydrogen gasses concentration for combustion is 20.000 $\mu\text{mol} / \text{mol}$ (ISO 2019). The type of impurity might also play a big role. Ammonia gas could impact an industrial process differently compared to other gasses. In the case of fertiliser production, ammonia gas in the hydrogen gas supply is not expected to influence the production process in any significant way. A purification step could be implemented to purify the hydrogen gas. Using a palladium membrane, ultra-pure hydrogen can be produced but this treatment step should of course only be used if necessary. It also introduces many potential problems like membrane damage, pressure fluctuation, and losses (Gornick & Bossard 2012).

6.4 Impact of ammonia on effluent

Both the nitrate and ammonia that were found in the electrolyte could have negative operational effects. The spent electrolyte contains additional contaminants which might cause an additional treatment step to be necessary. No research could be found on the treatment of spent electrolyte. In theory, if ultra-pure water and pure potassium hydroxide are used to produce the electrolyte, electrolysis can be carried out indefinitely by just adding water periodically. In practice, while the electrolysis process can be carried out continuously, it is likely that part of the electrolyte gets taken out periodically to maintain a certain purity. The spent electrolyte might contain some impurities that were corroded from the electrodes or the membrane. This wastewater could be treated in several ways. Due to the high potassium hydroxide concentration, somehow recycling the wastewater would save a lot of chemicals. In the case of fertiliser production, the high potassium concentration of the spent electrolyte can be valuable. The high temperature of the spent electrolyte is also useful for the fertiliser production plant. By redirecting the spent electrolyte back to the fertiliser production process, both energy and chemicals can be saved.

If the electrolyte used in the process contains ammonia, both ammonia and nitrate might be present in the spent electrolyte. It is likely that a large-scale operation would produce relatively small volumes of spent electrolyte. The ammonia in the electrolyte would get enough time to oxidise. This means the ammonia concentration in the spent electrolyte might be negligible, but the nitrate concentration could be high. Ironically, the nitrate concentration could be treated using electrochemical reduction (Garcia-Segura et al. 2018).

7. Conclusion

Adding ammonia to the electrolyte caused a decrease in current density. This indicates that the ammonia oxidation reaction competed for catalytic surface which decreased the OER rate. Literature suggests that electrode poisoning could occur due to elemental nitrogen chemisorption. However, this effect was not measurable in the relatively short experiment time in this report. Although ammonia oxidation also produces hydrogen, a decrease in Faraday efficiency could have occurred due to the introduction of new side-reactions. The experiments did not show a decrease in Faraday efficiency. However, if the decrease in current density were to be compensated, the voltage would have to be increased. This increase would lead to a decrease in voltage efficiency and thus a decrease in overall efficiency as well.

While some of the ammonia was oxidised in the cell, there was also a decrease in ammonia concentration due to ammonia stripping. After the experiment there also remained a significant ammonia concentration in the electrolyte. Considering that the overpotential for the ammonia oxidation reaction was very large and that there were significant ammonia concentrations present in the spent electrolyte, indicates that nickel electrodes are a poor catalyst for ammonia oxidation.

Both the cathode and anode showed signs of electrode degradation. The cathode showed the most degradation turning completely black. However, this degradation is likely to have been caused by stopping and starting the electrolysis process repeatedly. The anode showed less signs of degradation. While adding ammonia indicates to have accelerated the electrode degradation processes, the experiments that were carried out in this paper do not prove this.

The experiments showed that multiple contaminants were produced due to the addition of ammonia to the electrolyte. Ammonia was stripped out as a gas. This gas got captured with the hydrogen and oxygen. A lower hydrogen gas purity could be problematic depending on its use. Some ammonia and nitrate remained in the spent electrolyte. This means additional treatment might be necessary before disposal.

The overall negative effects of having ammonia in the electrolyte for alkaline water electrolysis were quite significant. Therefore, it is recommended that ammonia is removed from the influent of an electrolysis operation. In case of a temporary breakthrough of a low concentration of ammonia, negative consequences are expected to be negligible.

8. Recommendations

Although this report made a few steps toward researching the use of steam condensate in alkaline water electrolysis, further research is necessary to get a better understanding of the effects of ammonia on the electrolysis process. It is predicted that the global electrolyser capacity will increase exponentially in the coming years. Therefore, it is important to find sustainable water sources. Steam condensate would be a great sustainable water source. By further researching this topic, a clear consideration between the advantages and disadvantages of using steam condensate can be made. There are multiple knowledge gaps that further research must fill. Firstly, the degradation of the electrolyser components due to ammonia should be compared to a system that is free of ammonia. Secondly, more accurate measurements can give an insight into the effect of ammonia on the hydrogen production and the efficiency of the production. Lastly, the effect of additional components has to be understood. The ammonia in steam condensate will lead to ammonia and nitrogen gasses being released, and result in the production of nitrate. Furthermore, steam condensate might contain additional components that affect the alkaline electrolysis process. All these components must be accounted for to get a proper understanding of the effects of using steam condensate as electrolyte. Some of the analyses that are proposed are measuring nickel in the spent electrolyte, and using scanning electron microscopy to get insight into electrode degradation.

To more thoroughly research the effects of ammonia on alkaline water electrolysis, it is recommended that a different experimental setup is used. In this report, a setup was used that quite accurately represents a cell that could be used in a large-scale production facility. However, there were some downsides to the setup. The cell was closed off which means visual observations of the production process could not be made. Also, all the vials and tubes that were used in the experimental setup reduce the accuracy of measurements. Produced gasses mix with the gas that is already present in the vials and tubes which would make gas measurements quite unreliable. In experiments that measure the produced gasses, it might be better to use a setup that more closely represents a Hofmann electrolysis apparatus (Von Hofmann 1865). This allows for more accurate gas measurements. To get insight into the degradation of equipment, it is recommended to use a dual setup. By using a dual setup, electrodes affected by ammonia could be accurately compared to electrodes that used a pure electrolyte.

It might be beneficial to focus future research on individual aspects like equipment degradation, production rates, or pollutants in the electrolyte. This guarantees that an adequate experimental setup is designed instead of designing an experimental setup that tries to do everything at once. Overall, pursuing this research topic is worthwhile since hydrogen can play such an important role in a sustainable society.

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10. Appendix

10.1 Background information

Principles of Alkaline electrolysis

Alkaline electrolysis is one of the more mature technologies used to produce green hydrogen (Chi & Yu 2018). To produce hydrogen using alkaline electrolysis, a current is supplied to the cell. In the cell, water is split into hydrogen and oxygen. The hydrogen produced in this process is a great energy carrier. By using electricity that was produced using renewable methods, green hydrogen can be produced. This gives alkaline electrolysis a great potential to help reduce overall carbon emissions in many industrial processes.

Figure 17 shows a schematic drawing of a conventional electrolysis cell design. On both sides are electrodes. At the cathode, H_2 is produced, and on the other side O_2 is produced at the anode. In the middle, a separator is placed to stop the gasses from mixing. The electrolyte between the electrodes and the separator is made up of water to which either potassium hydroxide or sodium hydroxide is added. Most often, electrolyte containing 20-30% KOH in weight is used (Chi & Yu 2018). This not only gives a very high pH to the electrolyte, but also guarantees an optimal conductivity which results in a higher process efficiency.

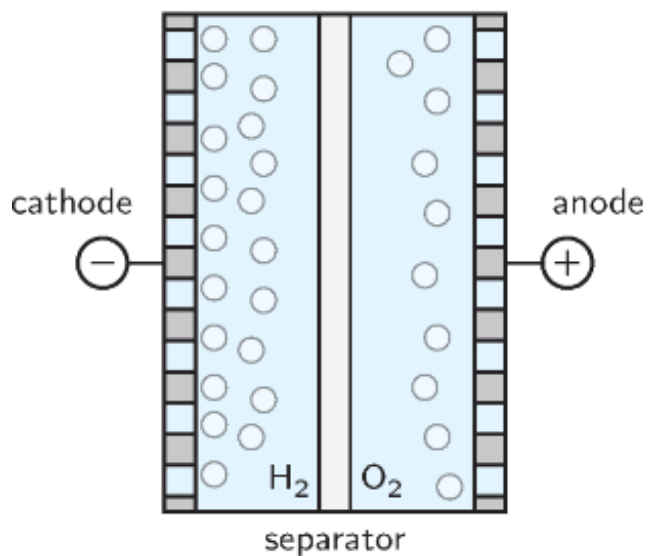
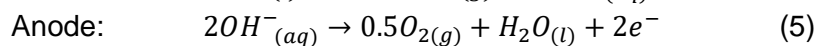
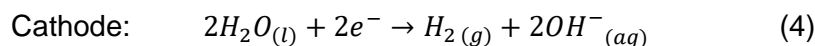


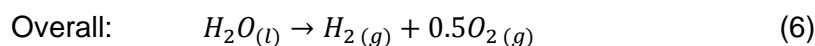
Figure 17: schematic of an alkaline electrolysis cell. From: Brauns & Turek (2020)

Reaction

There are 2 half reactions that take place in the electrolysis process which are known as the Hydrogen Evolution Reaction (HER), and the Oxygen Evolution reaction (OER) (Wang et al. 2021). Equation 4 and 5 below show these reactions:



These are the HER and OER in alkaline conditions (Brauns & Turek 2020). In acidic conditions slightly different reactions take place. Nevertheless, the overall reaction is the same and can be seen in equation 6:



The theoretical voltage that must be applied to let this reaction occur is 1.23 V. However, since this reaction is non-spontaneous at standard conditions, more energy is required. The

thermoneutral voltage is the required voltage at which the reaction can be sustained. At standard conditions this is at 1.48 V (Brauns & Turek 2020).

Electrodes

Additionally, an overpotential is required. This overpotential is reduced by using catalysts. Without catalyst, the HER and OER are very slow (Wang et al. 2021). Electrode material is usually chosen by considering its catalytic properties and the stability of the material. Nickel is a common catalyst; it lowers the required overpotential and is stable under alkaline conditions. However, there are many improvements that can be made. For example, making a structured nickel iron alloy to use as the anode is one of the ways to improve the OER (Koj et al. 2019). While using nanocrystalline nickel-molybdenum alloys as a cathode decreases the HER overpotential (Huot et al. 1991). The shape of the electrode plays an important role too. Electrodes are often covered in slits to enhance the gas bubble separation. The optimal diameter of the slits depends on the mean gas bubble diameter which in turn depends on the type of gas and the operating temperature. At 90 °C this is 0.1 mm for hydrogen gas and 0.7 mm for oxygen in alkaline conditions (Wendt & Kreysa 1999).

The catalytic properties of the electrodes should also be maintained throughout their lifetime. A common problem that many electrode materials face is electrode deactivation. For example, applying a 10 mA/cm² to a nickel electrode can cause nickel hydrides to form on the catalytic surface due to the high hydrogen concentration at the cathode (Mauer et al. 2007). On the long term this could affect the hydrogen production significantly. To guarantee a long lifetime of electrodes, such issues must be addressed. Some methods have been developed to reduce electrode deactivation. This is either done by applying an iron coating to the cathode to negate the formation of nickel hydrides (Mauer et al. 2007), or by dissolving vanadium in the electrolyte (Abouatallah et al. 2001).

Electrolyte

The electrolyte used, as mentioned before, is usually a solution of which 20-30 % of its weight is made up of KOH or NaOH. Usually, KOH is preferred over NaOH because it has a higher conductivity at its optimal weight percentage. However, NaOH has the benefit that it has a lower gas solubility (Brauns & Turek 2020). The purity of the solution plays an important role in both the efficiency of the electrolysis and the lifetime of the equipment. There are many impurities that can cause blockage due to deposition on the catalyst surface or in the gas separation membrane. Blockage is mostly caused by divalent cations like calcium, magnesium, and zinc (Barwe et al. 2018) (Zeng & Zhang 2010). Other ions can lead to unwanted side-reactions that lower the efficiency. Some can even be corrosive to the electrodes. This happens for example when chloride forms chlorine at the right current density (Zeng & Zhang 2010).

Separator

The gasses produced at each electrode must be kept separate. The separator in the electrolysis cell has to prevent the mixing of hydrogen and oxygen gasses, while letting the hydroxide ions pass through. Different separators can be useful depending on the experiment that has to be carried out. In some cases, a separator with a very low resistance might be beneficial, while a different experiment might need a corrosion resistant separator. Many types

of separators show great applicability. Anion exchange membranes, polymeric membranes, acrylic separators, and porous separators (Yuzer et al. 2020) (Sakr et al. 2017) (Kim et al. 2022) are all great separation technologies and are still being innovated upon.

Efficiency

An important parameter of water electrolysis is its efficiency. It helps in comparing technologies like alkaline water electrolysis and PEM electrolysis with each other. Moreover, efficiency is used to compare different alkaline water electrolysis cell setups. However, different definitions of efficiency can make comparing different electrolysis cells difficult. Lettenmeier (2021) describes efficiency in four ways, three of which are useful in this report and are defined in equation 7, 8, and 9.

Firstly, the Faraday efficiency ε_F , is defined as the actual volume of usable hydrogen V_u over the theoretical maximum volume V_m . The Faraday efficiency accounts for any diffusion losses, current losses, losses due to side-reactions, and downstream purification losses. To clarify, in a test setup the produced hydrogen might be bubbled through demi water before being captured and measured. In this case, the small portion of hydrogen that dissolves and diffuses in the demi water is accounted for when calculating the Faraday efficiency. The formulation of the Faraday efficiency is given in equation 7 below.

$$\text{Faraday efficiency:} \quad \varepsilon_F = \frac{V_u}{V_m} \quad (7)$$

Secondly, the voltage efficiency ε_V can be defined as the thermoneutral voltage E_{th} over the measured cell voltage E_{cell} . At standard conditions, the thermoneutral voltage is 1.48 V. This is higher than the 1.23 V that is required for the actual reaction due to the non-spontaneity of the reaction (Lide 1999). The activation overvoltage results in an even higher cell voltage on top of the thermoneutral voltage (Brauns & Turek 2020). By using nickel electrodes, the activation overvoltage is lowered significantly but not gone. Equation 8 shows how the voltage efficiency is calculated.

$$\text{Voltage efficiency:} \quad \varepsilon_V = \frac{E_{th}}{E_{cell}} \quad (8)$$

Lastly, the DC efficiency ε_{DC} or overall efficiency, can be calculated in two ways. In general, it is defined by the energy contained in the technically usable hydrogen over the power that is put into the system. A simple way to calculate this is by multiplying the Faraday efficiency ε_F by the voltage efficiency ε_V . This overall efficiency is generally useful when analysing experiments. However, an actual hydrogen plant would have to process and store the hydrogen which leads to an even lower efficiency than the overall efficiency defined here, but this is not relevant for this report.

$$\text{Overall efficiency:} \quad \varepsilon_{DC} = \varepsilon_F \times \varepsilon_V \quad (9)$$

It is good to compare overall efficiency between systems. However, in practice a higher than necessary overvoltage is usually applied because this increases the current density and thus

the hydrogen production. Therefore, it is important that every paper clearly describes what voltage and current density is used and explains why certain choices were made. In the next chapter voltage and current density of electrolysis setups is further explained.

Current density and voltage

As explained previously, by applying a higher cell voltage, the voltage efficiency decreases. However, the voltage used in practical applications is often a lot higher than the minimal voltage that would be needed for the reaction to take place. This is because a higher overvoltage increases the reaction rates of the HER and OER. While efficiency is important, the production rate of the cell should also be considered. If the cell voltage is minimised, the hydrogen production would be very low. This means that the cost of the electrolysis cell would be too high for the amount hydrogen it can produce. On the other hand, if the cell voltage is increased too much, the corrosion also increases while the efficiency decreases.

Instead of only focussing on the voltage, it can be beneficial to consider the current density as well. When the voltage is increased, the current density increases too. In modern big scale applications, a current density of 400-500 mA/cm² is common (Gandia et al. 2013). When comparing two electrolysis setups with each other both cell voltage and current density have to be considered to draw meaningful conclusions.

Ideally, the cell voltage can be plotted against current density. To do this, extensive measurements must be made. Figure 18 shows a theoretical example of such a plot. The figure also shows which components make up the cell voltage. As described by Brauns and Turek (2020), these components are the reversible cell voltage U_{rev} , the ohmic losses $I \cdot R_{ohm}$, and the activation overvoltage η_{act} .

The reversible cell voltage is a constant 1.23 V because that is the standard potential of the water electrolysis reaction. The ohmic losses increase linearly with voltage because capacitance or induction do not occur in the electrolysis cell. The resistance of the cell is composed of four parts. These are the resistance through both electrodes, the gas separator, and the electrolyte. These parts are added up to obtain the total resistance R_{ohm} . The distance between the electrodes has a big influence on the resistance of the electrolyte. Instinctively, one might think the distance should be as small as possible to minimise the resistance. However, at a very small distance between the electrodes, more gas will accumulate which lowers the conductivity of the electrode and blocks the electrode surface. Therefore, there exists an optimal distance that should be used (Balabel et al. 2014).

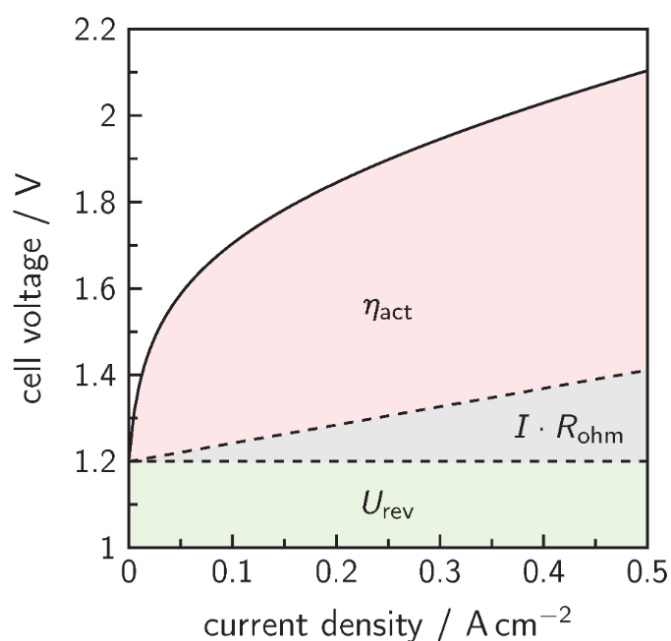


Figure 18: Theoretical example of the components that make up the total cell voltage against current density. From (Brauns & Turek 2020).

The activation overvoltage is the loss of voltage that is required to overcome the chemical bonds and drive the reaction forward (Zouhri & Lee 2016). The variables that affect the activation overvoltage are current density and temperature. The electrode material and electrolyte also play a role since these affect the exchange current density. As can be seen in figure 18, the activation overvoltage does not increase linearly with current density. Equations 10 and 11 are used to calculate the activation overvoltage of hydrogen and oxygen as described by Zouhri & Lee (2016):

$$\eta_{cathode} = 2.3 \frac{RT}{\alpha F} \log \left(\frac{i}{i_0} \right) \quad (10)$$

$$\eta_{anode} = 2.3 \frac{RT}{(1-\alpha)F} \log \left(\frac{i}{i_0} \right) \quad (11)$$

In these formulas,

$\eta_{cathode}$ = Activation overpotential at the cathode (hydrogen evolution reaction), V

η_{anode} = Activation overpotential at the anode (oxygen evolution reaction), V

R = Universal gas constant, $8.314 \frac{J}{mol \cdot K}$

T = Absolute temperature, K

F = Faraday constant, $\frac{C}{mol}$

i = Current density, $\frac{mA}{cm^2}$

i_0 = Exchange current density, $\frac{mA}{cm^2}$

α = transfer charge coefficient, depending on electrode and temperature

10.2 Water consumption

Society is trying to drastically increase green hydrogen production. Currently, government projects are on track to a total hydrogen production capacity of 134-240 GW in 2030. However, an even greater 720 GW is required in a net zero carbon emission society (IEA 2023). To reach these goals, very large hydrogen production plants have to be constructed. A source for the water consumption of very large plants was not found. Therefore, a calculation was made to get an estimate. This calculation makes several assumptions. First, it was decided to make the calculation for a 1 GW production plant. It was assumed that the 1 GW is the electrolyser capacity of the plant. Processes like storage, cooling, DC conversion, etc. also require electricity but are excluded. This means the actual electricity consumption of a 1 GW capacity plant would be a lot higher than 1 GW.

Efficiency plays a vital role when calculating the water consumption of electrolysers with a capacity of 1 GW. As of 2020, the efficiency of a nominal alkaline water electrolysis stack is approximately 70% (Brauns & Turek 2020). This efficiency might increase slightly in the future but seemed realistic for this calculation. This efficiency means that 700 MJ/s worth of hydrogen is produced. This number was converted to a mass of water that is required to store this energy. The calculation steps to do so are presented below:

- The water splitting reaction has an enthalpy change of 285.8 kJ/mol hydrogen.
- 1 mol of hydrogen weights 2.016 grams.
- 1 kg of hydrogen contains 496 moles of hydrogen.
- Therefore, 1 kg of hydrogen requires 141.77 MJ/kg to produce. (Excluding efficiency)
- At 70% efficiency, this means 4.94 kg of hydrogen is produced each second.
- 1 mol of water weighs 18.0153 grams.
- This means a production of 4.94 kg of hydrogen requires 44 kg of water.
- Therefore, a 1 GW capacity plant consumes 44 kg of ultra-pure water per second.
- 1 kg is equal to 1 litre for ultra-pure water.
- The daily ultra-pure water consumption is approximately 3800 m³.

Feeding a production plant with 3800 m³ of ultra-pure everyday can be challenging. Such a high water demand makes it harder to find a suitable water source. Water is constantly fed into the system. This replaces the water that is split. Having a constant process keeps the electrolyte at the right conductivity. A noteworthy problem that should be prevented is that water is consumed at the cathode, but water is produced at the anode. The electrolyte should not be mixed since part of the produced gasses are dissolved. Mixing the electrolyte flows could lead to a flammable gas mixture (Buttler & Spliethoff 2018). To negate this problem, circulation control is used which reduces the electrolyte flow and thus also reduces the mixing of the two electrolyte streams (Schug 1998). An overview of the flows in a large plant is given in figure 19. It was assumed that there is also an electrolyte effluent, but this is not shown in the figure. The lye that is fed into the system must also exit the system to maintain a constant concentration and conductivity.

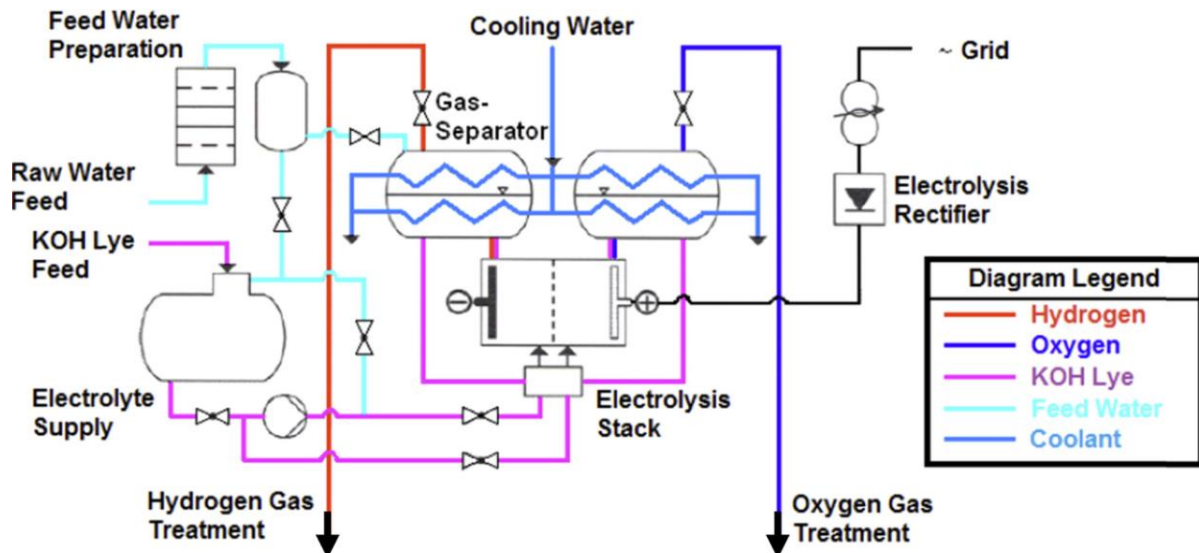


Figure 19: Layout of an alkaline water electrolysis system that is applicable on a large scale (Buttler & Spliethoff 2018)

As can be seen in figure 19, another important flow of water is the cooling water. This is another influent for which a water source must be found. Fortunately, the cooling water does not have to be ultra-pure water. Even seawater could be used although this can introduce problems like biofouling, inorganic fouling, and scaling (Rajala, 2016). Calculating the water consumption required for cooling depends on a multitude of factors. Some estimations should be made. Firstly, the operational temperature of the electrolysis cell must be approximated. A good estimate for the operating temperature is 75 °C since operating temperatures are generally between 60 °C and 90 °C (Buttler & Spliethoff 2018). Furthermore, it is assumed that the feed water and the cooling water both have a starting temperature of 15 °C. It is assumed that the feed water is added when it is still 15 °C which also helps cooling down the operation. It is assumed that the cooling water can reach an equilibrium temperature of 75 °C and thus cools as efficient as possible. An efficiency of 70% was used for the feed water calculation. This means 30% of the energy was lost. While in theory this 30% would not be converted to heat completely, in this calculation it is assumed that the lost energy is converted to heat completely. The performed calculation steps are shown below:

- 30% of the energy put in is converted to heat, this is 300 MJ/s.
- To increase the temperature of 1 kg of water by 1 °C, 4184 J are needed.
- The feed water and cooling water increase in temperature by 60 °C.
- 300 MJ can increase 1195 litres of water by 60 °C.
- Subtracting the 44 kg of ultra-pure water that is added each seconds gives 1151 litres.
- This means the plant needs 4100 m³/hr.

If the assumptions are correct, this means a 1 GW capacity electrolyser facility would need approximately 10⁵ m³ of cooling water per day. Such a large water demand makes finding a suitable fresh water source unlikely in many places. This would leave seawater as the best option.

10.3 supplementary information

Pumps and current source

The peristaltic pumps used in the experiments are from Watson Marlow model 120 U. The pump can be seen in figure 20. A calibration was performed which found that the pumps would pump electrolyte at a rate between 100-110 mL/min. The current was supplied by a TENMA 72-10500 digital control DC power supply. It can supply both constant voltage or constant current at a range up to 30 V and 3 A. It has a load regulation of 0.01% which is way more accurate than what is necessary for the experiments. Figure 21 shows a picture of the power supply.

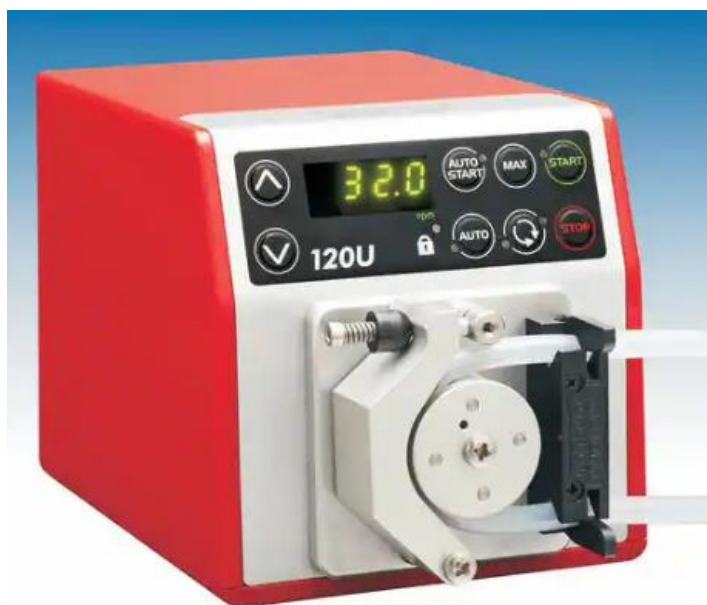


Figure 20: Peristaltic pump model 120U from Watson-Marlow



Figure 21: TENMA 72-10500 digital control DC power supply

Figure 22 shows the experimental setup. The entire setup took up about one square meter of space in the fume hood. The many black plastic objects on the tubes are the valves which were used to control the gas and electrolyte flows. The experiments were carried out inside the fume hood to prevent gas build-ups.



Figure 22: experimental setup that was used to carry out the experiments.

Conductivity after experiments

After the experiments, the conductivity was measured for a second time. Demi water was used to rinse the electrolysis cell after each experiment which causes the drop in conductivity. The slightly lower values are plotted in figure 23:

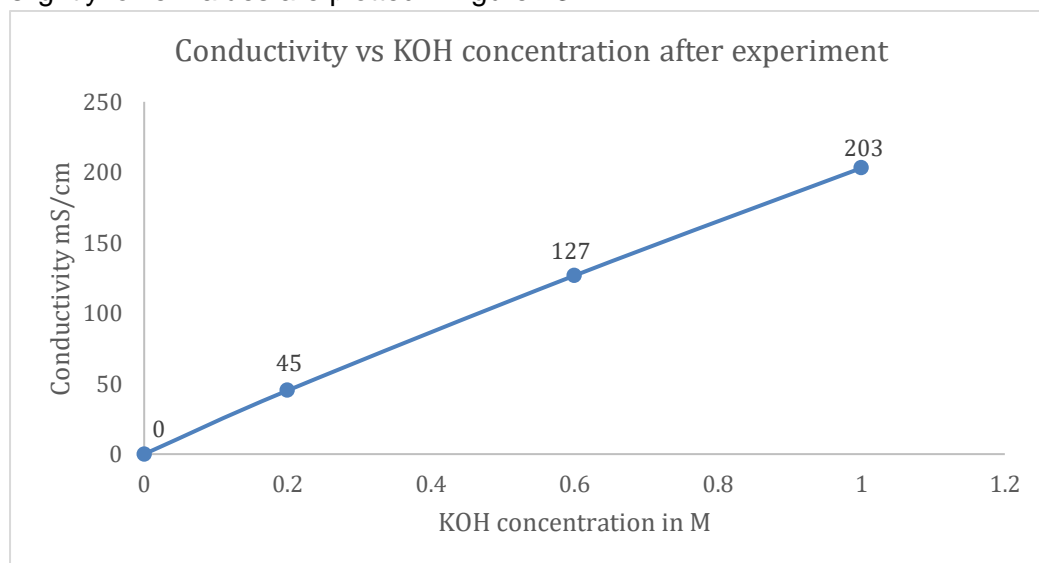


Figure 23: Conductivity vs KOH concentration measured after the experiment.

Gas production against concentration

Both current density and hydrogen production can be plotted against KOH concentration. These plots both give the same result. However, hydrogen production has a bigger error margin due to the way in which measurements are taken. Figure 24 shows the plot of hydrogen production against KOH concentration.

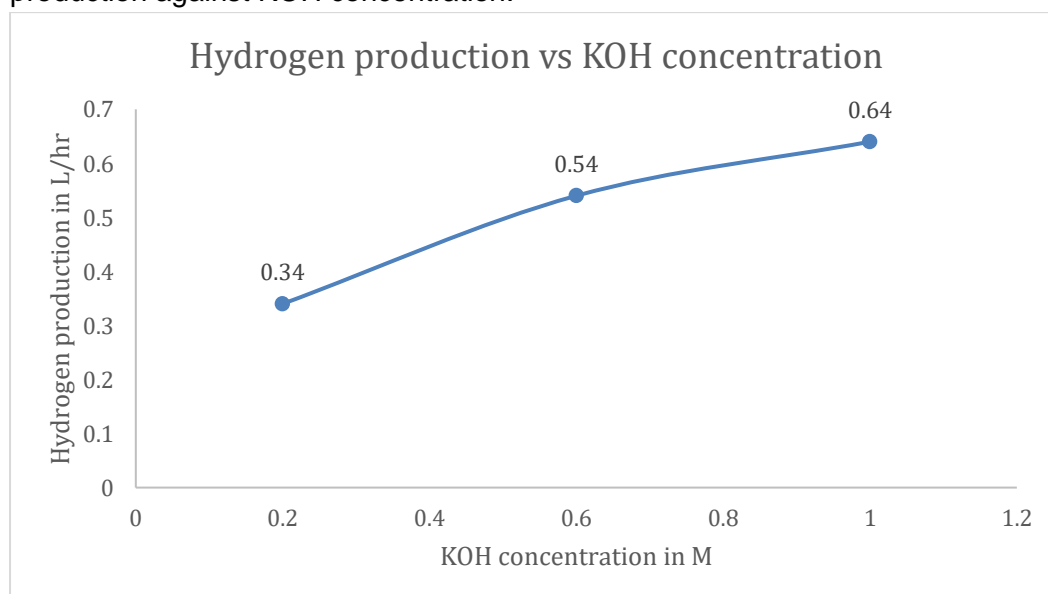


Figure 24: Hydrogen production against KOH concentration. Each point is the average of six experiments done at this concentration.

IC ammonia measurements

Figure 25 shows one of the IC chromatograms that were made to measure ammonium concentration in the spent electrolyte. The peak at approximately 7,5 minutes is caused by ammonium. The area under the peak is calculated to get the concentration. The peak to the left is caused by sodium. The samples all showed this sodium peak, but it is not sure why sodium is present in the samples. At 10,5 minutes, the conductivity spikes upward. This spike is caused by the high potassium concentration due to the use of potassium hydroxide as the electrolyte.

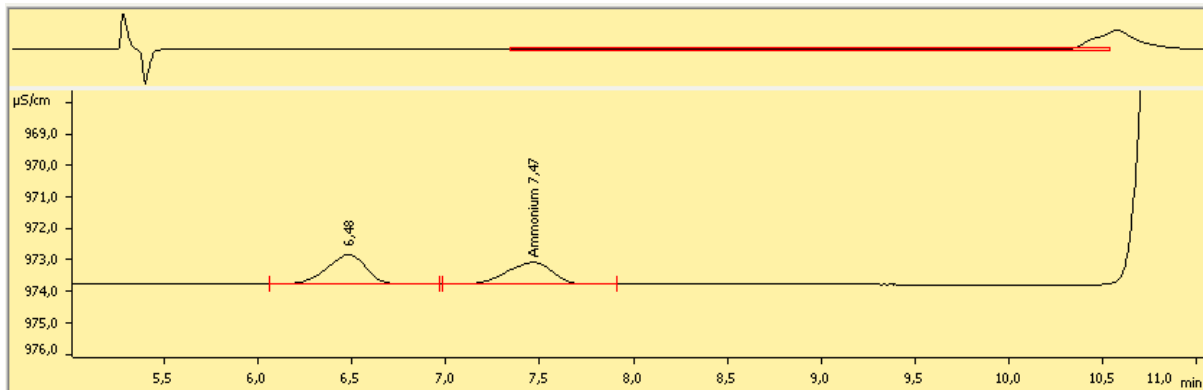


Figure 25: example of an IC chromatogram that was used to determine ammonia concentration in the electrolyte.

Figure 26 below, shows the calibration curve of the IC. The standards are used as a reference for the area under the curve of the measurements. The relative standard deviation is very low. Ion chromatography is a great way to get accurate ammonia concentration measurements.

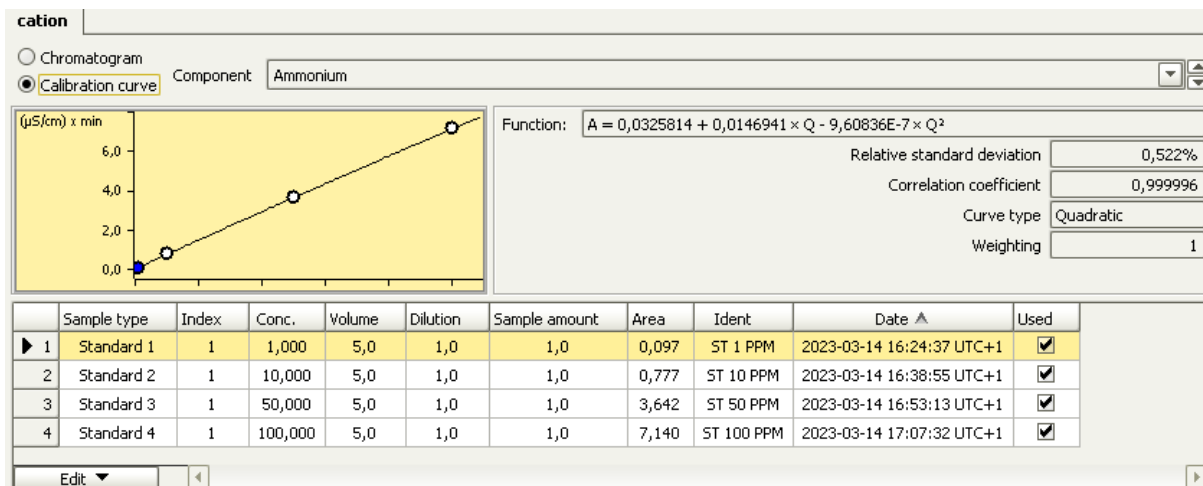


Figure 26: calibration curve of the ammonium measurements.

Pre-research questions

The questions below were used to direct the research that was performed. Originally, the focus lied on using steam condensate as the electrolyte for hydrogen production. However, many choices had to be made since this topic would have been far too broad. Questions had to be asked regarding the electrolysis method, the focus on different pollutants, and the focus on purity of the gasses or overall performance of the cell. Ultimately, studying the effect ammonia could have on the electrolysis process using nickel-based electrodes made the most sense to pursuit.

How important is electrolyte purity for hydrogen production?

The effect impurities have on the hydrogen production will depend on the type of impurity. For example, metal ions might travel with the protons through the membrane (solid polymer electrolyte). Then the metals with underpotential deposit at the cathode. When deposits form on the surface of the cathodic catalyst, the hydrogen evolution slows down (Kötz & Stucki 1987). Other Cations have a very negative Nernst potential. These cations will not be reduced at the cathode but instead might precipitate as hydroxides at the cathode due to the local pH difference. When experimenting with electrolysis of seawater, it was found that these deposits can be minimised by using turbulence, different current density, and the right cathode surface (Abdel-Aal & Hussein 1993). Due to the poor electrical conductivity of many hydroxides like ones that contain calcium for example, deposits formed in the membrane will also increase the ohmic potential (Wei et al. 2010).

What problems do the contaminants in the condensate cause?

The oxidation of ammonia and ammonium heavily depends on the pH of the electrolyte. When the electrolyte is alkaline, ammonia is the dominant species, while when the electrolyte is acidic ammonium is more dominant. The oxidation is favoured in alkaline conditions in which ammonia reacts with hydroxide ions to form water and nitrogen (Adli et al. 2018). In acidic conditions, direct electrochemical decomposition occurs which forms nitrogen. Ammonia and ammonium will form nitrogen at 0.9 V and -0.52 V respectively (Candido & Gomes 2011). However, experiments also show that different compounds can also be produced at the anode like nitrate. This nitrate could then be reduced to ammonium at the cathode again under the right conditions (Candido & Gomes 2011). Overall, it is likely that nitrogen is produced since oxidation potential of both ammonium and ammonia are lower than the oxidation potential of water.

How important is the purity of the hydrogen produced?

The standards for purity of hydrogen depends on the application that uses it. For vehicles it is very strict. For example, the maximum total non-hydrogen gasses concentration should not exceed 300 $\mu\text{mol} / \text{mol}$ (ISO 2019). However, these vehicles use a fuel cell and therefore need very pure hydrogen. For applications like combustion the purity does not have to be as high (Hy4Heat 2019). The maximum total non-hydrogen gasses concentration for combustion is 20.000 $\mu\text{mol} / \text{mol}$ (ISO 2019). If hydrogen is produced from untreated condensate, it is likely that it will contain some contaminants. If the hydrogen is used in a process that requires high purity, it could be filtered using a palladium membrane purifier. This type of membrane is usually used to purify hydrogen that is made from fossil fuel. Using a palladium membrane, ultra-pure hydrogen can be produced but this treatment step should of course only be used, if

necessary, it also brings many potential problems like membrane damage, pressure fluctuation, and losses (Gornick & Bossard 2012).

Can steam condensate be used directly?

Treating the water before using it for hydrogen production could be the best way to make the overall process more efficient. One important aspect that makes this difficult is the introduction of new contaminants while trying to get other contaminants out. This means the best method would be through adsorption. Using Zeolite as an absorbent is a great way to reduce the total ammonia nitrogen of water (Soetardji et al. 2015). The benefit this treatment could have, is that there is less corrosion of the electrodes and that the produced hydrogen is purer. Nevertheless, this treatment step should only be introduced if the added benefit is significant enough. Alternatively, a more thorough treatment step could be applied. Nanofiltration combined with zeolite has shown to have the potential to be very effective in removing ammonium (Rohani et al. 2021). This method specifically showed to be effective at low concentrations. Additionally reverse osmosis could be used to produce very pure water. The three methods described in this paragraph come with a greater and greater increase in cost respectively. It would be very beneficial if hydrogen can be produced efficiently without having to treat the water first.

What are the main electrolysis techniques?

Two very promising techniques to produce green hydrogen are alkaline electrolysis and proton exchange membrane (PEM) electrolysis. As of now, the technique that seems to be best commercially applicable is alkaline liquid electrolysis (Chi & Yu 2018). Nickel containing alloys can be used as electrodes for this technique (Colli et al. 2019), which are significantly cheaper than the electrodes used in other techniques which usually contain platinum. Another technique is polymer electrolyte membrane (PEM) electrolysis. This method is not as developed as alkaline liquid electrolysis but great potential. Plans to build electrolysis plants that use both alkaline and PEM have already been made (ISPT 2022). It is still more costly and has less durability but also a higher efficiency and higher current densities (Kumar & Himabindu 2019).

The efficiency, capital and operational costs, gas purity, etc. all play a role in making one technique more attractive than the other. Furthermore, the main advantage is that balancing a PEM electrolysis plant is easier which makes it more suitable to run on unpredictable renewable energy sources. An important difference with regards to the electrolyte is that PEM uses acidic electrolyte, while alkaline liquid electrolysis uses an electrolyte that contains 20-30% NaOH or KOH (Chi & Yu 2018). An advantage of PEM electrolysis is that the membrane can keep the gas produced at both electrodes completely separated (Hermann et al. 2005) and thus any nitrogen or nitrate would not contaminate the produced hydrogen gas.