HELSINKI UNIVERSITY OF TECHNOLOGY
Faculty of Information and Natural Sciences

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DIMETHYL ETHER REFORMING FOR HIGH TEMPERATURE PEM FUEL CELLS

Master's Thesis, submitted for fulfilment for the degree of Master of Science in Technology.

Espoo, 25.11.2009

Supervisor:	Prof. Peter Lund
Instructors:	Dr. Jens Oluf Jensen Dr. Qingfeng Li

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Työ käsittelee synteettisen polttoaineen nimeltä dimetyylieetteri (DME) soveltuvuutta polttokennoille. Työssä on laaja kokeellinen osuus, joka on tehty Danmarks Tekniske Universitetin kemian osastolla Energy and Materials Science Group -tutkimusryhmässä.

Metanoli on toistaiseksi kenties lupaavin pienen mittakaavan polymeerielektrolyyttimembraani (PEM) -tyyppisten polttokennojen polttoaine. DME, kemialliselta kaavaltaan CH_3OCH_3, on huonelämpötilassa kaasumainen, helposti nesteytettävä metanolista jalostettu polttoaine. Se palaa puhtaasti dieselmoottorissa ja sitä voidaan käsitellä nestekaasun tavoin. DME:n valmistus vaatii energiaa, mutta metanoliin verrattuna DME:llä saavutetaan monta systeemiä yksinkertaistavaa etua.

Työssä rakennettiin ja kalibroitiin laboratorioon koejärjestely, jolla tuotettiin sekä metanolista että DME:stä sähköä reformeri-polttokennosysteemillä. Tutkimuksen pääpaino oli vertailla itse valmistettuja katalyyttimateriaaleja, jotka auttavat DME:n hajoamisreaktiota vetypitoiseksi kaasuksi.

Reformaattikaasun koostumukseen vaikuttavia parametreja on lukuisia ja niiden vaikutusta tutkitaan. Kaasun koostumus analysoitiin massaspektrometrillä ja kaasua syötettiin polttokennoon. Polttokennotyyppi on korkealämpötila PEM, joka kestää verrattain suuria epäpuhtausmääriä myrkyttymättä.

Koejärjestelyllä saavutettiin hyviä tuloksia metanolin reformoinnissa. DME:n reformoinnissa saavutettiin parhaimmillaan hyviä tuloksia, mutta toivottua reaktiota ei pystytty ylläpitämään kauan.

Avainsanat: Dimetyylieetteri, DME, reformointi, vety, korkealämpötila PEM, PBI

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ABSTRACT OF
THE MASTER´S THESIS

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The work studies the suitability of the synthetic fuel dimethyl ether (DME) for fuel cells. The work includes a large experimental section, which has been done in Technical University of Denmark, Department of Chemistry, Energy and Materials Science Group.

Currently, methanol is seen as probably the most suitable fuel for small scale polymer electrolyte membrane (PEM) fuel cells. DME, with a chemical formula of CH_3OCH_3 is a further synthesized fuel, which is a gas at room temperature but can be easily liquefied. It burns in a diesel motor with low emissions and can be handled as liquefied petroleum gas (LPG). Although synthesizing DME consumes energy, by doing so there are benefits gained when considering a fuel cell system.

In this work, a setup was built to produce electrical power from methanol and DME via a self-built reformer–fuel cell system. Self-made reformer catalysts which help the chemical reaction towards hydrogen-rich gas are under focus.

There are numerous parameters affecting the reformate gas composition and this effect is studied. The reformate gas was analysed by a mass spectrometer and led to a fuel cell. The fuel cell type is a high temperature PEM, which has a considerable tolerance to high impurity levels without poisoning.

The setup worked well for methanol reforming. In DME reforming, a high hydrogen yield was gained but could not be sustained.

Keywords: Dimethyl ether, DME, reforming, hydrogen, high temperature PEM, PBI

Preface

The experimental part of this Master's Thesis was carried out at the Energy and Materials Science Group, Department of Chemistry, Technical University of Denmark from February to August 2009. The extent of the whole project corresponds to 30 ECTS points.

I want to thank my professor Peter Lund for supervising this work and allowing me to try my wings abroad on the fascinating field of hydrogen and fuel cells. I gratefully thank my instructors Jens Oluf Jensen and Qingfeng Li for always being there for questions and troubleshooting, and all of the Energy and Materials Science Group personnel I had the honour to work with. Especially the laboratory assistants Claus Burke Mortensen and Steen Blichfeldt deserve an acknowledgement for their professional help in the construction and maintenance of the setup. I also want to acknowledge Danish Power Systems for their helpful attitude and the preparation of the membrane electrode assemblies.

Furthermore, I use the opportunity to thank my faculty's English teacher William Martin for help with revising the language, my parents for their advice and encouragement, and last, but not least, my old and new friends Susan, Pia, Tapio, Ricardo and good old Kisällit for their collegial support throughout the journey.

Helsinki, 24.11.2009

Mikko Kotisaari

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Abbreviations

CFC	Chlorine-fluorine-carbon
DME	Dimethyl ether
DPS	Danish Power Systems
DTU	Technical University of Denmark (Danmarks Tekniske Universitet)
FC	Fuel cell
HT-PEM	High temperature proton exchange membrane
LHV	Lower heating value
LPG	Liquified petroleum gas
MEA	Membrane electrode assembly
MS	Mass spectrometer
MTG	Methanol-to-gasoline
PBI	Polybenzimidazole
PEM	Proton exchange membrane
PFSA	Perfluorosulphonic acid
S/C	Steam-to-carbon
amu	Atomic mass unit

1 Introduction and research objectives

The advantages of fuel cells in future power production are significant. The concept of the fuel cell itself is old, invented in the 19th century, but becoming real now as the world strives towards a cleaner and more energy efficient future. Despite the fact that their price is still prohibitively high, fuel cells are currently under a lot of research and growing global interest because of their high energy efficiency.

Visions of future vehicle fleets are plenty, and electrical vehicles will most likely have their role. Still, it is likely that there will also be a lasting need for convenient and safe transportation fuels in the post fossil fuel era. Fuels should have high energy density to allow reasonable driving distances between fuelling. Fuels should also be safe and easy to handle. Hydrogen, ultimately the best fuel for fuel cells, unfortunately faces unsolved questions concerning these particular issues. Problems associated with leakage and the need for large storage containers, in spite of large gas compression call for research in alternative solutions.

The scenarios for hydrogen storage are many. This work studies the hydrogen-rich synthetic fuels methanol and dimethyl ether (DME) as hydrogen carriers for a fuel cell. While methanol is a widely known and used liquid, DME is rather new to the public. Its production is slightly more energy intensive than methanol's, but this costly drawback is paid back in some interesting characteristics of the fuel. DME is a gas at atmospheric pressure but is easily liquefied for convenient storage and transportation. DME can run both a diesel engine and a fuel cell, a benefit which eases the challenge of implementing a new fuel to the current infrastructure. These arguments are addressed in Chapter 2.

DME can be directly led to a fuel cell. Alternatively, it can be pre-processed before entering the fuel cell. This work studies the latter way, using catalytic chemical reactions, *reforming*, to obtain hydrogen out of DME gas and using this hydrogen-rich reformate gas to fuel a fuel cell. From many different types of fuel cells, the proton exchange membrane (PEM), and especially the high temperature PEM seems the most suitable for these kind of reformate gases and is used in this work.

The main objective of the work is to build up, calibrate, test and run a reformer–fuel cell system. The goal is to produce electrical power from DME through this system. The performance of self made catalysts for DME reforming is among the most interesting parameters. Different types of in-house membrane electrode assemblies (MEAs) for fuel cell are tested as well. Reforming theory is described in Chapter 3 and the experimental part in Chapter 4.

The results of the experiments are presented in Chapter 5. Chapter 6 consists of analysis of the results and discussion. Conclusion of the work done is given in Chapter 7.

2 Fuels and fuel cells

2.1 Hydrogen and its storage

Ultimately, the cleanest and best performing fuel for fuel cells is hydrogen. Hydrogen is the lightest of all elements, presented with letter H in the periodic table. It has the atomic number of 1 and molecular weight of 1.008 g/mol (1). Hydrogen is by far the most abundant substance in the universe, covering about 75 % of the universe's elemental mass. However, on Earth hydrogen as such can be found practically nowhere because of its high reactivity. Hydrogen is present in various chemical compounds like water or acids but as well in hydrocarbons and in every living organism (2). Hydrogen is a diatomic gas with chemical formula of H_2 and at room temperature it is odourless and colourless. (3, 4)

Hydrogen is widely used in the chemical industry with total annual consumption of 50 million tons. Two major hydrogen-consuming sectors are petroleum refining and ammonia production. One other, quite exotic utilization method of hydrogen is as a propellant for rockets and space shuttles. (2)

Because of its high energy density by mass, hydrogen is a tempting candidate for a future energy carrier, i.e. fuel. If combusted, it burns clean, the only product being water vapour. If used in fuel cells, there are no emissions either. Moreover, the energy conversion efficiency is higher. As far as fuels are concerned, hydrogen's properties are very different from what mankind has been used to. The lightness of hydrogen represents a handicap for its storage and transmission. The small H_2 molecule can also diffuse through most materials and, for example, make steel brittle (2).

As mentioned, hydrogen is rarely found in its free form on Earth and thus has to be generated from whatever source locally available. Ways for achieving this are many, as seen in Figure 1. Hydrogen is today mainly produced from fossil resources by reforming hydrocarbons. Natural gas, which consists mainly of methane covers 48 % of global hydrogen production sources (2). Another established way, although not large in quantity, is hydrogen production by electrolysis. Electrolysis means using electricity to split water into hydrogen and oxygen. The reaction is the reverse to that taking place in a fuel cell. This may at first seem perverse, because the purpose of fuel cells is to provide electricity. The point is that electrolysis produces the cleanest hydrogen, which would act as an energy carrier, later to be combusted or used in a fuel cell. Powering electrolysis by nuclear power is considered in some scenarios. If electrolysis is done by power from renewable sources, the cycle is free from emissions. This is the long term ideal of the so called *hydrogen economy*. Electrolysis methods and materials are under research (5). Unfortunately, electricity costs for electrolysis are so high today that although some large production facilities exist around the world, it covers only 4 % of global hydrogen production. There are also promising ways of using biological methods based on enzymes, bacteria or light for hydrogen production. Arguments of inexhaustible renewable energy sources like algae which can be used in bio-photolysis and the use of biological wastes as substrates for bio-hydrogen production make this ongoing research tempting (6). Only the future will tell how much these nature-like methods can be scaled up and harnessed. (2, 7)

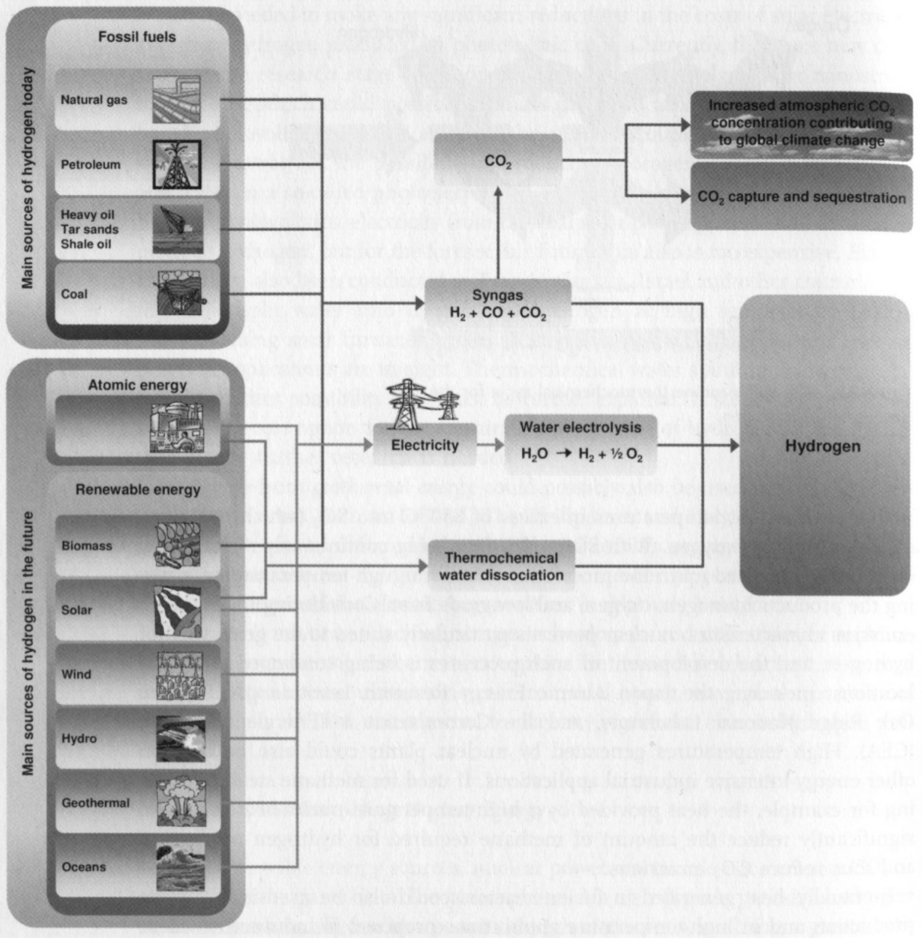

Figure 1: Different ways of hydrogen production. Figure from (2).

The small size of the hydrogen molecule and the low volumetric density of the gas make a major technical problem: how to store hydrogen. Lot of attention has to be put on preventing leakage. The storage tanks are massive in size, even when hydrogen gas is compressed to pressures of several hundred bars. Many ways of physical and chemical storing of hydrogen are currently being researched to overcome this complex challenge.

Technically, the most straightforward method, and also the most widely used one, is simply to compress the gas to high pressure. Although hydrogen has high energy density per mass, it is very low per volume. This results in containers of very high pressure or considerable volume, which is a major drawback considering mobile applications. Storing hydrogen as liquid is currently the only widely used method of storing large quantities of hydrogen. Such large amounts of hydrogen are used, for example, in petroleum refining and ammonia production. The storage of hydrogen as a liquid has been tested for fuel cell vehicles as well, but it faces unsolved questions because of the extremely low temperatures required. Hydrogen's boiling point is -253 °C and, over time, hydrogen evaporates from the storage tank. Liquefying hydrogen is also rather energy intensive and the energy density per mass still remains poor, under that of both gasoline and methanol. (7)

There is also a way of storing hydrogen which may be less obvious, namely using solid absorbing materials like reversible metal hydride hydrogen stores. Certain metals, particularly mixtures of titanium, iron, manganese, nickel and chromium can react with hydrogen to form a metal hydride in a reversible reaction, which is very easily controlled. This is a safe and compact method, usable in a wide range of applications where small quantities of hydrogen are stored. Then again, there are disadvantages such as the great weight of the metal alloy. Practical metal hydrides contain merely few weight percents hydrogen, and on system level the practical storage capacity is not more than 1 wt%. There are also critical aspects of long refill time and the need for high purity hydrogen. (2, 7)

2.2 Methanol and dimethyl ether (DME)

In this subchapter two distinct substances are brought up as practical examples of indirect hydrogen storage. In this method hydrogen is first produced in large chemical plants and then used to produce hydrogen-rich chemicals or man-made fuels (7).

The existing infrastructure uses liquid fuel like gasoline or diesel to fuel vehicles. Therefore, a liquid hydrogen carrier would be relatively easy to implement in the foreseeable future. The liquids rich in hydrogen are compact and easy to store. To be usable in large scale applications, they have to meet three major requirements. Firstly, easily giving up their hydrogen; secondly, having simple and energy efficient manufacturing process; and, finally, be safe to handle. Methanol, with a chemical formula of CH_3OH, has been widely studied and has gained a lot of attention for fuel cell use. Applications like fuel cell based external power source that delivers power to mobile digital consumer products are already being introduced to the market (8). This thesis concentrates on methanol and an alternative fuel called dimethyl ether, DME. DME is the simplest ether, with a chemical formula of CH_3OCH_3. As a chemical it is close to methanol, but further refined. The refining process naturally requires energy, but by doing so there are also quite a few benefits to be gained. (2, 7)

Today DME is commonly used in aerosol spray propellants as a CFC replacement. Because of its clean burning properties and ease of handling, DME is seen as being suitable for three primary applications: the immediate market allows the use of DME as a blend-stock with liquefied petroleum gas (LPG) for home heating and cooking, there is potential for DME in electric power production and finally, a new and developing market is exploring DME as a transportation fuel. The potential is huge, especially in Asia. (9)

The growing popularity of DME in China is such that annual production is expected to grow from 2 million metric tons as of 2008 to 20 million metric tons by 2020 (10). Most of the new Chinese production will be used for transportation. Some other countries that have recognised DME's potential are Japan, US, Canada, Sweden and Iceland (11, 12). Volvo in Sweden is currently running a project to field test 14 trucks running on Bio-DME (13).

Both the gravimetric and volumetric energy densities of DME are slightly higher than that of methanol. A peculiar characteristic of DME is its low boiling point of -24.9 °C (2). It is a gas at room temperature, but easily liquefied by cooling or modest pressurising. DME is stored and transported as a liquid but can be ejected as a gas. Considering a fuel cell system, the fact that DME is a gas at room temperature is a significant benefit: there is no need either for a DME pump or for an evaporator.

A parameter called *cetane rating* characterizes a fuel's propensity to self-ignite under high heat and pressure. DME has cetane ratings in the range of 55-60, compared with

40-55 for conventional diesel fuel. For methanol the figure is 3, an order of magnitude lower. This high cetane number of DME makes it attractive to be used in diesel engines. (2)

DME burns with a visible blue flame and is non-peroxide forming in the pure state or in aerosol formulations. Like methanol, DME is clean-burning, produces no soot, black smoke or SO_2, and only very low amounts of NO_X and other emissions even without exhaust gas after-treatment (2, 14). DME is a volatile organic compound, but non-carcinogenic, non-teratogenic, non-mutagenic and – one of the most significant differences compared with methanol - practically non-toxic. In order to keep things in perspective, methanol still appears to be a more environmentally benign fuel compared to conventional gasoline. This is based on a lengthy report on the human and aquatic toxicity aspects of methanol, executed by Malcolm Pirnie Inc (15). DME has a sweet ether-like odour so it does not require an odorant (14).

Moving towards more DME use in vehicles would not be that difficult, because of the similarities it has to diesel fuel. Only a new fuel injection system is needed to be added to an ordinary diesel engine. The performance stays the same, and emissions decrease dramatically. Therefore DME also has a nickname *diesel minus emissions* (16). (14)

DME's physical properties are similar to those of liquefied petroleum gases (LPG) like propane and buthane (14). The currently used LPG infrastructure could be easily adapted for handling and transporting DME, the large LPG importer Japan leading the way in research. These issues are not that simple with methanol, which demands more modifications to the fuel distribution and storage infrastructure because of its corrosive nature (2). Implementing DME as a fuel would hence be relatively easy and reasonable because it can be used in combustion engines and perhaps later in hybrids with DME fuel cells. It is inevitable, though, that synthesizing DME from methanol consumes energy. It remains an open question, whether the benefits achieved overcome the excess energy needed for producing DME.

The following Table 1, Figure 2 and Figure 3 present comparisons between fuel characteristics. It is essential to note the speciality of hydrogen in the graphs. Its energy density is pre-eminent by mass, but poor by volume. DME energy density stays behind of gasoline and diesel, but is slightly higher compared to methanol.

Table 1: Comparison of fuel properties. Data from (2) and others, cited below. DME density is peculiar, because DME actually is a gas at 20 °C. It is in any case liquefied with only a modest pressure. The liquid phase makes the most sense in this comparison, because that is what matters concerning storage and transport. LHVs are rounded to full numbers.

		Hydrogen	Methanol	DME	Diesel
Chemical formula		H_2	CH_3OH	CH_3OCH_3	$C_{14}H_{30}$
Molecular weight	g/mol	2.0159	32.04	46.07	198.4
Hydrogen content	wt%	100	12.5	13	13
Carbon content	wt%	0	37.5[a]	52.2[a]	87[a]
Boiling point	°C	-252.9	64.6	-24.9	125-400[a]
Density at 20 °C	g/cm^3	0.0001 (g)	0.791 (l)	0.668 (l)	0.80-0.89 (l)[b]
Energy content (LHV)	MJ/kg	120	20[a]	29[a]	42[a]
Energy content (LHV)	MJ/L	0.01[c]	16[c]	19[d]	31[c]
Flammability limits in air	vol%	4-74	5.5-44[e]	3.4-17	0.6-6.5

[a] (17)
[b] (2, 3)
[c] (18)
[d] Reproduced from (19)
[e] (20)

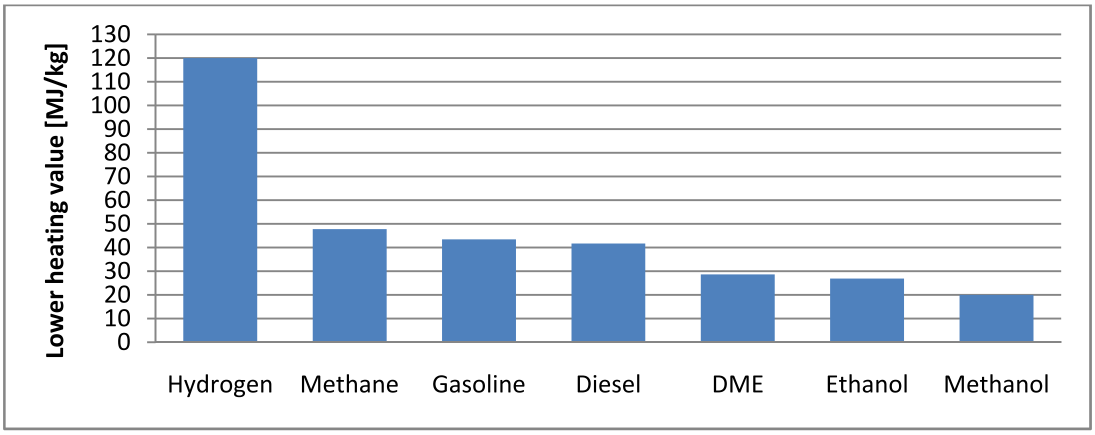

Figure 2: Comparison of gravimetric energy density between fuels. (2, 17)

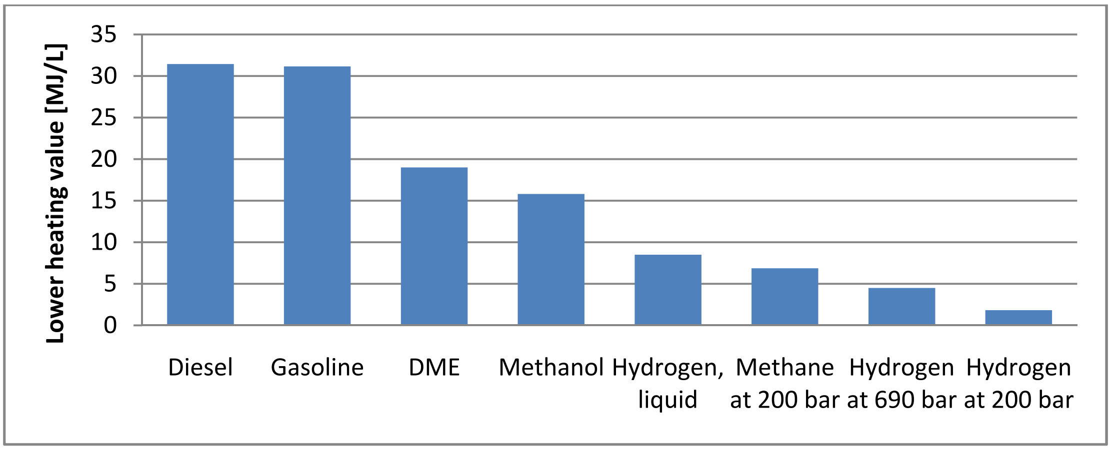

Figure 3: Comparison of volumetric energy density between fuels. (18, 19)

2.3 Production of methanol and DME

As well as with hydrogen, DME is today mainly produced from fossil resources, but scenarios for a carbon neutral cycle exist. To start with the state-of-the-art method, there is an established way of steam reforming practised industrially on a large scale to produce methanol and DME from hydrocarbons. The production starts with a fossil fuel. Methane (CH_4), the main element of natural gas is the most suitable because of its highest hydrogen/carbon ratio in fossil fuels. Higher hydrocarbons obtained for example during oil refining can also be used, and coal as well. Whatever the feedstock, it is reacted with water or oxygen in order to break it into *syngas*. The name syngas derives from synthesis gas and refers to a gas consisting of H_2 and CO in some proportion. Methanol is produced from these elements by further reaction and DME by yet further reaction. The last step of the dehydration of methanol to DME itself is an easy process, but it is questionable, whether it is economical or not in the long run. The process is schematically

Hydrocarbons ⇨ Syngas ⇨ Methanol ⇨ DME .

A Danish company, *Haldor Topsøe*, has developed a process that yields DME directly from syngas without going through the methanol phase (10), however that process remains an industrial secret. To be more specific, the reactions for the traditional DME production are presented. First, the reforming reactions for methane and a generic hydrocarbon C_nH_m as presented by (7):

$$CH_4 + H_2O \rightleftarrows CO + 3H_2 \qquad \Delta H = 206\frac{kJ}{mol} \tag{\{1\}}$$

$$C_nH_m + nH_2O \rightleftarrows nCO + (\frac{m}{2} + n)H_2 \tag{\{2\}}$$

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad \Delta H = -41\frac{kJ}{mol} \tag{\{3\}}$$

The reforming reactions {1} and {2} and the associated water-gas shift reaction {3} are carried out normally over a supported nickel catalyst at elevated temperatures, typically over 500 °C. Reactions {1} and {3} are reversible and normally reach equilibrium over an active catalyst, as at such high temperatures the rates of reaction are very fast. Over a catalyst that is active for reaction {1}, reaction {3} nearly always occurs as well. The combination of the two reactions taking place means that the overall product gas is a mixture of carbon monoxide, carbon dioxide, and hydrogen, together with unconverted methane and steam. (7)

For syngas production from methane there are also methods like dry reforming:

$$CH_4 + CO_2 \rightleftarrows 2CO + 2H_2 \qquad \Delta H = 247\frac{kJ}{mol} \tag{\{4\}}$$

and partial oxidation:

$$CH_4 + \frac{1}{2}O_2 \rightleftarrows CO + 2H_2 \qquad \Delta H = -247\frac{kJ}{mol} \tag{\{5\}}$$

Partial oxidation can be carried out at high temperatures (typically 1200-1500 °C) without a catalyst. Moreover, autothermal reforming is a concept where the endothermic steam reforming reaction and exothermic partial oxidation reaction are combined. (7)

The reactions for DME synthesis from syngas are the following, as presented by (17):

Methanol synthesis:

$$CO + 2H_2 \rightleftarrows CH_3OH \qquad \{6\}$$

Methanol dehydration:

$$2CH_3OH \rightleftarrows CH_3OCH_3 + H_2O \qquad \{7\}$$

Water-gas shift:

$$H_2O + CO \rightleftarrows H_2 + CO_2 \qquad \{8\}$$

Net reaction:

$$3H_2 + 3CO \rightleftarrows CH_3OCH_3 + CO_2 \qquad \Delta H = 259\frac{kJ}{mol} \qquad \{9\}$$

The relevance of water-gas shift reaction grows if the stoichiometric ratio of CO and H_2 is not the optimal in the syngas. The chemical formulas above show expicitly that methanol and DME can be seen as carriers of hydrogen. Compared with pure hydrogen obtained from syngas, methanol and DME obviously require energy to be produced. On the other hand, after that price has been paid, they both act in our current fuel infrastructure as much more convenient fuels.

DME production is, of course, not only limited to natural gas or other fossil fuels. In principle, all there is needed for the synthesis is carbon dioxide, hydrogen and water. For example, one raw material for syngas available now is black liquor from the wood industry. Companies *Chemrec* and *Haldor Topsøe* collaborate to build a pilot plant in Piteå in northern Sweden to produce Bio-DME. It is a part of a co-operative venture between the European Comission, the Swedish Energy Agency, fuel companies and transport industry companies to investigate the potential for full-scale investment in Bio-DME as a vehicle fuel (21). Also a Canadian DME company called the *Blue Fuel Energy Corporation* is planning to use renewable energy, such as wind and hydro, as well as waste carbon dioxide and water, to produce DME (11).

A study from Ulf Bossel and Baldur Eliasson (22) promotes liquid hydrocarbons, such as DME, instead of pure hydrogen for the future energy economy. For this to be renewable, however, there are closed clean natural cycles of water and CO_2 needed. Water can be split into hydrogen by electrolysis, powered by electricity from renewable energy or perhaps by nuclear power. Hydrogen can then be combusted or used in a fuel cell and the product water is again in the natural cycle. What comes to carbon, if it is recycled from power plants, taken from the biosphere or even from the atmosphere as more futuristic scenarios present (2), the *Synthetic Liquid Hydrocarbon Economy* will be environmentally as benign as a *Pure Hydrogen Economy*. (22)

2.4 High temperature PEM fuel cell

Fuel cells are electrochemical devices, which convert chemical energy of hydrogen and oxygen straight to electricity without burning. The essentials of the fuel cell itself are simple and it is quiet in use. The system built around the fuel cell to run it optimally, however, can reduce these benefits. In most applications the fuel cell needs a quite complex system of auxiliary components like pumps, blowers or compressors. Fuel cell systems are often proposed as energy converters in a sustainable energy system. They are discussed as a replacement of internal combustion engines, steam turbines and batteries, and are proposed for use in numerous applications. Vehicles are the ones with probably the most media interest, but the potential applications range from small electronic devices to back-up power for buildings and right up to large-scale power plants. There are different types of fuel cells for different applications, all having their benefits and drawbacks. (23, 24)

Indeed, the capability of producing power practically in any range explains part of the attraction of fuel cells. Another significant benefit is that the energy efficiency is high, not limited by Carnot efficiency as is the case with internal combustion engines. The overall fuel cell system efficiency scales down along with the balance-of-plant, though. If hydrogen is the fuel, the only by-product is pure water. Fuel cells could hence be seen as zero emission devices. As discussed earlier, however, the question of hydrogen production must be addressed before that.

The abbreviation PEM stands for both *polymer electrolyte membrane* as well as *proton exchange membrane*. The first one follows the convention to name fuel cells after the electrolyte type, in this case polymer membrane. The second one refers to the charge carrier going across the membrane. In PEM fuel cells the charge carrier is the proton, H^+. PEM fuel cells are usually run at about 80 °C and use perfluorosulphonic acid (PFSA) membranes, most commonly Nafion® from *DuPont*. The essential functioning of a PEM fuel cell is presented in Figure 4. Figure 5 shows in detail the composition of the interface between the porous electrode and the electrolyte membrane. The membrane is the core of the fuel cell. Even in this brief description of a fuel cell, it deserves special attention. It is a proton conductor, but ideally impermeable to other molecules or ions, e.g. H_2 or O_2. Most importantly, it is an electronic insulator. This means that electrons are forced to take a roundabout route via an external circuit. This flow of electrons is the electrical current.

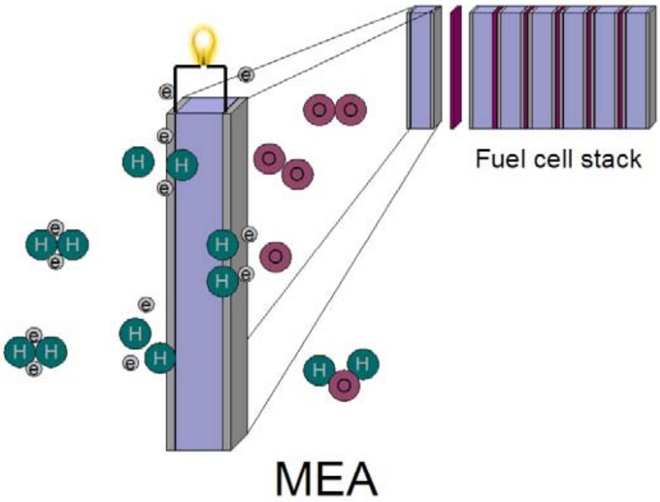

Figure 4: Membrane electrode assembly. H_2 molecules are broken into protons and electrons with the help of a catalyst on the anode electrode. The membrane in the middle is an electronic insulator, so electrons go via an external circuit and power is produced. Protons diffuse through the membrane. On the cathode side, these components meet again together with an oxygen molecule. Water (H_2O) is formed. Figure from (24).

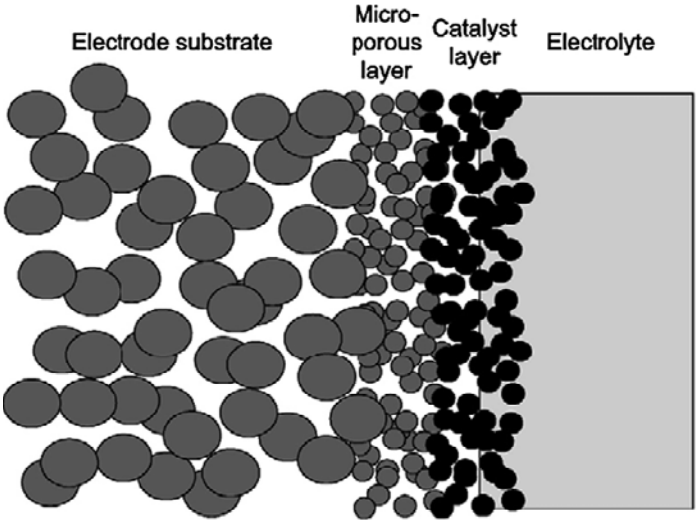

Figure 5: Zoom-in of the interface between the anode electrode and the electrolyte. Figure from (25).

In addition to the famous Nafion® membrane, there are new types of membranes introduced. In this work, a high temperature PEM (HT-PEM) is used. The membrane consists of phosphoric acid doped polybenzimidazole (PBI). Its operation temperature is high, 120-200 °C, which brings numerous advantages considering not only the fuel cell, but the whole fuel cell system. Water management is significantly simplified, since all the water is in gas phase. In traditional PFSA membranes the role of liquid water is a shuttle to conduct protons through the membrane. Water acts as a base to accept protons from the sulphonic acid groups. In HT-PEM, instead of liquid water, the phosphoric acid is used for proton conductance (26). In a fuel cell system the waste heat can be taken advantage of, for example, by being used to heat up an evaporator unit (27, 28).

An even greater advantage of a PBI fuel cell is its tolerance against impurities, especially CO. Nafion®-based cells operating typically at 80 °C can tolerate 10-20 ppm CO. PBI cells operating at above 150 °C can tolerate up to 1 % CO and 10 ppm SO_2 in the fuel stream. At operating temperature of 200 °C the figure for CO tolerance is up to 3 % CO, i.e. 30 000 ppm. This high CO tolerance makes it possible to simplify the fuel processing system and to use reformed hydrogen from the reformer without further cleanup of the CO. It also allows for possible integration of the fuel cell stack with fuel processing units. (23, 29)

Considering the fuel cell itself, oxygen would be an optimal cathode side reactant. On a system level the most reasonable reactant is in any case air. The simpler the system, the better. As far as an application is considered, if it can use ambient air it saves a lot compared to having compressed oxygen carried onboard.

The fuel cell type used in this work is phosphoric acid doped polybenzimidazole high temperature proton exchange membrane fuel cell, H_3PO_4/PBI HT-PEMFC.

2.5 Separate reforming and direct DME fuel cell

Like methanol, DME could be used as a direct fuel for the fuel cell. The benefits of direct use are obvious especially in mobile applications. If a separate reformer unit is cut out, the fuel cell system will become simplified and save in weight and volume. HT-PEM is seen suitable for the fuel cell type, because the problem described earlier about low temperature PEMFC and low tolerance against impurities.

One of the major disadvantages in direct methanol fuel cells is the fuel leakage through the membrane, resulting in crossover and a lowering of the overall performance of the cell. The DME molecule is larger in size than the methanol molecule and its polarity is lower, resulting in lower permeability through the electrolyte membrane (26). Still, the fuel crossover through the membrane will be an issue. The cell should also be tolerant to the remaining products of direct oxidation, including traces of poisonous CO. There is not yet much experience gained and documented from using direct DME.

Catalyst materials are often expensive and wherever they can be saved, they should be. This question is not a trivial. Compared to a fuel cell designed to be run by hydrogen, direct DME fuel cell definitely needs more catalyst, and more expensive catalyst, on the electrodes. This should still be seen in the light of *saved catalyst* from the separate reformer unit. Although separate reforming is more complex than direct use concerning the whole system, in the long run reforming could still be expected to be more reliable. The more hydrogen-rich fuel will allow the fuel cell to have a longer lifetime. By using a separate reformer, the fuel crossover problem through the membrane is overcome and cell poisoning is much slower. This work concentrates mostly on DME use with a separate reformer unit. The fuel cell MEAs were not optimized for direct DME use, but it was still tested as well out of interest.

3 Reforming

3.1 Catalyst definition

A catalyst is a term used for a substance which accelerates a chemical reaction. The catalyst forms bonds with the reacting molecules and allows these to react with a product. The product then detaches from the catalyst and leaves it unaltered, available for the next reaction. A catalyst offers an alternative path for the reaction. The reaction is obviously more complex, but energetically much more favourable. The catalyst changes the kinetics but not the thermodynamics of a reaction. A general catalytic reaction can be, for example:

$$A + B \xrightarrow{Catalyst} AB \qquad \{10\}$$

Catalysts come in a multitude of forms, varying from atoms and molecules to large structures such as zeolites or enzymes. In addition, they may be employed in various surroundings: in liquids, gases or at the surface of solids. About 85-90 % of the products of the chemical industry are made in catalytic processes. A catalyst offers there an alternative, energetically favourable mechanism to the non-catalytic reaction, thus enabling processes to be carried out under industrially feasible conditions of pressure and temperature. The next sections introduce the use of catalytic chemical reactions, *reforming*, to obtain hydrogen out of methanol or DME. (30)

3.2 Reforming review

Whereas methanol reforming is a widely studied field, hydrogen production from DME has been studied for less than ten years. The subject is under growing interest, however, and there is a very thorough work about steam reforming of DME by Semelsberger (31). The DME reforming process is essentially a two step process.

The DME molecule is first broken down to two methanol molecules over a solid acid catalyst. This is known as DME hydrolysis, because the reaction needs water. It is the rate-determining step of DME steam reforming (32). The following reaction equations are from (17).

$$CH_3OCH_3 + H_2O \rightleftarrows 2\ CH_3OH \qquad \Delta H = 37 \frac{kJ}{mol} \qquad \{11\}$$

Methanol is thereafter decomposed to hydrogen and carbon monoxide:

$$CH_3OH \rightleftarrows CO + 2\ H_2 \qquad \{12\}$$

Carbon monoxide will further react with water, resulting in more hydrogen and carbon dioxide. This is called water-gas shift:

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad \{13\}$$

Traces of CO will in most cases still be present, but assuming 100 % conversion, the methanol steam reforming reaction is these two reactions combined:

$$CH_3OH + H_2O \rightleftarrows CO_2 + 3H_2 \qquad \Delta H = 49 \frac{kJ}{mol} \qquad \{14\}$$

The net DME steam reforming reaction is a compilation of the equations above:

$$CH_3OCH_3 + 3\ H_2O \rightleftarrows 2\ CO_2 + 6\ H_2 \qquad \Delta H = 135 \frac{kJ}{mol} \qquad \{15\}$$

Naturally, there are many other possible options for these reactions. Figure 6 shows the reaction network for DME steam reforming.

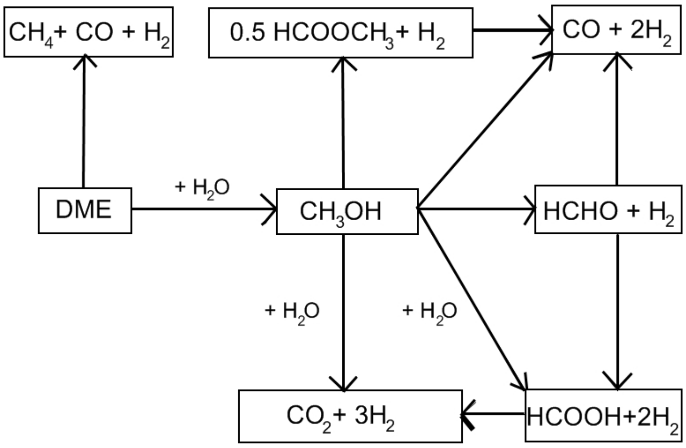

Figure 6: Reaction pathways for DME steam reforming. Reproduced from (33).

In general, DME hydrolysis to methanol {11} takes place over acidic catalysts such as alumina or zeolite, while methanol steam reforming to hydrogen and carbon monoxide {12} proceeds over metal catalysts such as Cu-, Pd-, and Pt-based catalysts. Among these, the Cu-based catalyst is considered to be superior due to the cost effectiveness and the level of activity (34). Aluminium oxide Al_2O_3 is used as a support for copper and zinc in methanol reforming. Cu-Zn/Al_2O_3 is the standard methanol reforming catalyst.

Gamma aluminium oxide γ-Al_2O_3 works well as the solid acid catalyst for DME hydrolysis, but only in the rather high temperature range of 300-400°C. Other catalysts studied for this step are, for example, zeolites Y and ZSM-5 and ZrO_2 (35). Among these, zeolite ZSM-5 has gained attention. An important parameter is the Si/Al ratio of the zeolite. From the literature survey conducted, figure 25 for this ratio seemed to lead to rather high hydrogen yields (35).

Something peculiar to be seen in Figure 6 is the route from DME to methane. Semelsberger et al. (35) have studied this. Of their catalysts tested, Cu-Zn/ZrO_2 and Cu-Zn/γ-Al_2O_3 were the only catalysts that produced methane, with low concentrations and at as high temperature as 400 °C. All other catalysts produced only hydrogen, methanol, carbon monoxide and carbon dioxide.

Let us now address the question of ratio between copper, zinc and solid acid in the DME reforming catalyst. The optimal copper-to-zinc molar ratio for methanol steam reforming is normally reported to be one-to-one (35). As for the ratio between the metal catalysts (Cu/Zn) and the solid acid catalyst, the research group of Feng et al., having many papers on DME reforming, has used mostly a weight ratio of 1:1. (32, 33, 36)

Feng et al. (33) report the activities of different catalysts. The effect of additives in Cu-Zn/ZSM-5 to higher hydrogen yields is studied. Cu-Zn-Al/ZSM-5 and Cu-Zn-Zr/ZSM-5 give slightly better results. The best of the tested ones is Cu-Zn-Al-Zr/ZSM-5, with a hydrogen yield of over 65 % at 260°C. The more tuned and complex the catalyst, the better the hydrogen yield. The yield is, however, a function of several other parameters, especially temperature. One more parameter in reforming is the ratio between the actual fuel meaning in this context methanol or DME, and the other compound necessary for the desired reactions, water. It is intuitive to use ratios water/methanol or water/DME. However, to make comparison easier, another ratio is introduced: steam to carbon ratio (S/C). It tells how many water molecules there are for each carbon atom. In the case of methanol, the ratios H_2O/CH_3OH and S/C are the same. In the case of DME, the S/C ratio is half of the H_2O/CH_3OCH_3 ratio because of the two carbons in DME.

4 Experimental

Building the setup started from an empty table, took a long time and had several changes along the way. Some of the orders were heavily delayed and in addition to the setup itself, a lot of work was done with the analysis equipment. The principal setup structure, however, can be introduced simply with Figure 7 below. On the anode side, DME and distilled water are fed to a reformer unit. The reformer has a catalyst inside and chemical reactions take place. The reformate gas is then fed to the anode side of the fuel cell. The cathode side is fed by compressed air. The un-reacted surplus gasses are sucked away from the fuel cell gas exits.

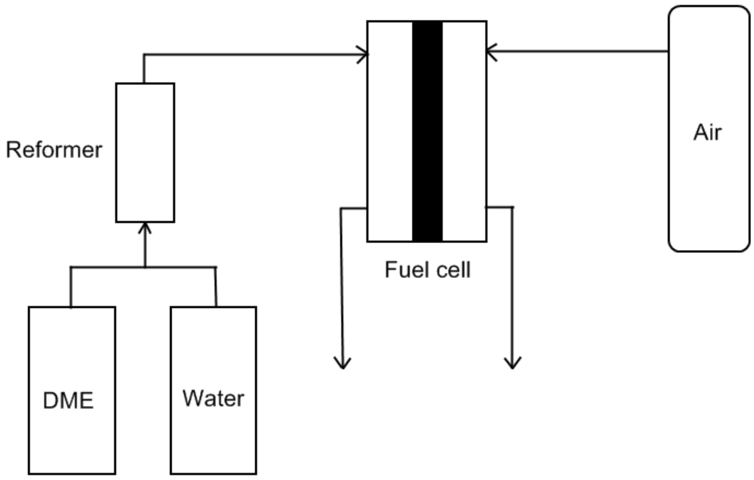

Figure 7: Schematic diagram of the setup.

4.1 Reformer setup

Since high temperatures and poisonous gases were expected, a small fume cupboard from JRV Jørgen Rasmussen's Ventilation A/S was first mounted on a laboratory table. Also a small CO alarm was hung next to the setup. In the following sections the setup is presented thoroughly piece by piece. For overview and later reference, see the picture of the final setup, Figure 8.

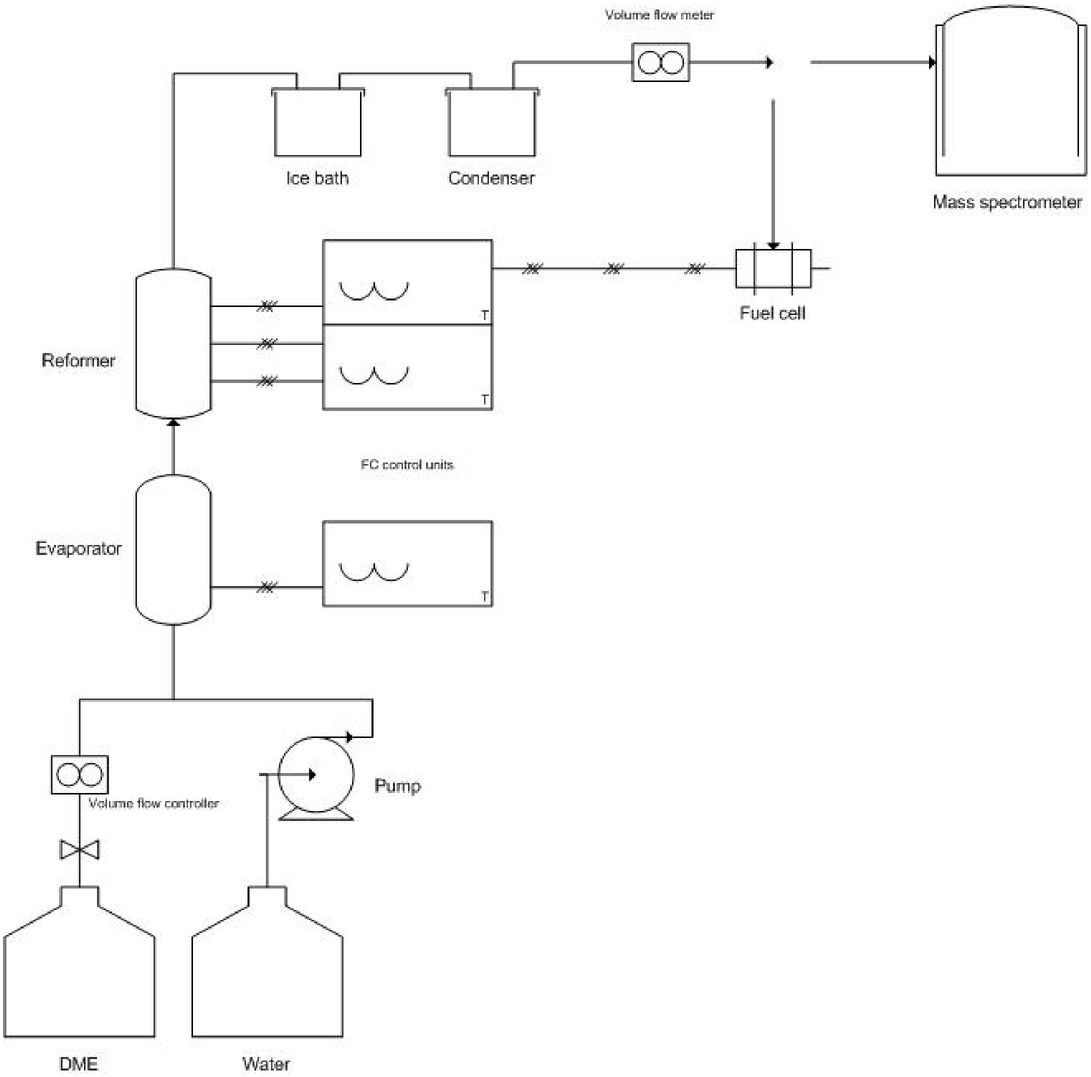

Figure 8: Final setup.

In the setup of Figure 8, DME gas and liquid water flows are controlled before letting them enter the same tube. This liquid/gas phase substance enters the evaporator and reformer units. Together with the fuel cell, the reformer is the scientifically most interesting part of the set up, with the catalyst inside. Temperature controllers from the three control units control the heating of the evaporator, reformer and fuel cell. The evaporator temperature is about 170 °C, the reformer temperature 200-425 °C and the fuel cell temperature 160-170 °C. After the reformer, the gas is led to a condenser bottle to liquefy and hence filter out as much of the soluble gases as possible. After that the outlet gas is analysed or led to the fuel cell. The parameters varied include catalyst material, reforming temperature, feed flow rate and the ratio between the fuel and water.

The fuel cell's cathode side reactant was air. It is not indicated in Figure 8, but one of the FC control units worked also as an air flow controller.

4.1.1 Pump

A pump was used in methanol reforming experiments to pump methanol/water solution and in DME reforming experiments to pump water. Two pumps were calibrated and tested for the setup: Cole Parmer MASTERFLEX CONSOLE DRIVE (Model no. *77521-47*) and peristaltic Cole Parmer MASTERFLEX L/S ECONOMY DRIVE (Model no. *7554-95*) with L/S ® Easy-Load ® 3 Pump Head (Model no. *77800-50*). The first one was a very accurate device, but on the other hand the second one could manage larger flow rates. The second pump was not fully functioning, however. It could not be calibrated for the full scale, but only for part of the scale at a time. Moreover, this kind of peristaltic water pump is not the most accurate, because the plastic pipe is under stress when the device is under operation and is hence slightly worn out over time. This was not considered to be such a significant effect for these measurements, but because of the scale of the desired pump rate the first pump was chosen. The calibration charts in Figure A 1 are presented in Appendix A: Calibration charts.

4.1.2 DME flow meter

The plan was to measure all the flows electronically. However, no electronic mass flow meter specifically for DME was available. Modifying one specified for methane was considered but the gas factor, which is used for comparing the suitability of flow meters between gases, was judged to be too large. Instead, an analogue flow meter

SHO-RATE was assembled straight after the DME outlet. The flow meter was calibrated with the help of a long gas burette with a known volume. Soap was contained in a small holder at the end of the tube. When the holder was pressed, the DME stream hit it and made bubbles go through the tube. From the time it took for the bubble to climb an accurate volume of 100 ml in the glass tube, the flow rate could be calculated and the flow meter calibrated. The molar volume of gas is a function of temperature. When pressure drops, volume increases and temperature falls. This was important to consider with the DME inlet. The pressure drop between the DME pressure in the bottle and the outlet valve was as large as possible. The outlet pressure was kept at 1 bar. The pressure drop between the outlet valve and flow meter was rather small, so that gas would not cool significantly there. The calibration chart Figure A 3 can be found in Appendix A: Calibration charts.

4.1.3 Reformer

Two similar metal units to be used as evaporators or reformers were tailor-made in in-house workshop of the university. Figure 9 below presents the design. The units were built around stainless steel pipes which had an inner diameter of 1.5 cm and length of 25.0 cm. Each unit had six holes through the metal for heating cartridges. The other unit had holes suitable for 6.5 mm diameter heating cartridges and the other one for 10.0 mm cartridges. This does not really make a difference because the heating power was the same for both of the cartridges. The heating cartridges used were Svend A. Nielsen A/S, model number *844010* (diameter 6.5 mm, length 50 mm, power 200 W) and *844082* (diameter 10.0 mm, length 50 mm, power 200 W).

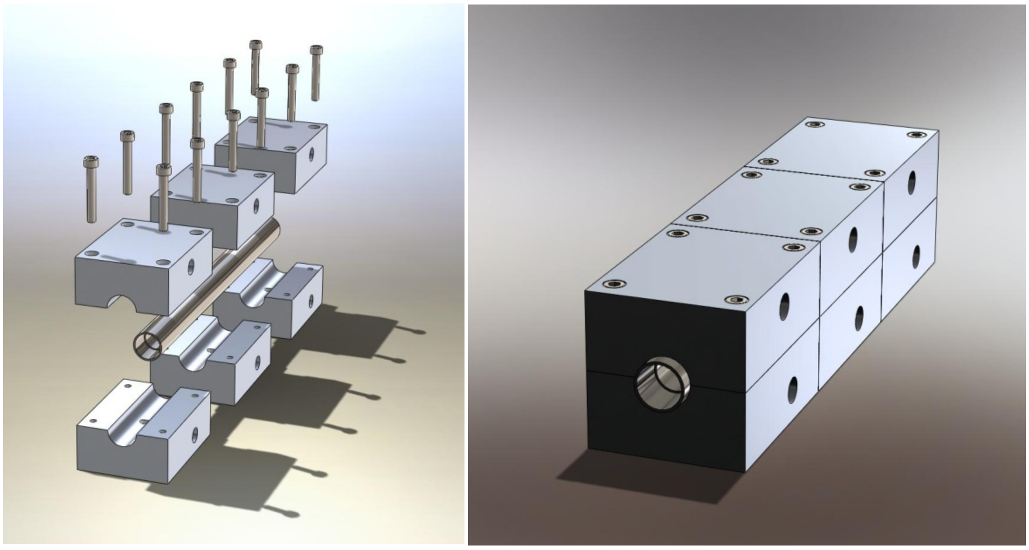

Figure 9: Left: View of evaporator/reformer unit. The tube in the middle is surrounded by large metal blocks to ensure steady heat distribution. Right: Note the six holes for heating cartridges on the right side of the block. Figures made by DTU workshop.

There were also three holes for thermocouples, so that each of the units could be controlled as a set of three heating zones. The holes for the thermocouples were drilled in each unit and the thermocouples welded by the workshop. The heads of the thermocouples went inside the pipe to ensure measurement of the actual temperature of the reforming process. The thermocouples used were type K, *RS 397-1236* (1.5 mm x 150 mm) with plug *RS 455-9764*. See Figure 10.

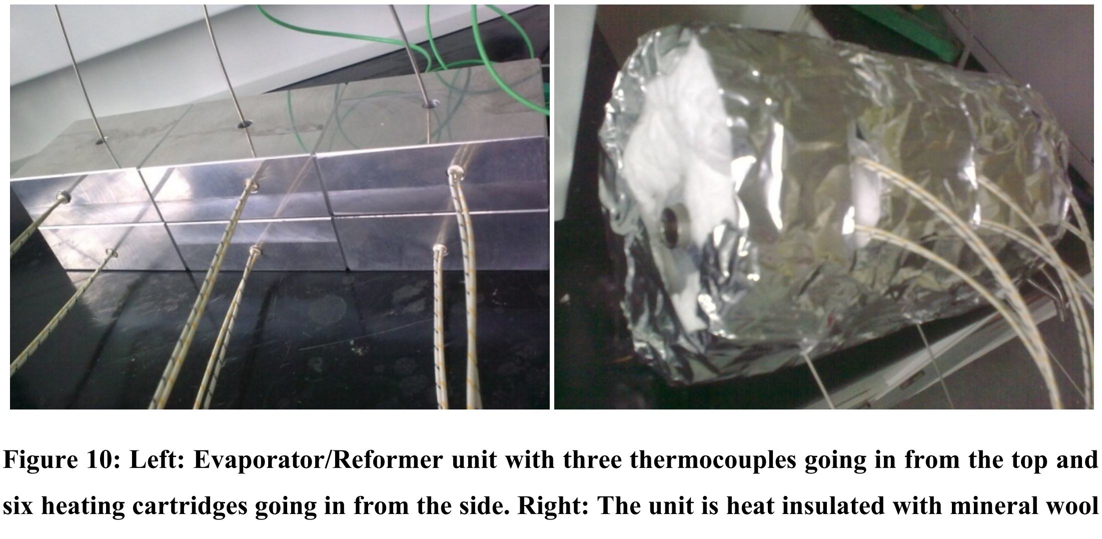

Figure 10: Left: Evaporator/Reformer unit with three thermocouples going in from the top and six heating cartridges going in from the side. Right: The unit is heat insulated with mineral wool and covered with aluminium foil for more convenient handling.

All in all the units can be considered as high quality equipment. They were especially manufactured for this work. The order included also connector part for the two units and specially made copper fitting rings, not shown in the pictures.

4.1.4 Tubing

For all the external tubing, the material chosen was preferably Teflon. The reforming temperatures were expected to be even higher than 400 °C and because Teflon can tolerate temperatures no higher than 250 °C metal tubes were used as well. Just before and after the reformer unit, the tubing material used was stainless steel. The short stainless steel tubes were connected to copper tubes because copper is easier to bend. The point of having a snatch of stainless steel just after the reformer is that copper could lose so much heat that some of the out coming gas could liquefy and the drops could fall back to reformer. Stainless steel retains the heat better and ensures that the gas stays hot.

4.1.5 Cooler and condenser

The copper tube coming from the reformer was twisted into a spiral and placed in an ice bath to cool the gas down. After the cooler, the gas was led via Teflon tubing to a condenser bottle with the purpose of condensing soluble gases like water vapour, methanol and DME. The condenser bottle was the last element of the reforming part of the setup. The outlet gas flow was measured again with a gas burette as described in the flow meter calibration in Section 4.1.2. After that the gas was led either to analysis equipment or to a fuel cell.

4.2 Gas analysis equipment

Two devices were thoroughly tested for the reformate gas analysis: *Hewlett Packard 6890 Series Gas Chromatograph* and *Balzer AG quadruple mass spectrometer*

(QMS). After the major effort of testing and calibrating both devices, the previous one was judged to be unsatisfactory for the desired analysis. The second one was found suitable, but with a boundary condition of only qualitative analysis. The essential functioning of mass spectrometry is briefly given here. The design of the specific QMS and the range of its different components are thoroughly presented in Appendix B: Mass spectrometer hardware.

Mass spectrometry is a very versatile technique for measuring the contents of a gas flow. A mass spectrometer works by separating the different atomic mass components of a gas flow and recording their amount separately. Each gas leaves a distinctive mass spectre, and comparing that with spectra of known substances the individual gases can be identified qualitatively. It is typical that different gases have overlapping peaks, which can make identification of individual gases difficult. (37)

All the mass spectrometry scans were done from atomic mass unit (amu) 0 to 60. One scan like this is called a cycle. For each analysis, at least three consecutive cycles were recorded in order to see if the gas composition changes with time. All the plots in this document are in similar scale. Figure 17 is an example of a mass spectre plot. The x-axis gives the atomic mass unit from 0 to 50 (the last ten were left out because of no data points were found in that range). The y-axis value is the mass spectrometer output value (current) for each amu with logarithmic scale. It is underlined that there is no quantitative result of the gas compositions. Although the peak heights in the graphs give an indication of the amounts of gases, they are not comparable between each other. Qualitative analysis still gives a lot of information for the objective of this work. The hydrogen peak at atomic mass unit two is under special focus. For easier interpretation of the coming mass spectre plots there is a table of the relevant gases and their atomic mass units included in Appendix C: Mass spectra.

4.3 Fuel cell and control devices

The fuel cell hardware was one of the regular single cell units used in the laboratory's experimental courses, see Figure 11. The single-channel straight flow fields were of flexible graphite material PAPYEX® from CARBONE LORRAINE. The white gaskets were carefully cut from Teflon to make them fit but not overlap with electrodes. The momentum for tightening the end plate nuts was 5 Nm.

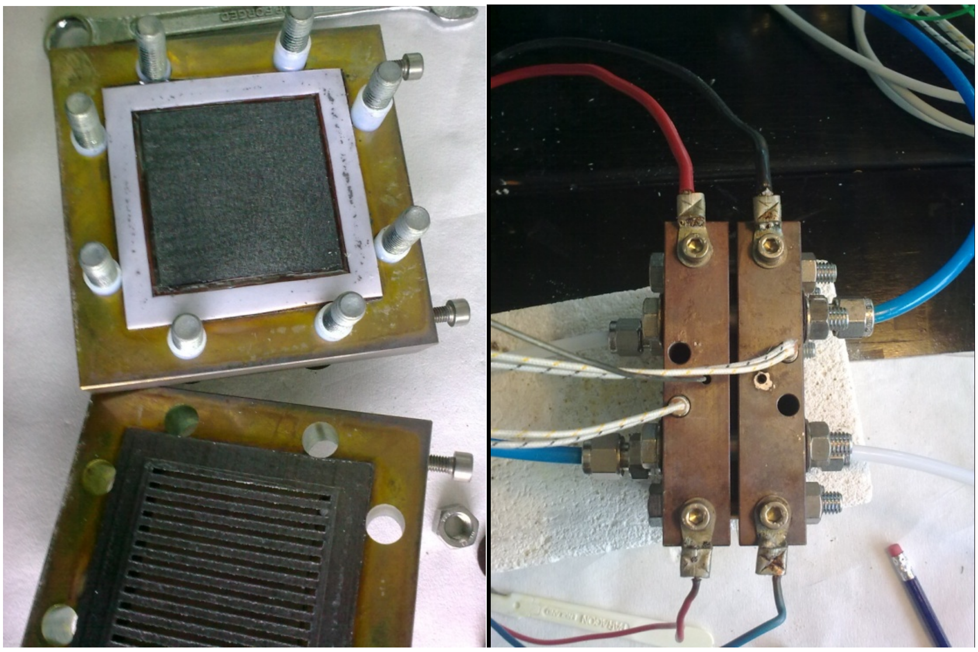

Figure 11: Fuel cell unit open and closed.

The view from the top of the fuel cell in Figure 11 shows the cabling and tubing. The white pair cables in the middle are wires for the heating cartridges. The metal stick is a thermocouple. The red and black cables on the top are for current flow and the small cables on the bottom for voltage measuring. On the sides, white Teflon tubes are for the gas inlet and the blue plastic tubes for gas outlet.

The laboratory's own design *Fuel-Cell Set-up* control boxes were used for temperature controlling and electrical measuring, see Figure 12. The temperature controllers were *CAL3300* from CAL Controls. Each control box had two temperature controllers, two sockets for heaters and two sockets for thermocouples.

Because the reformer unit’s three heating zones occupied three of these kinds of sockets, and moreover there were one required for the fuel cell and one for the evaporator unit, in the end altogether three control boxes were assembled to the setup. Temperature controlling had rather big marginal. The measured temperature kept sometimes oscillating ± 3 °C around the set point.

For electrical measurements, the screw on the left side of Figure 12 was used. After setting the current to the set point value, the voltage kept oscillating some millivolts. After half a minute’s saturation time, the voltage was read from the display, rounded downwards to an accuracy of 10 mV and written down.

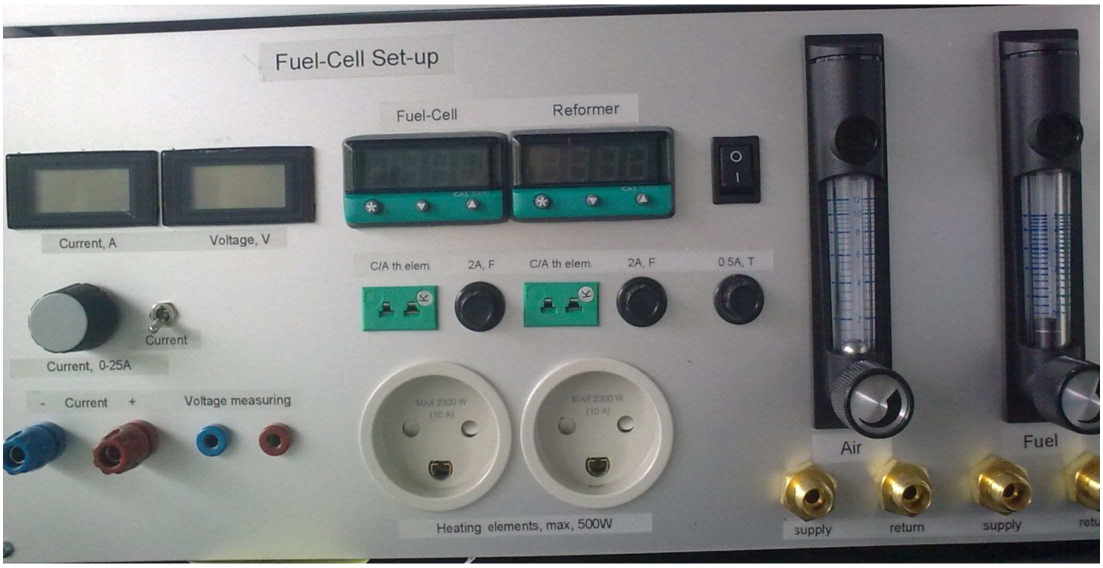

Figure 12: Fuel cell control box for temperature, current and air flow controlling.

One of the control boxes worked also as air flow controller. Hydrogen flow was controlled with BROOKS INSTRUMENTS B.V. H_2 mass flow controller, connected to BROOKS INSTRUMENTS B.V. controller/monitor unit (Model no. *0154/BC1B1*). The calibration charts are presented in Figure A 4 in Appendix A: Calibration charts.

4.4 Catalyst preparation

Four types of catalysts were prepared for placing inside the reformer. They were made into small solid pieces. The preparation procedure is described in detail in the following subchapters. The catalyst for methanol reforming was done with an established laboratory procedure. For DME reforming, three batches of new catalyst with different weight ratios between components Cu-Zn and zeolite ZSM-5 were prepared. Table 2 below lists the catalysts and the weight ratios between the DME reforming components. Densities of the prepared catalyst tablets were measured by micromeritics® AccuPyc 1330 device (model *133/34010/00*).

Table 2: Densities of the prepared catalyst tablets.

Catalyst	Cu-Zn/Al_2O_3	Cu-Zn/ZSM-5 2:1	Cu-Zn/ZSM-5 1:1	Cu-Zn/ZSM-5 1:2
ρ[g/cm^3]	4.19	5.43	4.60	3.79

4.4.1 Catalyst for methanol reforming

The preparation started with making two litres of water solution, containing:

- 0.5 mol $Zn(NO_3)_2 \cdot 6H_2O$
- 0.5 mol $Cu(NO_3)_2 \cdot 3H_2O$
- 0.14 mol $Al(NO_3)_3 \cdot 9H_2O$

The metal ions were co-precipitated at 50 °C by adding 10 wt% Na_2CO_3 solution until the pH value of the solution reached roughly 7. The solution was allowed to digest at 50 °C under stirring for one hour to complete the reaction. After the digesting the solution contained $CuCO_3$ and $ZnCO_3$ powder and dissolved $NaNO_3$. The solution was filtered and thoroughly washed with hot distilled water to remove the nitrate and sodium ions. In order to obtain the oxide form of the catalysts, the catalyst was calcined in a furnace LYNGBYOVNEN (type *K 30*) with the following program:

- Heating up to 95 °C with heating rate of 120°C.
- Maintaining the temperature at 95 °C for five hours in order to slowly remove water traces.
- Heating further to 400 °C with the same heating rate.
- Maintaining the temperature at 400 °C for five hours.

The pictures before and after are shown in Figure 13. The calcined catalyst was collected and put into 1.5 litres of 0.5 wt% NH_4HCO_3 solution in order to remove the residual Na_2O. The solution was left stirring for more than the instructed minimum time of one hour. The slurry was filtered and thoroughly washed with distilled water. Finally, the catalyst cake was dried in a furnace ELEKTRO HELIOS (type nr. *284 52C*) at 120 °C overnight.

Figure 13: Catalyst production. Left and middle: before and after calcination in oven. Right: stirring the catalyst in 0.5 wt% NH_4HCO_3 solution.

4.4.2 Catalyst for DME reforming

The catalytic reaction of DME reforming is a two step process. In the first step the catalyst material helps to convert DME to methanol. The second step is methanol reforming. For the second step, the catalyst was prepared from copper and zinc nitrates as described above. The first catalyst was purchased, but before that other options were looked into as well. In following subchapters the preparation is described in detail.

To make a single catalyst for the whole reaction, the catalysts for each reaction were mixed. Three batches with different weight ratios between the two components were prepared in order to experiment how much the weight ratio affects the results. The ratios were 1:1, 1:2 and 2:1.

4.4.2.1 Step 1: splitting of DME molecule

A zeolite *Ueticon 13X-1001* molecular sieve (current name *Zeochem Z10-01*) was available in the laboratory and planned to be used as a catalyst. The product had a shelf life of two years. Because it had been stored for much longer time than that, the plan to use this zeolite was abandoned. There was also a jar of small balls with note Al_2O_3, which seemed promising. In the case of gamma-aluminium form, Al_2O_3 would have been suitable for the desired reactions. Unfortunately, X-ray analysis gave a result of completely different compound.

Finally, a commercial solid acid zeolite for the reaction to split the DME molecule was purchased from Zeolyst International. The trade name of it is *CBV2314* and product description ZEOLITE AMMONIUM ZSM-5 POWDER. It is fine white powder and has characteristics of SiO_2/Al_2O_3 mole ratio 23 and surface area 425 m^2/g. This product had the closest available SiO_2/Al_2O_3 mole ratio compared to the Si/Al ratio of 25 that several research groups have previously used for DME steam reforming as explained in Chapter 3.

4.4.2.2 Step 2: methanol reforming

Cu-Zn catalyst was prepared with the procedure described in Section 4.4.1 with the difference of leaving $Al(NO_3)_3 \cdot 9H_2O$ out.

4.4.3 Pressing the catalyst tablets

The work was not ready yet, because the catalysts could not be used as powder. Powder would fill up the reformer tube so impermeably that the gas coming into the tube would not have enough space to enter, react and the reactants flow out. Therefore, the three powder mixtures were pressed into small tablets with appropriate manual equipment and a PERKIN-ELMER hydraulic press. Before pressing the tablets, 7 wt% of graphite powder was added to the mixtures as lubricant for the pressing equipment. 1 g of powder was weighed for each tablet. The tablet diameter was 13 mm and thickness 3-4 mm. The tablets were too big as such for the reformer tube, so they were each cut into about four pieces. See Figure 14. The DME reforming catalyst pieces did not unfortunately stay that well as chunks but were rather easily broken back to powder. This was most probably because of the soft form of zeolite powder. The batch with most zeolite did not even make proper tablets, and the powder made the tablet pressing equipment to become stuck very easily.

Figure 14: Catalyst tablet preparation.

4.5 MEA preparation

Altogether nine pieces of MEAs were prepared in-house for this work. They were made according to the procedure of the DTU spin-off company Danish Power Systems (DPS) with much help from the personnel working there. Five of the MEAs were DPS standard MEAs, described below in Section 0 and four of them of new type with special catalyst on anode electrode, described in Section 4.5.2. The five standard MEAs were called *S1-S5* and the four special ones *R1-R4*, see Table 3. The electrode pieces themselves were 5.0 cm x 5.0 cm, but since the gaskets covered 1 mm from each side, the active area became $(4.8\ \text{cm})^2 = 23.04\ \text{cm}^2$.

Table 3: MEA nomenclature.

Name	Anode catalyst	Cathode catalyst
S1	Pt/C	Pt/C
S2	Pt/C	Pt/C
S3	Pt/C	Pt/C
S4	Pt/C	Pt/C
S5	Pt/C	Pt/C
R1	Pt/Ru/C	Pt/C
R2	Pt/Ru/C	Pt/C
R3	Pt/Ru/C	Pt/C
R4	Pt/Ru/C	Pt/C

4.5.1 MEAs with Pt/C catalyst

First of all, the catalyst ink was prepared by DPS. The composition of it was the following:

1.83 g	40 % Pt/C catalyst, previously made in laboratory
1.28 g	85 % phosphoric acid
87.49 g	Formic acid
29.75 g	0.5 % PBI and 0.5 % phosphoric acid in formic acid

This ink was manually sprayed on a large sheet of carbon paper inside a fume cupboard. In between the several spraying layers the sheet was dried once in an ELEKTRO HELIOS oven (type nr. *284 52C*) at 125°C for 30 minutes in order to make the next ink layers absorb better. After the spraying, the sheet was placed in the oven at 125°C overnight. The next day ten pieces of 5 cm x 5 cm were cut out, corresponding to five anodes and five cathodes. The PBI membranes were made by DPS and had a molar weight of approximately 50 000 g/mol as a mixture of seven different batches from molar weight scale 40 000 – 70 000 g/mol.

For each MEA, the two electrodes, two transparent plastic gaskets and PBI membrane were assembled together by hand with two aluminium end plates. The aluminium had an acid resistant coating because of the presence of formic and phosphoric acid. The plates were adjusted together and moved to a hot press machine 30 TON PRESS *C-30* (Research & Industrial Instruments Company, London England). The hot press temperature was 160°C, the pressure was equal of 6 ± 1 tons and the press was on for seven minutes for each MEA. Finally, the platinum loading was 22.76 wt%, corresponding to 0.69 mg/cm^2.

4.5.2 MEAs with Pt-Ru/C catalyst

Four special MEAs with a slightly different catalyst material were prepared. The idea was to promote the reforming reaction even more, meaning that reforming could still take place at the fuel cell anode. On the cathode side, the ink used was as described above. On the anode side, the ink, prepared again by DPS, composed of the following components:

• 0.29 g	40 % Pt 20 % Ru on Alfa Aesar 044172 carbon black
• 0.09 g	85 % phosphoric acid
• 8.39 g	Formic acid
• 1.36 g	PBI/phosphoric acid solution

The Pt-Ru loading became 45.78 wt%, corresponding to 0.61 mg/cm^2.

4.5.3 Break-in

The MEAs were made in-house and not on a factory production line, so there was already a natural variation in quality. Each MEA had an overnight break-in with sufficient gas flows and low current of 3 A, but an advanced break-in procedure like in (38) was not executed. The numerous results with different parameters are to be compared to that best performance with hydrogen for each specific MEA. A reference run with pure hydrogen was always recorded as the first thing on fuel cell experiment days in order to ensure comparability of the test with the same MEA.

5 Results

5.1 Validation of MEAs and FC reference runs with H_2

The very first test was a comparison of MEAs. The performance of standard MEAs S2 and S5 made for this work was compared with the data of a similar MEA earlier produced and tested by DPS, although not in an identical test setup. The test temperature was 170 °C. As seen in Figure 15, comparability is rather good. The results are well within the validation marginal. The effect of hydrogen flow rate was measured and is indicated in Figure 16. The measurement was made in order to have a reference for later experiments when hydrogen is supplied from the reformer. The hydrogen flow rate can then not be explicitly measured but can be estimated with the limiting current.

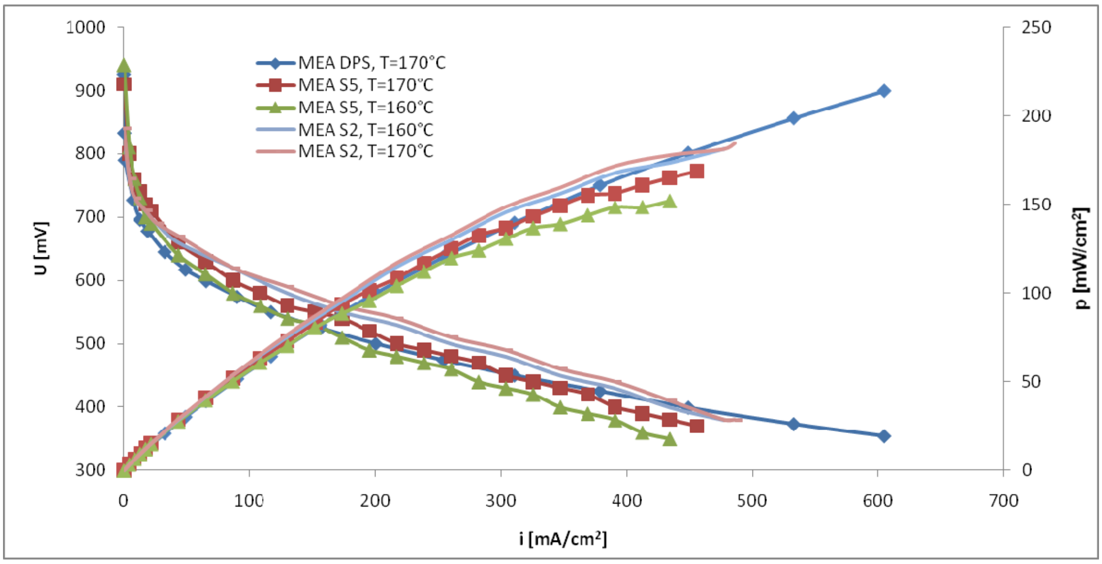

Figure 15: Comparison of MEAs S2 and S5 performance with reference data of similar MEA tested by DPS.

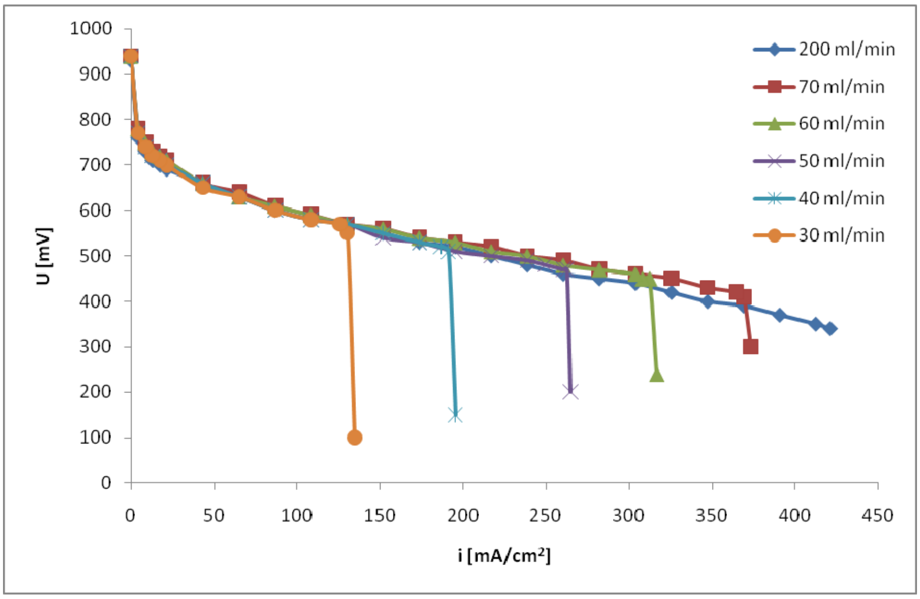

Figure 16: Effect of hydrogen flow rate. MEA S5, T = 160 °C.

5.2 Methanol reforming

Methanol reforming experiments were made in order to approach step by step more complicated DME reforming. Methanol reforming is a widely studied field and there was lot of knowhow for it in the laboratory. The purpose of these experiments was to test the setup, because the catalyst itself was known to function well, to test the mass spectrometer for analysing the gas coming out and also to gain experience in performing measurements all in all.

The reformer tube was filled with 23.43 g of Cu-Zn/Al_2O_3 catalyst. It occupied about 12 cm of the 25 cm long tube and the rest of the volume was filled up with steel wool. The function of steel wool is manifold. It functions as a heat conductor, and moreover, it helps the liquid drops to evaporate. The reformer was heated up to 150 °C and a small hydrogen flow of 30 ml/min was left running into it overnight. This procedure prepares the catalyst for reforming. It reduces ZnO and CuO to Zn and Cu. Two batches of feed were mixed: methanol and water in molar ratios of 1:1 and 1:1.5. With S/C notation these are S/C=1.0 and S/C=1.5, respectively.

5.2.1 Gas analysis

A 1:1 molar solution of methanol and water was pumped into the reformer by pump rate 0.9. It corresponds to 350-360 ml/min of post reformer gas flow rate (Appendix A: Calibration charts, Figure A 3).

Altogether six cycles of mass spectrometer scans from atomic mass unit 0 to 60 were run. Figure 17 shows the mass spectre of the final cycle. The peak at amu 2, corresponding to hydrogen, is an order of magnitude higher than the next highest peak at amu 44, corresponding to CO_2. The CO peak is at amu 28. The ratio of hydrogen, carbon dioxide and carbon monoxide after the methanol/water solution has reacted with $Cu\text{-}Zn/Al_2O_3$ is known to be in range

74-75 %	H_2	amu: 2
24-25 %	CO_2	amu: 44
0-2 %	CO	amu: 28

Figure 17's spectre indicates that this is likely to be the case with peaks on amus 2, 44 and 28. In addition to these three gases, amus of 12, 16 and 18 were detected, most probably corresponding to carbon, methane and water, respectively. Carbon atoms are not expected from the reaction, but might be formed as breakdown products during ionization in the MS.

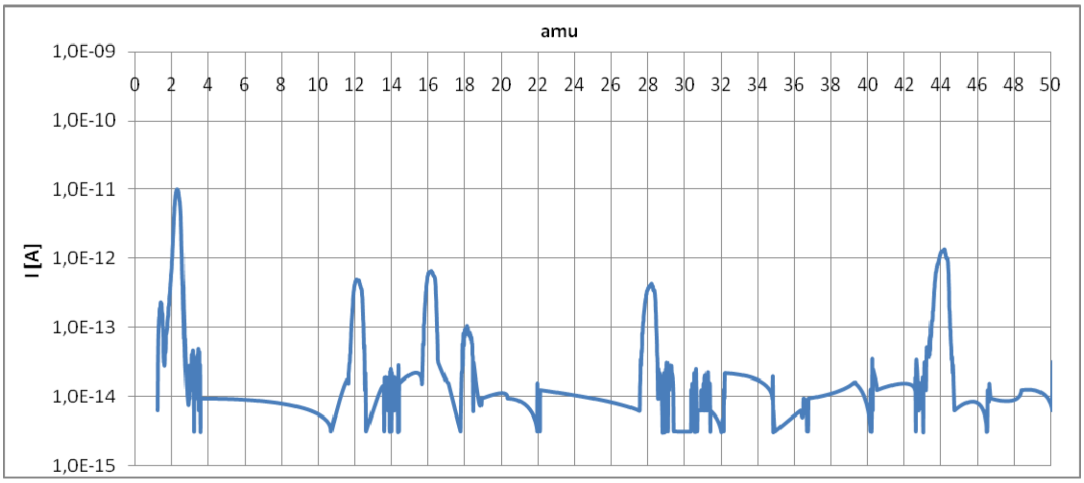

Figure 17: Methanol reformate gas. S/C 1.0, pump rate 0.9, $T_{reformer}$ = 225 °C.

5.2.2 FC performance

A lot of fuel cell performance data was harvested. The parameters studied were reformer temperature, fuel pump rate to the reformer and steam to carbon ratio (S/C). The fuel pump rate is given as the scale number. The pump rates in ml/min are given in Appendix A: Calibration charts, Figure A 1. As far as the S/C 1.0 methanol/water solution is concerned, also the flow rate of the gas coming out from the reformer is plotted as a function of the pump scale, see Figure A 2 in Appendix A: Calibration charts.

With optimal parameters, the performance with the reformate gas was very close to that of pure hydrogen. As an example, Figure 18 plots the effect of reforming temperature on the fuel cell polarization. Obviously, enough hydrogen is produced in all cases and mass transport does not limit the performance. Around the reforming temperature of 225 °C, the performance with the reformate gas is very close to one with pure hydrogen. The performance gradually drops as the reforming temperature is increased.

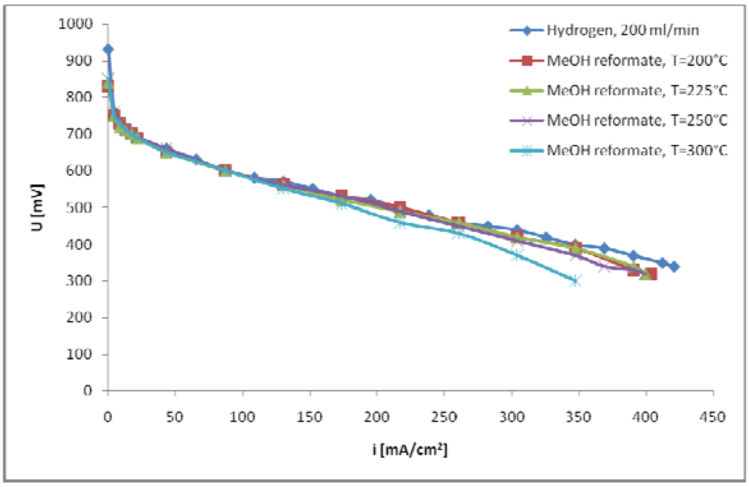

Figure 18: Effect of reforming temperature. MEA S5, S/C = 1.5, pump rate 0.7, $T_{\text{fuel cell}}$ = 160 °C.

Rest of the polarization curves from the numerous experiments can be found from Appendix D: FC performance with methanol reformate gas. The thorough methanol reforming experiments proved that the setup works well. The next job was to modify it for more advanced experiments.

5.3 DME reforming

The next issue was direct DME. The reformer unit was taken out from the setup and replaced by an evaporator unit. It was filled up with steel wool and heated up to 170 °C, ten degrees higher than the fuel cell operation temperature. The gas coming out from the evaporator was led straight to the fuel cell anode inlet. The results were poor with both S and R type MEAs (see Table 3) and are not plotted.

All the four prepared catalysts were tested for DME reforming. The first experiment was to test how the fuel cell performance is with DME and water run through the traditional methanol reforming catalyst Cu-Zn/Al_2O_3. After that the three special catalysts were tested one after another, the reformate gas analysed and FC performance recorded with different parameters. The most relevant mass spectrometer plots of reformate gases are presented in the following subchapters. All of the plots can be found in Appendix C: Mass spectra.

As for the hardware, the separate evaporator unit before the reformer was added to the setup only for the last experiments with catalyst Cu-Zn/ZSM-5 1:2 and the final Cu-Zn/ZSM-5 1:1 revisited. Before that the evaporating took place in the reformer. See Figure 8 for a schematic picture of the setup.

The S/C ratio was now trickier to control than earlier with methanol. Methanol and water, both liquids, could be easily mixed to batch, but DME is a gas when taken out of the container with moderate pressure. The calculation is shown in detail in Appendix E: Flow rate calculation.

5.3.1 Catalyst Cu-Zn/Al_2O_3

Expectations for the FC performance with DME and this distinctive catalyst were not high. Still, it was interesting to see what happens. The experimental procedure was the following. The first thing was again to record the standard FC performance with hydrogen as a fuel. Then the hydrogen tube fuelling FC anode was replaced by the tube from the reformer setup. The reformer was fed by H_2O/DME vapour in a molar ratio of 3:1, corresponding to the S/C ratio of 1.5. The DME flow rate was set to about 165 ml/min and liquid water flow rate to about 0.36 ml/min.

The FC polarization was recorded at reformer temperatures of 250 °C, 300 °C, 350 °C, 400 °C and 425 °C. As seen in Figure 19Figure 19 below, the performance is poor even with the highest temperature. After the reformer had cooled down and the FC run with pure hydrogen for a while, another set of measurements were taken. This time the H_2O/DME molar ratio was 3.5:1, corresponding to a S/C ratio of 1.75. In practise this means that the liquid water flow was increased to 0.42 ml/min. The FC polarization was recorded at reformer temperatures of 300 °C, 350 °C, 400 °C and 425 °C.

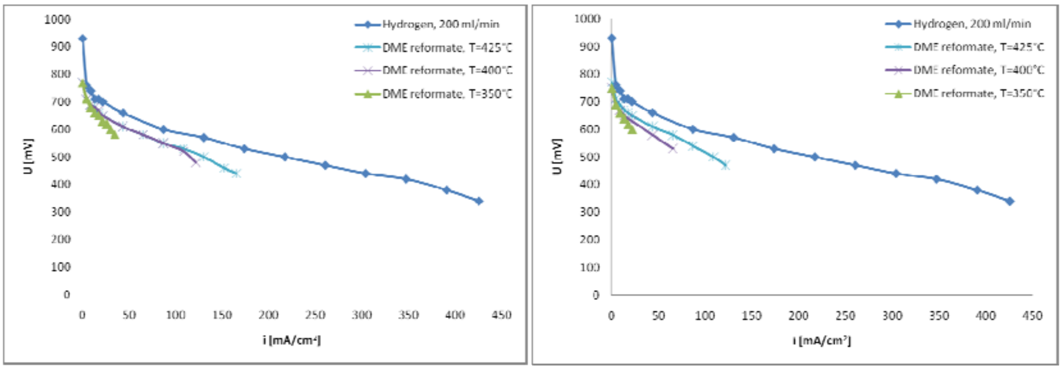

Figure 19: Effect of reforming temperature. MEA S5, $T_{\text{fuel cell}}$ = 160 °C. Left: S/C=1.5. Right: S/C=1.75.

Comparing the two consecutive sets of potential scans in Figure 19, the second one looks like. The reason could be in S/C ratio, in the fuel cell degradation or in that the catalyst has suffered and the level of hydrogen is decreasing. With pure hydrogen the fuel cell performance did not change, indicating that the problem lies somewhere else. To study this further, and as a last experiment with the Cu-Zn/Al_2O_3 catalyst, methanol reforming was tested once more. Figure 20 shows that the performance really had dropped. It is likely that the catalyst has suffered. The calcination temperature in the catalyst production process had been 400 °C. The temperature scan in this set of experiments exceeded that, which probably caused irreversible damage.

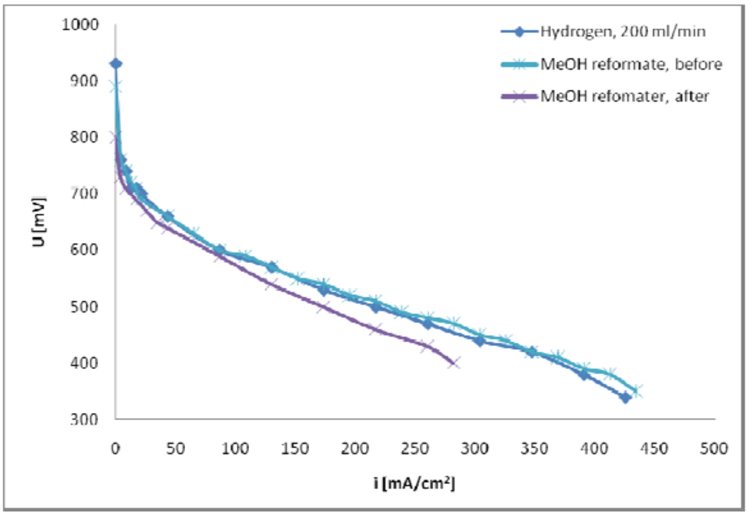

Figure 20: FC performance with methanol reformate gas before and after DME reforming experiments. MEA S5, S/C = 1.0, pump rate 1.0, $T_{\text{fuel cell}}$ = 160 °C.

5.3.2 Catalyst Cu-Zn/ZSM-5 1:1

The reformer was filled up with 26.34 g of catalyst and the remaining volume with steel wool. Mass spectre analysis was done twice: as a first and last thing with this catalyst. Both analyses had three cycles. The catalyst was not even reduced before the first analysis. The result of it was promising at first but not for long. Figure 21 and Figure 22 plot the spectre of the first and the second cycle. As can be seen, the amount of hydrogen as well as other gases drops dramatically, indicating a sudden decrease in catalyst performance.

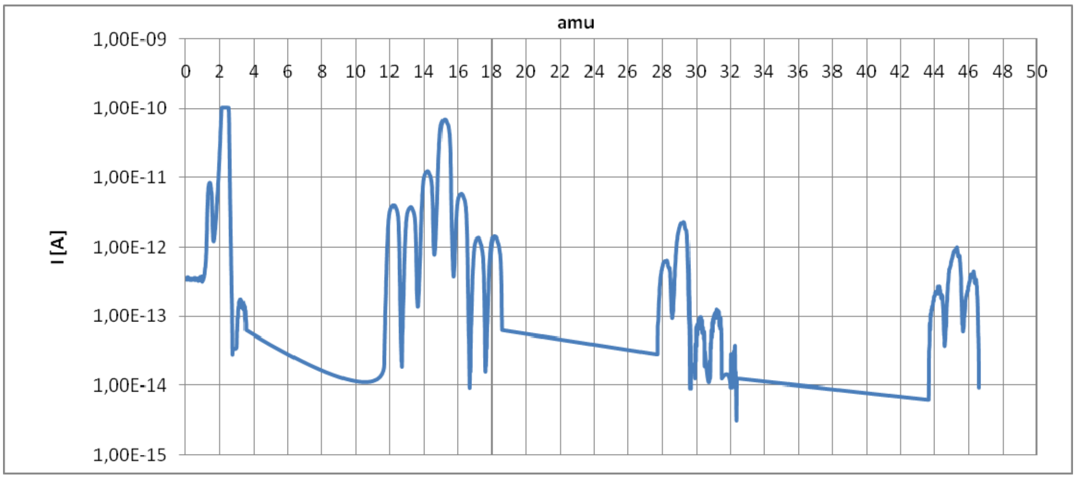

Figure 21: Cycle 1/3. S/C = 1.5, T$_{reformer}$ = 300 °C.

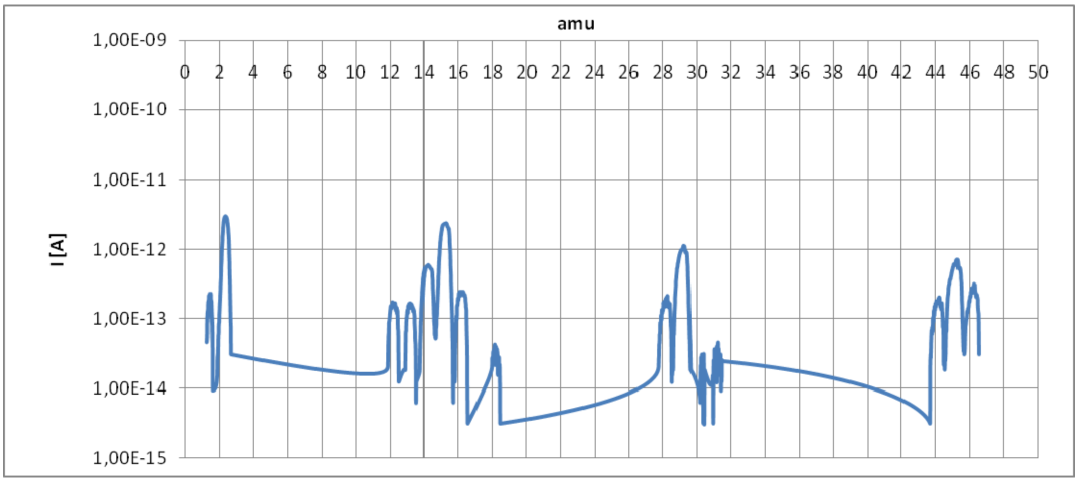

Figure 22: Cycle 2/3. S/C = 1.5, T$_{reformer}$ = 300 °C.

The well behaved MEA S5 was still in use and it was now tested with the reformate gas. Figure 23 plots the polarization curves in permutation of parameters 300 °C, 350 °C, S/C=1.5 and S/C=1.75. The performance does, as expected, not climb as high as with methanol, but is pretty good with S/C=1.50 and 350 °C.

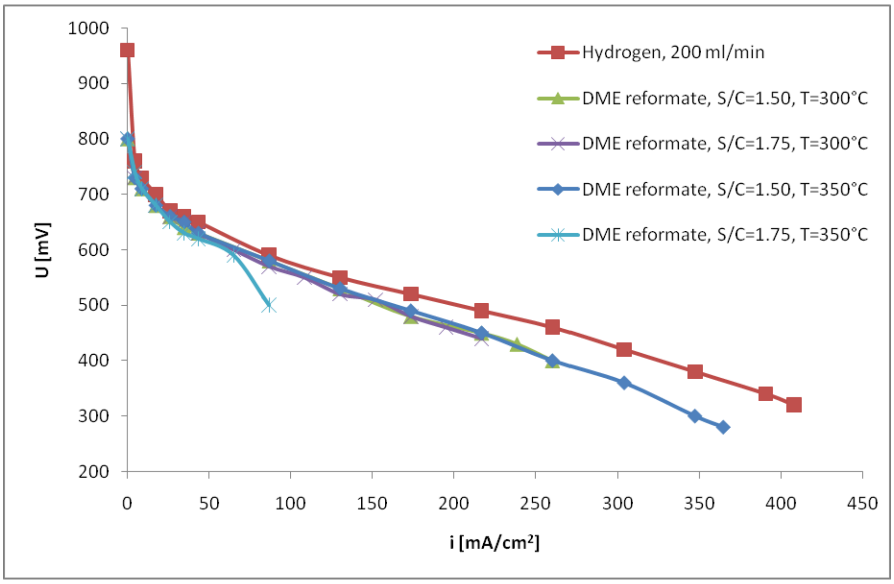

Figure 23: Performance with DME reformate gas by catalyst Cu-Zn/ZSM-5 1:1. The index is in chronological order of measurements from top to bottom. MEA S5.

After all these fuel cell experiments, the catalyst was under reduction at 150 °C overnight with 30 ml/min hydrogen flow for as long as six days. The goal was to make CuO and ZnO react with H_2 to form Zn and Cu and water vapour. It did not help; with similar input parameters as before the flow coming out was minimal. This could be directly observed from the amount of bubbling in the condenser bottle.

The experiments continued with other catalysts, but as a very last experiment, this catalyst was loaded again to the reformer and mass spectrometer analysis run once more. The mass of the catalyst inside the reformer was 20.99 g and the remaining volume in the ends of the tube was filled up with steel wool. The goal of this experiment was to study if a separate evaporator unit before the reformer would have an effect and even if not, what is the composition of the gas. For the final time, the catalyst was reduced overnight at 150 °C with 30 ml/min hydrogen flow. Contrary to all the other MS recordings, this was done at a reforming temperature of 350 °C instead of 300 °C. This was because the flow rate from the reformer was too moderate at 300 °C. The first MS cycle indeed indicated a trace amount of hydrogen, but very much lower compared to that of the first analysis. The second and third cycle had no hydrogen anymore. The figures are presented in Appendix C: Mass spectra.

5.3.3 Catalyst Cu-Zn/ZSM-5 2:1

The reformer was filled up with 28.28 g of catalyst and the remaining volume with steel wool. Before the analysis, the catalyst was used for one day of experiments. After that the catalyst was reduced at 150 °C overnight with a 30 ml/min hydrogen flow. To stabilise the flow to the MS, pure Argon was added to the MS inlet. Argon flow rate was set to 300 ml/min, whereas the reformate flow rate was adjusted to about 100 ml/min. For the rest of the MS scans, the Argon peaks 20 and 40 are present. The gas is not as hydrogen-rich as with the previous catalyst. Moreover, the amount of hydrogen drops dramatically again already in the second cycle. The number of recorded cycles was nine, but the last seven were so similar to the second that only the three first cycles are presented in Appendix C: Mass spectra and two first here below in Figure 24 and Figure 25.

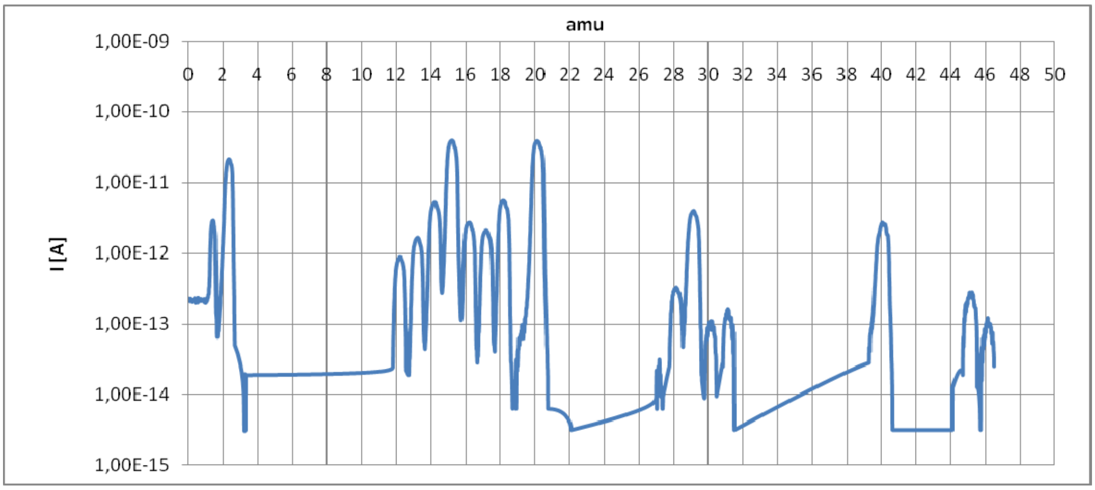

Figure 24: Cycle 1/9. Argon as a carrier gas. S/C = 1.5, $T_{reformer}$ = 300 °C.

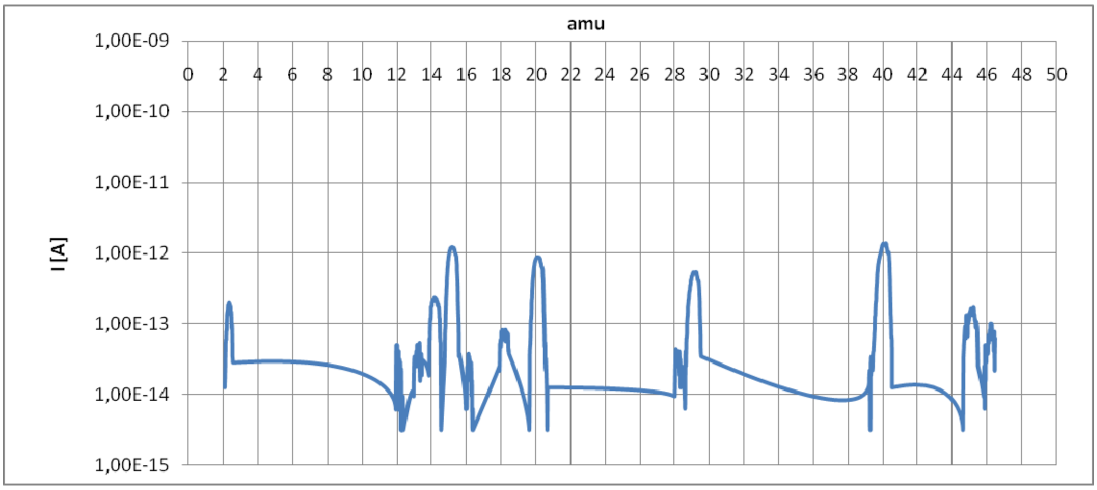

Figure 25: Cycle 2/9. Argon as a carrier gas. S/C = 1.5, $T_{reformer}$ = 300 °C.

MEA S5 was tested with pure hydrogen and compared with the earlier similar tests. The MEA had suffered a lot, so fresh MEAs *R4* and *S2* were taken into use instead. Before the experiments, they had following break-in procedure:

- T = 160 °C
- I = 3 A / i = 130 mA/cm^2
- H_2 flow = 50 ml/min
- Ait flow = 100 ml/min

MEAs *R4* and *S2* were compared with pure hydrogen as a fuel and the output was identical. The reformate gas was fed to the fuel cell with *R4* and parameters varied. The results are plotted in Figure 26.

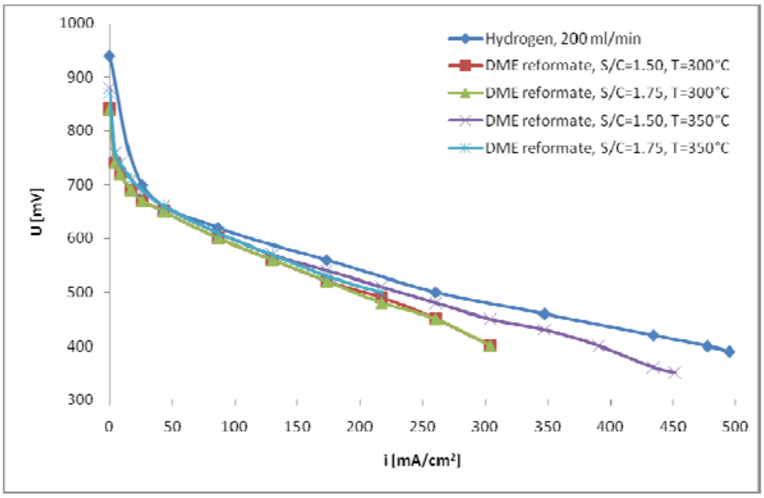

Figure 26: **Performance with DME reformate gas by catalyst Cu-Zn/ZSM-5 2:1. The index is in chronological order from the top to the bottom. MEA R4.**

MEA *R4* performance was recorded with pure hydrogen after these experiments and it was similar to that of before the experiments so the MEA was not damaged.

5.3.4 Catalyst Cu-Zn/ZSM-5 1:2

The reformer was filled up with 13.36 g of catalyst and the remaining volume with steel wool. This catalyst had been reduced at 150 °C and a 30 ml/min of hydrogen flow over the weekend. The mass spectre analysis of five cycles was recorded first. The result from each cycle was more or less similar. A separate evaporator unit was mounted before the reformer. The evaporator unit was filled with steel wool and heated up to 200 °C to guarantee that the DME and water were in gas phase before entering the reformer. The second recording had again five cycles and their results were quite similar. Only the last cycles of both recordings are plotted in Appendix C: Mass spectra, Figure C 15 and Figure C 16. The plots are very similar with merely a tiny trace of hydrogen. Apparently, the evaporator unit did not have any effect on the mass spectre. The fuel cell was tested with both MEAs *S2* and *R4* fuelled by this reformate gas, but the performance was practically zero.

6 Discussion

Based on the work done and the data harvested it can be summarised that the setup and the operation of it were well functioning for methanol reforming, but not sufficient enough for proper DME reforming.

Since the focus of the study was the fuel cell's anode feed, all the other fuel cell operation conditions were kept optimal as far as possible. The operation temperature of the cell was all the time at 160 °C, high enough for high performance but not too high to cause short term degradation of the membrane. The air flow on the cathode side was kept sufficient all the time.

Methanol reforming was executed with a high hydrogen yield. Comparing the fuel cell polarization curves when fuelled by pure hydrogen and the reformate gas, the difference is small. Flow rate reduction had its natural effect of limiting current, plotted in Appendix D: FC performance with methanol reformate gas, Figure D 1. Only when the reforming temperature was raised to 300 °C the performance started to sink, see Figure D 3 and D 4. That is unexpected, but it is not necessarily consequence of the temperature. The runs at the highest temperatures were made as the last experiments of the sets, so there is a chance that something degraded or the numerous parameters could not be held optimal for as long as needed.

In DME reforming, a high hydrogen yield was gained but could not be sustained. At first it was experimentally confirmed that the mere methanol reforming catalyst Cu-Zn/Al_2O_3 did not perform well. Out of the three batches of new zeolite catalysts two worked. They were the weight ratios 1:1 and 2:1. The best polarization curve with the DME reformate feed was recorded with the catalyst Cu-Zn/Al_2O_3 2:1 and MEA *R4* and is plotted in Figure 26. R type MEAs had a ruthenium loading in addition to platinum, which most probably had a helping effect. The ruthenium sites absorb water molecules that react with CO.

For the functioning zeolite catalysts, the hydrogen yield was measured to be high in the beginning, but then to drop and stay low. All in all, the fuel cell performance figures that are plotted are the ones with the highest performance. After those recordings, the performance kept decreasing, no matter which MEA type or flow rate.

The DME reforming results indicate that the reason was inside the reformer. Because of this the numerous fuel cell potential scans with different parameters like S/C ratio lose some of their importance. If the catalyst caused problems for the desired reactions more and more over time, the different input parameters become irrelevant. Catalyst poisoning could be a potential reason. Reducing zeolite catalysts with low hydrogen flow was tried, but with no success. The gas coming out did not contain hydrogen anymore.

Still, the most probable reason for the catalyst behaviour is too high reforming temperature for the zeolite material. Based on research by (39), the temperature range from about 275 °C upwards changes the dominant reaction over the zeolite catalysts. Instead of DME hydrolysis, conversion of methanol and dimethyl ether to higher molecular weight species, commonly referred to as methanol-to-gasoline (MTG), starts to dominate. The temperatures used in this work are at the upper limit for DME hydrolysis over zeolites, 300 °C or even higher, 350 °C. As set in the initial experiment conditions, the mass spectrometer scans were executed to amu not higher than 60 so there is no data to verify this theory. However, if lower reforming temperatures are tested in further studies, there is a good reason to expect the hydrogen yield to stay high.

The control of water addition is another critical issue and might have caused problems. The fact that the DME was controlled in the gas phase and water in the liquid phase in the inlet made the controlling of the S/C ratio tricky. The meters were volume flow meters, not mass flow meters. Volume is a function of pressure and temperature, and although these factors were maintained as far as possible at desired values in DME feed, even a minor change has an effect on the S/C ratio.

The separate evaporator unit was not a part of the setup from the beginning on. Instead, the reformer tube had steel wool in it as well and was expected to vaporise liquid water. Speculatively, there is a chance that the reformer volume was not large enough for the liquid water to evaporate with the flow rates used. On the other hand, the reformer temperatures were throughout the experiments far higher than water boiling point in the inlet and the assembly of the setup was made keeping the control of water in mind.

In this work, a mass spectrometer was used to qualitatively distinguish different components from the reformate gas stream. A quantitative analysis would give a lot more information and make the plots comparable, so updating the equipment is suggested for further research on the topic. Suitable device for the analysis would be a mass spectrometer, a gas chromatograph, or for more reliability a combination of these two.

7 Conclusion

The aim of the work was to build a setup for methanol and DME reforming and high temperature PEM fuel cell experiments. That was successfully done and a lot of reforming data and especially fuel cell performance data was harvested. One methanol reforming catalyst and three different batches of DME reforming catalyst were made and tested. Altogether nine membrane electrode assemblies (MEAs) of two different types were made in-house for this work.

Building and calibrating the setup took considerably much time and effort within the scope of a Master's Thesis. The main difficulties were with the equipment for analysing the reformate gas. Qualitative analysis was done with a mass spectrometer and different components in the gas stream could be recognised.

The methanol reformate gas was hydrogen-rich and worked well as a fuel cell feed. The performance was close to that of pure hydrogen. A zeolite catalyst was proven to split the DME molecule and hydrogen-rich gas was produced, but only for a while. Two of the new zeolite catalysts performed weaker and weaker over time, resulting in smaller and smaller hydrogen yield. One of them did not give any hydrogen yield. The lowering of the hydrogen content in the reformate gas was proven both with mass spectrometry and the fuel cell performance over time. This is most probably explained by too high reforming temperatures. The best fuel cell performance with the DME reformate gas as a fuel was measured with the Cu-Zn/ZSM-5 2:1 catalyst and Pt-Ru/C MEA.

The work studied the reforming of DME for high temperature PEM fuel cells. Even with a relatively simple setup like this, the amount of parameters became much larger than initially planned and unexpected issues were encountered. This gives an indication of all the research and willpower needed in catalytic chemistry as well as in the level of system development required to bring into use a new potential fuel like DME.

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Appendix A: Calibration charts

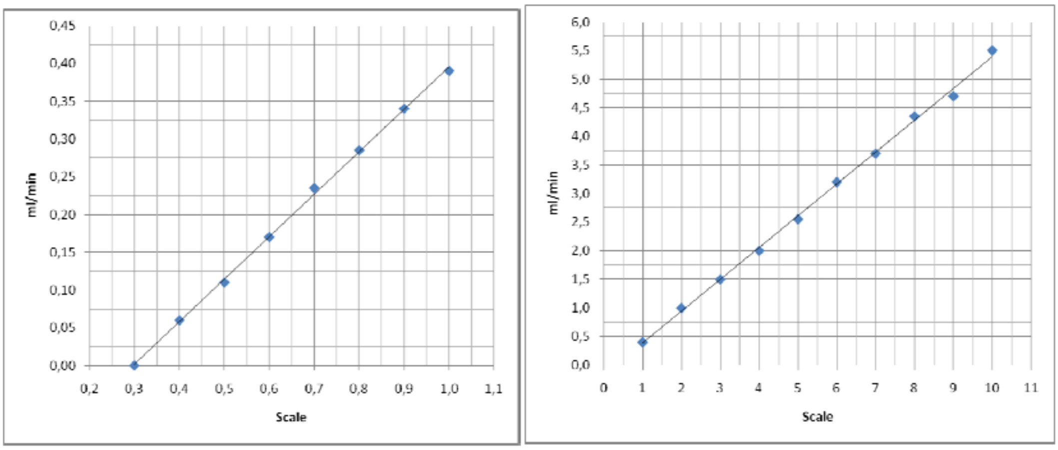

Figure A 1: Pump rate of Masterflex Console drive as a function of scale numbers. Linear fit. Left: Small scale numbers. For each scale value, volume filled in 10 minutes was recorded and then divided by 10. Right: Big scale numbers. For each scale value, volume filled in 1 minute was measured twice.

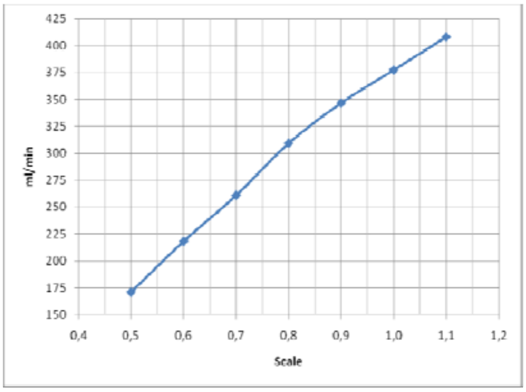

Figure A 2: Reformer outlet gas flow rate as a funtion of methanol – water 1:1 molar ratio solution pump rate with Masterflex Console drive. Averaged from at least ten data points for each scale value. There was a 15 min flow rate stabilation time after changing the scale value.

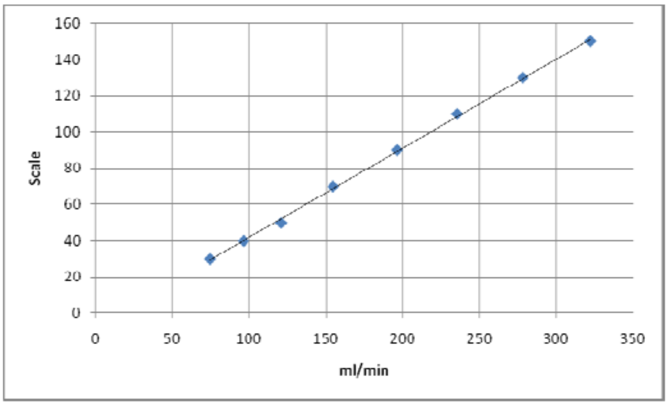

Figure A 3: DME flow meter SHO-RATE calibration chart. Values averaged from three measurements. Linear fit.

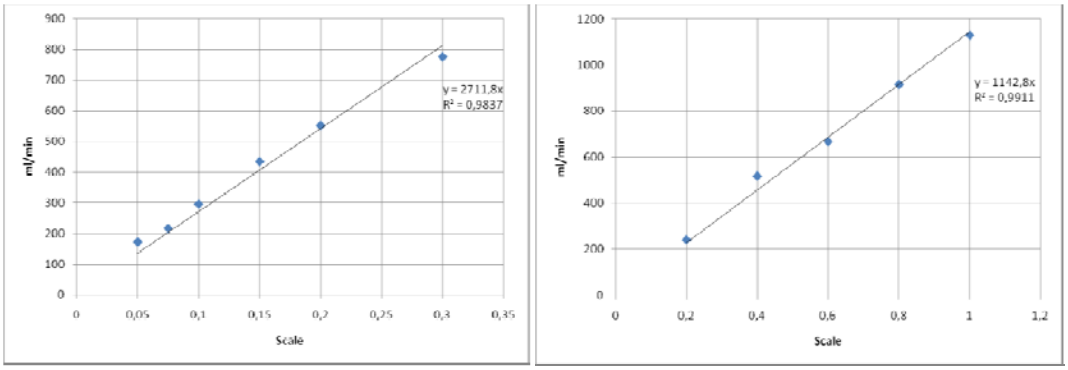

Figure A 4: Flow charts for FC reactants hydrogen (left) and air (right). Linear fit.

Appendix B: Mass spectrometer hardware

This appendix presents the design and components of the quadruple mass spectrometer (QMS), which was used for gas analysis. It was manufactured by Balzer AG, now Pfeiffer Vacuum. The description is based on the Ph.D. thesis of Lars Nilausen Cleemann (37).

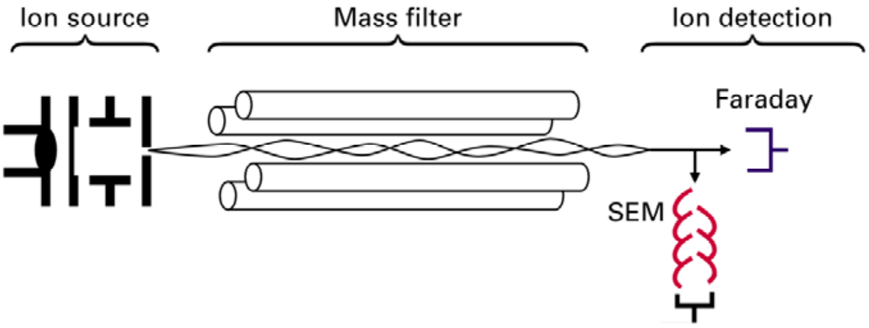

Figure B 1: Basic principle of QMS mass spectrometer (40)

A QMS mass spectrometer can be separated into three parts as shown in Figure B 1. The functions of the different parts are as follows.

Ion source

A small sample of gas is passed into the ion source, where it is ionised by electron impact. The electrons are thermally emitted from the filament in the ion source. After ionisation the positive ions are focused, accelerated and led into the mass filter (41). The ion source used is a crossbeam Tungsten filament.

Mass filter

QMS is named after the way the mass filter works. The ions are sorted and separated according to their mass and charge. The mass filter consists of 4.8 mm molybdenum rods connected to both direct current (DC) and radio frequency (RF) voltages. Each pair of rods is 180 °C out of phase with the other pair. By varying the DC and RF voltages only a specific mass relative to charge is allowed to stay in the centre of the filter and thus to pass through to detection. The DC and RF voltages are varied with time, and this allows for the whole mass range to be detected (42).

Ion detection

After separation, each mass fraction is detected electrically using either a Faraday or secondary electron multiplier (SEM) detector. The choice of detector is dependent on the needed accuracy and speed of measurements. Throughout the experiments the Faraday detector was used. It is less accurate than the SEM, but more stable and the accuracy is sufficient for the experiments.

The QMS used in the work was manufactured by Balzer AG, now Pfeiffer Vacuum, and built up of the following components (40).

The quadruple mass analyser QMA 400. The main part of the spectrometer consists of the ion source, mass filter and detectors, as well as a turbo molecular drag pump for controlling the pressure. At standby the pressure is around $1 \cdot 10^{-8}$ mbar. During measurements the pressure is raised to between $1.0 \cdot 10^{-5}$ and $2.0 \cdot 10^{-5}$ mbar, something which is easier said than done. The screw to adjust the pressure acted very easily to the smallest moves. The more accurate the pressure, the better. The goal value was $1.4 \pm 0.1 * 10^{-5}$ mbar. During the runs, the pressure fluctuated $\pm 0.2 * 10^{-5}$ mbar.

The quadruple multichannel sequential measuring unit QMS 421. This unit houses the systems power supply, as well as a range of boards for controlling different functionalities.

The quadruple controller board QC 421. Links the different parts of the system together. An external computer is connected to the board for recording measurements. The measurements are done using Quadstar sotware, ver. 7.00 from Pfeiffer Vacuum. The board also links the controlling software to the RF generator, and supplies power to the generator.

The Ion source power supply board IS 420. Supplies power to the ion source filament.

The high voltages power supply HV 420. Supplies voltages for the SEM detector.

The RF generator QMH 410. Produces the radio frequency high voltages for use in mass separation.

The Electrometer preamplifier EP 112. Two of these are used. They connect the detectors with the RF generator and amplify the ion voltages (from the Faraday detector) or electron voltages (from the SEM detector) and convert them to a voltages signal.

In addition to these components, some vacuum equipment is also used for measuring and controlling the vacuum of the analyser.

Appendix C: Mass spectra

This appendix consists of mass spectrometer data. Table C 1 lists the relevant gases with their chemical formulas and atomic mass units for easier plot interpretation. The mass spectra of all the reference gases and the analysed gases are plotted. Argon is a speciality: it is not part of the chemical processes in the work, but merely added as a stabilising carrier gas to the mass spectrometer (MS). Argon flow increases the total gas flow to a suitable range.

Table C 1: Atomic mass units of relevant gases.

Name	Chemical formula	amu
Hydrogen	H_2	2
Methyl radical	CH_3	15
Methane	CH_4	16
Water	H_2O	18
Argon split	½ Ar	20
Carbon monoxide	CO	28
Formaldehyde	CH_2O	30
Methanol	CH_3OH	32
Argon	Ar	40
Carbon dioxide	CO_2	44
Dimethyl ether	CH_3OCH_3	46
Formic acid	HCOOH	46

Reference gases

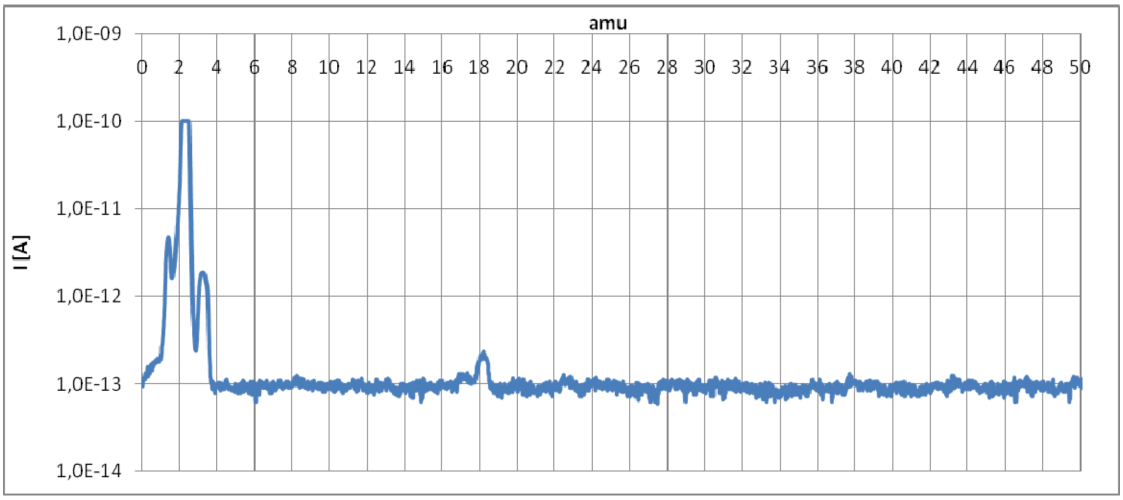

Figure C 1: H2.

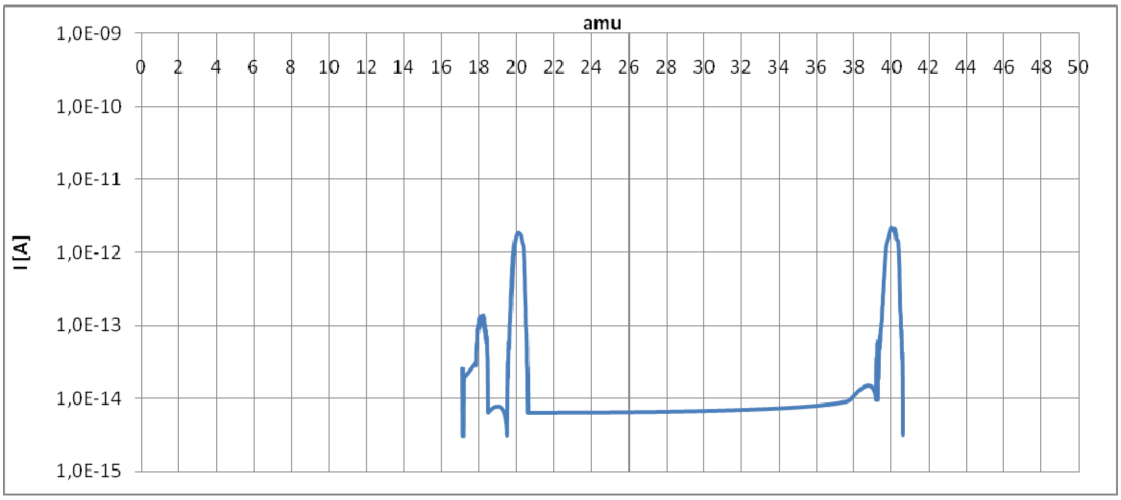

Figure C 2: Ar.

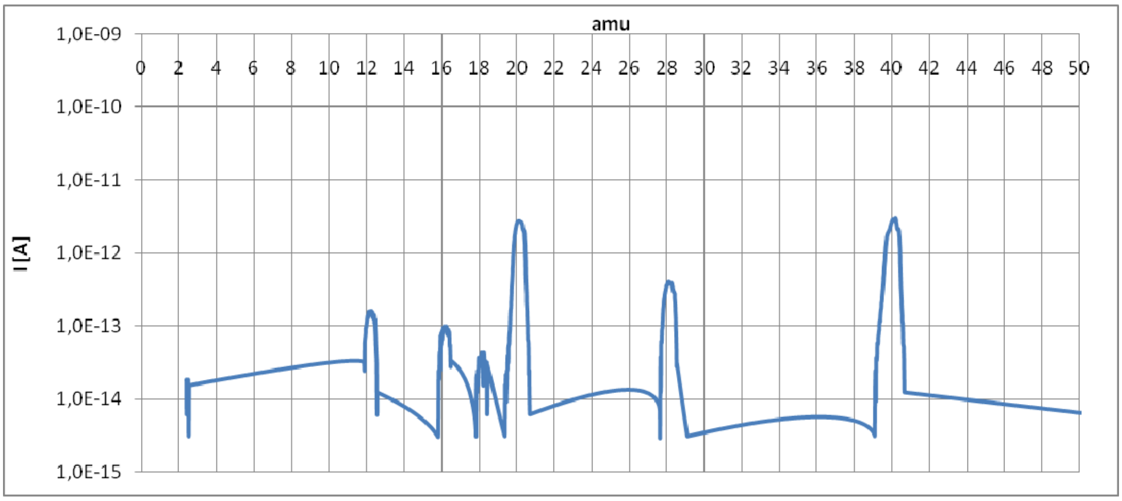

Figure C 3: CO 5 % + Ar 95 %. Argon was added because maximum CO flow was too low for MS.

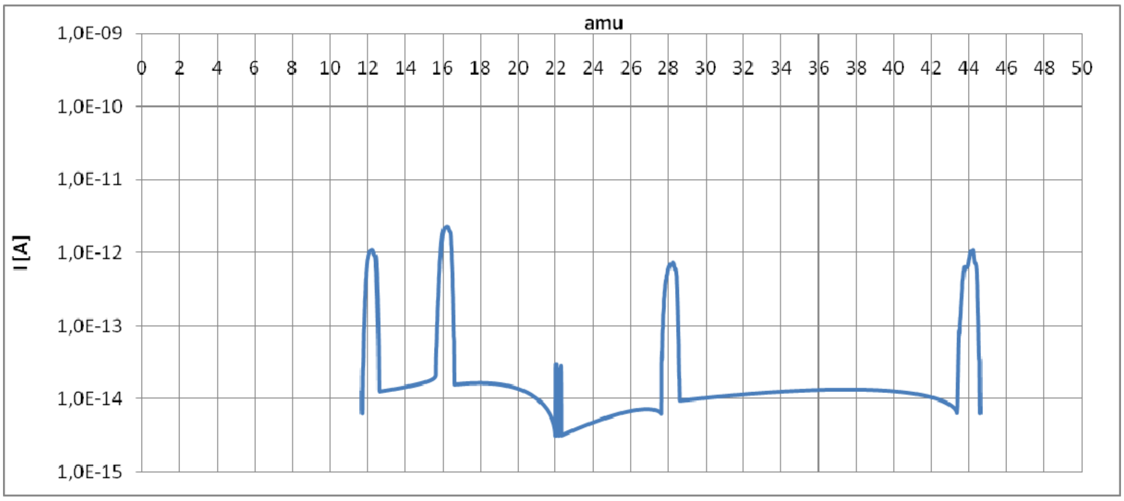

Figure C 4: CO2.

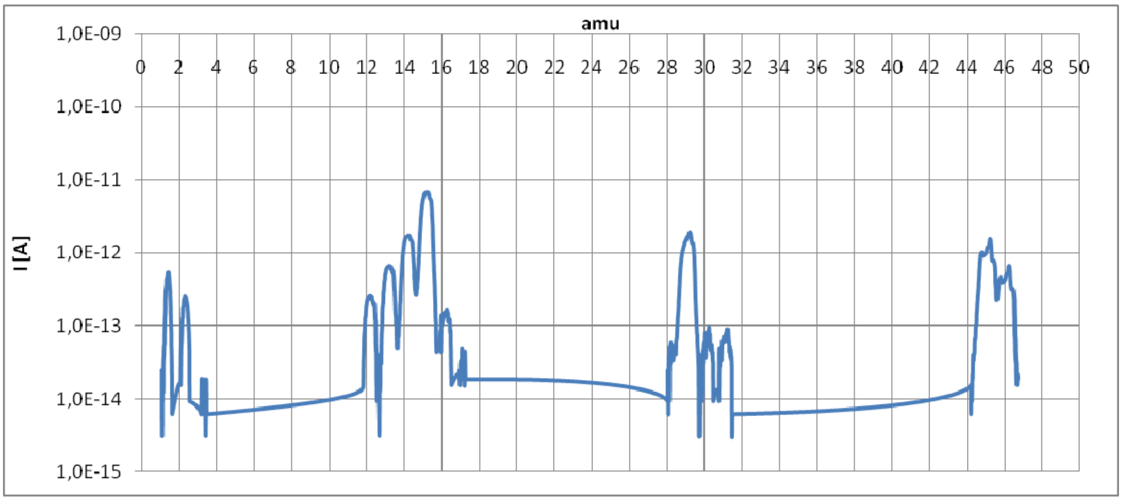

Figure C 5: DME.

Cu-Zn/ZSM-5 1:1

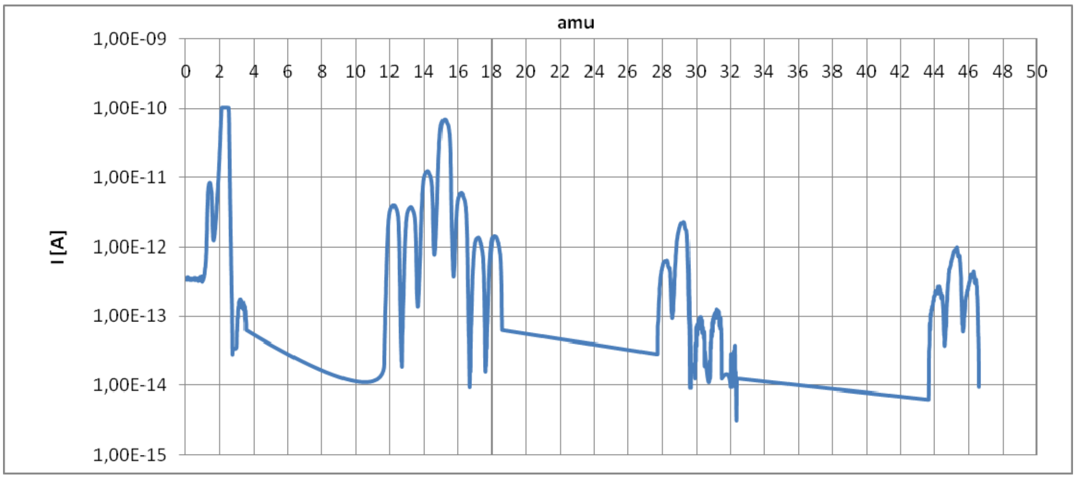

Figure C 6: Cycle 1/3. S/C = 1.5, $T_{reformer}$ = 300 °C.

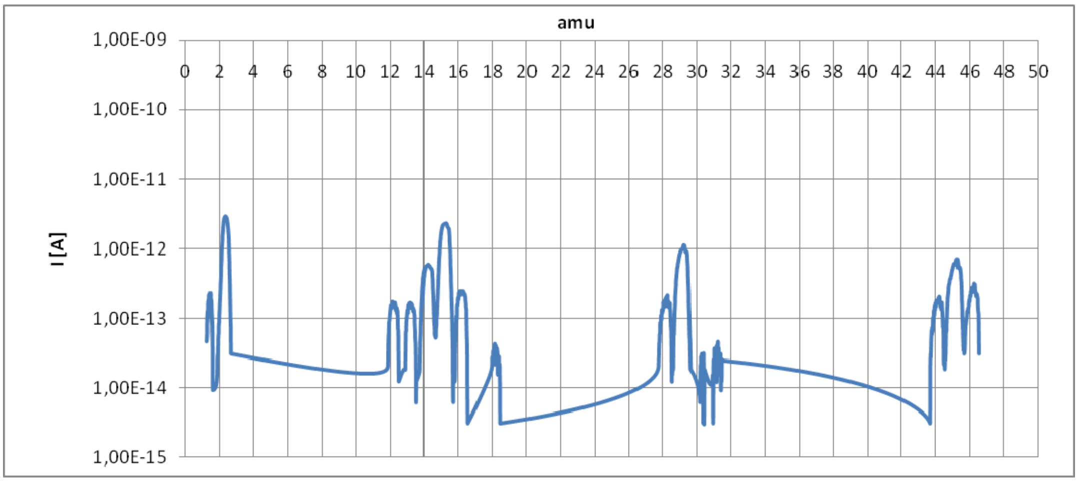

Figure C 7: Cycle 2/3. S/C = 1.5, $T_{reformer}$ = 300 °C.

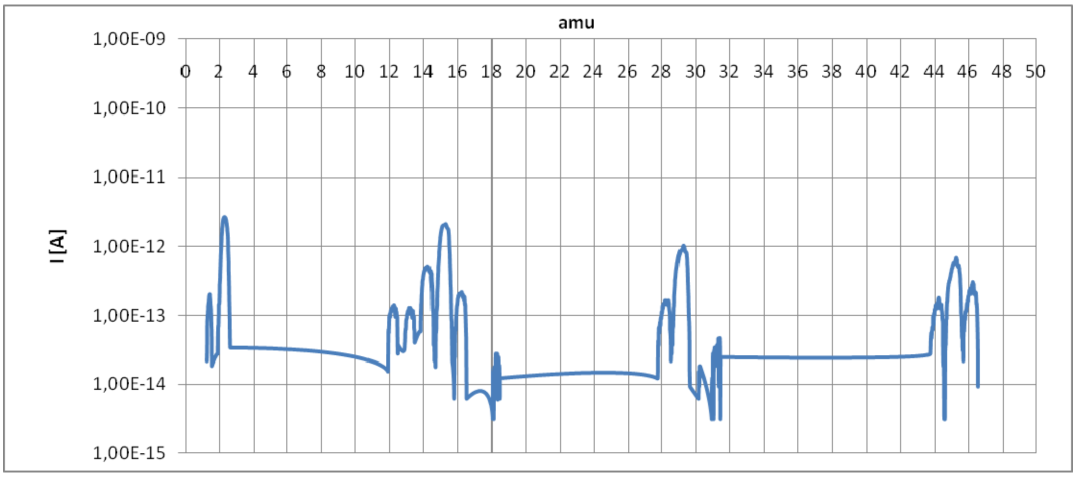

Figure C 8: Cycle 3/3. S/C = 1.5, $T_{reformer}$ = 300 °C.

Cu-Zn/ZSM-5 1:1 revisited

Reforming temperature was 350 °C instead of the normal 300 °C. This was because the flow rate from the reformer was too moderate at 300 °C.

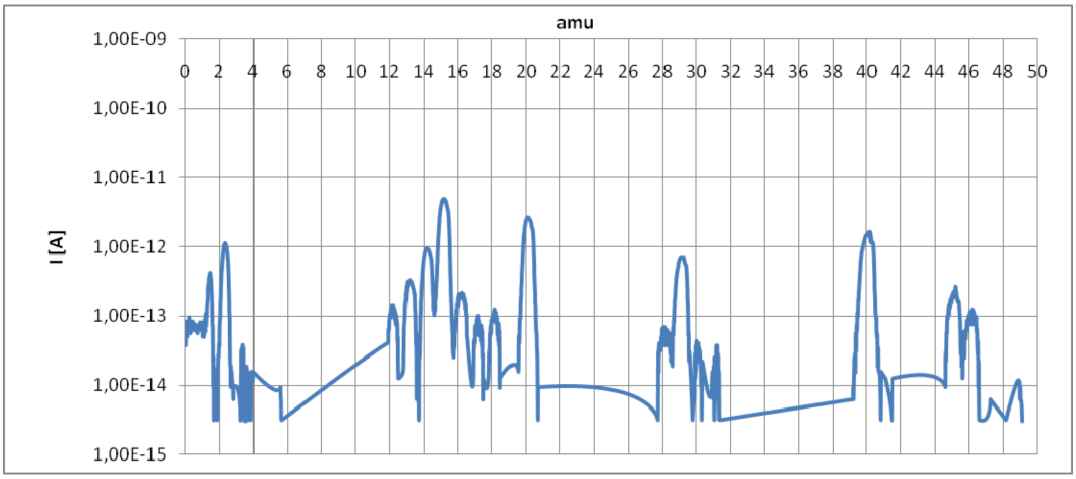

Figure C 9: Cycle 1/3. Argon as a carrier gas. S/C = 1.5, $T_{evaporator}$ = 185 °C, $T_{reformer}$ = 350 °C.

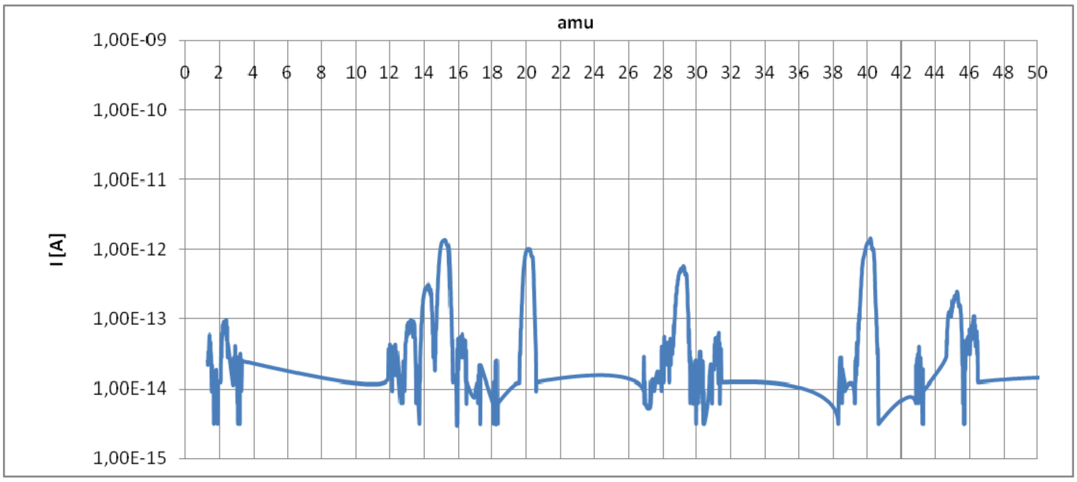

Figure C 10: Cycle 2/3. Argon as a carrier gas. S/C = 1.5, $T_{evaporator}$ = 185 °C, $T_{reformer}$ = 350 °C.

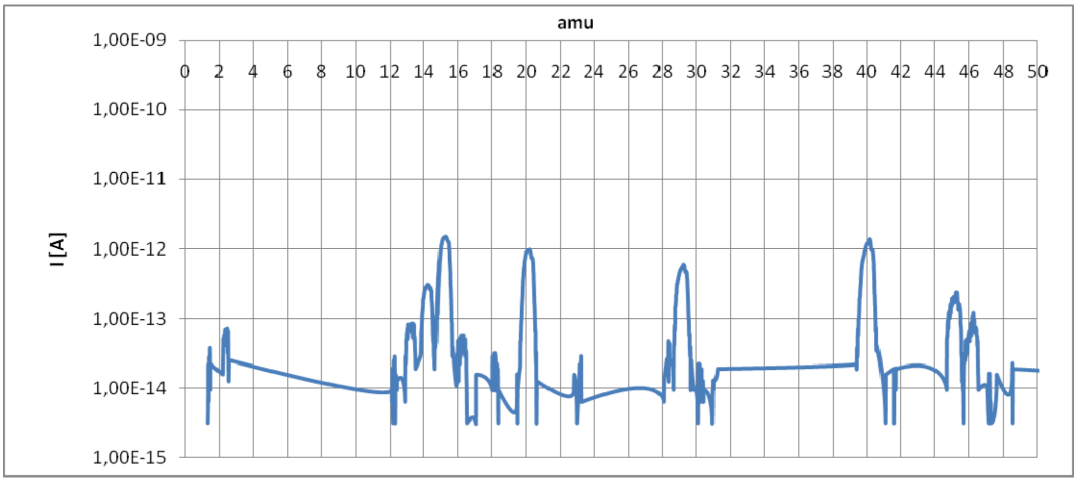

Figure C 11: Cycle 3/3. Argon as a carrier gas. S/C = 1.5, $T_{evaporator}$ = 185 °C, $T_{reformer}$ = 350 °C.

Cu-Zn/ZSM-5 2:1

Before the analysis, catalyst was used for one day of experiments. After that the catalyst was reduced at 150 °C overnight with 30 ml/min hydrogen flow.

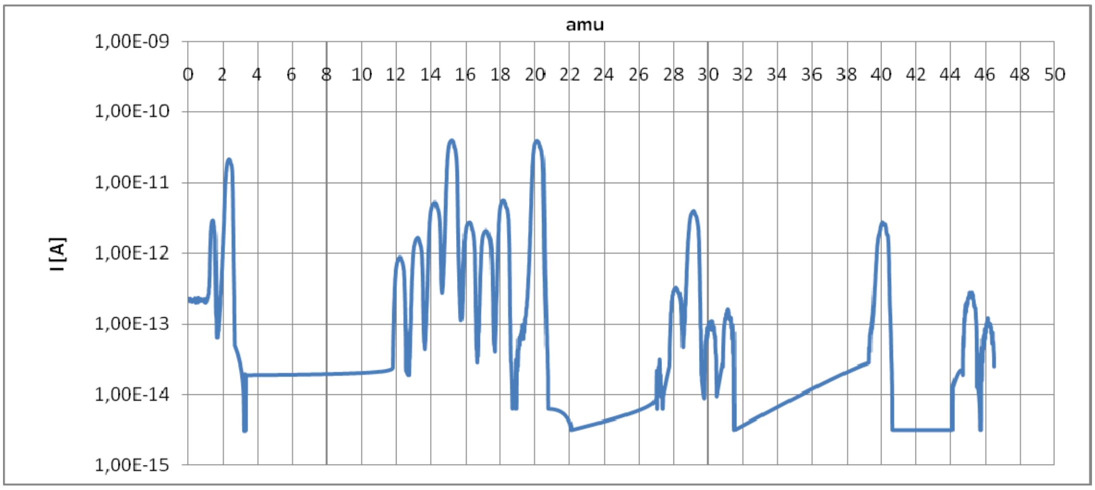

Figure C 12: Cycle 1/9. Argon as a carrier gas. S/C = 1.5, $T_{reformer}$ = 300 °C.

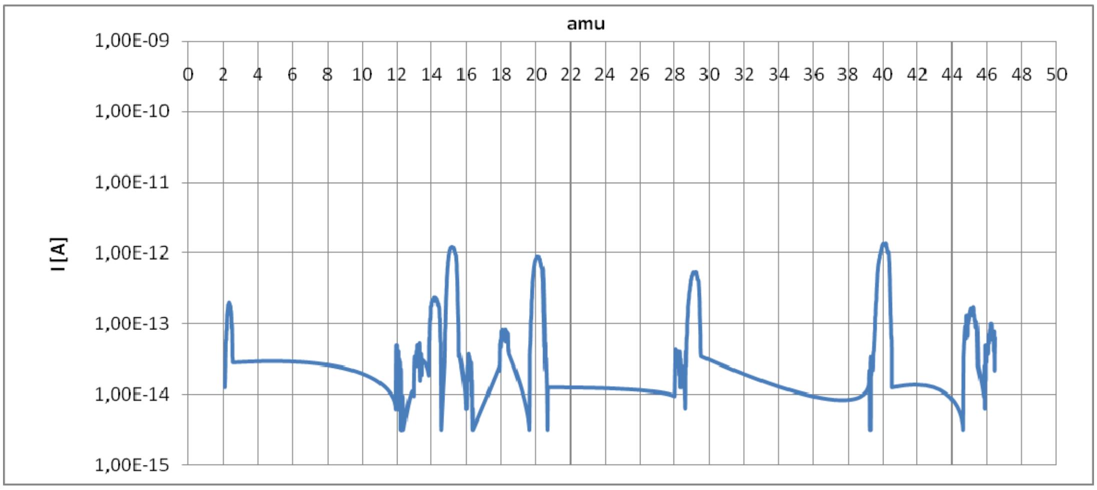

Figure C 13: Cycle 2/9. Argon as a carrier gas. S/C = 1.5, $T_{reformer}$ = 300 °C.

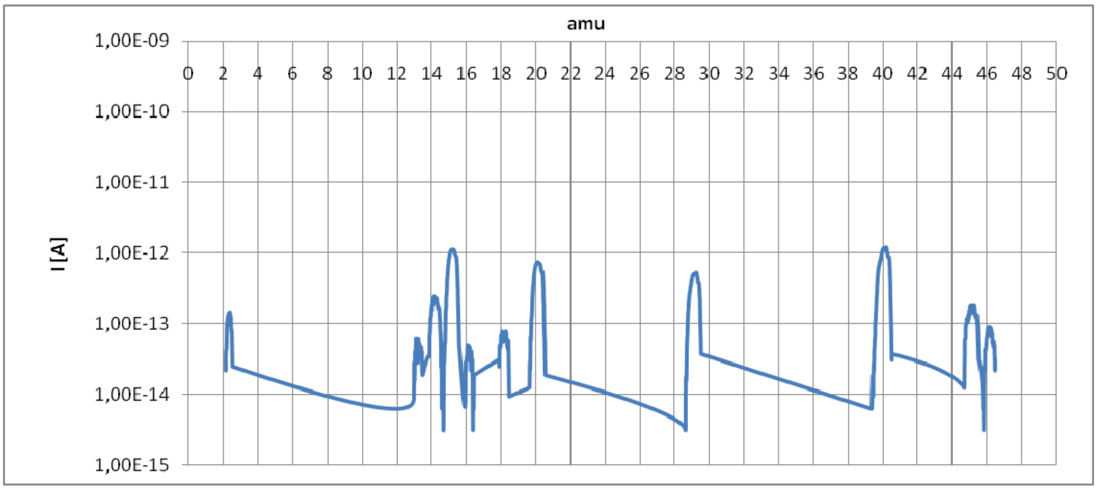

Figure C 14: Cycle 3/9. Argon as a carrier gas. S/C = 1.5, $T_{reformer}$ = 300 °C.

Cu-Zn/ZSM-5 1:2

This catalyst had been in reduction at 150 °C and 30 ml/min of hydrogen flow over the weekend before recording the mass spectra. After the first recording, including five more or less similar cycles, a separate evaporator unit was mounted before the reformer. The evaporator unit was filled with steel wool and heated up to 200 °C to guarantee that the DME and water are in gas phase before entering the reformer. The second recording had again five quite similar cycles. Only the last cycles of both recordings are plotted below in Figure C 15 and C 16. Apparently, the evaporator unit did not an have effect on the mass spectra

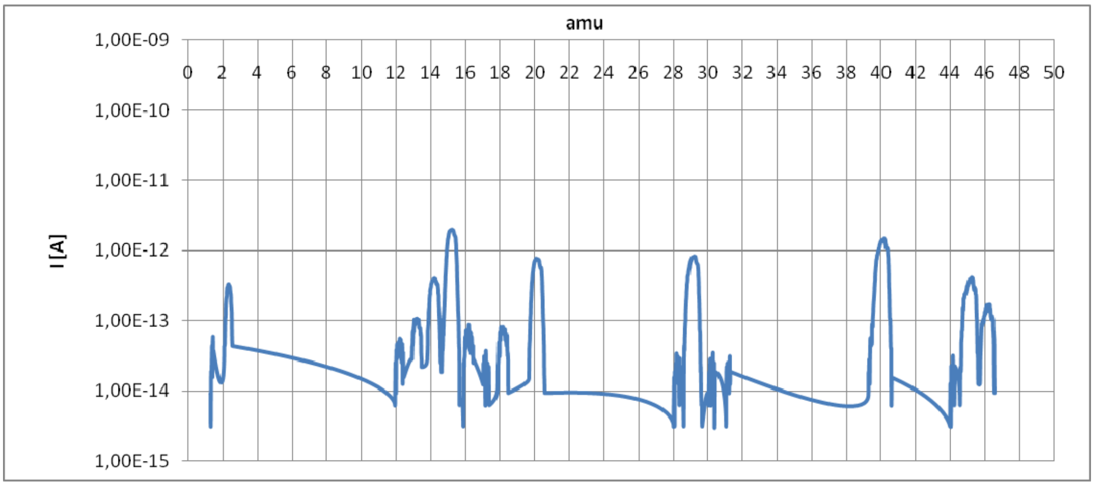

Figure C 15: Cycle 5/5. S/C = 1.5, $T_{reformer}$ = 300 °C.

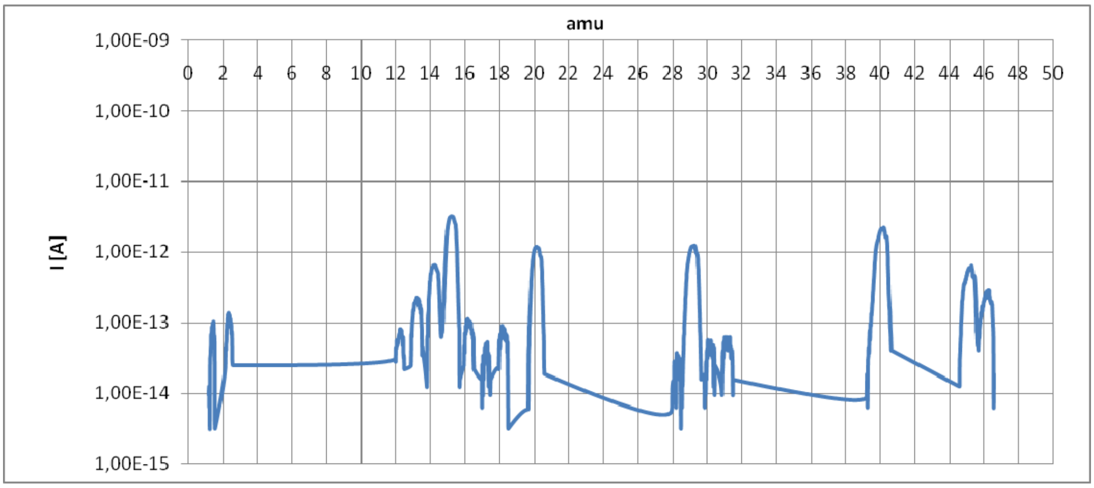

Figure C 16: Cycle 5/5. S/C = 1.5, $T_{evaporator}$ = 200 °C, $T_{reformer}$ = 300 °C.

Appendix D: FC performance with methanol reformate gas

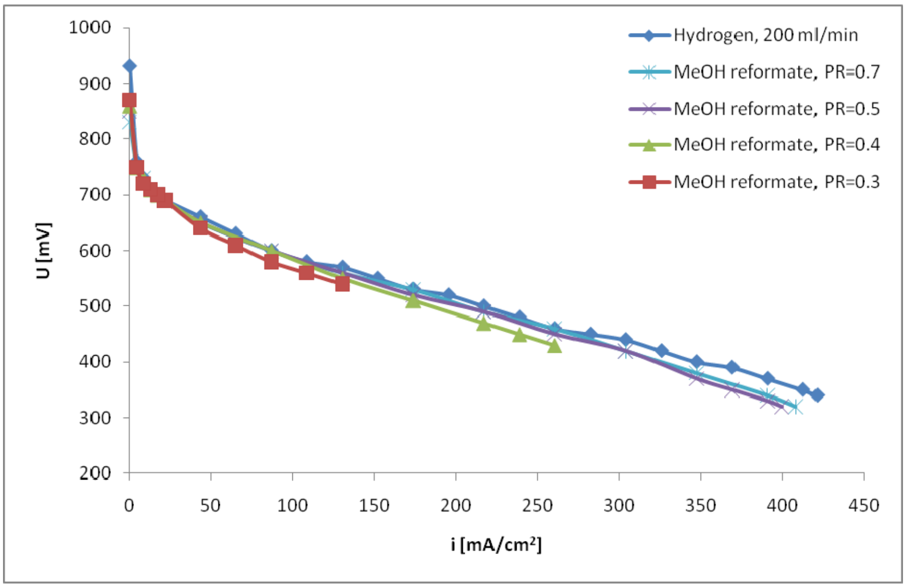

Figure D 1: Effect pump rate (PR). MEA S5, S/C = 1.0, $T_{reformer}$ = 225 °C, $T_{fuel\ cell}$ = 160 °C.

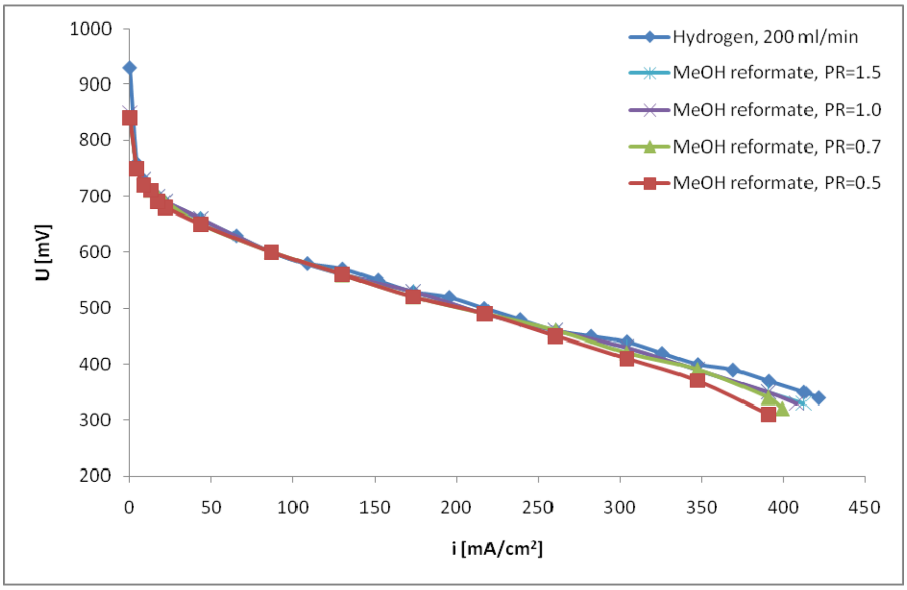

Figure D 2: Effect of pump rate (PR). MEA S5, S/C = 1.5, $T_{reformer}$ = 225 °C, $T_{fuel\ cell}$ = 160 °C.

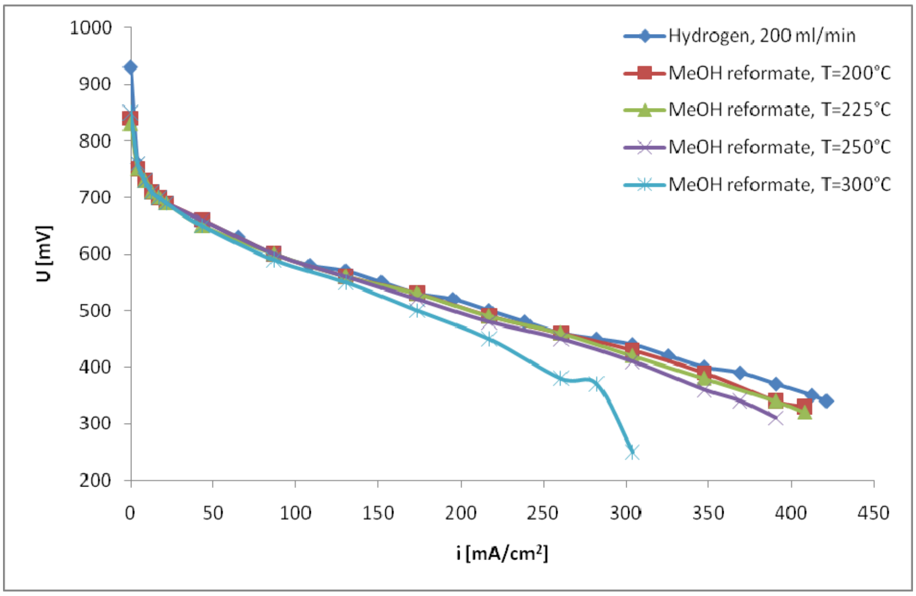

Figure D 3: Effect of reformer temperature. MEA S5, S/C = 1.0, pump rate 0.7, $T_{\text{fuel cell}}$ = 160 °C.

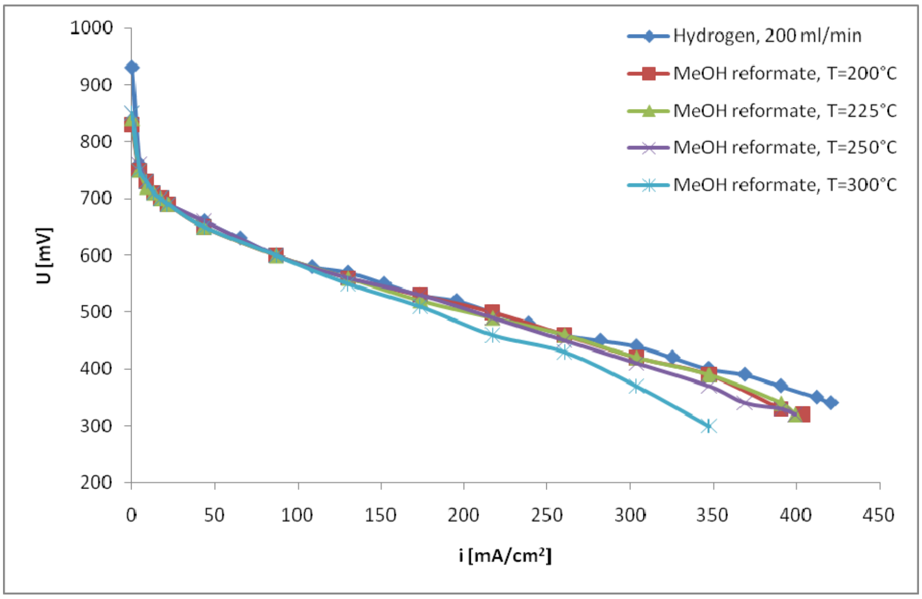

Figure D 4: Effect of reformer temperature. MEA S5, S/C = 1.5, pump rate 0.7, $T_{\text{fuel cell}}$ = 160 °C.

Appendix E: Flow rate calculation

This appendix presents a calculation for the right proportion of gaseous DME and liquid water to be pumped into the reformer.

The DME reforming reaction is

$$CH_3OCH_3\ (g) + 3\ H_2O(l) \rightleftarrows 2\ CO_2\ (g) + 6\ H_2(g)$$

Let's assume 100 % conversion.
Let the desired hydrogen flow be $\dot{V}_{H_2}$= 500 ml/min.
The molar ratio of DME to the product gases is $\frac{1}{8}$.
Hydrogen makes $\frac{6}{8}$ = 75 % of the total flow of products.

$$\dot{n}_{DME} = \frac{1}{8} \cdot \dot{n}_{products} \Leftrightarrow \dot{V}_{DME} = \frac{1}{8} \cdot \dot{V}_{products}$$

$$\dot{V}_{\mathrm{DME}} = \frac{1}{8} \cdot \dot{V}_{\mathrm{products}} = \frac{1}{8} \cdot \frac{\dot{V}_{H_2}}{0.75} \approx 83.3\ \frac{\mathrm{ml}}{\mathrm{min}}$$

$$\dot{V}_{\mathrm{H_2O}}(\mathrm{g}) = \ 3 \cdot \dot{V}_{\mathrm{DME}} \approx 250.0\ \frac{\mathrm{ml}}{\mathrm{min}}$$

The volume flow of *liquid* water still needs to be calculated. The relation of molar flow $\dot{n}$ to volume flow $\dot{V}$ is proportional. 1 litre of water at T = 25 °C and p = 1 bar is 55.56 mol. The molar volume of an ideal gas is 24.79 litres. It thus expands by factor

$$55.56\ \frac{\mathrm{mol}}{\mathrm{l}} \cdot 24.79 \frac{\mathrm{l}}{\mathrm{mol}} = 1377.2$$

$$\dot{V}_{\mathrm{H_2O}}(\mathrm{l}) = \frac{250.0 \frac{\mathrm{ml}}{\mathrm{min}}}{1377.2} \approx 0.1815\ \frac{\mathrm{ml}}{\mathrm{min}}$$

It is concluded that in the case of a H_2O/DME molar ratio of 3:1, corresponding to S/C=1.5, the flow rate proportion of liquid water to gaseous DME is

$$\frac{0.1815\ \frac{\mathrm{ml}}{\mathrm{min}}}{83.3\ \frac{\mathrm{ml}}{\mathrm{min}}} \approx 0.0022$$

For a H_2O/DME molar ratio of 3.5:1, corresponding to S/C=1.75, the proportion is

$$\frac{3.5}{3} \cdot \frac{0.1815 \frac{\mathrm{ml}}{\mathrm{min}}}{83.3 \frac{\mathrm{ml}}{\mathrm{min}}} \approx 0.0025$$