# Development of a Fuel Cell Vehicle

With On-Board Hydrogen Production by

Nanoporous Aluminum

M.W.G. van der Pluijm





HYDROPORE



y university of groningen



# Development of a fuel cell vehicle with on-board hydrogen production by nanoporous aluminum

M.W.G. van der Pluijm s2162601

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#### Abstract

Due to the ever-increasing usage of power by humans, more and more greenhouse gasses are added to the atmosphere every year. Because of this, alternative ways for the production of this power needs to be found. In this work, steps towards a more hydrogen-based economy are made. Companies and startups like Hydropore and Elysis are finding a way towards a carbon-free and cost-effective hydrogen production. To achieve this, the possibilities of the use of nanoporous aluminum has been researched and applications have been developed. With the high surface-to-volume ratio of nanoporous aluminum, because of its nanometer sized ligaments, a very fast reaction with water is present when the two are combined. With this, hydrogen can be generated on-board fast enough for multiple applications. Here, optimizations of the nanoporous aluminum have been researched by changing the size of these nanometer sized ligaments. A light electric vehicle has been modified with a fuel cell to be able to run on hydrogen, and thus nanoporous aluminum. The project is therefore appropriately named the Nanoporous Aluminum Fuel Cell Car project, or in short, the NAFCAR project. Although not completely finished, a well-established base has been laid for further development on this project, and the optimization of the nanoporous aluminum.

RESEARCH INTERNSHIP, UNIVERSITY OF PENNSYLVANIA MASTER'S THESIS, UNIVERSITY OF GRONINGEN M.W.G.VANDERPLUIJM@GMAIL.COM

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In today's economy of a well-developed country it is not exceptional if an average citizen uses up to 80 times more energy than produced by their own metabolism in the same time span [1]. This energy is needed to produce raw materials, goods and services, and transportation. Most of that energy comes from the use of fossil fuels, as can be seen in figure 1.1 below [1, 2]. The advantages of fossil fuels are very clear:

- Available in large quantities
- Very high energy density
- Relatively cheap
- Can be burned to generate usable energy
- Relatively safe to handle
- Easily transportable

This all helped build up our economy and still drives most of the global economy today [3].



# U.S. primary energy consumption by energy source, 2018

Figure 1.1: US energy consumption as an example of primary energy consumption by energy source. Note: the sum of components may not equal 100% because of independent rounding [2].

The biggest downside, which is widely known for a while now, is the great amount of greenhouse gas emissions from these fossil fuels. These emissions are causing climate change with, for example, global warming as a consequence [4–6]. The disastrous effects of climate change can cause huge devastating storms or even cause a mass extinction level event [7, 8]. Whereas there are numerous benefits of using fossil fuels, and humanity is so powerful partially due to the use of these fossil fuels, our knowledge surrounding this topic increased and shows humanity needs to change. To minimize the climate change, a (rapid) development to renewable energy sources is needed.

These renewable sources include

- Solar/wind/hydro energy
- (Advanced) nuclear energy (e.g. nuclear fusion)
- Bio-energy and bio-fuels
- Hydrogen (produced with renewable methods)

The addition of hydrogen to a sustainable economy has been up for discussion for a long time already, and the idea is becoming more and more popular. Hydrogen is a highly abundant substance on Earth in the form of water. Jules Verne wrote about it in 1874, saying "water will be the coal of the future" [9], and, as one of many examples, U.S. President George W. Bush proposed \$1.2 billion in research funding towards developing clean hydrogen powered vehicles back in 2003 [10].

In this thesis the focus lies on hydrogen as a renewable energy source. Here it will be shown how hydrogen can be produced (with ideally no carbon footprint), how it can be stored (indirectly), and how it can be used to drive a light electric vehicle (LEV) in the future, where the latter had the main focus of the research done for this thesis. In this work the LEV is an example and a proof of concept of the future application of hydrogen in a carbon-free economy.

## 1.1 Hydrogen

The biggest downsides of hydrogen as a renewable energy source are the capability of the cheap production of *renewable* hydrogen, its storage and its transport [3, 11, 12].

Most of the hydrogen used today comes from water, natural gas, coal or biomass. Over 95% of this hydrogen is produced from natural gas via steam methane reforming [10, 13–16]. It is the cheapest way to produce hydrogen and also produces a lot of CO and CO<sub>2</sub>. Therefore, it is only a small reduction in greenhouse emissions compared to current hybrid vehicles and thus evidently is not sustainable [10, 16]. More renewable ways of producing hydrogen by for example biomass or electrolysis from renewable energy sources have a very high price tag attached to them [17, 18]. An alternative should thus be focused on.

Because of the extremely low density of hydrogen, the energy density of hydrogen per volume (MJ/L) is also very low, as seen on the bottom right in figure 1.2 below [3, 19, 20]. This makes it difficult and inefficient to transport and store hydrogen. Common tricks for this are, for example, to compress hydrogen or to make it a liquid [21]. Both require a lot of energy which lowers their efficiencies dramatically. There are also a lot of restrictions on the use of high-pressure hydrogen cylinders due to safety considerations associated with high pressure flammable gasses [22]. Another example is storing hydrogen in metal hydrides [3, 12, 23]. Usually this is expensive and these metals can only hold around 1% of their weight in hydrogen and thus are not very efficient [3, 23]. Also, to get people to adapt to, for example, hydrogen fuel cell driven vehicles, the availability of hydrogen (e.g. hydrogen fuel stations) needs to increase dramatically.

Please note from figure 1.2 that, opposite to the low energy density per volume of hydrogen, it has a very high gravimetric energy density/specific energy (MJ/kg) [24]. This density is 143 MJ/kg and shows why hydrogen is so viable as a fuel when compared to the 46 MJ/kg for petroleum used in combustion engines [20]. This high density gets drastically lowered when the pressure tanks and storage infrastructure are also taken into account [3].

Hydrogen also burns clean, i.e. the only combustion product is water if the reaction takes place at low temperatures. This means the carbon footprint of hydrogen as a fuel is solely determined by the carbon footprint of the source used to produce it [3].



Figure 1.2: Energy density chart of selected materials [25].

## 1.1.1 Hydropore LLC

To tackle the above-mentioned problems, Prof. E. Detsi and J. Corsi from the University of Pennsylvania (UPenn) have collaborated with CleanTech Penn from UPenn to start a new startup called "Hydropore LLC" (Hydropore). The goal of Hydropore is to make a jump towards a more sustainable hydrogen orientated economy by enabling high-volume hydrogen production through the reaction of nanoporous aluminum and pure water, with costs below \$2/gge (gasoline gallon equivalent) [26]. With this sustainable vision, the author of this thesis honorably mentions that this work has been done in collaboration with Hydropore.

As stated on their website, "[Hydropore] aim[s] to achieve this low cost by selling the following three products made during the reaction of aluminum and water: hydrogen, activated alumina and heat". Aluminum is a perfect match for this application. Besides that it is able to react with water to form hydrogen, it is the most abundant metal on Earth (after the metalloid silicon) [27]. This reaction takes place through the following equation:

$$2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2 + heat$$
(1.1)

Hydropore will first produce sustainable **hydrogen** by using secondary (recycled) aluminum. In the long term a collaboration with Elysis will be preferred, where Elysis will be able to produce carbon-free primary aluminum [28]. Elysis claims to be able to commercialize the production of carbon-free aluminum, and is aiming to have the technology commercialized by 2024. When this technology is available, sustainable hydrogen will be produced using both these primary and secondary aluminums.

The other products of the reaction, **activated alumina** and **heat**, are sold to reduce the cost of the hydrogen production. The activated alumina is high purity nanoporous alumina and the heat can be used to drive steam generators to generate electricity.

When all of these factors are combined, and when the technology for the mass production of sustainable hydrogen by Hydropore is commercialized, this can lead to a leap forward into a more sustainable hydrogen economy.

#### 1.1.2 Nanoporous aluminum

The research on nanoporous aluminum is on the top of modern nanophysics. As close as before the year 2000, researchers could not imagine the full impact of nanotechnology in science today [29]. A review article from 2007 "Towards the Hydrogen Economy?" [30] mentions nanomaterials once, where it is written that the results of experiments with carbon nanotubes are considered to be an experimental error, and even a review paper from 2018 "Recyclable Metal Fuels for Clean and Compact Zero-Carbon Power" [31] only dedicates a sub-subsection towards the use of nanoparticles as a fuel.

As mentioned above, aluminum is widely available and is the most abundant metal found on the Earth's crust [27]. It can potentially be recycled carbon-free and reacts with water to form hydrogen and alumina [10, 13, 28]. Aluminum has one of the highest hydrogen generation capacities, with a gravimetric hydrogen capacity of 3.7 wt % and a volumetric hydrogen capacity of 46 g H<sub>2</sub>/L [32, 33]. Quite high compared to, for example, a gravimetric hydrogen capacity of 1.97 wt % for zinc (Zn), another popular material to produce hydrogen [33, 34]. On top of this, aluminum also has a very high volumetric energy density as seen on the top left in figure 1.2. Please note that the energy densities for aluminum given in figure 1.2 are the values when there is a complete burning of the fuel with oxygen, producing heat. This is not the case for this thesis as the aluminum is reacted with water instead of oxygen. This generates heat plus hydrogen, which can be burned again. The heat and the energy generated by the hydrogen each contribute to approximately half of the total generated energy [35].

The reaction of aluminum with water as seen in equation 1.1 is thermodynamically favorable [32, 33]. Despite this, it is a self-limiting reaction because of the formed metal hydroxide layer. The aluminum at the surface is converted into alumina. This creates an envelope around the surface early on during the reaction, preventing water to come in direct contact with the metal underneath. To make sure all of the aluminum reacts, various methods have been proposed to enhance the reaction. This includes:

- The addition of catalysts such as salts to the metal to disrupt the hydroxide envelope. Salts like Ga, Li, Ln and Sn are added in the metal to make alloys or mixtures with a high water reactivity [32, 33, 36–40].
- The addition of catalysts such as, for example, NaCl or NaOH to the water to disrupt the hydroxide envelope [32, 33, 41–44].

Despite these catalytic properties these methods also add a lot of mass to the system, significantly lowering the gravimetric hydrogen generation capacity of the reactant. On top of this, the catalysts add impurities to products of the metal-water reaction. This impedes the recyclability of the fuel. To get rid of these impurities one needs to go through the complex so called "Bayer purification process" before the alumina can be recycled back to aluminum. Both of these reasons made sure no real breakthrough has been made yet [32, 45, 46].

To circumvent these problems it would be best if just the aluminum itself will be used. This is exactly what J. Corsi et al. proposed to do in their paper "Hierarchical Bulk Nanoporous Aluminum for On-Site Generation of Hydrogen by Hydrolysis in Pure Water and Combustion of Solid Fuels" [33]. Corsi et al. have modified the microstructure of the aluminum through nanoengineering, instead of modifying the chemical composition. As mentioned, the self-limiting properties of the reaction in equation 1.1 are present because of the development of an alumina envelope, which has a thickness of about 3.5 nm [47]. So when one, for example, has an aluminum sheet with a thickness of  $\sim$ 7 nm, the whole sheet will be converted into alumina as the metal hydroxide envelope will form on both sides.

Corsi et al. thus proposed to create nanostructured aluminum particles with an approximate ligament size of 7 nm. With this they aim to produce aluminum hydroxide and hydrogen gas with ideally a 100% yield [33]. They introduced hierarchical nanoporosity in bulk aluminum, characterized by the coexistence of both macroscopic and mesoscopic ligament and pore structures. This can be clearly seen in some of their SEM results shown in figure 1.3, where the macroscopic ligaments are seen in the left image, and the slightly more zoomed in image on the right shows the mesoscopic ligaments. In another paper the researchers found that water reaches the mesoscopic ligaments because of this hierarchical architecture [34]. The bigger macroscopic pores facilitate the flow through the bulk aluminum and let the water reach the so called nanopores. The mesoscopic ligaments were found to be in the range of 10-20 nm. Without any catalyst or reaction promoter, they reacted their sample with water and produced hydrogen with a yield of about 52-90%. Also, because of these structures, the nanoporous aluminum (NP-Al) has a very high surface-to-volume ratio, increasing the reactivity of the system. This nanoporous aluminum, or an optimized form, is the material Hydropore seeks to utilize for the mass production of hydrogen. In addition, this material can be attractive for solid fuel combustion, as its reactivity is much higher than ordinary aluminum powder [48].



Figure 1.3: The hierarchical nanoporosity of the aluminum, characterized by the coexistence of both macroscopic (left) and mesoscopic (right) ligament and pore structures [33].

Aluminum has to go through some special treatments to obtain this kind of hierarchical nanoporosity. To achieve this, Corsi et al. have made an aluminum-magnesium alloy with nominal composition of  $Al_{30}Mg_{70}$  at. % [33]. Where a wide range of nanoporous metals have been produced by chemical or electrolytic dealloying with aqueous electrolytes, here an air-free (argon) non-aqueous electrolytic (all-phenyl complex [APC] electrolyte) dealloying route has to be taken because of the reactive aluminum [33, 49–53]. Here, the Mg from the alloy is electrochemically removed and plated onto the counter electrode, as seen in figure 1.4. The sacrificial element and the reduced working ion in the non-aqueous electrolyte (Mg and Mg<sup>2+</sup> respectively) are of the same nature. The benefit here is that the Mg is recovered during this process, which is not possible when dealloying by galvanic replacement or in an aqueous electrolyte where the reduced working ion and the sacrificial element are not the same [33].



Figure 1.4: Schematic of electrolytic dealloying setup before (left) and after (right) the dealloying process [33].

Even though this research has not been done by the author of this thesis, the method and results of the work of Corsi et al. will be disclosed in the thereby corresponding sections of this thesis. There is a lot of overlap and most of the work for this thesis was done in cooperation with Corsi et al. Their findings and results set a base for the work on this thesis, so a lot of their work is a good way to introduce some topics in more depth than in this more general introduction.

#### 1.1.2.1 Ligament size

As previously mentioned, the ligament size plays a mayor role in the percentage yield of hydrogen and alumina. Corsi et al. have produced NP-Al with ligament sizes between 10 and 20 nm, generating a yield in the range of  $\sim$ 52-90% [33]. As stated, the ideal ligament size would be  $\sim$ 7 nm. To understand how to decrease this ligament size, and thus increase the yield percentage, one can look at the free surface diffusion. As seen in figure 1.5, one starts off with a solid mixture (alloy) of Al and Mg. When you remove Mg atoms, the Al left behind will diffuse to form Al clusters [54, 55]. Finally, ligaments and pores start to form as the Al clusters grow.

In cooperation with Corsi et al., the research conducted at the University of Pennsylvania also contained tests to optimize the ligament size of the NP-Al and increase its hydrogen yield. To decrease the ligament size it was proposed to take a look at the free surface diffusion coefficient, as shown in equation 1.2, where  $D_{s0}$  is the maximal diffusion coefficient (at infinite temperature in m/s<sup>2</sup>),  $Q_s$  the activation energy for diffusion (in J/mol), R the universal gas constant (8.314 J/mol·K) and T the absolute temperature (in K) [56]. Now one can see that if the temperature is decreased, also the diffusion coefficient will be decreased, in turn decreasing the pore and ligament size of the dealloyed NP-Al [57, 58].

$$D_s = D_{s0} exp\left(-\frac{Q_s}{RT}\right) \tag{1.2}$$



Figure 1.5: Example of pore growth. Following the arrows: solid mixture of Al (yellow) and Mg (grey) atoms  $\rightarrow$  selectively remove Mg atoms  $\rightarrow$  Al atoms left behind to form Al clusters  $\rightarrow$  ligaments and pores start to form as the Al clusters grow.

## 1.2 Fuel cell vehicle

Now some of the basics of the physics behind this new and renewable way of hydrogen generation is introduced, and why it is important for the development of a sustainable economy, let us see how this can be applied to the original goal of the thesis: "The Development of a Fuel Cell Vehicle".

When looking for a way to show off a new tech like this NP-Al, and bridge the gap between fundamental materials science research and its application, it was fast determined to build a vehicle. Vehicles are a tangible subject and fuel cell (FC) vehicles, powered by hydrogen, have a high potential to reduce  $CO_2$  emissions. Also, because of this low density of hydrogen, storing it in a moving vehicle is difficult and not very efficient if the hydrogen gas has to be pressurized [21, 22]. And finally, safety will be an issue when a vehicle with a high pressure, highly flammable hydrogen gas tank crashes [22, 59]. These restrictions can be overcome with a new hydrogen storage technology, increasing the popularity and adaptation of fuel cell powered vehicles.

#### 1.2.1 PEM Fuel cell

A vehicle powered by hydrogen usually uses a fuel cell stack (a stack of multiple fuel cells). The most popular fuel cells used in vehicles today are the "proton-exchange membrane" fuel cells, also called the "polymer electrolyte membrane" (PEM) fuel cells (PEMFC) [60–62]. These PEM fuel cells generate electricity without emitting any greenhouse gasses, which the vehicle uses to drive.

PEM fuel cells have been developed in the United States in the 1960s and are thus fairly new [61]. The polymer electrodes work at low temperatures so it starts up quickly, and the membrane electrode assembly is thin, so the fuel cells can be compact. Also, there are no corrosive fluid hazards and the PEM fuel cell works in all orientations [61]. All these reasons make PEM type fuel cells fitting for fuel cell vehicles. Research in the more recent years have led to current densities of about  $1 \text{ A} \cdot \text{cm}^{-2}$  while reducing the use of platinum (the catalyst splitting hydrogen and oxygen into their ions) by over a factor 100 to about  $0.2 \text{ mg} \cdot \text{cm}^{-2}$ . Because of these improvements, a great reduction in cost per kilowatt of power has been achieved [61].

Figure 1.6 shows the operation of a fuel cell. The electrolyte in the middle is an ion conduction polymer, with a catalyzed porous electrode on each side (the anode and cathode) [61]. This anodeelectrolyte-cathode group is thus assembled as one item, which can be very thin as mentioned above. These assemblies are then connected in series (hence, fuel cell *stack*) to increase the power output, generally by using bipolar plates. These bipolar plates conduct electrical current, uniformly distribute the fuel (air and hydrogen), prevent leakages and remove heat from the active area [63]. The catalyst splits the hydrogen and oxygen molecules into their ions, generating electrons, after which the mobile  $H^+$  ion is conducted through the polymer [61]. After this it recombines with oxygen to produce  $H_2O$ , generating electricity and not emitting any greenhouse gasses in the process.



Figure 1.6: Diagram of a PEM fuel cell [64].

## 1.2.2 NAFCAR

To get to a proof of concept, all the above-mentioned preparations are combined and put into a LEV (see figure 1.7), powered by a 2.4kW PEM fuel cell stack and named the Nanoporous Aluminum Fuel Cell Car (NAFCAR). This proof of concept aims to show people the potential of nanoporous aluminum for use on-board or on-site hydrogen generation. The goal of the project is to drive the NAFCAR on hydrogen produced by the nanoporous aluminum, and ideally drive it up and down the "Locust walk", a 2 km pathway right through the center of the UPenn campus.

This project is currently supported by the University of Pennsylvania, Penn Engineering, the Laboratory for Research on the Structure of Matter (space), the Vagelos Institute for Energy Science and Technology (VIPER program), the CleanTech Penn startup Hydropore and the University of Groningen.





Figure 1.7: Photos of the 2007 GEM eL XD, used for the NAFCAR project.



## 2.1 Nanoporous aluminum

#### 2.1.1 AI-Mg Alloy

Corsi et al. prepared the Al-Mg alloy with a near-eutectic composition [33]. Since the characteristics of the composition and test values were known, and because this work would partly be compared to the work of Corsi et al., the choice was made to stay as close as possible to their methods of producing this alloy.

The alloy was made using pure Al and pure Mg. Both materials were put in a graphite crucible which was put inside a quartz tube. This quartz tube was heated up to 750 °C in a OTF-1200X tube furnace from MTI Corporation to melt both metals, all under an argon flow. The tube has been shaken a little to improve mixing of both liquid metals.

Corsi et al. distinguished these two phases doing low-magnification scanning electron microscopy using a JEOL 7500F scanning electron microscope (SEM), depicted in figure 2.1 [33]. To enhance the phase contrast of the SEM images, the alloy was pretreated by etching with an acid. To confirm the existence of both phases, the alloy was further characterized by X-ray diffraction (XRD) using a Rigaku D/Max-B X-ray diffractometer.



Figure 2.1: The JEOL 7500F scanning electron microscope, equipped with energy-dispersive X-ray spectroscopy capabilities.

To determine the real chemical composition of the Al-Mg alloy, energy-dispersive X-ray spectroscopy (EDS) and Inductively coupled plasma (ICP) spectroscopy has been done [33]. EDS has been done with the JEOL 7500F SEM, which is also equipped with EDS capabilities. Because the interaction volume of EDS is relatively thin, ICP spectroscopy has been done with a Spectro Genesis ICPOES device to determine the bulk composition of the alloy [34]. From averaging these two, a nominal composition of the Al-Mg alloy has been determined.

For more in-depth details of the exact procedure on these phase and composition determinations, please refer to the work of Corsi et al. [33].

## 2.1.2 Dealloying

Also for dealloying the choice was made to stay as close to the work of Corsi et al., except for necessary changes in the procedure (e.g. cooling), to have better comparable results.

The dealloying process has been done by selective electrolytic removal of Mg from the abovementioned Al-Mg alloy in an air-free (argon) environment, using non-aqueous electrolytes [33, 65]. Because of the reactivity of the nanoporous Al with ions such as  $H^+$  and  $OH^-$ , the environment and materials needed for dealloying need to be chosen carefully. To electrochemically remove Mg from the starting alloy and plate it onto the counter electrode, the reduced working ion on the counter electrode in the non-aqueous electrolyte,  $Mg^{2+}$ , is the same as the sacrificial element Mg. The big benefit here is that the sacrificial element Mg is recovered during dealloying, whereas the downside of this electrochemical removal method is that it is a lot more time consuming. To reduce the time needed for the dealloying process, the Al-Mg alloy has been crushed to small pieces to increase the surface-to-volume ratio and therefore increase the Mg removal rate. As mentioned in the ligament size introduction section 1.1.2.1, the setup has to be cooled down when dealloying to decrease the ligament size of the NP-Al. For this two slightly different setups were made:

- A fridge was used to cool the setup down to  $\sim 0$  °C.
- A bath of dry ice + isopropyl alcohol (IPA) was used to cool down the setup to -78.5 °C, the sublimation temperature of dry ice.

The fridge could not be put into a glovebox as a whole to produce the NP-Al in an air-free argon environment. Therefore, the setup was prepared in an airtight glass container with electrodes as seen in figure 2.2. This container has been prepared in an argon filled glovebox and was sealed well before being put in the fridge, and thus air environment.

The glovebox was kept in atmospheric pressure and the water and oxygen levels stayed below 0.1 ppm [66]. Note that the use of argon as the inert gas is not critical, e.g. nitrogen could also be used. Inside the closed container there is a 50 ml closed off vial with a 0.4 M all-phenyl complex electrolyte as a magnesium ion conducting electrolyte. The APC electrolyte was prepared following the procedure of previous work done in the research group at the University of Pennsylvania [66]. Furthermore, the Al-Mg alloy was used as the working electrode in the vial, and a pure Mg foil was used as counter (and reference) electrode. The electrodes were attached to a Bio-Logic VMP-300 multichannel potentiostat, which controlled the selective removal of the Mg from the alloy as seen in figure 1.4 [33, 67, 68]. Since a too high voltage will have a destructive effect on the APC, a constant voltage of 1 V versus Mg/Mg<sup>2+</sup> has been maintained between the working and reference electrodes. This to dissolve the Mg after which the corresponding Mg dissolution current between the electrodes is measured.



Figure 2.2: Left a schematic overview of the dealloying setup with the fridge. Right a photo of the same setup inside the fridge.

As with the fridge, the dry ice dealloying setup could not be put inside the glovebox. Therefore, the same vial, with the same kind of contents, was prepared inside the glovebox and closed off with a rubber cap to prevent air from coming in. The electrical wire could pierce this rubber cap and make contact with the Bio-Logic VMP-300 multichannel potentiostat, while the vial was kept air tight. The vial was submerged in IPA to cool the vial down evenly. IPA was chosen since its melting temperature is below -78.5 °C, the sublimation temperature of dry ice. A schematic overview and photo of this setup are shown in figure 2.3 below.



50ml closed off vial filled with an APC electrolyte, counter electrode and Al-Mg alloy

Isolating container filled with dry ice and IPA at -78.5  $^{\rm o}{\rm C}$ 



Figure 2.3: Left a schematic overview of the dealloying setup with dry ice. Right a photo of the same setup in the dry ice container.

After the dealloying processes were completed, the samples were checked with EDS in the JEOL 7500F to check the resulting composition.

## 2.1.3 Ligament size

The ligaments of the dealloyed samples were checked with the SEM capabilities of the JEOL 7500F, and with Small-angle X-ray scattering (SAXS) with the Xenocs Xeuss 2.0. The X-ray source used for the sample was Copper K- $\alpha$ . This has an energy of 8.04 keV, corresponding to an X-ray wavelength of 1.506 Å. The corresponding prefactor then becomes  $k = \frac{2\pi}{\lambda} = 4.0784$  Å. Ligament sizes were measured and compared with the ligament sizes of the nanoporous aluminum from the work of Corsi et al. to check if the ligaments are indeed smaller [33].

## 2.2 Hydrogen generation

Additionally, Corsi et al. investigated the amount and rate of hydrogen generation from the reaction of water and the fabricated hierarchical bulk nanoporous aluminum [33]. This is done with a customized Scion 456 gas chromatography (GC) system [34]. As this work is done solely by Corsi et al., the results of this setup are also given here. The author did choose to mention this, as it is important to have confirmation of hydrogen generation by nanoporous aluminum and pure water, and knowledge on how this is tested. For more in-depth details and results, please refer to the work of Corsi et al. [33].

A schematic setup to measure hydrogen is shown in figure 2.4 a [33]. The setup was prepared and sealed in an argon environment in a glovebox, after which deionized (DI) water could be injected using a syringe. To transfer hydrogen produced from the reaction flask to the GC, helium was used. Figure 2.4b shows typical raw GC data. The black, red and blue curves show the amount of hydrogen produced 30, 185 and 380 minutes after injection of water, respectively [33]. Finally, figure 2.4c shows the cumulative amount of hydrogen produced as a function of time [33].



Figure 2.4: (a) A schematic of the setup for hydrogen measurement with GC. (b) Typical raw GC data associated with the amount of hydrogen produced 30, 185, and 380 min after injection of water. (c) Cumulative amount of hydrogen produced as a function of time. [33]

To visualize and appreciate the process of hydrogen generation, Corsi et al. made a video supporting their work. They crushed bulk NP-Al into powder to enhance its hydrogen generation kinetics when in contact with water and put it in a closed off flask on top of a Horizon H-racer, a toy vehicle operating on hydrogen [33]. DI water is then added with a syringe, after which hydrogen is generating and the H-racer starts driving. Their video can be found when clicking the link "sc9b00481\_si\_002.avi (22.95 MB)" on the website of their publication "Hierarchical Bulk Nanoporous Aluminum for On-Site Generation of Hydrogen by Hydrolysis in Pure Water and Combustion of Solid Fuels" [33].

To increase the hydrogen generation rate, one can grind the NP-Al into a fine powder. This increases the density of the NP-Al and thus the surface area per volume reacting with the DI water.

## 2.3 NAFCAR

For the biggest part of this thesis, a more engineering approach had to be taken. The NAFCAR project is applying a lot of physics into a light electric vehicle (LEV). As engineering was a completely new branch for the research group supervised by Prof. E. Detsi at the University of Pennsylvania, it has been a great and fun adventure to be the first to set it up. This did come with some difficulties, which will become clear and will be discussed in the thereby corresponding subsections throughout the rest of the thesis, starting here, in the experimental setup section of the NAFCAR project.

A light electric vehicle which was chosen for the NAFCAR project, the 2007 GEM eL XD (see figure 1.7). Since the LEV is too big to be worked on at the Laboratory for Research on the Structure of Matter (LRSM) at UPenn, a garage was rented at Pennovation Works, a blend of offices, labs, and production space developed by The University of Pennsylvania for many projects, thus including the NAFCAR project.

The 2007 GEM eL XD was chosen since it is light, safe, has a fairly strong 72 V DC motor with a continuous 5 horsepower (hp) and 12 hp peak rating and has a large payload capacity because of the 1.8 m by 1.2 m boot to carry the fuel cell and hydrogen generation setups [69]. This all while keeping the costs inside the budget. The LEV is able to run at a maximum velocity of 25 mph. It comes with nine 8 V batteries connected in series, able to deliver 72 V to the DC motor. It was chosen, despite the weight, to keep these batteries in the LEV as a backup system when the fuel cell system fails to produce (enough) power to run the motor. For safety and simplicity, it was chosen to have manual switches between the fuel cell and battery systems. A simple schematic of this is shown in figure 2.5 below. To reduce the weight, the doors of the LEV were taken off and some interior and exterior weight reduction was done.



Figure 2.5: A simple schematic overview of the electrical circuit and switches for manually switching between the battery and fuel cell systems of the NAFCAR.

#### 2.3.1 PEM fuel cell system

To power this LEV outside of its batteries and run it on hydrogen, it was chosen to add a PEM fuel cell to the vehicle. Since, as a proof of concept, it is not necessary to drive the LEV at 25 mph, the DuraPEM W240 fuel cell stack was chosen [70]. A picture of this FC stack is shown in figure 2.6. This is a relatively cheap 2.4 kW (3.2 hp) PEM fuel cell stack from the company Asia Pacific Fuel Cell Technologies (APFCT) and is believed to be powerful enough to move the LEV [71]. As hydrogen is a dangerous gas to work with, especially in combination with the high voltages and currents coming from the fuel cell, a hazard control plan (HCP) has been made for future use of the fuel cell and all its subsystems. It is highly recommended to read this HCP before handling the

fuel cell system. The HCP will not be discussed in more detail in this thesis, however, all requests for a copy of this HCP will be fulfilled by the author.



Figure 2.6: The DuraPEM W240 fuel cell stack. [72]

Unfortunately, the low costs came with the big drawback that the fuel cell came without any of the necessary subsystems to monitor and/or control output current and voltage, cooling, air (oxygen) flow, hydrogen flow, or show data like temperature and voltage levels of the stack. Since these systems are crucial for the good operation of a PEM fuel cell, building the whole FC system has occupied most of the research time for this thesis. Since this was a major and unexpected setback on the limited time available for this research, the help from three undergraduate students from the University of Pennsylvania, Asaph Lee, Jonathan Mui and Randy Chen, has been very welcome and has been much appreciated. Without the help of these students, the author would not have been able to finish the fuel cell system in time.

Below, in figure 2.7, a schematic overview and design of the FC system is shown. This schematic shows all necessary systems, i.e. the cooling system (top left), air, and thus oxygen, supply system (bottom left), the hydrogen supply system (bottom right) and power control system (top right). All these systems are controlled by an Arduino MEGA 2560 microcontroller, programmed in MATLAB.

Please note that not all parts of the fuel cell system will be mentioned or discussed. The important designs, choices and parts are mentioned in the thereby corresponding sub-subsections below.

As a base, the DuraPEM W240 PEM fuel cell stack from Asia Pacific Fuel Cell Technologies was chosen due to the relatively low cost, while still being able to deliver 2.4 kW of electrical power. The big downside of this stack is that it is only the base stack, without any of the subsystems as mentioned above, which often comes with a fuel cell stack and is set up and calibrated accordingly.

The dimensions (in mm) of the stack in different viewpoints are shown in figure 2.8 [72]. It shows that the FC stack is approximately 17 x 24 x 24 cm, and is thus relatively small and easily fits in the boot of the LEV. The stack weighs  $\sim$ 10.5 kg and the interfaces for the fluids (i.e. hydrogen, air and coolant water) are shown in figure 2.9, where the anode inlet represents the hydrogen inlet



Figure 2.7: A schematic overview and design of the fuel cell system. Top left: the cooling system. Bottom left: air, and thus oxygen, supply system. Bottom right: the hydrogen supply system. Top right: the power control system. All of these systems are controlled by an Arduino MEGA 2560 microcontroller, shown at the bottom.

[72]. Note that also the plus and minus poles of the electrical circuit of the FC are shown on the left image in figure 2.9. The stack can be mounted in vertical directions only, i.e. with the blue bars shown in figure 2.6 facing downwards. The right orientation is shown in figure 2.9.

The operating conditions for the DuraPEM W240 are quite extensive and will be summarized here [72]. The rest of the subsystems are all based on these conditions.

- The stack is able to deliver 0-120 A of current, with a recommended current operating range from 37.5 to 100 A.
- It is able to deliver 0.5-1 V per cell, and has a total of 40 cells.
- The purity of the hydrogen needs to be grade 4 (99.99%  $H_2$ ) or higher.
- A hydrogen flow of 1.2 stoic is needed, i.e. a flow of 1.2 times as much hydrogen as the fuel cell consumes, and needs to have a relative humidity (RH) of 85-100%.
- The hydrogen inlet pressure should always be kept below 0.48 bar.
- The oxidant inlet is ambient air where the flow needs to be 2.8 stoic (with a minimum of 80 L/min), with a maximum inlet pressure of 0.34 bar and a RH of 90-100%.
- The composition of the coolant ideally is deionized water with a flow of at least 10 L/min.
- The conductivity of the coolant should always stay below 10  $\mu$ S/cm at a temperature of 25 °C.
- The target operating temperature is 60 °C, while the environmental temperature range is -20 to 60 °C.



Figure 2.8: Physical dimensions of the DuraPEM W240 (units in mm). [72]



Figure 2.9: Indications of the interfaces for the fluids (i.e. hydrogen, air and coolant water), where the anode inlet represents the hydrogen inlet. [72]

Figure 2.10 shows the polarization curve for a fully conditioned stack operating at nominal conditions [72]. The dashed lines indicate a stack to stack manufacturing variability. Here it is seen that ideally the FC is run at 100 A and 24 V, generating the 2.4 kW of power.



Figure 2.10: The polarization curve for a fully conditioned stack operating at nominal conditions. [72]

#### 2.3.1.1 Cooling system

For the cooling system it was chosen to build a custom loop for the cooling, with a 12 V DC SEAFLO SFDP1-055-060-55 diaphragm pump and two fin tube heat exchangers with 12 V DC radiator fans, all connected by non-conducting rubber hose. The pump is able to deliver a coolant flow of 20 L/min, well above the recommended 10 L/min. These systems are all on or all off for simplicity. This can be controlled with the Arduino microcontroller and, for safety, can be manually shut down. The coolant consisted of ~80% DI water, ~20% ethylene glycol and a bit of an anti-corrosive and anti-bubble forming liquid to minimize corrosion and keep the electrical conductivity of the coolant as low as possible. To keep the electrical conductivity below the recommended 10  $\mu$ S/cm, a deionizer was added. The flow through the deionizer, and thus how much fluid is deionized per time unit, can be manually controlled by opening or closing the needle valve of the diversion loop around the deionizer. The temperature of the fuel cell stack is monitored via the internal thermistor. This thermistor was read by the Arduino microcontroller and showed live. A photo of this setup is shown in figure 2.11 below.

It was chosen to run all the subsystems on an additional 12 V battery, with the exception of the humidifiers which run at 24 V (two 12 V batteries in series). It was chosen to power these subsystems independent from the FC stack and LEV for simplicity and to make sure the subsystems work independently from the other systems. Please remember that a schematic overview of this, and all other subsystems, is shown in figure 2.7.

#### 2.3.1.2 Air supply system

Since it is recommended to have at least a 2.8 stoic air flow, a 12 V SEAFLO SFIB1-130-01 air blower was chosen to have an abundant flow, with a maximum of 3650 L/min. An air filter was added to ensure no dust or other unwanted particles are coming into the fuel cell.



Figure 2.11: The cooling subsystem for the fuel cell. In blue the coolant tank, black the fin tube heat exchangers with radiator fans, orange the coolant pump, white the deionizer and silver the FC stack, all connected by non-conducting rubber hose.

It is common to add a membrane based humidifier to humidify the air supply [73]. Here it was not chosen to go with this method of humidifying the air supply, since there was no well-suited membrane humidifier and to reduce costs. Instead, a humidifier system was designed and made, as seen in figure 2.12. This humidifier system consisted of two clear tanks fit together with their openings pointing towards each other. The bottom tank contains DI water and eight 400 ml/h ultrasonic humidifiers, closed off by a clear plate with holes for the water vapor to go through. The plate separating the two tanks was added for stability of the height of the water on top of each humidifier when the vehicle is driving, to increase the efficiency of the humidifiers. The top tank seals off the whole so only air from the blower goes in, and humidified air flows out of this top tank to the fuel cell. Finally, holes for the electronics and a refilling cap for refilling the DI water were added, all placed such that the top tank remains airtight.



Figure 2.12: Humidifier design (left) and prototype system (right). The system consists of two clear tanks fit together. The bottom tank contains DI water and eight 400 ml/h ultrasonic humidifiers, closed off by a clear plate with holes for the water vapor to go through. The top tank seals off the whole so only air from the blower goes in, and humidified air flows to the fuel cell. Finally, holes for the electronics and a refilling cap for the DI water were added.

## 2.3.1.3 Hydrogen supply system

For the hydrogen supply system a few different designs were thought of and made. The nanoporous aluminum is not allowed to come in undesired contact with air or water. The occupied volume at atmospheric pressure increases drastically when the NP-Al reacts with water and forms hydrogen. The materials used should be able to withstand heat from the reaction, and the hydrogen exiting the

hydrogen supply system should be of high purity. This all needs to hold while keeping the occupied volume as low as possible. With these conditions, one can imagine a solid design had to be made.

As an example of these multiple designs, a design which did not make it to the final fuel cell system is shown here. It is included here to get a wider view on possibilities for solutions, and as a possible base design for future applications with NP-Al. In figure 2.13 a side view schematic of a NP-Al dispenser is shown. This dispenser uses hydroxy propyl methyl cellulose (HPMC) capsules, dissolvable in water, to hold certain amounts NP-Al. The volume of these capsules was chosen to be  $\sim 1 \text{ cm}^3$  to fill for about half with 1 gram of NP-Al and the other half argon gas, as the preparation of these capsules would happen in an argon filled glovebox. With this, the user of the dispenser system can easily choose how much NP-Al gets used to the gram precise. These capsules will be dispensed into a tank with DI water. by a specially designed rotating mechanism to close off the capsule holder from the water and hydrogen tank. The benefit of having a tank with a large enough amount of water here is that heat doesn't influence the system. Which also is the downside as the heat energy coming from the reaction gets lost in this design. The tank is designed to withstand a pressure of at least 10 bar because of the volume increase of the reaction products versus the reactants. Finally, the rotating mechanism as shown in a CAD design in figure 2.14 has been designed such that it opens up when the cavity is on top to let gravity push a capsule in, while it being closed when the capsule is dropped into the tank so there is no, or as little as possible, gaseous water coming into the capsule holder. A supporting video can be found by clicking here, or by following the link in reference [74].



Figure 2.13: Side view schematic of the NP-Al dispenser.

Figure 2.14: CAD design of the rotating mechanism for the NP-Al dispenser.

Unfortunately, due to time and resources, this design has never been finalized and no prototype has been made. Major simplifications were made, cutting the possibility of using a variable amount of NP-A1. As seen in figure 2.15, the design used contained two stainless steel tanks, both able to withstand at least 10 bar, one containing NP-A1 and the other containing DI water with a volume of 20 and 7.5 L respectively. The NP-A1 tank needs to be 20 L so that the pressure of the generated

hydrogen gas will always stay below 10 bar when a maximum of ~150 g of NP-Al has been fully reacted. The orientation of the setup is trivial since the H<sub>2</sub>O tank holds the DI water in a with air pressurizable rubber bladder to push the water out. Metal tubing is used because of the permeability of hydrogen through various materials. To start off, DI water is in the H<sub>2</sub>O tank, NP-Al in the NP-Al tank (for example filled with unreactive argon or nitrogen gas), and all valves are closed. A check valve is placed to prevent fluids from going into the H<sub>2</sub>O tank. Both valves 1 and 2 are being opened, allowing the DI water to flow into the NP-Al tank, after which both valves will be closed again. Time will be passed to let reaction develop. Valve 1 can be opened after which the 2-step pressure regulator is able to read out the generated pressure. The valves on the regulator can then in turn be opened such that the user determines the flow and pressure of the hydrogen gas into the fuel cell.



Figure 2.15: Schematic overview and photo of the hydrogen supply system. Here the 2-step pressure regulator is missing from the photo.

As seen in figure 2.7, additional solenoid valves have been added which are controlled by the Arduino microcontroller, a check valve is added for a recirculation loop to reuse the leftover hydrogen of the outlet of the fuel cell and a flashback preventer is added to prevent fire from coming into the fuel cell when hydrogen at the outlet accidentally ignites. Note that there is no humidifier added, even though the recommended conditions indicate an 85-100% relative humidity. This was done to simplify and reduce the costs of the hydrogen supply system, because it is believed that the water reacting in the NP-Al tank add to the RH and because it is believed that the impact of a lower than 85% RH does not impact the performance of the fuel cell too much. This is thus far unknown and needs testing when aiming for a higher efficiency.

#### 2.3.1.4 Power control system and test load

The voltage generated by the fuel cell is varying from 20 to 40 V while the engine in the LEV runs at a stable 72 V. For this a DC-DC converter needed to be added. Because high load DC-DC converters are relatively expensive, it was chosen to have four lower power DC-DC converters in parallel to distribute the load through each converter as shown in the schematic in figure 2.16. Each converter is able to handle a maximum of 30 A, totaling to 120 A, the maximum current from the fuel cell system. The converters are able to boost the varying input voltage to a stable 72 V. Because the voltage is boosted, the current needs to be lowered since the total power (P = VI) needs to be conserved. Rectifier diodes, with a high resistance in one direction and a low resistance in the other direction of

the current, have been added after each converter to ensure a current flow in one direction, and to ensure there is an equal load on all four converters. Finally, circuit breakers have been added before each converter to cutoff the power when there is a current of more than 30 A.



Figure 2.16: Schematic overview of the DC-DC converter setup.

For testing the FC system without the need to add the whole system to the LEV, a custom load was added. This load was made out of three connected high resistance NiCr-A ribbons to distribute the load in three parts. NiCr-A is nickel-chromium wire with 80% nickel and 20% chromium. This resistance wire heats up under load, converting electrical energy into thermal energy.

#### 2.3.1.5 Arduino microcontroller

An Arduino MEGA 2560 was used to monitor and control all in- and outputs from the fuel cell system. This microcontroller was programmed in MATLAB to graph both pressures from the pressure sensors and the fuel cell temperature versus time. It does this in real time by sending data over Bluetooth to a connected computer so the operator does not need to be in direct contact with the FC system. The Arduino is able to control the cooling system (pump and fans), air blower, humidifiers and the two solenoid valves of the hydrogen supply system by turning them on or off. An image of the graphical user interface (GUI) is shown in figure 2.17 below. Here, valve 1 is controlling the solenoid valve of the hydrogen supply system input and valve 2 is controlling the solenoid valve of the hydrogen supply system of hydrogen in the hydrogen supply system, while Pressure 2 indicates the pressure of hydrogen in the hydrogen supply system on or off. With the Connect button the Arduino gets connected with the computer via Bluetooth, and the Read button lets the Arduino start plotting the pressure and temperature graphs.

Since the Arduino controls currents at 5 V, relays were added to the system to control the 12 V systems. The setup here is made such that when there is a current flowing from the Arduino, the 12 V system is allowed to have a current flow. When testing this it worked perfectly, however, after turning the system off and then on again, often sparks appeared and the system shut down. This was due to possible residual current in each one of the loads (e.g. air blower). When turning the system on again, this induced a very short but high peak current, short circuiting the setup. Therefore, also here rectifier diodes were added on a loop around each of the loads. These rectifier diodes again have a high one-way resistance, in this case in the opposite direction of the desired current flow. This means that when the system is on, no current is flowing through the rectifier diode, yet when it is off, current is able to flow through the diode in the opposite direction. This means that when the system is on the opposite direction. This means that when the system is able to flow back into the load where is gets used, making sure this high peak current is gone. In figure 2.18, a schematic overview of the relay with rectifier diode setup is shown.



Figure 2.17: A screenshot of the GUI as shown on a computer connected to the Arduino with Bluetooth.



Figure 2.18: A schematic overview of the relay setup, including rectifier diode to ensure a stable control over the various 12 V systems.



## 3.1 Nanoporous aluminum

#### 3.1.1 Al-Mg alloy

From the experiments as described in section 2.1, the resulted alloy had a nominal composition of  $Al_{30}Mg_{70}$  at. %. This near-eutectic alloy contained two microstructural phases, as can be expected when looking at the Al-Mg equilibrium phase diagram seen in figure 3.1 [33, 75, 76].



Figure 3.1: Al-Mg binary phase diagram. [75]

As seen in figure 3.2, the darker areas correspond to Mg and the lighter areas to  $\beta$ -Al<sub>12</sub>Mg<sub>17</sub>, indeed indicating two phases [76].

The EDS resulted in a measured hypoeutectic composition of  $Al_{24}Mg_{76}$  at. %, where the ICP spectroscopy resulted in a measured hypereutectic composition of  $Al_{37}Mg_{63}$  at. % [76]. From averaging these, a nominal composition of  $Al_{30}Mg_{70}$  at. % has been determined [33].

For more in-depth results from these phase and composition determinations, please refer to the work of Corsi et al. [33].



Figure 3.2: Low-magnification SEM image of the Al-Mg alloy. This alloy has been pretreated by etching to enhance the contrast. The darker areas indicate the Mg phase and the lighter areas indicate the  $\beta$ -Al<sub>12</sub>Mg<sub>17</sub> phase. [33]

## 3.1.2 Dealloying

First of all, the dealloying process of the dry ice setup at -78.5 °C could not be completed. This is most likely due to the solubility of one or multiple salts in the APC electrolyte, as there were crystals found in the APC solution after cooling down the vial. This was found for both the fridge (figure 3.3 left) and dry ice (figure 3.3 right) setups, although only affected the dry ice setup enough to keep the Al-Mg alloy from dealloying properly. The salts in the dry ice dealloying process were crystallized so much that the conductivity of the electrolyte went down. As a result, the current was measured to be as low as  $\sim 3 \mu$ A. When compared to the work of Corsi et al., this would ensure a dealloying process of about 6 years [33]. Therefore, the dealloying process inside dry ice was aborted after three days. After the vial was heated up to room temperature, indeed, after some mixing, the found crystals were dissolved again.



Figure 3.3: Crystalline structures found in the cooled down vials. Left the APC electrolyte solution at 0  $^{\circ}$ C, right the APC electrolyte solution at -78.5  $^{\circ}$ C.

Figure 3.4 shows a typical current profile as a function of time (I vs. t) for magnesium removal from the Al-Mg alloy inside the fridge. This was done at a constant potential of 1 V vs Mg/Mg<sup>2+</sup>, over a total time of ~253 hours at 0 °C and with an average current of ~0.32 mA. Unfortunately, due to the setup short circuiting (seen by the peak at the end of the first graph) and a power outage of

the building (second cutoff), the dealloying needed to be restarted twice within the same process. The higher current at the start of every process is coming from a slightly higher temperature of the solution. This because the solution has not been cooled down completely to 0  $^{\circ}$ C yet, and therefore, already dissolved ions in the APC are plated onto the magnesium foil easier. The higher bump at the first 20-25 hours of the process is coming from an easier electrolytic removal of Mg ions on the surface of the crushed Al-Mg alloy pieces. Although lots of small peaks are expected in these curves, it is unknown why the second graph shows more and higher peaks than the other two parts. It is believed that this has no influence on the dealloying process itself.

The dealloying process could not be finished completely due to the large amount of time it takes to fully dealloy a sample. First of all it was checked if the dealloying process took place at all. As seen in table 3.1, the EDS results of three samples from three different pieces show an Al at. % ranging from 79.4% to 94.5%, compared to a 30 at. % before dealloying. The density of the retrieved NP-Al was measured to be  $\sim 2 \text{ g/cm}^3$ . Most importantly here is the comparison between room temperature and freezing point dealloying, which will be made in section 4.1

Sample #	<b>Al</b> (at. %)	<b>Mg</b> (at. %)
1	79.4	20.6
2	91.4	8.6
3	94.5	5.5

Table 3.1: EDS results of three samples of the mostly dealloyed Al-Mg.

#### 3.1.3 Ligament size

Since the electrolytic removal of Mg goes from the surface of a piece of Al-Mg alloy slowly inwards, the ligament size of the nanoporous aluminum at the surface of a piece could be measured with the help of SEM imaging, even though the dealloying process has not been completed entirely. Some of these resulting SEM images are shown below in figures 3.5 and 3.6. The images show a hierarchical nanoporosity with both macro- and mesoscopic ligaments because of the hypo- and hypereutectic compositions of the Al-Mg alloy. Here it is seen that the macroscopic ligament sizes range from  $\sim 0.3 \ \mu m$  to  $\sim 2 \ \mu m$ , and the mesoscopic ligament sizes range from <5 nm to  $\sim 20 \ nm$ .

Additionally, the SAXS results as seen in figure 3.7 show the pore size distribution. Here on the x-axis the Q values are shown on a logarithmic scale. From this the pore size d can be calculated with  $d = \frac{2\pi}{Q}$ . The y-axis shows the intensity of the corresponding pore size on a logarithmic scale and in arbitrary units. Most of the pores (i.e. intensity > 2.0) are distributed between  $Q = 10^{-2} \text{ Å}^{-1}$  and  $10^{-1.22} \text{ Å}^{-1}$ . This corresponds to d values of ~63 nm and ~10 nm respectively. As additional examples, the corresponding pore sizes of  $Q = 10^{-1.62} \text{ Å}^{-1}$  (value corresponding to the highest intensity) and  $10^{-0.8} \text{ Å}^{-1}$  are ~26 nm and ~4 nm respectively.



Figure 3.4: Typical current profile as a function of time of the Mg removal from the Al-Mg alloy at a constant potential of 1 V vs.  $Mg/Mg^{2+}$ . Three different curves are seen for the same single process as there has been two power cutoffs, interrupting the dealloying process. Please note that the x-axes show different ranges of time.



Figure 3.5: SEM images of the fabricated hierarchical nanoporous Al at various magnifications. Here both macro- and mesoscopic (smallest features on bottom right image) ligament sizes are seen.



Figure 3.6: Two high magnification SEM images of nanoporous aluminum with ligament sizes in the range of <5-20 nm.



Figure 3.7: SAXS results. Here the x-axis shows the Q values on a logarithmic scale. The y-axis shows the intensity of the corresponding pore size on a logarithmic scale and in arbitrary units.

## 3.2 NAFCAR

#### 3.2.1 Cooling and supply systems

The cooling system was able to deliver a coolant flow of 8.9 L/min, slightly less than the 10 L/min advised by the fuel cell manufacturer [72]. Since two radiator fans produce a lot of cooling power for this setup, 8.9 L/min was considered enough for the NAFCAR project.

The air supply system was able to deliver an airflow of over 1500 L/min with a relative humidity of 81-100%.

At the time of writing, the hydrogen supply system has not been able to sustain a long and high enough hydrogen flow to run the fuel cell system. Therefore, a grade 4 (99.99%  $H_2$ ) hydrogen cylinder with high pressure has been attached to the FC system for testing purposes.

#### 3.2.2 Fuel cell system

The PEM fuel cell system worked first try, i.e. it turned on when all the systems were turned on and there was a hydrogen and air flow. The fuel cell ran for 85 seconds with the hydrogen cylinder attached. This was seen by red LED indicators on the DC-DC converters turning on. The fuel cell was able to generate a current of ~51 A. Unfortunately it was not possible to measure the voltage, this will be discussed in corresponding section 4.2.2. After a quick check up on all the systems, the fuel cell was turned on for the second time. This time it ran for 202 seconds, confirming the results from the first run. The high resistance ribbons indeed became hot, although no temperature measurement was done. The DC-DC converters did not convert the electrical power as the current of ~51 A was found both before and after the converters. Although not measured, because of the conservation of power (P = VI), the voltage also remained the same before and after the converters.

After these two tests, a third and fourth test were done, both unsuccessful. The third test was done with hydrogen generated by combining bulk aluminum and 2 molar sodium hydroxide dissolved

in DI water as reactants. Sodium hydroxide acts as a catalyst proceeding the hydrogen reaction as shown in equations 3.1 and 3.2 [77, 78]. This was done as a test for future runs with nanoporous aluminum. NP-Al was not chosen for this run, as it takes a lot of time and resources to be produced. This run was unsuccessful due to a too low pressure in the NP-Al tank generated by the aluminum and sodium hydroxide. After this, it was tried to run the FC system on pure hydrogen from the hydrogen cylinder again, though also unsuccessful. Reasons for this will also be discussed in section 4.2.2. An image of the prototype fuel cell system is shown in figure 3.8. Please note that this is a first prototype, which needs some wiring cleanup etc., and that the  $H_2O$  tank from the hydrogen supply system is not attached in this image as it was being prepared for use at that moment.



Figure 3.8: An image of the prototype fuel cell system. Note that this is a first prototype, which needs some wiring cleanup etc. The  $H_2O$  tank from the hydrogen supply system is not attached as it is being prepared for use.

$$2Al + 6H_2O + 2NaOH \rightarrow NaAl(OH)_4 + 3H_2$$

$$(3.1)$$

$$NaAl(OH)_4 \rightarrow NaOH + Al(OH)_3$$
 (3.2)

After these four tests, there was not enough time left for the author of this thesis to disassemble some systems, figure out what went wrong, fix it and do more tests. Fortunately, research on running the fuel cell system has not ended and, at the moment of writing, progress is still being made by other students at the University of Pennsylvania. A successful fifth test has been done, without any additional measurements. This test was solely done to check if the fuel cell worked again. No changes to the system were made for this test.

## 3.2.3 GEM eL XD

As one would conclude based on the previous paragraph, the LEV has not been run on hydrogen yet since the FC system is not finalized. First the FC system needs to be running stable and at known voltage, current and total power outputs.



## 4.1 Nanoporous aluminum

Since nanoporous materials, and thus NP-Al, are fairly new to research, let alone applications, some big steps towards the mass production of usable NP-Al have been made. Still, a lot has to be done before nanoporous aluminum can be found in profitable products. As mentioned before, unfinished research still exists. Here in the discussion section these partial findings, and some still existing problems will be discussed, after which ideas to solve these problems are given in the future research section 5.

#### 4.1.1 Dealloying and ligament size

When dealloying, it was expected and found that the dealloying time increases due to a lower current compared to the work of Corsi et al. [33]. This lower current is due to the lower temperature of the dealloying setup influencing the solubility of the salts in the APC electrolyte solution [79, 80]. Although it looks like a successful first attempt to dealloy on a lower temperature, the process has to be redone because of the two power cutoffs during dealloying, and the dealloying process not being completed entirely.

A comparison between SEM results of the work of Corsi et al. [33] and SEM results of this thesis is shown below in figure 4.1. The findings on the ligaments sizes of this thesis definitely needs to be confirmed and validated with higher resolution SEM images with less noise (astigmatism etc.), and with EDS and SAXS. Nevertheless, it seems that there is a fairly clear difference between the ligament sizes of the nanopores when dealloying happens at room temperature, and when dealloying is done at around 0 °C. The maximum ligament sizes are about the same, where the smallest ligaments seem to definitely be smaller, and the average ligament size seems to be smaller too. From figure 3.5 it can be seen that there is a hierarchical nanoporosity too, beneficial for water flow when producing hydrogen. This confirms that the two Al-Mg alloy phases also existed in this sample.

The average pore size found with SAXS is higher than the SEM images show. This can be contributed to the fact that there is a hierarchical porosity, because the samples have not been fully dealloyed, and that the sample used for SAXS was different as the sample used for SEM imaging, though both samples came from the same batch. As mentioned above, these tests should be done again to confirm the results and remove these final uncertainties. SAXS results should be used as a confirmation on top of the SEM results, since it gives a good overview on the distribution of the pores both inside and on the surface of the sample imaged by the SEM, but does not show structural details.

#### 4.1 Nanoporous aluminum



Figure 4.1: A comparison between ligament sizes of the work of Corsi et al. [33], dealloyed at room temperature (right), and when dealloyed at  $\sim 0$  °C (left). Please note that the image of Corsi et al. has been edited to be comparable to the findings from this thesis by cropping the image, and downsizing the measuring bar by a third from 150 nm to 100 nm to be the same for an easy comparison.

## 4.1.2 Hydrogen production

The biggest question here is how to increase the hydrogen generation yield to 100%, with an as high as possible hydrogen yield rate. As explained throughout this thesis, the ligament size can have an effect on the hydrogen generation yield. In future research section 5.1, it will be discussed on how to start checking for the effect of the ligament size.

After the period of research had ended some additional thoughts were laid on the table, indicating another factor possibly influencing the hydrogen yield from nanoporous aluminum. As explained in subsection 1.1.2, Corsi et al. created a hierarchical nanoporosity. This helps to get the water to places faster and easier within the, let's say "bulk", NP-Al. The images in figure 1.3 on page 5 clearly show this hierarchical nanoporosity. On the right it is seen that the ligaments (bulk NP-Al) of the macropores is much larger than the ligaments of the NP-Al. In this image it is already seen that the middle of the three ligaments is over 500 nm in diameter, and this is not the biggest macro ligament, by far.

Also, the nanopores have been generated by removing magnesium from the Al-Mg alloy. This means that there has been a way for the magnesium to be removed from inside this bulk Al-Mg alloy and, when partially dealloyed, also through the bulk NP-Al. At first thought one would think that if a magnesium ion can be removed from the Al-Mg alloy, through this bulk NP-Al, water (assuming it has not reacted to form  $OH^-$  yet) should be able to go inside. This is not necessarily the case though, as the crystal *ionic* radius of the magnesium is 0.86 Å [81], whereas the *molecular* radius of water is 1.38 Å [82], approximately 1.6 times as large. When water reacts with the top layer of the bulk pieces of NP-Al it forms alumina. At standard pressures and temperatures aluminum has a face-centered cubic structure [83], whereas alumina can have different types of crystalline structures [84]. This means that besides the difficulty of water flow through the bulk NP-Al, there is also a structural change when aluminum is converted into alumina by the water. One layer of this alumina should not be a big problem, although a 500 nm thick macro ligament, containing at least 25 layers of (20 nm thick) NP-Al layers can potentially become a problem for water flow in the bulk NP-Al. While water (and potentially OH<sup>-</sup>) can diffuse through alumina [85–88], it can

still potentially close off the gateway for this water flow because of all these layers, or at least slow down the process of hydrogen generation. As a first thought, the diffusion of water through these few nanometers of alumina on each nano ligament is probably quite fast, where the diffusion through these multiple layers of NP-alumina in the macro ligaments will take those approximate 22 hours which Corsi et al. needed for their NP-Al sample to nearly fully react [33, 86, 88]. This would mean the nano ligament size is more important for reaction rate, where the size of macro ligaments are more important for total hydrogen yield. Additionally, H. Nie et al. found that when a small spherical core of aluminum reacts with liquid water, the reaction mainly occurs at the surface of the shrinking aluminum core, thus inside the growing aluminum hydroxide layer [89]. When this aluminum reacts with water vapor, it gives different results. Water vapor can be formed when the NP-Al reacts with water because of the very high reactivity and the production of heat during this reaction. In this case, the reaction likely occurs at the outer surface of the growing alumina shell. This shell is rigid and is fractured multiple times while it is growing. After a shell is fractured, a new shell grows around this oxidizing aluminum core [89]. These findings can again influence the formation of alumina, and thus influencing the hydrogen yield (rate).

Since this field is quite new for (mass) production of hydrogen, and there are quite a few uncertainties and unknowns, a lot of research and development needs to be done. It is definitely possible the ligament sizes are not the only factor influencing the hydrogen yield and the rate at which hydrogen is produced. Both are essential for a profitable company taking the route of NP-Al to fulfill the increase in hydrogen demand. Ideas for future research on this will again be given in the associated section 5.1.

## 4.1.3 Sustainability and costs

Hydrogen produced from NP-Al and water, including the production of aluminum used for this NP-Al, can only be considered sustainable when there are no greenhouse gas emissions during these processes. There are many energy intensive processes involved. One of these processes convert  $Al_2O_3$  (l) to Al (l) and  $O_2$  (g), at temperatures above 1000 °C [45, 46, 90]. Fortunately, there is thermal energy released during the process of hydrolysis of NP-Al. However, because of the need for a high temperature in the aforementioned process during aluminum smelting, the carbon-based anodes used in this process react with the released oxygen to produce  $CO_2$ . Therefore, this process has a carbon footprint and an alternative is needed. Prof. E. Detsi and J. Corsi, together with their startup Hydropore, proposed to use recycled secondary aluminum [33]. The 2016 global market of high purity secondary aluminum was over 22 million tons and is expected to keep growing [91]. So, there is enough secondary aluminum for large scale production of hydrogen with a reduced (or no) carbon footprint. Also, as mentioned in section 1.1.1, the company Elysis claims to be able to commercialize the production of carbon-free aluminum in the near future [28]. This would allow a sustainable hydrogen production from primary aluminum.

To reduce the costs of producing hydrogen via NP-Al, and make the process more feasible, Corsi et al. also proposed to heat treat the high purity aluminum hydroxide [33]. This high purity aluminum hydroxide is co-produced during hydrolysis of NP-Al and, when heat treated, makes nanostructured alumina with a high specific surface area, also known as activated alumina. This activated alumina is highly valuable and can be sold to reduce the costs of producing hydrogen. Examples of applications for this activated alumina include fluoride adsorbents for water treatment, catalysts and catalyst supports, desiccants, bio-ceramics and separators for lithium-ion batteries, with a 2016 global market of over 11 million tons, also expected to keep growing [92]. This indicates it is unlikely that the activated alumina from the processes of Corsi et al. will saturate the activated alumina global market.

# 4.2 NAFCAR

Since the research and development on the NAFCAR project has not finished at the time of writing, it is hard to discuss and/or compare this work to other findings. Therefore, a lot of the discussion will also be on how to the process of the development done so far could be improved, and why the development has not finished yet. Plans and ideas for the future of this project will be given in section 5.2.

For the NAFCAR project, before the project even began, some critical underestimations were made. Initially it was thought that a fuel cell system would "just" need an air and hydrogen supply, after which it would be attached to the vehicle and the vehicle would be able to drive on the generated power. This, although very much simplified, would indeed be possible if one chooses to purchase a very expensive fuel cell setup, which would be prepared by the selling company. These types of fuel cells, in the range of power we need ( $\sim 2$  - 5 kW) can be way more than twice the price of a bare fuel cell stack as the one from Asia Pacific Fuel Cell Technologies used for this thesis. These high prices are not feasible for a proof of concept like the NAFCAR project. Therefore, which at the same time was the underestimation for this project, the subsystems described in section 2.3.1 had to be designed, developed and made. This, in combination with a predetermined limited amount of time ( $\sim$ 6 months) available for this thesis, made it unrealistic to finish the NAFCAR project in time with only one person working on it. To get as far as possible, supervising professor E. Detsi from the University of Pennsylvania rapidly found three undergraduate students willing to assist with this project, for which the author is very grateful. Without the help of these students, even the fuel cell systems would likely not have been finished in time. Additionally, the procedure of purchasing an expensive item like the fuel cell, including the delivery time of Asia Pacific Fuel Cell Technologies, took about two months. This did not speed up the development process, although gave the author and helping students enough time to start well prepared. Unfortunately, APFCT was not prepared to be helpful during the design process. The information for the fuel cell stack they delivered was minimal, and further contact was ignored after the purchase was completed. The author therefore does not recommend a collaboration with APFCT, unless enough in-house experience is present.

#### 4.2.1 Cooling and supply systems

In the cooling system, the diaphragm pump is exactly right. Its specifications fit the fuel cell system well, and also its dimensions for tubing fit. The radiator fans are excessive though. These have not been necessary so far, and as a proof of concept project, the fuel cell will not be running for large amounts of time and thus not heat up too much. This means the two fin tube heat exchangers, without the radiator fans, or only one set of heat exchanger + radiator fan will suffice for cooling for this specific project. As seen in the results, the pump was able to deliver a flow of 8.9 L/min, a bit lower than the recommended specs of 10 L/min, while the specifications of the pump indicated it was able to deliver a higher flow of 20 L/min. The highest measured flow was 18.6 L/min, where there was minimal tubing present. This lower flow is due to the internal frictional forces of the whole tubing system. The fine tube heat exchangers have a large tube length with a lot of 180-degree corners. For example, removing one of these heat exchangers, which is thus possible for this setup, will most likely increase the flow to above the recommended 10 L/min.

For the air supply system, the air blower is also excessive. Since there is a *minimum* airflow specification of the fuel cell, this does not matter too much for a proof of concept like the NAFCAR project. Since there is more air going through the fuel cell, this air also needs to be humidified. This greatly decreases the efficiency of this fuel cell system, as those eight humidifiers need quite some power to run, and also the DI water used for humidification has to be prepared for the system too. If efficiency is of importance, an air blower with such an excess of airflow like this is unnecessary and not recommended.

For the hydrogen supply system, a lot of different setups could be designed and tested. It was chosen that the most easy, cheap and fast to be prepared system would be made. Also, the initial test of the fuel cell system was done with a provided grade 4 hydrogen cylinder, which indeed was successful. As mentioned in the results section, the hydrogen supply system has not been able to sustain a long and high enough hydrogen flow to run the fuel cell system from NP-Al. There was not enough NP-Al to begin with. To still try and test if the fuel cell would run on on-site generated hydrogen,  $\sim$ 35 g of bulk Al and 2 M NaOH in DI water was put in the NP-Al tank shown in figure 2.15. This generated a pressure of about 7 psi above atmospheric pressure inside the NP-Al tank. There was indeed a flow through the system, though no current was generated by the fuel cell system. There are multiple mistakes made during this test. The two most important ones are that there needs to be a lot more (nanoporous) aluminum to generate a lot more hydrogen, and that the two reactants need to be mixed in an oxygen free environment so that there is no oxygen going into the hydrogen fuel input of the fuel cell. This was not the case in our test, where it was done in an atmospheric environment. Increasing the hydrogen pressure mainly has two advantages, it increases the amount of hydrogen to be used so a longer runtime is possible, and the percentage of hydrogen gas inside the tank increases. That there is always another gas than hydrogen inside the NP-Al tank does not have to be a problem, as long as the gas or other material is not reactive with the fuel cell. A list of undesired materials is given in tables 4.1 and 4.2 below. If the NP-Al tank is prepared in, for example, an argon environment in a glovebox, and hydrogen is generated such that the tank contains a pressure of 2 bar (50% H<sub>2</sub> + 50% Ar), only the hydrogen flow needs to be doubled, meaning a stoic of 2.4 instead of 1.2.

Description	Specification oxidant
Sulfur dioxide (SO <sub>2</sub> )	< 0.01 ppm
Nitrogen monoxide (NO)	< 0.01 ppm
Nitrogen dioxide (NO <sub>2</sub> )	< 0.01 ppm
Carbon monoxide	< 1 ppm
Carbon dioxide	< 1% vol

Table 4.1: Undesired materials in the oxidant for the fuel cell. [72]

#### 4.2.2 Fuel cell system

Since the end of the research period was near, it was a big relief that the system worked at first try. As mentioned in the results, the fuel cell has run for a total of  $\sim 287$  s, generating a current of  $\sim 51$  A. Since the voltage and current meter available was the same device, and the author and fellow researchers preferred to know the current over the voltage, no voltage measurements have been done since there have only been two successful tests.

The DC-DC converters did not work during both tests, although the converters let the current

Description	Specification fuel	
Composition	Grade 4 hydrogen gas (99.99% H <sub>2</sub> )	
Total hydrocarbons	< 2 ppm	
Total sulfur compounds	< 0.004 ppm	
Total halogenated compounds	< 0.05 ppm	
Oxygen	< 1 ppm	
Carbon monoxide	< 1 ppm	
Carbon dioxide	< 10 ppm	
Formaldehyde	< 0.01 ppm	
Formic acid	< 0.2 ppm	
Ammonia	< 0.1 ppm	

Table 4.2: Undesired materials in the fuel for the fuel cell. [72]

pass through. They have been thoroughly tested and setup individually, and as a collective before put into the FC system. It is unknown why the converters were not working properly, and further research is needed.

There are a few proposed reasons on why the succeeding tests could be unsuccessful, and resulted in no current generated from the fuel cell. These reasons will be listed below. Ideas or solutions to these problems will be given in the future research section.

- Since the airflow and humidification are way higher than the specified amount, this could have a negative impact on the system. Condense could have formed on the platinum stack, negatively impacting the possibilities of reactions to occur with oxygen at the interface. Since the air supply system is closed off from the atmosphere, with as only exception the exhaust, condense could have remained on the stack for multiple days.
- The oxygen in the fuel supply could have had a destructive effect on the FC stack. As indicated in table 4.2, a maximum of 1 ppm is allowed, where in our system it is possible that the mixed gas contained  $\sim 14\%$  of oxygen.
- Although thoroughly tested, a malfunctioning in one of the subsystems or wiring of the system could have been the impeding factor. The weakest link in the system is the multiple valves in the hydrogen supply system. These valves are, besides indicated by the microcontroller, confirmed open by listening to a clicking noise made when the valves open or close. Problems with other subsystems can visually inspected and seemed fine at the moment of testing.

As mentioned in the results, a fifth and successful test has been done without the presence of the author. According to Prof. E. Detsi and J. Corsi, no changes were made to the whole of the setup. Testing was done with hydrogen from a grade 4 hydrogen cylinder. They have indicated one of the valves had difficulties opening, most likely due to some wiring issues. This problem could have been present at the time of the first set of tests, although was not found at the moment. If condense has been the problem for the unsuccessful third and fourth tests, it makes sense the fifth test did have a positive result. This because the condense had nearly 1.5 month to evaporate. No further tests have been done at the time of writing.



Since research on the subjects for this thesis has not finished yet, a section about the future of research on the development of nanoporous aluminum for the production of hydrogen and a section about the future of the NAFCAR project is added here.

## 5.1 Nanoporous aluminum

For nanoporous aluminum there will be multiple ideas for the future proposed. This includes ideas for upscaling the production of nanoporous aluminum, and ideas for research on how to increase the hydrogen yield.

#### 5.1.1 Scaling up the production of NP-AI

To get to the goals of Hydropore, hydrogen mass production on a global scale via nanoporous aluminum, a lot of upscaling steps need to be done. Here, some near future upscaling ideas will be given. It is chosen to not jump too far into the future, as the production of nanoporous aluminum has just started and is still on the lab scale and produced for research. Nevertheless, there is always a shortage on NP-Al, even for the amounts of research done at the moment. And to scale up these processes, also the research on NP-Al needs to be scaled up, which will become clear in the hydrogen production section below.

To make more Al-Mg alloy is not too big of a problem. A bigger oven, or other ways to melt the materials, needs to be installed and prepared for these materials. At the moment the author left the research group at the University of Pennsylvania, this was in the middle of being set up.

Dealloying is a harder task to scale up. Since the voltage cannot be increased as it will break the electrolyte, other solutions need to be thought of. Dealloying by electrolytic removal is a long process at the moment. One of the things that can be done to scale up the dealloying process is to increase the surface area of the alloy, so more area is prone for the removal of magnesium. This can be done by, for example, crushing the alloy into a fine powder, or by increasing the size or number of alloy and counter electrode plates in the dealloying setup shown in figure 2.2. An example of increasing the production of NP-Al by increasing the size of the working and counter electrode plates is shown in figure 5.1. Here both setup (a) and (b) will be dealloyed in about the same time because they have the same thickness. Since (b) has a larger surface, the total volume of resulting NP-Al is higher. Theoretically, this can be increased many times, to the scale of mass production. Another idea for lab-scale dealloying is shown in figure 5.2 [33]. In this setup Al-Mg alloy in powder form is added in a platinum (non-reactive) container. This can already be done with the available equipment in the research group, and is one of the ideas for the near future of dealloying in the lab, after the production of the Al-Mg alloy is scaled up.



Figure 5.1: Illustrations showing the effect of thickness and surface of the electrodes on dealloying. [33]



Figure 5.2: Setup to scale up the dealloying process in the lab. Al-Mg alloy in powder form is used as the working electrode to increase the dealloying rate. [33]

## 5.1.2 Hydrogen production

Depending on the goal of why one would research NP-Al, and its ability to produce hydrogen, the specific research conducted would be different. If one wants to fundamentally understand the mechanics behind the hydrogen yield, and the rate at which it happens, tests like the one Nie et al. [89] have done should be included and edited for the specific research. Here, some ideas for future research on how to maximize the hydrogen yield and the hydrogen production rate will be discussed, as that is more in-line with the conducted research for this thesis, and more in-line with the views of startups like Hydropore.

First of all it needs to be checked whether the hydrogen yield indeed increases with a decreasing ligament size. If this is the case, then a whole set of dealloying temperatures should be taken, where all other factors remain constant. With this, one can determine the dealloying temperature with the highest yield of hydrogen. A setup comparable as the one for this thesis, as explained in section 2.1.2, should be used. This setup is closed off airtight, and can thus be put in any type of fridge or freezer to get to the desired temperatures. It would be best to generate a whole range of temperatures and check what the effect is on the ligament size. Theoretically, the lower the temperature, the smaller the ligament sizes. It is expected that a nice curve will come out, showing the connection between temperature and ligament size. Since it is not needed to have a smaller ligament size than  $\sim$ 7 nm, on

optimum can be obtained from these tests. This way the NP-Al can be optimized as desired, and dealloying can be done as efficient as possible, since lowering the temperature too far will increase unnecessary costs for cooling. One of the biggest obstacles to overcome for this research would be the dealloying rate, which gets lowered together with the temperature. This is mainly due to the solubility of the magnesium conducting electrolyte. Optimizations in this area, where e.g. salts are used which are better soluble in the APC at lower temperatures, are strongly recommended. Note that the electrical power used should not break down this new APC solution, as for example in the case for this thesis, the voltage could be a maximum of 1 V vs  $Mg/Mg^{2+}$ . And finally note that the hierarchical nanoporosity should remain intact. The macro pores facilitate the flow of water through the NP-Al. Without this, hydrogen yield will be very slow, and most likely (far) below 100%.

Still the question remains if the ligament size indeed is the factor influencing the hydrogen yield from nanoporous aluminum. One of the easiest ways to check whether the effect of the alumina envelopes is impeding the hydrogen yield and/or yield rate as discussed in section 4.1.2, is to produce NP-AI with large pores. This is likely to be done when dealloying in a heated environment. It is expected that the hydrogen yield rate will be decreased, while it is unknown what it will do to the hydrogen yield itself. If indeed these alumina envelopes have a negative effect on the hydrogen yield, it will most likely be shown in this test, where the total yield is investigated using the customized gas chromatography system as mentioned in experimental setup section 2.2.

## 5.2 NAFCAR

Even though the nanoporous aluminum and its hydrogen generation are not optimized yet, some prototype systems using it can already be designed and, the same as this project, be made. Let us focus on the future of the NAFCAR project in this section.

#### 5.2.1 Fuel cell system

For a first try the subsystems work close to fine. There are some quirks left to polish, though the gross of these systems are working. In general, the electrical wiring should be redone. Very rarely some of these wires, or connections between wires, fry and become useless. Also, junctions should be redone with proper equipment and the connections with the relays should be redone, as they are very small.

Additions to these subsystems can include a variable control by current of the air blower and coolant pump instead of only being able to turn them on or off. This will increase the efficiency of the FC system. As mentioned in discussion section 4.2.1, one of the two fin tube heat exchangers with its radiator can be removed. This will also increase the systems efficiency, while maintaining enough cooling capacity.

Also, since one of the problems of the fuel cell system could potentially be condense forming on the platinum plates, adding a humidifier pad to the outlet of the humidifier system could solve this. First of all, one should test whether it is the condense. This can be done by first making sure all condense in the system has gone. After this, all systems should be turned on after which the fuel cell should be working fine. If this is the case, and the fuel cell stops working after a while, turn off the eight humidifiers. The air blower will now blow dry air into the system, which should get rid of the condense quickly. If this indeed is the case, a humidifier pad could do the trick. A humidifier pad is a sponge-like pad with a membrane which can be made wet and let gasses pass through. When there is an airflow through the pad it humidifies the air. When this humidifier pad is added right before the outlet of the humidifier tank as shown in figure 2.12, it is expected that the with water oversaturated air will release the excess water to the humidifier pad, which in turn distributes it more evenly over the air exhaust and releases the excess water into the water tank again.

For this project it is thought that the current hydrogen supply system is the way to go. It is not the most easy to prepare for each use as the NP-Al tank and water tanks both need to be refilled in an oxygen free environment. Still, this is a fairly easy to use system, where flaws are quite easily found and minimized. It is recommended to first do some more attempts with bulk Al and NaOH for hydrogen generation. This way a good amount of Al can be determined by weight for proper use of the FC system.

Finally, the not working DC-DC converters should be tested thoroughly. They have been tested on converting different voltages to 72 V, though never tested with a high current. The converters should be tested and tuned with high currents and different voltages, individually and as a collective.

## 5.2.2 GEM eL XD

Once the fc system runs stably, it should not be too difficult to add it to the trunk bed of the GEM eL XD. The bed is more than big enough to hold all systems, and as shown in section 2.3, there are only minor additions needed to connect the fuel cell, battery pack of the GEM and the motor of the GEM. It is expected that the fuel cell system will be able to run the vehicle, although not for a long amount of time, and not with a lot of power. The power of the DC motor is 5 hp, whereas the power of the fuel cell can only reach a maximum of  $\sim$ 3.2 hp. It is thought that this will be enough as 5 hp is able to accelerate the LEV quickly to, and drive the car at a velocity of 25 mph, which is not needed for this proof of concept project. As soon as the car drives one should check how far it can be driven, say, per gram of aluminum. When this is known, some ideas on the efficiency of a system like this can be determined. Although efficiency is not on the top priority list of the NAFCAR project, a comparison with vehicles running on other forms of fuel can be made to give a general idea.

An addition which can be made to the NAFCAR project is to transform it into a hybrid vehicle. This means the batteries originally found in the GEM eL XD and the fuel cell system work in conjunction for a higher efficiency. This has been found in several projects and, for efficiency, is the preferred setup [93–99].



In this work, steps towards a more hydrogen-based economy are made. The development on the production of nanoporous aluminum has continued, and the development of a prototype LEV, running on NP-AI, has finished and its assembly is nearly finished. With this a basis for future NP-AI based applications has been laid, together with a base for further research on different properties of this nanoporous aluminum.

It is shown that temperature indeed relates to the ligament size of the NP-Al. Exact numbers need to be found, although it is shown that ligament sizes can be tuned with the help of a change in temperature while dealloying. Also on lower temperatures a hierarchical nanoporosity is found, beneficial for the flow of water to react with the NP-Al. It is expected that ligament size at least influences the hydrogen yield rate. If it indeed is the factor (mostly) determining the hydrogen generation yield still needs to be found. It is possible alumina envelopes close of some of the pathways for water to flow, after which the water needs to dissipate through layers of alumina, before being able to reach the NP-Al underneath. This can both influence the hydrogen yield and hydrogen yield rate, though needs more research for any conclusion to be made.

Although Hydropore has a great vision, and lots of good initiatives have already been done, still research and tests need to be done before there is a sustainable mass production of NP-Al. Some big steps need to be made to scale up the processes involved. It is shown that mass production of NP-Al can be cost-effective with zero carbon footprint, although collaborations with companies like Elysis are needed.

The application of such new technologies has proven to be more time consuming than expected. Despite this, lots of progress has been made towards the development of a LEV running on on-board produced hydrogen by nanoporous aluminum. Although most subsystems worked well, and the complete fuel cell system worked first try, a reliable power generation has not yet been obtained. At the time of writing, some final obstacles are filtered out of this fuel cell system. After this it will be attached to the LEV, which is expected to be able to drive on this system.



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From left to right: M.W.G. van der Pluijm, R. Chen, A. Lee and J. Mui.



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