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Further development of a fuel cell-electrolyser test bed and developing a microcontroller-based control system for it

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ABSTRACT OF THE
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As the energy consumption of mobile devices is increasing and their size is decreasing there is a need for a new type of power supply that gives a longer mobile usage time than traditional batteries. To achieve this goal, which is the goal of the IPPES project that this work is a part of, a mobile usage time extender system based on a passive hybrid 1.5 W PEM fuel cell – electrolyser system has been developed. The system also involves a rechargeable battery and a supercapacitor. The system is unique as no system using a methanol electrolyser together with a hydrogen fuel cell was found in literature.

A control system was developed in LabVIEW on basis of the previous IPPES-prototype after analysing the strengths and weaknesses. Though simple, the control system was able to complete controlled start-up, mobile time extension duties for a mobile phone, and safe shutdown of the system. The same control system could be also used together with higher power fuel cells and electrolysers with only minor changes to parameters.

Keywords: PEM, Fuel cell, methanol electrolysis, control system, hybrid

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Mobiililaitteiden energiankulutus kasvaa samalla kun niiden koko pienenee ja olemme lähestymässä pistettä, jossa perinteisten akkujen suorituskyky ei enää riitä. Näin ollen tarvitaan uudenlainen tehonlähde, joka tarjoaa pidemmän mobiilin käyttöajan. Tämä on tavoite IPPES projektissa, johon tämä työ sisältyy.

Tässä työssä kehitettiin mobiilia käyttöaikaa pidentävä järjestelmä perustuen passiiviseen 1.5 watin PEM polttokenno – elektrolyyserijärjestelmään. Järjestelmä on hybridi, sillä siihen kuuluu myös akku ja superkondensaattori. Kehitetty järjestelmä on ainutlaatuinen, sillä järjestelmää jossa käytetään vetypolttokennoa metanolielektrolyyserin kanssa ei löytynyt kirjallisuudesta.

Ohjausjärjestelmä kehitettiin LabVIEW-ohjelmiston avulla hyödyntäen tietoa edellisen IPPES-prototyypin heikkouksista ja vahvuuksista. Ohjausjärjestelmä kykeni järjestelmän automaattiseen käynnistämiseen, mobiililaitteen käyttöajan pidentämiseen ja hallittuun järjestelmän alasajoon. Samaa ohjausjärjestelmää voisi myös käyttää suurempitehoisen polttokenno – elektrolyyserijärjestelmän ohjausjärjestelmänä.

Avainsanat: PEM, polttokenno, metanolielektrolyysi, ohjausjärjestelmä, hybridi

Preface

This master's thesis was completed at the automation technology laboratory at the Aalto University as a part of the IPPES-project in which a small fuel cell – electrolyser system for extending the mobile usage time of mobile devices is developed.

I would like to thank my supervising professor Aarne Halme for a very interesting subject as well as for advice and guidance throughout the work process. I would also like to thank Sami Kielosto for conducting the mobile phone consumption test as well as building electrical components for the system, Jorma Selkäinaho for help with the practical testing, and Anja Ranta for valuable comments on this work.

Otaniemi, 7.9.2011

Axel Kohonen

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Abbreviations

AC	Alternating Current
AFC	Alkaline Fuel Cell
CHP	Combined Heat and Power
CPU	Central Processing Unit
DBFC	Direct Borohydride Fuel Cell
DC	Direct Current
DM	Direct Methanol
DMFC	Direct Methanol Fuel Cell
DVS	Dynamic Voltage Scaling
EEPROM	Electrically Erasable Programmable Read Only Memory
FC	Fuel Cell
FPGA	Field Programmable Gate Array
GAL	Generic Logic Array
HDS	HydroDeSulphurisation
HHV	Higher Heating Value
IPPES	Innovatiivinen Polttokennojärjestelmä PienElektroniikan Sovellutuksiin, Innovative biofuel cell system for portable electronics applications
ISP	In System Programming
LH2	Liquid Hydrogen
MC	Molten Carbonate
MCFC	Molten Carbonate Fuel Cell
MEA	Membrane Electrode Assembly
NI	National Instruments
NTP	Normal Temperature and Pressure (20°C, 101.325kPa)
PA	Phosphoric Acid
PAFC	Phosphoric Acid Fuel Cell
PAL	Programmable Array Logic
PCFC	Protonic Ceramic Fuel Cell or Proton Ceramic Fuel Cell
PEM	Proton Exchange Membrane
PEMFC	Proton Exchange Membrane Fuel Cell (aka PEFC, Proton Electrolyte Fuel Cell)
PID	Proportional-integral-derivative
PLA	Programmable Logic Array
ppm	Parts Per Million
RAM	Random Access Memory
SLPM	Standard Litres Per Minute
SO	Solid Oxide
SOEC	Solid Oxide Electrolysis Cell
SOFC	Solid Oxide Fuel Cell

x

1 Introduction

Fuel cells have raised a lot of interest ever since their working principle was discovered in 1838. Sir William Grove discovered that two platinum electrodes having one end immersed in sulphuric acid and the other ends in sealed containers of oxygen and water at one electrode, and hydrogen and water at the other one, created a constant flow of current between the electrodes. He also noted that pairs of electrodes could be connected in series to produce a higher voltage – the first fuel cell was created. (Ortiz-Rivera et al. 2007, p. 117)

Although the progress has been slow, the oil cheap, and environmental pollution not considered a problem, the development of the fuel cells have continued since their invention. According to Andújar and Segura (2009, p. 2314) military and space applications have been key factors sustaining the interest in fuel cells during the 20th century.

Today when fossil fuels are estimated to run out in a not too distant future and fuel cells are seen as a possible solution for producing clean energy from renewable resources, it is easy to understand the growing interest in fuel cells. Fuel cells are available for various applications, with a power range from a few watts up to megawatts, are more efficient than combustion engines, have simple design, low emissions and are almost silent. For the moment the cost for producing energy is their primary drawback. (Larminie and Dicks 2003, p. 23) The cost will likely decrease as the technology matures and is more widely commercialised, thus further increasing the attractiveness of fuel cells. Larminie and Dicks (2003, pp. 23-24) emphasize that the advantages of fuel cells are possibly strongest in combined heat and power systems and mobile power systems.

The focus in this work is on mobile power systems, as it is a part of the IPPES project at the Aalto University in which a micro fuel cell system for mobile electronics in the power range 0.5-20 W is developed. The system is based on the local production of hydrogen and a novel micromechanical proton exchange membrane (PEM) fuel cell structure, which maximises the volumetric power density. (Aalto University, 2008) Local production of hydrogen is achieved through catalysed electrolysis of methanol, which is beneficial, since a methanol electrolyser combined with a PEM fuel cell using hydrogen as fuel is more efficient, considering watt hours produced per millilitre of methanol, than a direct methanol (DM) fuel cell using methanol as fuel. This is true even though some of the energy produced by the fuel cell in the first case is used when converting the methanol into hydrogen. (Aalto University, 2010b) Methanol electrolysis also eliminates the problems with methanol crossover present in the DM fuel cells, while preserving the benefit that methanol, which is liquid at room temperature, is much easier to transport than hydrogen. Methanol fuel transporting and refuelling of the fuel cell can be made simple by e.g. providing the fuel and the catalyst in replaceable cartridges.

The fuel cell stack in this hybrid system is connected in parallel with an electrical system, which balances power peaks, letting the fuel cell stack function at the optimal operating point. This increases the systems efficiency and as a result a smaller and cheaper fuel cell stack can be used,

as it only has to be able to produce enough power for average consumption. In this work, the fuel cell – electrolyser system will be used to extend the mobile usage time for e.g. a laptop computer or a mobile phone. The fuel cell will extend the time one can use the device without grid power by providing a part of the power needed when the device is turned on, while the battery of the device provides the rest, and reloading the battery when the device is turned off or in low power mode. This provides a solution to the energy storage problem arising in mobile devices as their functionality is expanding, causing their power consumption to increase, while their size is decreasing. (Aalto University, 2008)

In this work a previously developed fuel cell – electrolyser test bed is further developed. The system is unique since no system using a methanol electrolyser together with a hydrogen fuel cell was found in literature, only research about using methanol electrolysers separately was found. Through a literature survey the existing control system is analysed and improved, and the optimal ratio between the fuel cell stack and the electrolyser stack is investigated. Also, the minimum size of the hydrogen storage between the electrolyser and the fuel cell is evaluated. Then the possibility to improve the electric efficiency of the system by increasing the system voltage and using a rechargeable battery together with the supercapacitor is examined, on the basis of literature and power consumption measurements done on a laptop computer. Since the final goal is to implement the control system using a microcontroller so it can be placed in e.g. a laptop computer, we will also discuss issues concerning how to choose a microcontroller for a specific application, and especially what kind of microcontroller would be suitable for the application presented in this work.

The second chapter provides a description of the working principle of fuel cells, the PEM and DM fuel cell types, and the parts of a fuel cell system. Additionally the IPPES prototype system is presented and digital design basics as well as important criteria when choosing a microcontroller are discussed. Literature is reviewed only for areas that are central for this work, i.e. the control and electrical systems as well as the use of electrolysers. In the third chapter the existing system is analysed and the new design is presented. The conducted tests and their results are presented in chapter four. Chapter five gathers the results and conclusions from the experiments and chapter six provides a summary of the work.

2 Theoretical background

The first part of this chapter is a brief introduction to fuel cell systems, to give the reader an understanding of the basic principles, possibilities and limitations of fuel cell systems. The working principle of fuel cells, different fuel cell types and also fuel and energy storage, control, and electrical systems used in fuel cell systems are considered. The IPPES system being developed in this work is presented as an example. The last part of this chapter presents different digital design technologies, as well as criteria used when selecting a microcontroller for a specific situation.

In sections discussing areas not developed in this work, i.e. the section about fuel cells, fuel storage and most of the section about fuel processing, only the theory and available methods are presented. However, in the section about fuel processing the literature concerning electrolysers is reviewed since electrolysers are an important part of the used system. Literature is also reviewed for the other parts of the fuel cell system that are developed in this work, i.e. the control and the electrical systems.

2.1 Fuel cells

2.1.1 Working principle

Fuel cells are devices that convert the chemical energy of a fuel into electrical energy, heat, and by-products, as long as fuel is supplied. In the case of a hydrogen fuel cell, the chemical energy is transformed through reversed electrolysis of water. As we can see in figure 2.1a, water is electrolysed, i.e. separated into oxygen and hydrogen, when an external electric current is applied to two platinum electrodes, with one end immersed in an acid electrolyte and the other ends in sealed containers. Figure 2.1b shows how the oxygen and hydrogen recombine, creating a small current. (Larminie and Dicks 2003, p. 1)

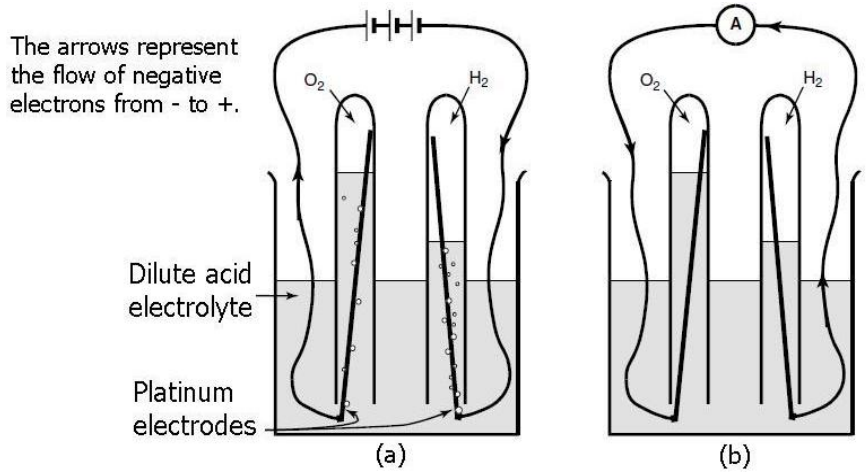

Figure 2.1: (a) Water is electrolysed into hydrogen and oxygen when an external electric current is applied. (b) Oxygen and hydrogen recombine creating a small current. (Adapted from Larminie and Dicks 2003, p.1, fig. 1.1)

Another way to understand the fuel cell is looking at the reaction, seen in equation (1), in which the fuel, in this case hydrogen, reacts with oxygen, thus creating electrical energy. (Larminie and Dicks 2003, p. 2)

$$2H_2 + O_2 \rightarrow 2H_2O \quad (1)$$

The experimental setup in figure 2.1 produces a very small current. This is because the reaction creating electrical energy only takes place where the gas, the electrode, and the electrolyte are in contact. In this case this area only is the ring around the electrode where it penetrates the surface of the electrolyte. The other main reason for the small current is the large distance between the electrodes, since the electrolyte resists the flow of electric current. (Larminie and Dicks 2003, p. 1)

The current can be increased by maximising the contact area between the gas, electrode and electrolyte, and by minimizing the distance between the electrodes. This is achieved by fitting a thin electrolyte between two flat porous electrodes, as in figure 2.2. The electrolyte together with the electrodes bonded on both sides of it is usually called a membrane electrode assembly, or MEA. The porous electrodes allow the gas from one side and the electrolyte from the other side to penetrate it, thus maximising the contact area. The current can also be increased by accelerating the reaction producing it with the help of a catalyst or by raising the temperature in the fuel cell. (Larminie and Dicks 2003, pp. 2, 6)

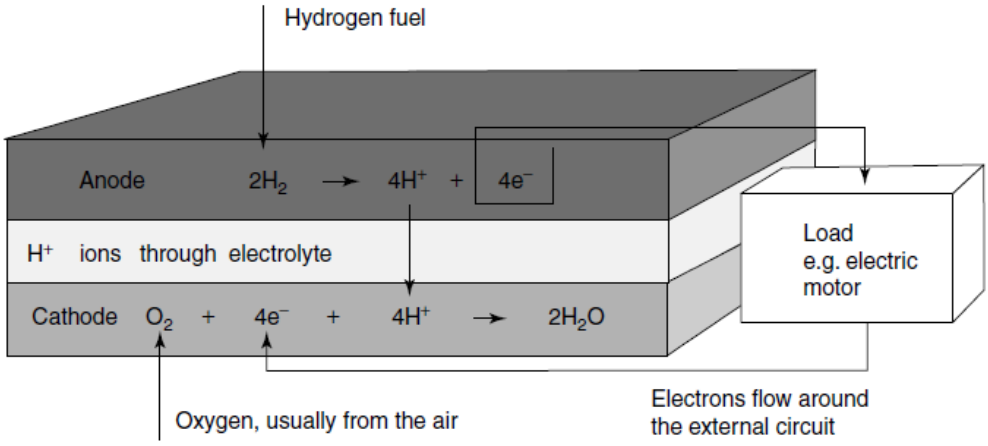

Figure 2.2: Charge flow in an acid electrolyte fuel cell. (Adopted from Larminie and Dicks 2003, p.3, fig. 1.3)

Figure 2.2 also shows how the charges flow in an acid electrolyte fuel cell. Firstly, hydrogen is ionized at the anode into H^+ ions and electrons according to equation (2). (Larminie and Dicks 2003, p. 2)

$$2H_2 \rightarrow 4H^+ + 4e^- \quad (2)$$

Secondly, the electrolyte lets the H^+ ions move through it, but forces the electrons to flow through the external circuit, creating a current. If the electrons could penetrate the electrolyte no current would be created. The electrolyte material is often a polymer, called a proton exchange membrane (PEM), since H^+ ions are protons. (Larminie and Dicks 2003, p. 2)

Finally the H^+ ions, electrons and the oxygen combine into water at the cathode as seen in equation (3). (Larminie and Dicks 2003, p. 2)

$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \quad (3)$$

Other types of fuel cells use different electrolytes and the cathode and anode reactions are also different. For example in an alkaline electrolyte fuel cell the OH^- ions, instead of the H^+ ions, are mobile and available, causing the anode and cathode reactions to be different, while the overall reaction is the same as for an acid electrolyte fuel cell. For the PEM fuel cell, which is used in this work, the reaction is the same as for the acid electrolyte fuel cell. (Larminie and Dicks 2003, p. 4)

By maximising the area of the electrodes, using a catalyst, and perhaps raising the temperature in the fuel cell as described earlier in this chapter, one can draw a satisfactory current from a fuel cell. On the other hand the voltage from a single fuel cell is limited to about 0.7 V, when the current is on a useful level. Multiple fuel cells are therefore connected in series to raise also the voltage to as useful level. Usually this is done using bipolar plates, which connect the cathode of one unit fuel cell with the anode of the next one over the whole surface of the electrodes. (Larminie and Dicks 2003, p. 6-7) However, the electrodes have an insulating coating in alkaline fuel cells, so often the connections between the cells in the stack are implemented by connecting the edges of the electrodes. Connecting only the edges does not cause major losses in this case since the electrode is built on a metal mesh with high conductivity. (Larminie and Dicks 2003, p. 137)

The bipolar plates do not only serve as conductors. They also have channels for feeding the reaction gases to the electrodes, as well as channels for a cooling fluid, since cooling often is needed in a fuel cell. The design of the bipolar plate is a compromise between electrical contact, gas flow, cooling fluid flow, and thinness, as they cannot be maximised simultaneously. This makes the manufacturing of the bipolar plates difficult and expensive. An example of a fuel cell stack consisting of three unit fuel cells connected with bipolar plates is found in figure 2.3. (Larminie and Dicks 2003, pp. 6-7)

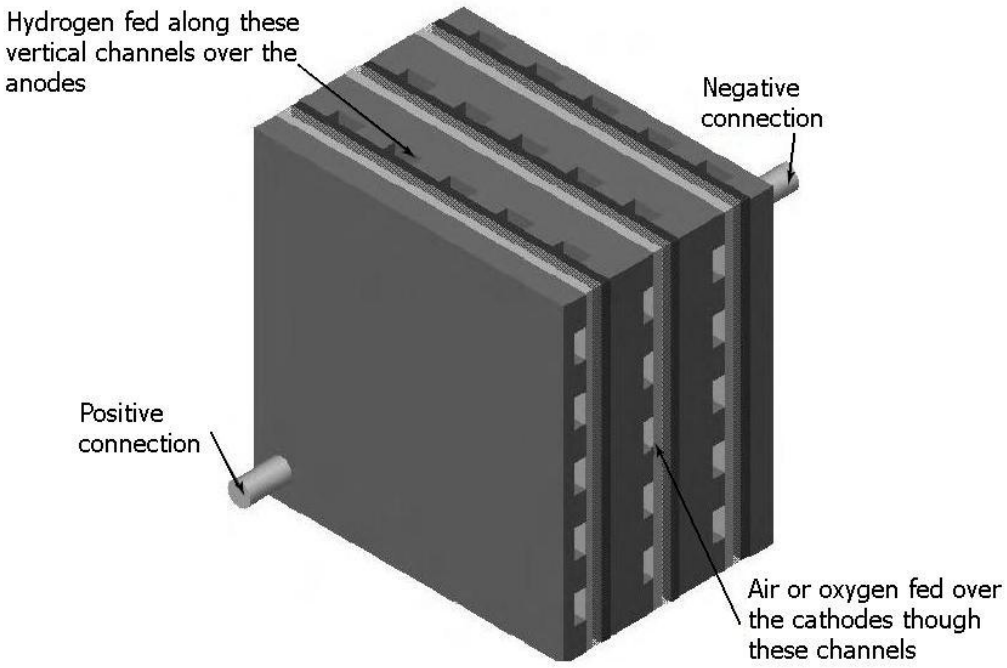

Figure 2.3: A fuel cell stack consisting of three cells and bipolar plates connecting the anode of one cell to the cathode of its neighbour. (Adapted from Larminie and Dicks 2003, p. 10, fig. 1.10)

2.1.2 Fuel cells types

There are many different types of fuel cells each with different solutions to the two basic technical problems present in fuel cells, i.e. the slow reaction rate and the use of hydrogen gas as fuel. The slow reaction rate causes low current and power output and hydrogen is not readily available yet. The main distinguishing factor is the electrolyte used, though many other differences exist. Basic types of fuel cells are briefly presented in table 1. (Larminie and Dicks 2003, p. 14)

Table 1: Six basic fuel cell types. (Adapted from Larminie and Dicks 2003, p. 15, table 1.1)

Fuel cell type	Mobile ion	Operating temperature	Applications and notes
Alkaline (AFC)	OH^-	50-200° C	Used in space vehicles, e.g. Apollo, Shuttle.
Proton exchange membrane (PEMFC)	H^+	30-100° C	Vehicles and mobile applications, and for lower power CHP systems
Direct methanol (DMFC)	H^+	20-90° C	Suitable for portable electronic systems of low power, running for long times
Phosphoric acid (PAFC)	H^+	~220° C	Large numbers of 200-kW CHP systems in use.
Molten carbonate (MCFC)	CO_3^{2-}	~650° C	Suitable for medium- to large scale CHP systems, up to MW capacity.
Solid oxide (SOFC)	O^{2-}	500-1000° C	Suitable for all sizes of CHP systems, 2kW to multi-MW.

The focus of this work is on PEM fuel cells and fuel cell types derived from this technology. These as well as a comparison between the most important fuel cell types for this work, i.e. the PEM and the DM fuel cells, will be presented in the following. Other fuel cell types are described more thoroughly in appendix 8.

Proton exchange membrane (PEM) **fuel cells** were invented in the 1960's to be used by the U.S. Army and Navy as portable, compact power supplies, but at that time the platinum catalyst used was expensive, making the fuel cells expensive. (Ortiz-Rivera et al. 2007, p. 119) Nowadays only very small amounts of platinum are needed to create the same catalytic effect, which has reduced the catalyst cost to a small part of the total PEM fuel cell cost. The PEM fuel cell design is simple, the electrode being a solid polymer, with mobile protons. (Larminie and Dicks 2003, p. 14) The solid, non-corrosive electrolyte, the stable building materials and the low operation pressures and temperatures make the PEM fuel cells robust and safe (Andújar and Segura 2009, p. 2319). Using the PEM fuel cells with hydrogen as fuel (H2-PEMFCs), high power density can be achieved in relatively low, only 80°C temperatures. They are suited e.g. for automotive applications where fast start-up is needed, and the output can be adjusted relatively fast when the load varies. (Ortiz-Rivera et al. 2007, p. 119) However, the hydrogen fuel has to be pure, since PEM fuel cells are sensitive to both carbon monoxide and sulphur. Additionally the reactive gases in many PEM fuel cells need to be humidified, which increases the complexity. The humidification also limits the operating temperature, as it has to be lower than the boiling point of the humidifier used, which often is water. Usually cells produce outputs between 50 W and 75kW. (Andújar and Segura 2009, p. 2319)

PEM fuel cells using methanol as fuel instead of hydrogen, are called **direct methanol fuel cells** (DMFCs). The electrolyte of the direct methanol fuel cells is a polymer membrane as in the PEM fuel cells, but no fuel reformer is needed since the liquid methanol is broken down into protons and electrons directly on the anode surface. These cells typically operate at 50-90°C and achieve efficiencies of about 40%. (Ortiz-Rivera et al. 2007, p. 120) Methanol is easier to transport and store than hydrogen as it is liquid, but the efficiency of DMFCs is low compared to hydrogen fuel cells (Andújar and Segura 2009, p. 2320). Ortiz-Rivera et al. (2007, p. 119) estimate that direct methanol fuel cells will replace traditional batteries, since their operating time exceeds the operating time of batteries, and they can be "recharged" in seconds by replacing the fuel cartridge. Therefore phones, laptop computers and other small devices could be powered by direct methanol fuel cells. (Ortiz-Rivera et al. 2007, p. 120)

Some special cases of fuel cell types under research are worth mentioning. **Direct formic acid fuel cells** (DFAFCs) are a special case of PEM fuel cells, in which formic acid is used directly as the fuel. They have the same benefits as direct methanol fuel cells, e.g. easy transport of the fuel. (Yu and Pickup 2008) Additionally, the fuel crossover is much smaller than for methanol, and the open circuit potential is about 0.1 volts higher. This gives higher power density, and better efficiency at low loads, compared to the DMFCs. Therefore direct formic acid fuel cells are one promising solution for powering portable devices in the future. (Rice et al. 2002)

Another technology trying to replace the direct methanol fuel cells is the **direct ethanol fuel cell** (DEFC). Song and Tsiakaras (2006, pp. 187, 191-192) argue that direct ethanol fuel cells would be a better option than direct methanol fuel cells since ethanol is non-toxic, environmentally friendly and causes a lower fuel crossover rate than methanol. Ethanol is also renewable and can be produced from natural resources or chemically. On the other hand, DEFCs have a lower maximum discharging current and peak power density than DMFCs for the moment. Therefore a lot of research is still to be done before direct ethanol fuel cells are competitive enough for the fuel cell market.

2.1.3 Comparison between the H2-PEMFC and the DMFC technologies

Both the H2-PEMFCs and the DMFCs are based on the PEM technology, which gives many similarities, e.g. low operating temperature, quick start-up, simple structure, and non-corrosive electrolyte. However, there are also many differences caused especially by the use of the different fuels. Since the H2-PEMFC uses hydrogen as fuel it achieves higher power densities than the DMFC (Andújar and Segura 2009, p. 2320). This is due to the higher energy density of hydrogen (Larminie and Dicks, 2003, p. 142) and the limitations of the DMFCs, which are methanol crossover and catalyst poisoning (Aalto University, 2010a). Methanol crossover increases with increasing methanol concentration and temperature, and occurs since methanol on the anode side permeates through the membrane to the cathode side.

On the other hand, hydrogen is harder to transport and store than methanol since it is gaseous at room temperature and has low density even when liquefied. Therefore it is easier to use the DMFCs, as they can be refilled easily. In both fuel cell types the fuel could be supplied in replaceable cartridges, but it might be impractical or expensive in the case of hydrogen, since the cartridges would have to be specially constructed e.g. to contain high pressure hydrogen, and therefore be heavy or voluminous. In the case of methanol the container is usually plastic (Aalto University, 2010a). Since methanol can be stored in simple plastic containers and hydrogen has to be liquefied, or stored under high pressure or in metal hydrides, the net energy density of methanol is very much higher, as can be seen in table 2. The net energy density is calculated by taking the mass of the storage device is into account. Hydrogen can also be produced using methanol electrolysis. The storage of hydrogen is more thoroughly discussed in section 2.3 and the use of methanol as an energy carrier in section 2.4.

Another clear difference between the H2-PEM and the DMFC is that the DMFC voltage degradation is faster. Typically the voltage degradation is 2-10 µV/h for a PEMFC and 10-25 µV/h for a DMFC (Knights et al. 2004, p. 128). Water management is especially important for the DMFCs since the liquid fuel easily causes cathode flooding, resulting in lower performance. The performance degradation is particularly severe if the DMFC is under constant load, since water builds up at the cathode causing gas diffusion limitations. According to Knights et al. (2004, p. 132) the gas diffusion degradation was around 370% for a DMFC working at a steady load for 16 hours, while it was only around 35% for a DMFC working nearly 2000 hours using load cycling. In load cycling the load is removed e.g. for 30 seconds every 30 minutes. It should be noted that many

DMFC applications have long lifetimes due to the naturally varying load, which also involves on-off cycles. While water management in DMFCs mainly involves removal of excess water, the water management of PEMFCs involves humidifying the gases so the membrane does not dry out. This is important since insufficient water content increased the ohmic resistance, which in turn lowers the output voltage of the cell.

Table 2: A comparison between the energy density of different hydrogen storage methods and methanol. An estimate for the reformer mass is included in the case of indirect methanol. (Adapted from Larminie and Dicks 2003, p. 142, table 6.1)

Storage method	Energy density of fuel	Storage efficiency (%)	Net energy density
H_2 at 300 bar pressure in composite cylinders	119.9 MJ kg^{-1}	0,6	0.72 MJ kg^{-1}
H_2 in metal hydride cylinders	119.9 MJ kg^{-1}	0,65	0.78 MJ kg^{-1}
H_2 from methanol - indirect methanol	119.9 MJ kg^{-1}	6,9	8.29 MJ kg^{-1}
Methanol in strong plastic tanks for direct use as fuel	19.9 MJ kg^{-1}	95	18.9 MJ kg^{-1}

2.1.4 Current fuel cell research trends

Today more research on fuel cell technology is conducted than ever before. Many companies are working on the commercialisation of stationary fuel cells and most vehicle manufacturers are developing fuel cells for automotive use. Currently, due to the high cost and limited lifetime of the other fuel cell types, the phosphoric acid fuel cells (PAFCs) are the only fuel cell type widely commercialised. However, it is estimated that also the lifetime of low temperature fuel cell, e.g. PEMFCs, will fill the requirements in a near future. Also, as demonstrated by some companies the bipolar plates and the MEAs in the PEMFCs can be mass-produced, which lowers the cost. Finding even better methods to reduce the cost and increase the lifetime are probably the main focuses in fuel cell research in the near future. Also new materials, e.g. for the catalysts and the polymer electrolyte membranes, need to be developed. If e.g. materials with high ionic conductivity in the absence of liquid water are found, then PEMFCs could be used at higher temperatures, thus making them more resistant to e.g. carbon monoxide. On the other hand, if solid oxide conductors with high conductivity at lower temperatures were developed, one could lower the temperature in the solid oxide fuel cells (SOFCs), thus reducing the degradation of the materials and increasing the lifetime. (Perry and Fuller, 2002, p. S66)

The PEMFCs are currently developed especially for mobile and automotive applications with 20-130°C operating temperatures. Research is conducted on all areas, e.g. on membranes and electrodes, fuel cell stack engineering and manufacturing, as well as modelling and prototyping. Membranes able to function at higher operating temperatures and lower humidity are developed as well as electrodes with less platinum loading and better gas diffusion layers. The fuel cell stacks are developed by optimising design, materials, and performance through modelling and prototype tests. For example fluid dynamics can be used to estimate the flow of reactants in the stack, which is helpful when e.g. improving the flow fields. (Squadrito et al., 2008, p. 1941)

2.2 Control systems

The control system is a central part of a fuel cell system as it keeps the system working, as well as takes care of start-up and shutdown (Larminie and Dicks 2003, p. 20). In the simplest case, it is supplying the required amounts of the reactant gases, e.g. hydrogen and oxygen, to the fuel cell. Supplying the right amount of reactant gases is more difficult than it first may seem, since the load connected to the fuel cell is varying over time, which changes the amount of reactant gases needed. Additionally, according to Vega-Leal et al. (2007, p. 194) the control system should keep the fuel cell at an optimal operating point, while minimizing the energy loss caused by other subsystems, thus maximising the efficiency. Control of the optimal operating point involves e.g. controlling the reactant gas concentrations as well as the temperature in the fuel cell. To achieve this, compressors, fans, pumps, blowers, valves, reformers and other devices in the different subsystems need to be controlled. Also, for the fuel cell system to produce a steady voltage output, the control system needs to control the electrical system consisting of e.g. voltage regulators, DC/DC converters and chopper circuits (Larminie and Dicks 2003, p. 331).

Vega-Leal et al. (2007, p. 194) present the following steps for designing a control system. Firstly, one needs to model the fuel cell system, i.e. the fuel cell stack, the manifold and other pneumatic systems involved. Secondly, control equations need to be calculated and the whole system simulated. Thirdly, the stack and the other pneumatic elements need to be emulated, and the system simulated using the designed control system. Finally, one should implement the physical control system and test it with the real fuel cell system.

A lot of research has been conducted on fuel cell system modelling. Cheddie and Munroe (2005, p. 72) state that models are beneficial since, they make it easier to understand how the fuel cells work, making it possible to predict their behaviour. Also, experimentation is faster and cheaper using models. This makes the innovation of new designs feasible, since new designs can be tried out with relatively low cost. Experimentation using hardware is expensive especially if many different solutions have to be tried out.

Many different kinds of model based control systems have been presented in literature. Pukrushpan, Stefanopoulou and Peng (2002) used a non-linear model with a feedforward and feedback controller to control the air supply of a PEM fuel cell stack system. Their model was constructed by combining equations for reactant partial pressures, load current, temperature and membrane hydration. It was then tuned using variables values from literature as well as fitting

variables to experimental data using regression. Their model was not fully validated, but they claim that it captures the transient phenomena, the dynamics of the compressor and the manifold, as well as the partial pressures of the reactant gases.

Vega-Leal et al. presented a more complex control system in 2007. Their system controlled the airflow using feedforward control, but also the hydrogen flow using proportional regulation valves and the temperature in the fuel cell stack using a proportional feedback controller. The air control loop adjusted the air fed into the cathode according to the current demand, trying to keep a constant oxygen excess ratio in the fuel cell. The hydrogen feed was simply proportional to the pressure difference between the hydrogen storage and the anode pressure. This approach can however only be used with closed anode circuits. The temperature was kept as close to optimal temperature as possible using a fan. Their control system was capable of keeping the system at optimal temperature and feeding air to the cathode while minimizing the parasitic load caused by the compressor.

In many cases simple PID-controllers provide satisfactory solutions to fuel cell system control problems. For example Thounthong, Raël, and Davat (2007) developed a hybrid system with a PEM fuel cell and a supercapacitor bank using only P-, PI- and PID-controllers and standard DC-link voltage regulation. Their system was able to keep the output voltage at a steady level while limiting the current and voltage in the fuel cell and the supercapacitor to effective levels. Remarkable in the system is that it does not use a state machine, but changes mode depending on the DC-link voltage regulation, which in turn depends on the state of charge of the supercapacitor bank and the power used by the load. Because of this no chattering problems arise, since there are no states the system could oscillate between. Using this experimentally validated control strategy, the system was able to deal with transient power demand, power peaks and regenerative braking, taking fuel cell and supercapacitor limitations into account.

Fuzzy logic is another strategy that can be used for controlling fuel cell systems. Melero-Pérez, Gao and Fernández-Lozano (2009, p. 203) state that fuzzy logic has many benefits. Fuzzy logic is written in natural language and it is easy to understand the basics. It can also use inexact data and does not need to be based on mathematical models making it flexible. Since the rules are natural language, e.g. if temperature is high, then use cooling system on full power, it is easy to use the knowledge of experts in the field when designing the control system. This also makes fuzzy logic advantageous with nonlinear systems. Finally fuzzy logic and conventional systems can be used simultaneously without problems.

Melero-Pérez, Gao and Fernández-Lozano (2009) used this kind of approach to design a control system for a fuel cell hybrid vehicle. Their system consisted of a fuel cell, a supercapacitor bank and a battery bank, which were connected using three DC/DC converters. The fuel cell provided steady power, and the battery bank was used for providing extra power at transients and storing surplus power when available. The supercapacitor bank was used to keep the DC-link voltage at a steady level and collecting energy from regenerative braking. They tested the system using load variations according to the Urban Dynamometer Driving Schedule (UDDS) (EPA, 2009). They found

out that their system kept the DC-link voltage at 400V ±20V and all the regenerative energy was collected. There were only sixteen changes in the fuel cell operating conditions during the almost 23 minute long schedule, which should give a longer lifetime for the fuel cell. Additionally, their fuel cell was designed for delivering average power instead of peak power, making it possible to use a smaller, cheaper fuel cell, therefore decreasing the hydrogen consumption.

Tekin et al. (2007) designed a fuzzy logic control system for controlling the airflow in a fuel cell. They used one fuzzy logic controller for airflow regulation and another for choosing the air flow set point. They also simulated their system and a PID-controller used to solve the same problem, and compared the results. The fuzzy controllers gave approximately ten per cent less energy consumption for the air supply, with the same rise time and almost no overshoot. Another clear benefit of the fuzzy controller was that a simulated water plug problem was easily solved using fuzzy logic, but not without it. According to the authors water plugs in the cathode compartment are usual in PEM fuel cells.

When choosing which kind of control system to implement one has to consider several aspects. Firstly, the platform on which the control system will be implemented constraints the computational power that can be used. Secondly, one has to consider how exact the solution needs to be. For research a possibly accurate model is often suitable, but for other purposes, less exact models can be used. Often it is beneficial to use the simplest solution that gives satisfactory results.

2.3 Fuel storage systems

There are many different solutions used to store energy in a fuel cell system. The basic hydrogen storage methods are presented in this section. It should be noted that storing energy as fuel often is used for long-term storage of energy, while short-term storage often is achieved by storing energy electrically, e.g. using batteries or supercapacitors (Bilodeau and Agbossou 2005, pp. 757,763). The electrical storage of energy is discussed in section 2.5.

Although hydrogen storage is associated with many problems (Bossel and Eliasson 2003, Bossel 2006), it still sometimes is beneficial to store energy as hydrogen. According to Larminie and Dicks (2003, p. 279) this can be favoured e.g. when storing energy from wind or water-driven generators, where the consumption and the production of energy seldom are equal. In this case electrolysers can be used to store excess energy as hydrogen, which in turn can be converted back to electricity when the consumption is higher than the production, e.g. on a windless day. They also suggest that hydrogen can be stored locally in small amounts, when using fuel cells for portable applications.

Larminie and Dicks (2003, p. 279) state that low power applications is another area where it is motivated to store energy as hydrogen, since a fuel processing equipment is too expensive to put in small devices. However more recently Morse et al. (2007) constructed a fuel cell producing 2-10 W, which reformed methanol using a microfluidic fuel processor. The fuel processor, which was built using microelectromechanical system (MEMS) manufacturing methods, used steam

processing together with heating elements to provide hydrogen pure enough to function in a PEM fuel cell using a phosphoric-acid doped polybenzimidazole (PBI) membrane. The PBI membranes tolerate higher temperatures than Nafion membranes, since they do not need water to conduct protons. Therefore they can tolerate more than 2% mole fraction of carbon monoxide without degradation of performance.

Nonetheless, many different storage solutions have been developed for hydrogen. They all try to overcome the problems that arise from the fact that hydrogen has a very low energy density, i.e. energy per volume unit, although the specific energy, i.e. energy per unit mass, is very high. Hydrogen can be stored using high-pressure containers, or storing the hydrogen as liquid, in metal absorbers, in carbon nanofibres or chemically. All the methods have their advantages and disadvantages, and they all have some major problem. (Larminie and Dicks 2003, pp. 279-280)

Storing hydrogen as pressurised gas is straightforward, but the high pressure brings some safety concerns. The tanks also need to be specially constructed, since the hydrogen molecules can penetrate very small holes, as well as embrittle some materials, e.g. carbon steel. Since the used pressure is very high, typically 200-300 bar, the tanks need to be strong, which makes them heavy. Therefore the hydrogen mass is usually less than 2% of the mass of the whole system. When the extra equipment is included, the price for the hydrogen energy is around 95€/kWh, when using a fuel cell with 45% efficiency to convert the hydrogen back to electricity. This is expensive compared to mains power, but less expensive than primary batteries. Since the storage of hydrogen as pressurised gas is easy, one can store it for long time, and there are no purity limits on the hydrogen stored, it is the most widely used method for small amounts of gas. It is used e.g. in hydrogen driven buses and for storing hydrogen produced by electrolysers when the energy demand is varying. (Larminie and Dicks 2003, pp. 282-284)

Hydrogen can also be stored as a liquid. Liquid hydrogen is often called LH2 or cryogenic hydrogen, since the gas has to be cooled to the liquid state. Storing hydrogen as liquid is for the moment the only used method of storing large amounts of hydrogen. Liquid hydrogen is used e.g. when refining petroleum and producing ammonia. While liquid hydrogen generally is less hazardous than pressurised hydrogen, it still has some problems. As the liquid hydrogen is very cold, only 22 K, all the pipes and tanks need to be carefully insulated as air could otherwise condense on the pipes, and liquid air on a combustible material, e.g. asphalt, can ignite. Another problem is that the density of liquid hydrogen still is low, only 71 kg/m3, which makes the required tanks large. The greatest problem is that liquefaction of hydrogen is a very energy intensive process, requiring at least 25% of the heating value of hydrogen. This makes liquefied hydrogen a very inefficient way of storing and transporting energy. Still liquid hydrogen can be used and is used, as it is approved as a fuel for use in cars in Europe. This proves that an infrastructure based on liquid hydrogen is possible to build. (Larminie and Dicks 2003, pp. 284-286)

When volume needs to be minimised and weight is not a problem, then metal absorbers can be used to store hydrogen. The metal absorber, e.g. titanium iron hydride, acts as a “sponge” which absorbs the hydrogen through an easily reversible chemical reaction. Hydrogen is supplied to the

metal hydride using pressure a bit above atmospheric pressure. The metal hydride, contained in a storage vessel, reacts with the hydrogen, producing some heat. When the metal hydride has fully reacted, the hydrogen supply is disconnected and the container is sealed. When hydrogen is needed the container is connected to e.g. the fuel cell and the reaction reverses. The heat needed for the reverse reaction is normally taken from the surroundings, but heat can also be provided to speed up the reaction. This limits the feasible size of the storage possible, since the reaction can only happen at a certain rate, without damaging the material. At a possible reaction rate, the typical recharge time is one hour for a 5 kg tank. This renders the method impractical for storing large amounts of hydrogen and it cannot therefore be used in e.g. vehicles. The metal hydride also easily reacts irreversibly with impurities, putting strict demands on purity of the hydrogen used. The method is however much safer than storing hydrogen under pressure or as a liquid, since the pressure in the container is low, and the tank is at ambient temperature. In the case of a leak, the hydrogen releasing reaction cools the tank, which slows down the reaction, and less hydrogen is released. Another benefit is that several hundred charge and discharge cycles can be completed without degradation of performance. Therefore storing hydrogen in a metal hydride is a good option when small amounts of hydrogen need to be stored in a small volume and weight is not an issue, as is the case e.g. in boats. (Larminie and Dicks 2003, pp. 286-289)

Hydrogen storage using carbon nanofibres has also been investigated, but shows no promising results yet. The different types of carbon nanofibres investigated are graphitic nanofibres and single and multi-walled carbon nanotubes. Of these the multi-walled carbon nanotubes show most promise for the moment. (Larminie and Dicks 2003, pp. 289-291)

A different method for storing hydrogen is chemical carriers, i.e. hydrogen rich fuels, from which it is easy to extract the hydrogen when needed. Apart from easy extraction of hydrogen, chemical carriers must also be cheap, simple, and energy efficient to manufacture as well as safe to handle. Taking these considerations into account e.g. methanol, alkali metal hydrides, sodium borohydride and ammonia are possible chemical carriers. Though the alkali metal hydrides provide an easy way of producing hydrogen and are not expensive, they require more energy to manufacture and transport than is released when reacted in the fuel cell. Additionally metal-air batteries are better, with fewer problems. On the other hand, when using sodium borohydride one gets carbon dioxide free hydrogen gas at an easily controlled rate. This solution does also work at room temperature, is safe to transport and the product gas can contain water vapour if needed, which is a clear benefit when using PEM fuel cells. The only problem with sodium borohydride is that the cost for producing hydrogen is approximately 470 €/kg, which is about ten times the cost of producing hydrogen using an electrolyser powered by mains current. Ammonia can be compactly stored, has low price and is readily available. However it is highly toxic and corrosive and to release the hydrogen, high temperatures are needed, which makes it very hard to use in small systems. Additionally internal reformation can be used at high temperatures, making other fuels a better option. For the moment methanol is the most promising chemical fuel, because of e.g. sufficient storage efficiency, low cost, availability, ease of transport and high hydrogen content. (Larminie and Dicks 2003, pp. 141, 293-304)

Table 3: A comparison between different ways of storing hydrogen. (Adopted from Larminie and Dicks 2003, p. 304, table 8.20)

Method	Gravimetric storage efficiency,% mass H2	Volumetric mass (kg) of H2 per litre	Comments
High pressure in cylinders	0.7-3.0	0.015	'Cheap and cheerful' widely used.
Metal hydride	0.65	0.028	Suitable for small systems.
Cryogenic liquid	14.2	0.040	Widely used for bulk storage.
Methanol	6.9	0.055	Low-cost chemical. Potentially useful in a wide range of systems.
Sodium hydride pellets	2.2	0.02	Problems of disposing of spent solution.
NaBH4 solution in water	3.35	0.036	Very expensive to run.

Choosing the hydrogen storage method is balancing between many different parameters including cost, safety, size, mass and available infrastructure. A comparison between different methods is found in table 3. Since storing energy as hydrogen often is inefficient, one needs to consider if it is beneficial. In the case where excess energy is available and long-term storage is needed, storing energy as hydrogen can be motivated. For short-term storage one should consider electrical storage of energy.

It should be noted that a pure hydrogen economy probably never will be realised, since around 75% of the energy is lost if the electricity is used to produce hydrogen, transport it to the customer and then use it in a fuel cell (Bossel 2006). This means that hydrogen energy would be at least four times more expensive than grid electricity, which makes it hard to sell. Bossel and Eliasson (2003) argue that a liquid hydrocarbon economy, using e.g. methanol or ethanol, is clearly more beneficial than a pure hydrogen economy. Liquid fuels have higher energy density at NTP than hydrogen that is stored at high pressure or liquefied. This provides easier transport with clearly less energy losses. Also, ethanol and methanol can be produced from plants using fermentation processes.

2.4 Fuel processing systems

Many fuel cell types use hydrogen as fuel. However, hydrogen is not readily available so it needs to be produced from available fuels. The produced hydrogen fuel might also need to be processed to remove impurities before use. Larminie and Dicks (2003, p. 238) define fuel processing as “the conversion of the raw primary fuel, supplied to a fuel cell system, into the fuel gas required by the stack”. Some of the possible paths for producing, storing and using various fuels are presented in figure 2.4. In this work methanol is electrolysed and the hydrogen is used in a mobile fuel cell. The methanol can be produced e.g. using renewable fuels with biological methanol production methods, but also other production methods are possible.

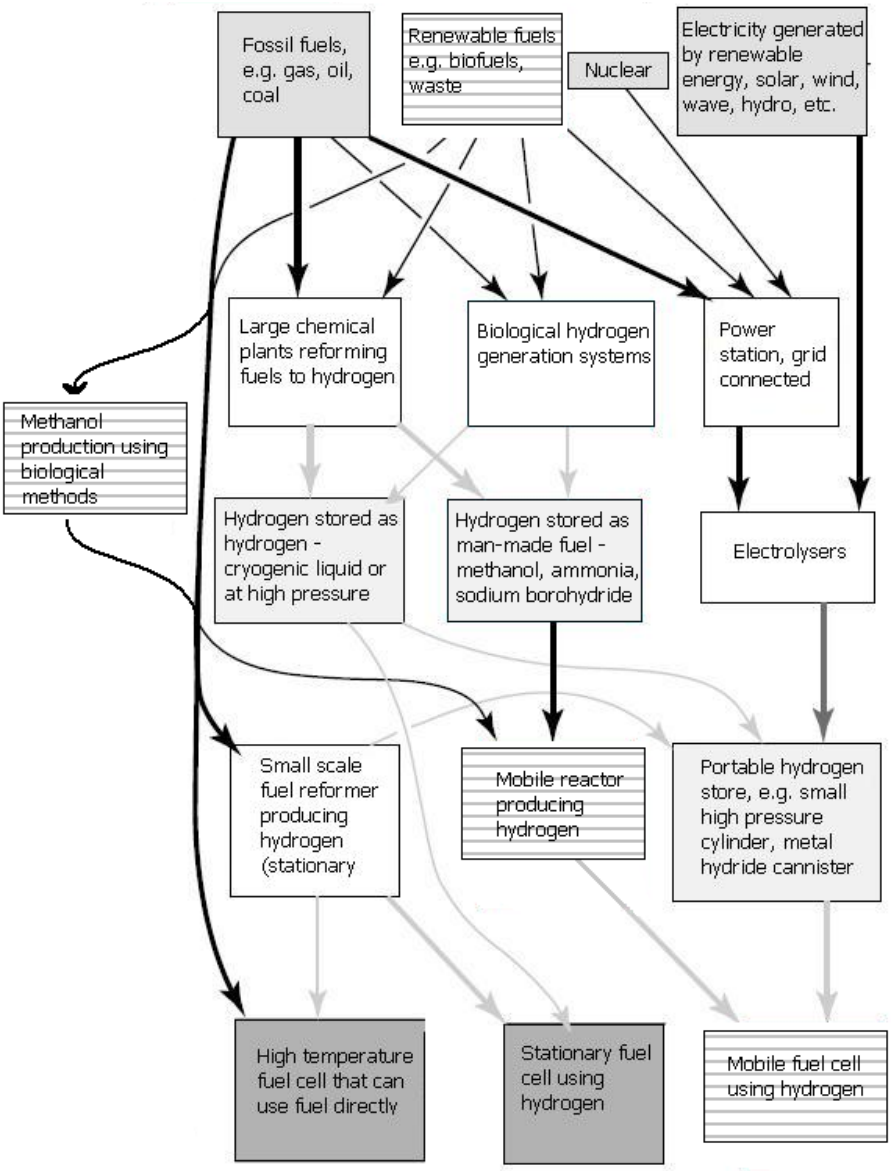

Figure 2.4: Different ways to produce, store and use fuels in fuel cells. One possible route which could be used for the system in this work is shown with the striped boxes. It involves using biologically produced methanol as the hydrogen carrier, which then is electrolysed and used in a mobile fuel cell. (Adapted from Larminie and Dicks 2003, p. 231, fig. 8.1)

In this section we will discuss hydrogen production using electrolysis and some uses of electrolysers found in literature. Conventional methods for producing hydrogen, e.g. reforming, direct hydrocarbon oxidation, partial oxidation, autothermal reforming, and pyrolysis will not be discussed, since they all require higher temperatures than what is suitable for PEMFCs in mobile applications. Biological hydrogen production methods on the other hand have not been successful yet and are therefore omitted from this work. Neither will common hydrogen refining methods, as sulphur, carbon and carbon monoxide removal, be discussed, since aqueous methanol electrolysis, which is used in this work, produces very pure hydrogen that can be used directly even in PEMFCs (Sasikumar et al. 2008). It should however be noted that water, carbon dioxide, and methanol

permeate the membrane into the cathode compartment. These substances are not poisonous for the PEMFC, but e.g. methanol is sometimes removed by bubbling the product gas through water and then drying it (Sasikumar et al. 2008). When PEMFCs are used the produced gas should not be too dry as the PEMFCs work better when the membrane is properly humidified. Methanol-water solution that has permeated the membrane can also be recycled to the anode, since the methanol concentration is almost the same for the permeated solution as for the original solution, as long as very low current densities are not used (Take, Tsuratani, and Umeda 2007).

2.4.1 Electrolysers

Electrolysers can be used for producing hydrogen. An electrolyser is the opposite of a fuel cell, since it uses electricity to split a substance into hydrogen and other substances. For example a water electrolyser split water into hydrogen and oxygen. The structure of an electrolyser is the same as for fuel cells, however some small differences exist. The electrode structure is made to expel the gas rather than to draw it and the electrolytes are often thicker to reduce water diffusion through the membrane. Though the membranes are thicker, some water permeates through the membrane, and therefore the product gas often needs to be dried before it is stored. (Larminie and Dicks 2003, pp. 270-272)

Alkaline electrolytes were previously mostly used, according to Larminie and Dicks (2003, pp. 270-272), but now PEM electrolysers are more common. They claim that PEM electrolysers are successful since the hydrogen produced is very pure and the main problems associated with PEMFCs, i.e. cooling and water management, can be easily solved. Cooling is easily solved since water needs to be circulated past the anode for the electrolysis to happen, and the water circulation effectively cools the cell. It is easily understood that since the main water management problem for PEMFCs was the flooding of the positive electrode, and the positive electrode should be flooded to achieve electrolysis, the problem no longer remains.

The electrolysis of water can be achieved using electricity to split the water as described above, and also with photo-electrolysis. Photo-electrolysis is a result of integrating a photovoltaic device and an electrolyser. The difference from using a separate photovoltaic device together with an electrolyser is that no separate electrical connections and converters are used. The integrated device collects light energy and splits water that comes in contact with it. These devices have been built using e.g. multi-layered amorphous silicon cells giving efficiencies of 7.8% for light energy to hydrogen conversion. Theoretically these systems could give an efficiency of 42%. (Larminie and Dicks 2003, p. 275) There are however also other useful electrolysis methods than the electrolysis of water. For example aqueous methanol (Sasikumar et al. 2008) and natural gas (Iora et al. 2010) can be electrolysed.

$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2 \quad (4)$$

Methanol electrolysis, see equation (4), is an attractive alternative to the electrolysis of water, since the voltage at which methanol disintegrates into hydrogen and carbon dioxide is theoretically only 0.02 V compared to 1.23 V using water (Sasikumar et al. 2008, p. 5906). Though

methanol actually starts to disintegrate at around 0.4 V it is still very much lower than the disintegration voltage for water. Thus the energy needed for methanol electrolysis is only around 60% of the energy needed for water electrolysis (Take, Tsuratani and Umeda, 2007). Very pure hydrogen can easily be produced using aqueous methanol electrolysis and it is therefore a good alternative to catalytic reforming of methanol (Sasikumar et al. 2008). In catalytic reforming the hydrogen needs to be separated from carbon monoxide and carbon dioxide present in the product gas before use in a PEMFC, while a PEM methanol electrolyser separates them already during electrolysis. Methanol electrolysis can also be used at very high current densities, while the voltage remains much lower than for water electrolysis. Additionally a methanol electrolyser combined with a PEM fuel cell using hydrogen as fuel is more efficient, considering watt hours produced per millilitre of methanol, than a direct methanol (DM) fuel cell using methanol as fuel (Aalto University, 2010b). This is true even though some of the energy produced by the fuel cell in the first case is used for the methanol electrolysis. Methanol electrolysis can be used in both portable and stationary devices for both small and large-scale hydrogen production e.g. for metallurgical processes, in gas chromatographs or for automotive use (Jeffries-Nakamura et al. 2002).

According to Barbir (2005) there are some issues that one needs to consider when choosing an electrolyser that operates together with a renewable energy source. For example the relative sizing of the electrolyser and the energy generating device, intermittent operation, efficiency, and output pressure needs to be considered. Most important when choosing the size of the electrolyser is the capacity factor, which describes how much the electrolyser is used compared to its capacity. For example if we have a photovoltaic device that produces varying power connected to a small electrolyser, then the small electrolyser is likely to use most of its capacity most of the time, and therefore have a large capacity factor. A larger electrolyser connected to the same photovoltaic device would have a lower capacity factor. However a small electrolyser cannot utilise all the energy provided by the photovoltaic device when the sunlight is intensive. Therefore the extra energy needs to be stored or else it is lost. The question that needs to be answered when considering the electrolyser size is therefore if it is more efficient and economical to have a large electrolyser or a small electrolyser combined with an energy storage system. One also needs to remember that the performance of the electrolyser degrades over time and this has to be taken into account when choosing the size.

Figure 2.5 shows a typical efficiency curve for a PEM water electrolyser. It can clearly be seen from the figure that low hydrogen generation rates give higher efficiencies. Since low hydrogen generation rates are given by low current densities it is seen that electrolysers are most efficient when working at low current densities. Low current densities are achieved by using low cell potentials, which makes the efficiency of the electrolyser inversely proportional to the voltage. However, low current densities give low hydrogen production rates, which means that a larger, and more expensive, electrolyser is needed to produce the same amount of hydrogen. (Larminie and Dicks 2003, p. 273) Additionally, Barbir (2005, p. 666) points out that some of the hydrogen permeates through the membrane instead of being collected, and the fraction that permeates

through the membrane is greater at low current densities. However, Barbir also states that using low current densities usually is no problem at low pressures, since the permeation is low. At high pressures more hydrogen permeates the membrane, which can create a highly flammable mixture of oxygen and hydrogen. Thus only high current densities are effective and safe if high pressures are used. If the electrolysers work at decent loads, but only short times at a time, the electrolyser efficiency is lowered since it takes some time before the electrolyser reaches the optimal temperature.

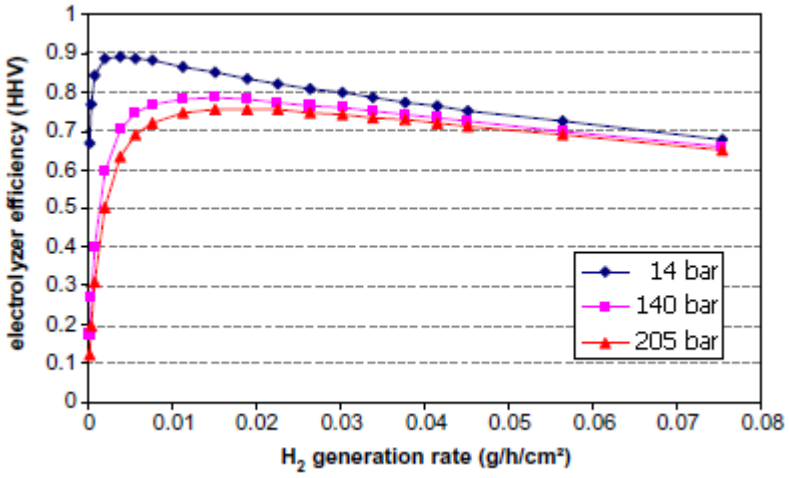

Figure 2.5: A typical PEM water electrolyser efficiency curve for various delivery pressures. The hydrogen generation rate is proportional to the current density. HHV stands for higher heating value. (Adapted from Barbir 2005, p. 667, fig. 9)

When calculating the efficiency of an electrolyser one must also remember that auxiliary equipment and possible voltage regulation can reduce the efficiency. The efficiency loss from voltage regulation arises mainly from power and voltage conversion. DC/DC converters have very high efficiencies in some power range, but since the power is varying in most applications the efficiency is lower. If a good match between the polarisation curves of the power generating device and the electrolyser can be achieved no converters are needed and the efficiency can be kept high over a much larger power range. Typical industrial water electrolysers reach an efficiency of 4.5-6 kWh/Nm^3 of hydrogen produced. (Barbir 2005, pp. 667-668)

Electrolysers can also be used to generate high-pressure hydrogen. To operate at high pressures the electrolyser needs to be designed to avoid material creep, the membrane needs to be supported, and the gasket strong. According to Barbir (2005, pp. 666-667) PEM electrolysers working at 14 bar are commercially available and electrolysers using 200 bar pressures have been operated in laboratories. Barbir also states that pressurising the hydrogen using the electrolyser is the most efficient way to compress the gas, since the only loss arises from the hydrogen permeation through the membrane. However, according to Larminie and Dicks (2003, pp. 272-273) the additional work done by the electrolyser to compress the gas is exactly the same as the work done when a compressor compresses the gas. This would imply that high-pressure electrolysers and compressors are equally effective. Compressors are however more likely to have

inefficiencies and it is easier to use only an electrolyser instead of an electrolyser and a compressor, while high pressure electrolysers are hard to construct.

When considering water electrolysis, the main problem is that the energy required for electrolysis, is greater than the energy which is released when the hydrogen is used e.g. in a fuel cell (Barbir 2005, p. 661). According to Larminie and Dicks (2003, p. 272) the use of electrolysers is therefore motivated only in certain applications, e.g. mobile use, at low usage rates and when surplus energy is available. Mobile use is motivated since mobile power is far more valuable than grid power. A large electrolyser using grid power could e.g. produce hydrogen used to power multiple boats or reload a fuel cell car during the night. According to Hammerli and Stuart (2000 in Larminie and Dicks 2003, p. 272) the running costs for a fuel cell powered car reloaded by an electrolyser would be less expensive than the same for a car using gasoline. Larminie and Dicks (2003, p. 272) also state that low usage rates also favour the use of electrolysers, since small electrolysers are available and it is simpler and cheaper to use an electrolyser instead of a small natural gas reformer. Electrolysers used together with fuel cells are convenient when surplus energy is available at some occasions and needed at others. The electrolyser can then convert the surplus energy into hydrogen, which the fuel cell converts back to electricity when needed.

There are also other advantages that motivate the use of electrolysers, especially at medium-scale production. Firstly, electrolysers produce very pure hydrogen. Secondly, the hydrogen does not need to be stored in large amounts since it is produced on demand, thus avoiding most of the safety problems associated with the storage of hydrogen, as electricity is easier and safer to provide than hydrogen. Thirdly, hydrogen produced with electrolysers has a much lower marginal cost than high-pressure hydrogen. (Larminie and Dicks 2003, p. 272)

2.4.2 Electrolyser state-of-the-art

In literature many different uses for electrolysers were found. According to Larminie and Dicks (2003, p. 272) most of the electrolysers are not used with fuel cells, since hydrogen is used for many different purposes, in e.g. chemical analysis. Barbir (2005) investigated the use of PEM electrolysers together with renewable power sources, primarily photovoltaic devices. He proposed five different setups in which electrolysers could be used. In the first hydrogen was generated with an electrolyser using only energy available from a photovoltaic device. The advantage of this approach is that hydrogen is produced only using renewable resources and grid power is not needed. The second used grid power when solar energy was not available to produce hydrogen at a steady rate. This raises the electrolyser efficiency and the capacity factor since intermittent operation of the electrolyser is eliminated. The third setup used an electrolyser to generate hydrogen from the surplus energy of a power plant. This is a possible solution if the grid operator requires that the power plant does not feed too much energy into the grid even during off-peak consumption hours. A variation of the third setup is to use the electrolyser at steady power for maximal efficiency and insert the surplus power into the grid. However, it is hard to guarantee that the power can be fed into the grid, which might make this solution unfavourable. The fourth solution used a photovoltaic device, an electrolyser, and a fuel cell to provide power to a steady or

varying load in the grid. This is done by storing energy as hydrogen when surplus energy is available, and converting the hydrogen into electricity when needed. This system requires a more complex power conditioning and control system, and the cost of the produced electricity is many times higher than when using e.g. a photovoltaic device alone. However, the electricity quality is high, which motivates the use of this system for some applications. The fifth system resembles the fourth, but is not grid connected. Instead of feeding power to the grid it can power e.g. a residential load and provide hydrogen for e.g. cooking or be used in an unmanned aircraft equipped with photovoltaic cells for long missions without the need to land for refuelling. Finally Barbir concludes that for the moment photovoltaic devices in combination with PEM electrolysers are well suited for hydrogen production only in demonstrations, remote areas or special applications due to the high cost.

Sasikumar et al. (2008) investigated the influence of different factors, e.g. methanol concentration, operating voltage and temperature, membrane thickness and hydrogen purity, on the electrolysis of aqueous methanol using a PEM electrolyser. They concluded that higher methanol concentration increases the hydrogen production up to a certain limit, where the production suddenly falls, perhaps due to Nafion membrane dissolution. Hydrogen production also increased when current density or temperature was increased. Thick membranes gave smaller methanol crossover and better mechanical stability, while thinner membranes gave better performance. For aqueous methanol electrolysis it was concluded that the best solution is to use a 7 mm thick Nafion 117 membrane.

Bilodeau and Agbossou (2005) used an electrolyser and a fuel cell together with a wind turbine and a photovoltaic array to power a residential load. They also used a battery stack to balance the DC-bus voltage to which all devices where connected. The whole system was controlled by a fuzzy controller, which was able to determine the appropriate hydrogen consumption and production needed to keep the load powered. Using this system they were able to keep the load constantly powered, keep the batteries state of charge over 50% all the time and guarantee that the fuel cell and the electrolyser always are run at least few minutes at a time, thus increasing their efficiency. They also concluded that storing energy as hydrogen is a good solution when energy for a residential load for a week has to be stored. Storing such a large amount of energy in batteries is not efficient. However, their system was not able to produce enough input energy to power the residential load when simulated using test data for a typical week in July. This implies that the system efficiency was too low, and more specifically that the power generating part of the system simply did not produce enough power for the load.

Iora et al. (2010) used solid oxide fuel cells (SOFCs) together with solid oxide electrolysis cells (SOECs) to produce pure hydrogen from natural gas. In their system multiple SOFCs turned natural gas into electricity and heat, which was fed into the SOECs. The SOECs in turn split the steam into hydrogen and oxygen. The hydrogen was collected and the oxygen could be collected or fed back into the SOFCs with the natural gas. Since a single SOFC produces less power than a single SOEC requires, Iora et al. simulated two different systems. In the first the same amount of SOFCs and SOECs where used and the extra power needed was taken from the grid. In the second additional

SOFCs where used to provide the extra power needed. They claimed that using intermediate temperature, i.e. 550-800°, SOECs the power required for hydrogen production was around 3 kWh / Nm^3, while they state it is around 4.3-4.8 kWh / Nm^3 for alkaline, and 6.7-7.3 kWh / Nm^3 for PEM state-of-the-art electrolysers. On the other hand natural gas steam reforming has an efficiency of 85% for large plants and less for smaller ones, while Iora et al. reported between 70 and 87% natural gas to hydrogen efficiencies for their different systems, 70% being approximately twice the efficiency of water electrolysis. Finally they conclude that SOFC/SOEC systems seem promising at small scale, while not competitive at large scale. However these systems are at an early stage of development so it is impossible to evaluate the economic competitiveness yet.

2.5 Electrical systems

The electrical system is a central part of every fuel cell system. Especially in the case of hybrid systems, where energy storage devices, e.g. batteries or supercapacitors, are used with the fuel cell, the electrical system is of central importance for the efficiency of the system. However, standard electrical equipment can mostly be used also with fuel cells, which makes the design of an electrical system for a fuel cell rather straightforward (Larminie and Dicks 2003, p. 331). In this section we will present some important matters concerning electrical systems in hybrid fuel cell systems.

The electrical system of a mobile fuel cell system often contains regulators, inverters, and electric motors. Regulators are needed, because the voltage and current a fuel cell generates is seldom directly usable for an electrical device, since the voltage of a fuel cell drops rapidly when the current is increased. Voltage regulators, DC/DC converters and chopper circuits are used to keep the voltage at a steady level. Inverters are readily available, low cost, standard electronics hardware used to convert the direct current produced by the fuel cells into alternating current, e.g. when connecting the fuel cell system with the grid (Larminie and Dicks 2003, pp. 339-349). Electric motors on the other hand are used in almost all slightly larger fuel cell systems for driving e.g. compressors and other auxiliary equipment. However, electric motors and inverters are usually not needed in small mobile fuel cell systems. Therefore we will focus on hybrid systems in the following.

2.5.1 Hybrid systems

Hybrid structures are often used to improve the performance of fuel cell systems, especially in applications where the load is highly variable (Guizzi, Manno, and De Falco 2009). Hybrid systems utilise multiple power sources, e.g. a fuel cell together with a supercapacitor or battery or both. If a fuel cell is used together with electric components the whole system is electric, which gives a simple design. A simple example of one of the benefits of a hybrid system is found in figure 2.6. In the figure we can see that the fuel cell lifts the voltage at low currents, while the battery keeps the voltage at a relatively steady level also when the current is increased.

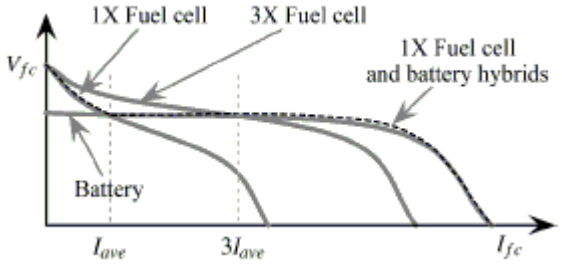

Figure 2.6: Benefits of a hybrid system. (Adopted from Zhuo et al. 2009, p. 25, fig. 4)

According to Thounthong, Raël, and Davat (2007) hybrid fuel cell systems are used since the dynamics of a fuel cell are slow and sudden high loads cause the fuel cell voltage to drop rapidly. They suggest that a faster auxiliary source, e.g. a battery or supercapacitor, should be used to keep the system output voltage at a stable level by providing energy at demand peaks. This also enables fuel cell sizing according to the average power consumption, instead of peak power consumption, which makes the fuel cell smaller, lighter and cheaper.

A stable voltage level also increases the lifetime of the fuel cell, since fast load variations increase wear (Guizzi, Manno, and De Falco 2009). Other benefits of hybrid systems are that peak powers provided by hybrid systems are much greater than the rated power of the system components alone, while maintaining high energy density (Jiang and Dougal 2006). This allows the hybrid system to have a much wider load range than e.g. a fuel cell alone (Guizzi, Manno, and De Falco 2009). Also, since supercapacitors can be charged with very low losses due to the very low internal resistance, hybrid systems using supercapacitors to provide energy at transients can achieve very high efficiencies. This makes it possible to connect the supercapacitors directly to the voltage bus in a system without need to control the supercapacitor voltage directly. Additionally, if hybrid systems are used the slow dynamics of some hydrogen storage methods, e.g. storing hydrogen in metal hydrides, can be overcome. The use of an electric energy storage system also makes it possible to use regenerative braking, i.e. slowing down the speed of a vehicle by converting the kinetic energy into electrical energy using a generator, often an electric motor (Thounthong, Raël, and Davat 2007).

In systems where both a battery and a supercapacitor are used with the fuel cell, there is usually a clear division between their functions. The battery provides energy, e.g. at system start-up, when the fuel cartridge is replaced, or at long loads with higher powers than the fuel cell can provide alone. It is beneficial to use batteries for this since they have two orders of magnitude higher energy density than supercapacitors. The supercapacitors are used to provide or absorb power at sharp transients, thus smoothening or almost eliminating the current transients for the rest of the system. This allows the fuel cell to work at steady power, and the battery currents stay on a lower level. When only small amounts of energy are required the supercapacitor can supply them fully, thus letting the battery rest. As a result of the lower battery currents, and the fewer charge and discharge cycles, the battery lifetime increases. A larger amount of charge and discharge cycles is no problem for the supercapacitor, which usually has a cycle life two orders of magnitude higher

than the one for high power lithium batteries. Supercapacitors also have the benefits, as opposed to batteries, that they do not get hot when they are discharged at high powers, and they can be charged and discharged using equal powers. Batteries need to be charged at lower power than they are discharged at. (Musolino and Tironi 2010)

Today supercapacitors cost around 50 €/Wh and batteries 1.2 €/Wh, when overhead for needed extra equipment, e.g. battery management systems, is included in the price. However, the price of supercapacitors is only a third of the previously mentioned price when produced in industrial quantities. Also, if the same amount of lifecycles is considered, the high power lithium battery cost approaches 200 €/Wh. (Musolino and Tironi 2010)

Adding a supercapacitor or battery to the fuel cell system is not beneficial if the load is nearly constant (Larminie and Dicks 2003, p. 363). On the other hand, if the load is varying, making a hybrid system advantageous, then one needs to choose whether to use a battery, a supercapacitor or both. Batteries have high energy density, but low power density, while supercapacitors have high power density, but low energy density (Bauman and Kazerani 2008, p. 760). This makes batteries better for storing large amounts of energy, while supercapacitors are better when sudden high powers are needed. One should also remember the previously mentioned advantages and disadvantages of the two technologies. The final decision on which type of energy storage to use, is dependent on the load profile of the specific application. For example Bauman and Kazerani (2008, p. 768) found that for a small hybrid sports utility vehicle (SUV) it is most efficient to use an approximately 40 kW fuel cell with a battery bank, or a fuel cell with a battery and a supercapacitor bank. The combination of a fuel cell and batteries was found to be slightly less expensive, while the combination of a fuel cell, batteries and supercapacitors was found to have a better fuel economy. The latter one also extended the lifetime of the batteries, since the supercapacitor bank handled most of the power transients. They reached their conclusions by optimising acceleration time, fuel economy and cost of the different power trains.

From the study of Bauman and Kazerani one can however not draw many general conclusions about what system to use, since their results apply mainly to a certain power range and application. The results can probably be applied to other applications with similar load profiles, if the power range is approximately the same, but it is difficult to estimate whether the results are valid for other load ranges. However, two general conclusions could be drawn. Firstly, fuel cells combined with only supercapacitor banks are not ideal when slightly larger energy storage is needed. Secondly, the use of supercapacitors prolongs the life of the batteries in systems, where large transients are present. Still, the choice of what kind of energy storage to use is application specific and depends on which system parameters need to be optimised. In section 4.1 we will therefore present power consumption measurements on two possible application devices, a small laptop computer and a mobile phone.

When designing a hybrid system one needs to choose the sizes of the components with care. The most important aspect is to fulfil the energy and power demand of the load. This can be achieved with many different configurations. For example if a hybrid system with a fuel cell, a battery and a

supercapacitor is used, then the battery must contain enough energy to provide energy for start-up, when the fuel cartridge is replaced or at long high loads, which the fuel cell cannot provide alone. The supercapacitor bank should be large enough to provide or absorb available energy at peaks so the battery and fuel cell currents stay at low enough levels. The fuel cell should be large enough to provide average power to the system. For minimal prise, volume and weight the components should be as small as possible while fulfilling the requirements. However, one should remember that the performance of the components decreases during their lifetime and this has to be observed in the design. Also, fuel cells are more efficient at medium load than at maximal load, which would make larger fuel cells preferable when considering the efficiency (Guizzi, Manno, and De Falco 2009). However, larger fuel cells are more expensive, which makes it more cost effective to use the fuel cells use at almost full power all the time (Larminie and Dicks 2003, pp. 362-367). These objectives are clearly opposite, and a compromise between size, cost, and efficiency has to be made.

One also needs to choose whether to use an active or a passive configuration in the hybrid system. The active configuration uses a DC/DC converter between the different power sources. Gao, Dougal and Liu (2003) evaluated the benefits of the passive and active configurations by constructing a hybrid power source consisting of a battery pack and a supercapacitor pack connected in parallel to a variable load. They tested their system both with an active and a passive configuration. In the active mode a DC/DC converter was placed between the battery and the supercapacitor. In the passive mode all components were connected directly in parallel.

Gao, Dougal and Liu (2003) noted that passive hybrid configurations have many benefits over systems with only a battery, e.g. higher peak power capacity, higher efficiency and longer battery runtime. Also, they might have higher efficiency than the active systems, since there is no DC/DC conversion loss. The problems with the passive configuration are firstly, that since the battery and the supercapacitor are connected directly in parallel, their voltages are always the same. This means that the components have to be sized to have the same voltage. Secondly, maximum peak power that can be achieved with the system depends on the power distribution between the components, which is mainly determined by the internal resistances of the components. There might also be large ripple in the battery current in this configuration. Thirdly, the terminal voltage follows the discharge curve of the battery.

The active configuration on the other hand allows the battery and supercapacitor packs to be of different size, since the voltages are not interdependent. For the optimised system this gives a smaller weight and volume than with the passive configuration. Also, the power capacity can be much higher, since the battery current can be kept at a safe level, while the supercapacitor current can be very high. Additionally, the efficiency might be improved if using lower battery currents saves more energy than is lost in the DC/DC conversion. Finally, the output voltage range is broadened, the battery current ripple is minimised, and the DC/DC converter keeps the terminal voltage almost constant while it also can be used as a battery charger or controller. (Gao, Dougal and Liu 2003)

2.5.2 Three non-automotive hybrid system examples

The study of Bauman and Kazerani (2008) mentioned in the previous section is only one in the large amount of studies on automotive hybrid systems. In literature only a much smaller amount of non-automotive hybrid systems was found. In the following three hybrid systems of different size will be presented.

Guizzi, Manno, and De Falco (2009) created a hybrid system for 125-1000W powers, consisting of a PEMFC, a battery and supercapacitor pack, and metal hydride canisters to store the hydrogen used in the fuel cell. Though the extra components in the hybrid system they reported overall system efficiencies, i.e. fuel cell stack efficiency multiplied with the auxiliary system efficiency, of over 36% for all test configurations. This is only slightly less than for a system with only a fuel cell connected to a load via a DC/DC converter. While slightly less effective, the hybrid system allows a much wider load range than the fuel cell alone. The fuel cell can also work at near optimal loads, which increases the efficiency and the lifetime, since the fuel cell is protected from rapid transients and high power peaks. The stable load of the fuel cell also makes it possible to use metal hydride storage as the hydrogen supply though the slow dynamics.

Boscaino et al. (2008) developed a power management control system for an active fuel cell-supercapacitor system used to power a digital still camera. The camera had three different modes, all with power consumption below 20W. The control system was designed to supply the stand-by power requirement of the modes using the fuel cell and the power peaks with the supercapacitor. That means that the fuel cell load changed only when the camera mode was changed. Simulation and preliminary tests validated that stable control was achieved with the proposed control algorithm.

A micro-scale MEMS DMFC and a thin-film Li-Ion battery were combined into an active hybrid system by Chen, Vogt and Rincón-Mora (2007). Their design optimised volume, energy and power to achieve high peak-power and long lifetime. The design, made to provide energy e.g. for ad-hoc wireless sensor nodes, worked at an average load power of 12.8 µW. Chen, Vogt and Rincón-Mora noted that with a fuel cell current of 30 µA the system lifetime was only 18 days, while with a fuel cell current of 44 µA, the lifetime of the system was 318 days. This was caused since the lifetime is very sensitive to fuel cell current changes when the usable fuel cell power is near load power. They concluded that both power and energy conditioning is important when controlling micro-scale systems for maximal lifetime.

2.6 The IPPES prototype system

The IPPES project at the Aalto University is developing an “innovative biofuel cell system for portable electronics applications”. This system is based on a 0.5-20 W novel micromechanical PEM fuel cell and local production of hydrogen through biocatalytic methanol electrolysis. The aim is to provide easy reloading and transport of the methanol fuel and the biocatalyst by distributing them in replaceable cartridges. This project seeks a solution to the energy problem in small mobile devices, e.g. laptop computers and mobile phones, arising from the growing energy demand due

to the steadily growing functionalities of these devices. Fuel cell technology is needed, since the capacity of batteries is lagging the fast growth in energy demand. Fuel cells also provide faster "reloading" of the devices than with rechargeable batteries. (Aalto University, 2008)

In this work we are further developing a hybrid system previously constructed for the IPPES project. The system functions as a mobile time extender for a mobile phone. Since the average consumption of a mobile phone is rather low the now designed system is low power. The fuel cell stack should give a voltage of around 1.6 V and a current of 1 A during operation, which would give a power of 1.6 W. Of this current 600 mA would be used for hydrogen production through methanol electrolysis, which means the system net power would be around 650 mW.

The system is started by powering the electrolysers with energy in the start-up source until the electrolysers have produced enough hydrogen for the fuel cell to start working. The start-up source can be a rechargeable battery, a supercapacitor or an external power source. It would also be possible to use the battery of the mobile phone as start-up source as long as it is not depleted. The external power source, which could be omitted, but is practical for testing purposes, can be a laboratory power supply or the power could be taken from the USB of a computer. However, primarily the rechargeable battery or the internal battery of the mobile phone would be used as start-up source due to the high energy density and the slow self-discharge of batteries.

When enough hydrogen has been produced the fuel cell starts producing power. This power is used for powering the electrolyser and recharging the start-up source. When the start-up source is fully charged it is disconnected and the surplus power from the fuel cell is used for charging the load. At shutdown the control system first checks that the start-up source is fully charged and recharges it as necessary. After this the system powers down.

The designed control system could also be used for recharging batteries of e.g. laptop computers. This however requires that a temporary source is used, and an additional DC/DC converter is added to the system. The extra components are needed, as a laptop computer requires a higher voltage and a higher charging current than the fuel cell can provide directly. In this case e.g. a supercapacitor would be installed where the load is in figure 2.7, and it would be charged to 5 V by the fuel cell. When at 5 V the supercapacitor would be emptied through another DC/DC converter into the battery of the laptop computer.

As can be seen in figure 2.7 and figure 2.8 the electrical components are a fuel cell stack, a battery, a supercapacitor, an external source, a digital switch, four DC/DC converters, three electrolysers, and a load. An electrical connection scheme can be found in section 3.1.1. The system also comprises a methanol storage for methanol used in the electrolysis, one pump for pumping methanol solution through the electrolysers, and one pump for pumping air to the fuel cell. The fuel cell has a manual purge valve, which is mostly closed, since the fuel cell currents in the system are rather small, which makes the water production small. See section 3.2.2 for more details.

The system works as follows: A water-methanol solution is pumped through the electrolysers, which turn it into hydrogen and carbon dioxide, according to equation (4). The biocatalytic

electrolysers are not functioning satisfactorily yet, so platinum catalyst is used in the electrolysers, see figure 2.9. When the biocatalytic electrolysers are functional, the methanol fuel to the biocatalytic electrolysers will be provided in replaceable cartridges, which would contain both the fuel and the biocatalyst used on the anode side of the electrolyser. The biocatalyst works in the same way as a metallic catalyst, i.e. it hastens the disintegration of methanol into hydrogen and carbon dioxide. Using replaceable cartridges with fuel and biocatalyst is advantageous, since the cartridges can be made of a material harmless to the nature or even biodegradable, and the cartridge may therefore be thrown away with the household waste or recycled after use, without the need to separate the metal first. (Ranta 2011)

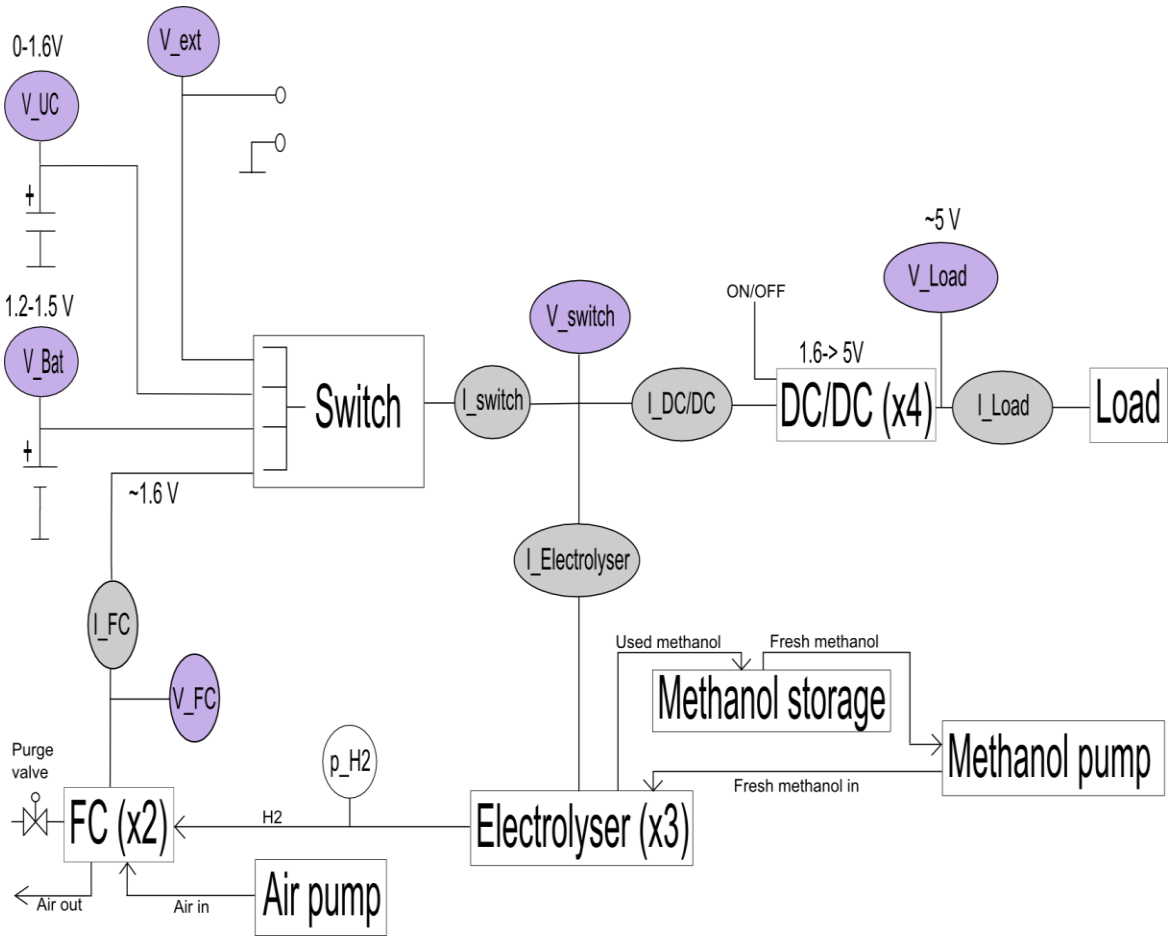

Figure 2.7: Schematic view of the developed system. The ellipses represent the measurements.

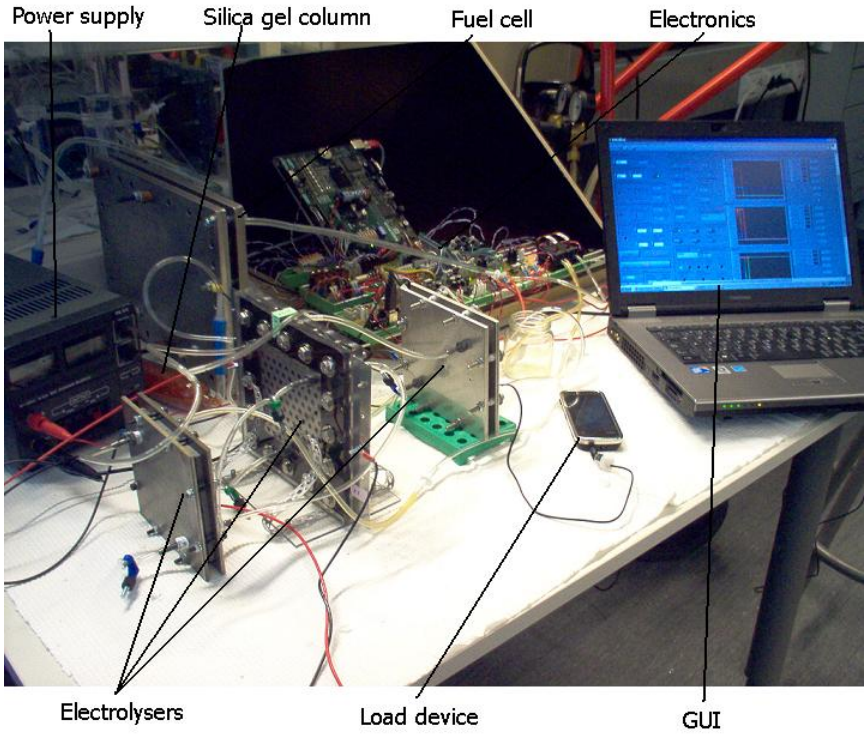

Figure 2.8: The IPPES prototype system. The three electrolysers are seen in the left foreground, the external power source, the silica gel column and the fuel cell is behind them.

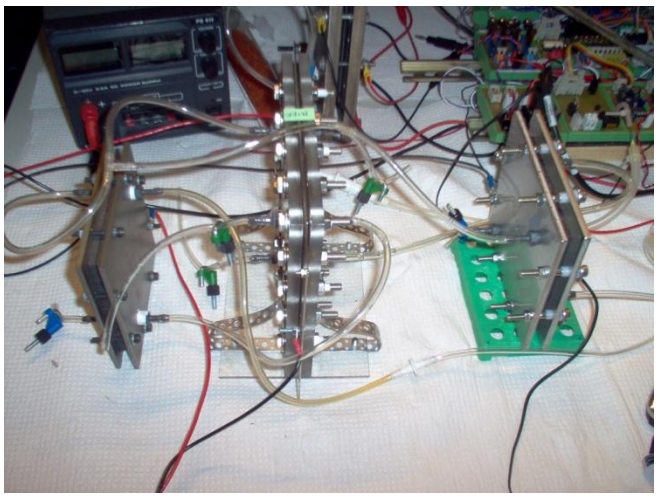

Figure 2.9: The platinum electrolysers used in the prototype system.

After electrolysis the produced hydrogen is transported to the fuel cell. The hydrogen pressure between the electrolyser and the fuel cell is monitored using a Honeywell ASDX series pressure sensor. In the fuel cell stack the hydrogen is transformed into electrical energy. The two-cell PEM fuel cell stack is passive, which means it uses oxygen from the surrounding air, and no cooling, heating or humidification is used. The air pump is used to force air through the narrow channels of the fuel cell stack. This ensures that enough oxygen is supplied to the cathode. The fuel cell is close-ended, with a manual purge valve at the fuel cell exit.

The main part of this is hybrid system is electrically passive. The electronics and the microcontroller board can be seen in figure 2.10. The fuel cell is connected directly in parallel with the start-up sources and the electrolyser, and the voltage of the currently connected energy storage device determines the operating point of the fuel cell. The load voltage on the other hand, is controlled using DC/DC converters. Four converters are used in parallel to achieve a high enough current to allow charging of the load battery. This is needed, since the load battery requires a certain amount of current before charging starts. The mostly passive configuration is inherently simple and has high efficiency, but the operating point of the fuel cell cannot be controlled. Using an active configuration, i.e. a DC/DC converter to control the voltage of the fuel cell, would make it possible to control the operating point of the fuel cell, but the additional DC/DC converter would lower the system efficiency.

The electrical flow is controlled by the digital switch and the on/off-switches in the DC/DC converters. The four gates of the digital switch are controlled independently. This as well as DC/DC converter switching is controlled by the control system. All four DC/DC converters are NCP1402SN50T1 type boost-converters with a regulated 5 V output. The converters are connected in parallel between the voltage bus and the load and boost the voltage from around 1.6 V to 5V. They are digitally controlled to be on when the load is charged and off otherwise. The parallel connection of many DC/DC converters is needed since a single converter of this type cannot handle larger currents. The efficiency at medium and large currents is also better when using many converters.

The supercapacitor is built from three 70 F capacitors connected in parallel, giving a total capacitance of 210 farads and rated voltage of 2.1 V. The capacitors can also be used separately, which makes it possible to also use capacitances of 70 and 140 F. The battery is a standard 2700 mAh rechargeable battery with a nominal voltage of 1.2 V.

The requirements for the control system are the following. The digital switch requires four digital outputs and the pumps require one digital output each. If a purge valve is used then additionally one digital output is required. The DC/DCs could be separately controlled with the current control system, but one digital output would be enough to control all DC/DCs since they are always on simultaneously. For thorough monitoring of the system 12 analog inputs are required, but only 5 analog inputs are needed for the control system to function. These are the voltage of the fuel cell, the battery and the supercapacitor, as well as the hydrogen pressure and the current flowing to the load. It might be possible to omit the hydrogen pressure measurement from the control system at a later stage of the development, if the fuel cell voltage is a clear enough indicator of when enough hydrogen has been produced and the fuel cell can start to function. The summarised requirements are: eight digital outputs and four to five analog inputs for the minimum case, and nine digital outputs and eleven analog inputs for thorough monitoring.

The control system is implemented in LabVIEW at this stage of the development. At a later stage it could be implemented using a small size microcontroller and perhaps a field programmable gate array and a standard programming language, e.g. C. The control system is now running on a

personal computer connected to a NI (National Instruments) sbRIO-9631 embedded control and acquisition device containing a microprocessor, an FPGA, and IO. See section 3.3.3.1 for more details. The user interface and data logging is handled by the personal computer, but the control system itself is running on the microprocessor, while the FPGA handles the IO. This means that the personal computer is not needed for automated control of the system, only for changing control parameters as well as logging and showing the measured data. If small modifications would be made control of the system could be performed using only the sbRIO-9631 device. However, prototyping is clearly easier using the user interface of the personal computer.

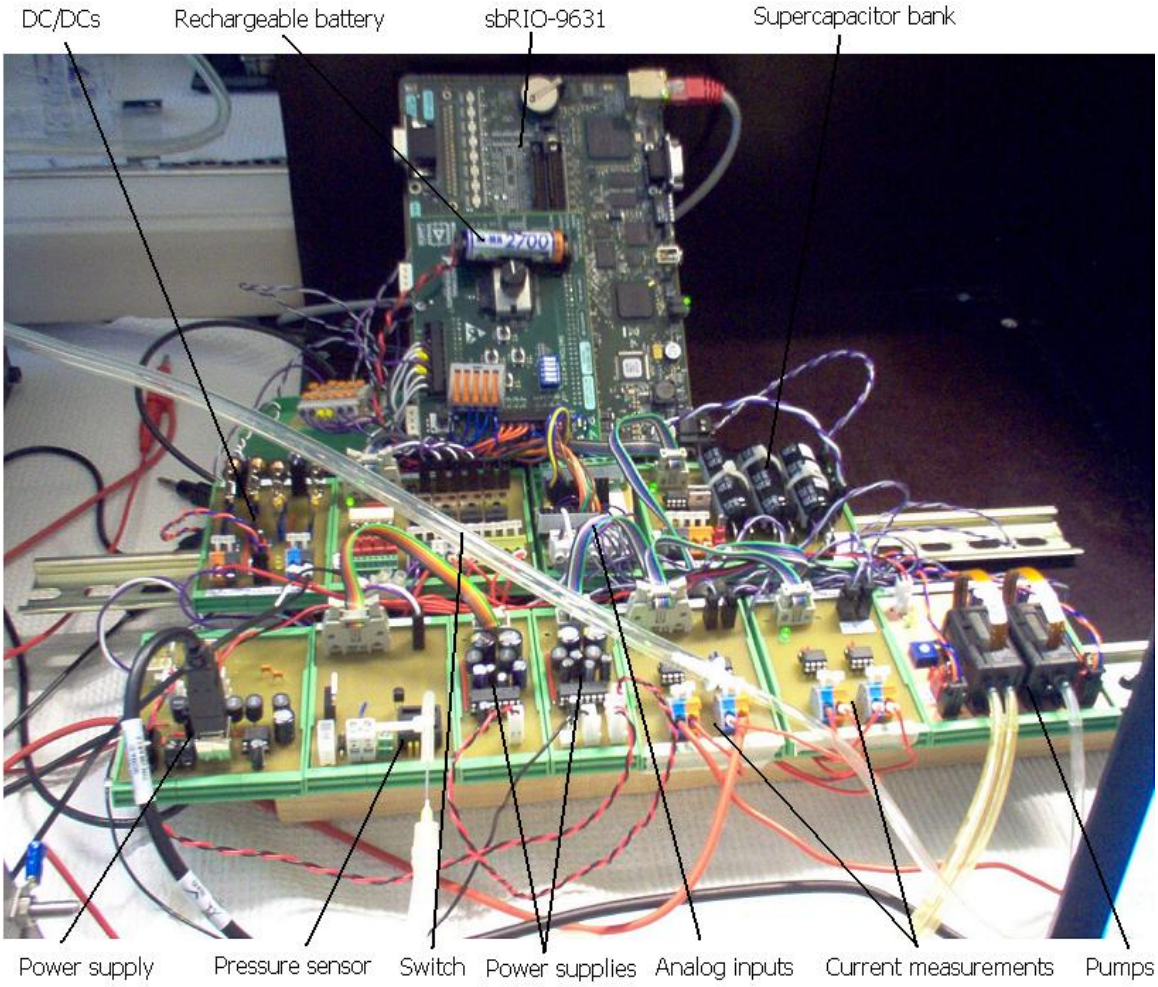

Figure 2.10: The electronics and the microcontroller board of the prototype system.

2.7 Digital design technologies

The choice of technology is a very important decision when one wants to solve a specific engineering problem (Barrett and Pack 2006, p. 12). In this section we will present the main digital design technologies available as well as discuss selection criteria for choosing a microcontroller for a specific application, as a microcontroller and an FPGA will be the technology used in this work.

There are four main technologies available when creating a digital design. Firstly, programmable gate arrays are, as the name implies, programmable logic hardware that can be configured using software. Programmable logic arrays (PLAs), programmable array logics (PALs), generic logic arrays (GALs), and field programmable gate arrays (FPGAs) are some of the available variants. FPGAs are especially used when very complex algorithms are needed. The programmable hardware in these devices consists of AND and OR gates and often also flip-flops. This makes it possible to construct both combinational and sequential circuits using these devices. The programmable gate arrays are usually programmed using Verilog hardware description language (VHDL), and can be used for fast implementation of complex digital designs. (Barrett and Pack 2006, p. 12)

Secondly, microprocessors, i.e. the main processor circuits of a personal computer (PC), can be used when many different problems need to be solved using a single processor. Microprocessors are hardly used for complex designs if only one problem needs to be solved, since standalone technologies offer more efficient solutions for this, saving both space and money. Thirdly, digital signal processors (DSPs) are used when more processing and analysis of the signals are needed, e.g. for sound processing in cellular phones. DSPs are also used when floating-point calculations are needed, since they are optimised for it. (Barrett and Pack 2006, p. 12)

Fourthly, and most important for this work are the microcontrollers. A microcontroller is a miniature version of a complete computer system containing all the needed subsystems. Microcontrollers have inputs and outputs, a time base, a timing system, memory, a unit that calculates arithmetic and logic calculations, and capability to produce control signals. According to Barrett and Pack (2006, p. 13) microcontrollers are used when “a moderate amount of local intelligence is required within a given application”. As opposed to digital signal processors, the microcontrollers are best suited for integer operations, though floating point operations are also possible.

Here we have presented the main technologies used in digital design. However, in some cases it is most beneficial to use many technologies at the same time instead of one. Barrett and Pack (2006, p. 13) claim that a current trend is using microcontrollers together with FPGAs.

2.7.1 Microcontroller selection criteria

As the designed system is using, and probably the next iteration of it will be using, a microcontroller as the heart of the system, we will discuss how to choose an appropriate microcontroller for a specific application. According to Barrett and Pack (2006, p. 44) one should choose the simplest microcontroller that fills the specifications. Firstly, one should list all the requirements that need to be fulfilled and secondly, choose the microcontroller that best fulfils

these requirements and fits the skills of the programmer while being as simple as possible. Barrett and Pack (2006, pp. 47-48) present that one should consider if the microcontroller has:

- Enough ports,
- Required subsystems,
- Right type and amount of memory,
- Required clock speed,
- Low enough power consumption,
- Needed special features?

Firstly, a sufficient number of ports and external pins are required. Secondly, subsystems, e.g. A/D conversion or serial communication, might be needed. Thirdly, the memory must be large enough for the programmed application, as well as of the right type so it is fast enough, and important data is not erased in case of power failure. Fourthly, the clock speed, which determines the microcontroller speed, should be fast enough to execute the needed algorithms in the given time. However, According to Barrett and Pack (2006, p. 44) the power consumption is directly proportional to the microcontroller speed. Thus, fifthly, the power consumption should be kept low enough. Sixthly, one should consider if special features, e.g. fuzzy logic or advanced signal processing, are required for the application.

For the embedded fuel cell control system designed in this work the most important characteristics are low power consumption and small size, as most microcontrollers have at least the required amount of inputs and outputs, as well as the A/D conversion capabilities needed. Also, most microcontrollers are small size, while the power consumption can vary greatly. The power consumption of the microcontroller is affected by the speed of the microcontroller, but also how long the microcontroller is asleep compared to awake. The possible sleep cycle lengths are primarily decided by the speed of the microcontroller, since a slower microcontroller needs to be on more often to complete the same calculations, and the control system designed, as some control systems require e.g. measurements to be done so often that the microcontroller cannot sleep. Microcontrollers can also use dynamic voltage scaling (DVS) to reduce the power consumption. Weiser et al. (1994) reported power saving of 50% with a time window of 50 milliseconds, i.e. so short that it does not affect the responsiveness of the software, and DVS between 5 V and 3.3 V. For the same time window and DVS between 5 V and 2.2 V, savings up to 70% were achieved. To give fast enough interactive response for human users a time window of 20-30 milliseconds should be used, which makes the powers savings slightly less. On the other hand, for a fuel cell control system the time window could possibly be a few hundred milliseconds, as the controlled process is rather slow, which could give even somewhat larger power savings.

Another important consideration is how the well the control system can be implemented using a specific microcontroller. The control system places certain demands on the properties of the microcontroller, as well as on the precision of the measurements, which are affected e.g. by the amount of bits used. The ease of programming is also a central concern. It depends on the programming language, the way the microcontroller is connected to the computer used for

programming, and if in system programming (ISP) methods can be used. Also, it might be important that the microcontroller is easily available, changeable, and low-cost if multiple devices will be built or there is a risk of device failure during the development or use of the microcontroller.

3 Analysis and design

As previously described, the aim of this work is to design and construct a system which extends the mobile usage time of a portable electronic device, e.g. a mobile phone or a laptop computer, by charging the battery of the device. The system does only need to provide somewhat less than the average power consumed by the device, as a five-hour mobile time extension is targeted. The power for charging the mobile device is produced by a fuel cell using in-situ produced hydrogen from a methanol electrolyser. The design also involves a control system that handles the charging process as well as the start-up and shutdown of the system.

The fuel cell – electrolyser test bench and the designed control system are based on a previous system built for the IPPES project. The problems of the previous system have been analysed and solved when appropriate for further development of the system. The main problems with the old system were low efficiency due to the DC/DC converters used, hydrogen leakage from the fuel cell, and high conduction losses in the electrical system due to modular design. Membrane drying was a problem at high loads. This section presents an analysis of the previous system and the design of the new one, and section 4 presents the conducted tests and the achieved results.

3.1 Electrical system

3.1.1 Implemented design

The electrical design is a major part of the overall system design, since the electrical efficiency of the components is a possible major source of losses. Therefore the new design, see figure 3.1, was made to maximise the electrical efficiency of the system. The problem with the DC/DC converter efficiency in the previous system was partly solved by choosing DC/DC converters more suitable for the current power range. The other part of the solution was to make the fuel cell – electrolyser part of the system passive, i.e. not using DC/DC converters to control the voltages and currents. This makes the efficiency higher, as DC/DC converters always lower the efficiency somewhat compared to using a direct electrical connection. However, to be able to connect the fuel cell and the electrolyser directly, the electrolyser stack has to be roughly 1.5 times the size of the fuel cell stack. This makes the voltages of the fuel cell stack and the electrolyser stack compatible. This is important as the electrolyser current depends on the voltage, and the current is directly proportional to the hydrogen production. This means that a too low voltage causes a too low hydrogen production, while a too high voltage gives a too high hydrogen production. Too low hydrogen production prevents the fuel cell from working properly, while too high hydrogen production wastes methanol resources and shortens the mobile time extension that can be achieved with the system.

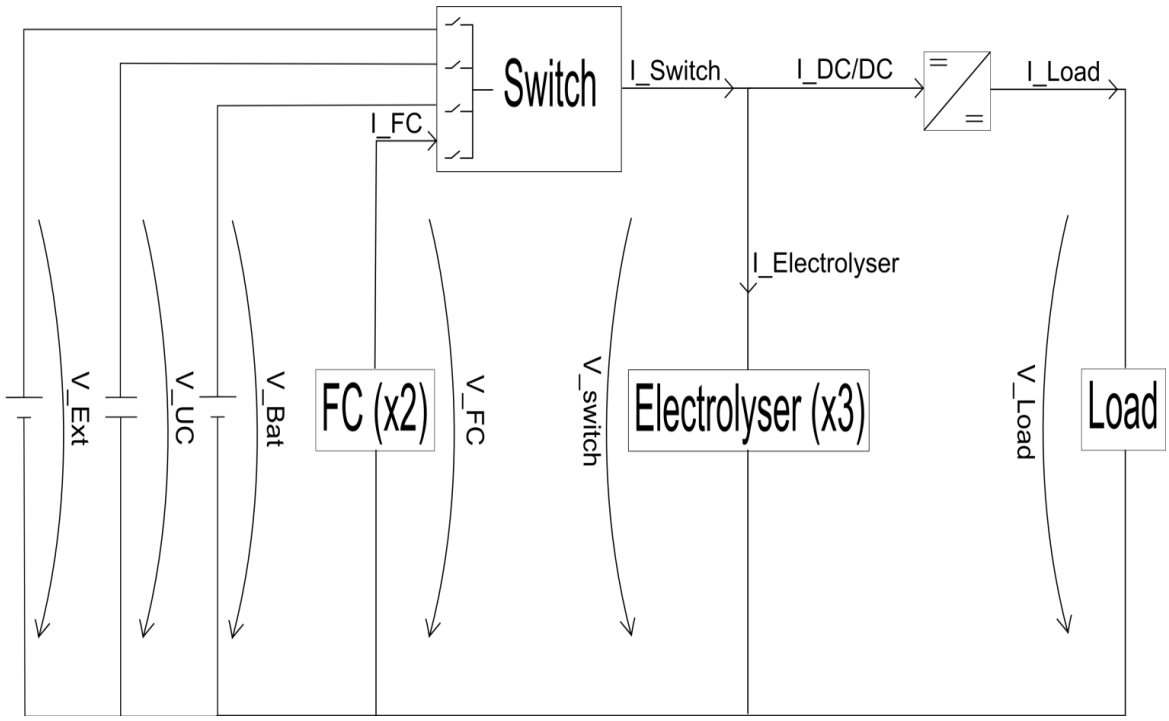

Figure 3.1: The electrical connection scheme of the designed system.

Since a small, i.e. low voltage, system was targeted DC/DC converters were needed for boosting the voltage to a suitable and stable level for the load. Using four NCP1402SN50T1 DC/DC converters in parallel the DC/DC efficiency was kept around 75%, see section 4.3.4. The higher DC/DC efficiency was achieved since the DC/DC converters were used only when charging the load, which only is done when the system has reached its operating point at around 1.6 volts. This means that the input voltage is relatively stable and the DC/DC converters work in their optimal power range.

The operating voltage of 1.6 V was chosen due to some considerations. Firstly, it could relatively easily be achieved with a fuel cell stack with two cells, and a two-cell fuel cell stack and three electrolyser cells could relatively easily be built. Secondly, the voltage is high enough so it can be boosted to the 5 V required by the load with only one DC/DC converter. The DC/DC conversion loss is proportional to the ratio of the input and output voltage, and the relatively small ratio kept the DC/DC conversion loss at an acceptable level. Thirdly, commonly used rechargeable 1.2 V batteries can be recharged with the chosen voltage without extra voltage modifying equipment.

As temporary energy stores we have chosen to use a standard 1.2 V rechargeable battery, and a supercapacitor built from three capacitors with 70 F and 2.1 V rated voltage, connecting the capacitors in parallel, thus raising the capacitance to 210 F. The battery is used mainly as start-up source because of its ability to store large amounts of energy for long times with only small self-discharge, and since they are readily available. The supercapacitor is used mainly as a temporary store as one has to charge the load with a larger current than the fuel cell can provide on its own. In this case the fuel cell charges the temporary store and when it is full, the energy in the

temporary store is discharged into the battery of the load. The supercapacitor is well suited for this since it has a low internal resistance, thus making the charging and discharging losses low.

3.1.2 Alternative designs

Another possible solution would have been to use only one cell in the fuel cell stack and two electrolyser cells. The use of two electrolyser cells would have caused a low voltage, 0.3-0.4 V, per electrolyser cell, which would have given a low hydrogen production when using our electrolyser cells with an active area of 50 or 100 cm^2. On the other hand, the hydrogen production, which depends on the electrolyser current, would have been lower than the fuel cell demand when producing the same current if only one electrolyser cell would be used. Using a smaller amount of cells would have had the benefit of smaller size and easier construction, but the voltage would have been around 0.8 V, which is too low for almost all rechargeable batteries, while capacitors still could have been used. The low voltage would also still have had to be boosted to 5 V for the load, which would have required two DC/DC converters in series causing a rather poor efficiency. For this very low power system, the power requirements of the auxiliary systems would easily have been too high.

A third option would have been to use more cells in the fuel cell and electrolyser stacks. This would have given a higher voltage, which in turn would have given a lower DC/DC conversion loss and smaller power consumption for the auxiliary devices compared to the total output power. The higher voltage would also have given lower currents, assuming a device with the same power, which in turn would have given lower conduction losses. The larger stacks would however been larger and harder to build, and the power could have been too high considering that the system only should extend the mobile usage time of the device.

The voltage could also have been raised using DC/DC converters or charge pumps instead of using a larger amount of cells in the fuel cell stack. As mentioned before a higher voltage would reduce the conduction losses, due to the lower currents. However, boosting the voltage with DC/DC converters or charge pumps possibly lowers the efficiency more than the conduction losses. Even very good DC/DC converters or charge pumps use at least 5% of the power for the conversion, most often more. As the conduction losses also depend on the wire diameters, it is more beneficial, and simple, to use thicker wire instead. For the prototype system now designed the simplicity of the system is a major concern, but calculations, see appendix C, show that also the losses are probably smaller when not using voltage boosting equipment. Since the wires are shorter, but also thinner in the future embedded system, the matter has to be reassessed when the exact specifications are available.

A third option for raising the voltage, actually a variant of the charge pump, would be to use multiple capacitors or rechargeable batteries together with two-way switches to lift the voltage, as seen in figure 3.2. In this configuration the fuel cell recharges one of the batteries or supercapacitors to 1.6 volts at a time. When all energy stores have been separately charged the energy stores are disconnected from the fuel cell and the switches are connected so all the energy stores are in series, thus creating a voltage of around 4.8 volts, which can be used to recharge the

load. In case one wants to use rechargeable batteries with a nominal voltage of 1.2 V then four batteries and switches would have to be used to reach the same voltage. To be able to use this configuration all the energy stores would have to have the same properties, so the charging and especially discharging would be even. The main advantage of this method is that no DC/DC conversion is needed, and thus the efficiency might be higher if the charging losses are small. On the other hand, one has no control over the voltage, which might be a problem with some devices that require a steady voltage for the charging. Additionally, a device to limit the charging current might be needed, and specialised DC/DC converters already have very high efficiencies so the efficiency gain is small or non-existent.

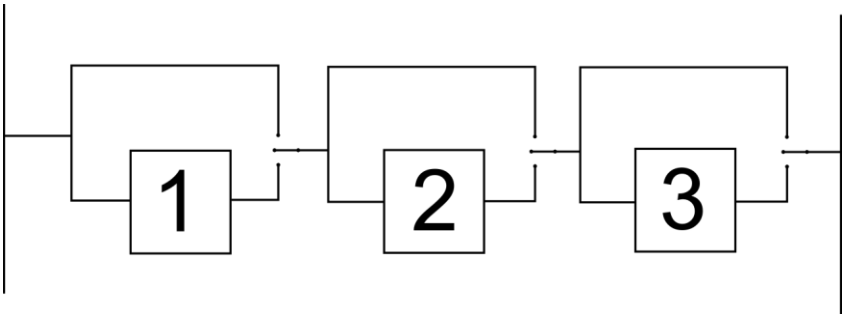

Figure 3.2: A possible solution for raising the voltage in the system by using multiple energy stores and two-way switches. The numbers represent energy stores, which could be either rechargeable batteries or capacitors.

If it is concluded that the system works well without a temporary energy storage device, then the supercapacitor can be omitted from the design. This is possible as the battery is very suitable to use as start-up source and can also be used to balance power peaks if necessary. Another perhaps more compact option could be to use the battery in the load device as the source of energy during start-up. This is problematic since it is not possible if the mobile phone contains some logic which disconnects the battery if the direction of the current is out from the phone, and we cannot know beforehand which phones have this kind of logic. The logic could be e.g. safety logic, since current out of the phone battery could indicate a short circuit. Additionally, using energy in the load device battery would probably require the voltage to be dropped down, from the 3.7 V of the mobile phone battery in our case, to a suitable level for the electrolysers, i.e. around 1.2-1.6 V. If the voltage is much higher the electrolyser current becomes too large, which would greatly increase the ohmic losses, and could damage the battery. Decreasing the voltage would require a DC/DC converter, which in turn would decrease the efficiency of the system. The configuration might however be beneficial if space is very constrained.

One could also use a hydrogen tank as the start-up source. This would have the benefits of no self-discharge as long as the tank would not leak, but because of safety issues, it is better to store the energy as electricity. The hydrogen tank would in addition to its own volume also need extra tubing and require a greater volume than a battery if the gas would not be compressed. On the other hand, compressing the gas would require extra equipment and use energy, which renders it unnecessarily complicated.

3.1.3 Optimal sizing of the components

As the purpose of the designed system is to extend the mobile usage time of a phone, one can calculate the optimal sizing of the components when the targeted mobile time extension and the requirements for the system are known. In this section the optimal sizing of the components are presented and the chosen alternative for implementing the prototype system are justified based on the requirements.

As the main target is a five-hour mobile time extension and the main load which is used is a mobile phone, the requirements for the system components can be deducted. As we want to be able to charge the mobile phone the system output needs to be close to 100 mA of current at a voltage of 5 V. Smaller currents can also be used, but that is outside the phone charging specifications and the efficiency of energy transfer to the phone is lower.

To get a rough estimate of the mobile time extension we can perform a simple calculation though it neglects the effects of battery aging etc., which also affect the extension time. As the phone battery has a capacity of 1320 mAh and the manufacturer promises 7 hours of talking time, the current during a call should be around 190 mA. To give a five-hour extension the fuel cell – electrolyser system needs to provide 80 mA on average.

Our tests however show, see section 4.1.2, that the current during a call is 430 mA at the beginning of the call when the backlight is on, and 350 mA during a call after the backlight has been turned off. With an average current consumption of 350 mA and an average charging current of 80 mA the mobile time extension would only be slightly more than one hour. On the other hand people very seldom do calls non-stop for seven hours, and since the current used by the phone is low when the phone has the keys locked and the backlight off, the average current also becomes lower. This means that a current of 80 mA should be sufficient to charge the phone and fulfil the mobile time extension target. If few calls are made also lower average currents should be able to provide the five-hour mobile time extension.

Since we want to build a passive fuel cell – electrolyser system, as the efficiency of a passive system is higher, we need to carefully balance the currents and the voltages of the fuel cell and the electrolyser. The current density is an exponentially growing function of the voltage over the electrolysers (Sasikumar et al. 2008, p. 5907). A possible and small solution that gives a good fit is to use 50% more cells in the electrolyser stack than in the fuel cell stack when the active areas of the fuel cell and the electrolysers are roughly the same, as explained in section 3.1.1. To get the smallest possible system we therefore use two cells in the fuel cell stack and three electrolyser cells.

A two-cell fuel cell stack gives approximately 1.6 V when connected to a load and since the load requires 5 V we need a DC/DC conversion. As we have a voltage of 1.6 V and need roughly 100 mA at 5 V and the DC/DC converter efficiency is around 75%, see section 4.3.4, the required current to the DC/DC converters is slightly more than 400 mA. Using three electrolysers, which splits the 1.6 V voltage in three equal parts, i.e. the electrolysers work at 0.53 V each, requires a current of near

to 600 mA and adding this with the current required for the load we see that the fuel cell should be able to supply at least 1 A of current.

If a high current density can be achieved the size of the fuel cell can be small, e.g. with a current density of 100 mA/cm^2 only ten square centimetres of fuel cell membrane is needed per cell. However, when higher current densities are taken from the fuel cell the voltage drops and thus the fuel cells cannot be made very small. The allowed voltage drop has to be chosen for each fuel cell system separately, but usually a current density of up to 400 mA/cm^2 is thought to be possible without a too large voltage drop (Larminie and Dicks, 2003, p. 46, 182). How much the voltage drops when the current density is increased depends e.g. on the type of fuel cell used.

Since the voltage of a fuel cell drops at higher currents, see figure 2.6, the fuel cells or fuel cell stacks are more efficient at medium load than at maximal load, which would make larger fuel cells preferable when considering the efficiency (Guizzi, Manno, and De Falco 2009, pp. 3117-3118). At low loads the power consumed by the auxiliary systems might be high in proportion to the power produced by the fuel cell thus making the lowest current densities inefficient. This of course depends on the auxiliary systems and if they can be controlled to reduce their consumption at low loads.

The prototype system uses a two cell fuel cell stack with an active area of 300 cm^2 per cell, which is unnecessary large, but is used since no other fuel cell capable of keeping the voltage above 1.6 V at higher current densities was available. Keeping the voltage as high as possible was required since the DC/DC conversion efficiency would otherwise become very low. The main problem with the fuel cell in the prototype system is the large internal volume. This means that the start-up takes quite some time as the whole internal volume has to be filled with hydrogen before the start-up source can be disconnected. On the other hand the large internal volume acts as a hydrogen buffer in case of power peaks, which clearly is beneficial.

As mentioned before we have fixed the amount of electrolyser cells to three to get voltages and currents compatible with the fuel cell stack. On the other hand, the size of the electrolyser or the sizes of the electrolysers must be chosen so that they can provide enough hydrogen for the fuel cell. Another important concern is the current density in the electrolysers since the efficiency of an electrolyser is inversely proportional to the current density as can be seen in figure 2.5. This means that a large electrolyser is more efficient at producing hydrogen, while the cost of course is smaller when using a smaller one.

For a commercial model the size of the electrolyser is therefore very important. For the prototype system in this work the efficiency is more important and the electrolysers that are used have the active areas of 50 cm^2, 50 cm^2 and 100 cm^2. An electrolyser stack could favourably be used, but it has proved hard to build good electrolyser stacks, and therefore three unit cells are used in the prototype system.

The main function of the battery is to provide energy at start-up and it has to be large enough to do this. Our starting point in the design was that the electrolysers in the prototype system require

a current of near 600 mA for effective hydrogen production and the start-up takes fifteen to twenty minutes. The starting time length was actually noted in the preliminary system tests and is that long since the prototype fuel cell has a rather large internal volume. This internal volume must be filled with hydrogen before the fuel cell can start producing power. Consequently the energy needed for start-up is close to 200 mAh, if we assume that the current is a constant 600 mA for twenty minutes. To ensure a successful start-up even after longer storage and some self-discharge of the battery a greater amount of energy is required. Since the prototype fuel cell has a large internal volume, the start-up time will actually be much shorter with the final system that will use smaller, more optimised components. This means that the battery also can be smaller. Another important concern with the battery is that it should be possible to recharge it directly with the fuel cell. This is possible with almost all rechargeable batteries as long as the fuel cell can provide a higher voltage than the battery uses. For the prototype system it was decided to use a standard 1.2 V, 2700 mAh rechargeable battery since it is standard, can be recharged with the fuel cell, and a non-rechargeable battery can be used instead of the rechargeable battery if needed. The capacity of the chosen battery is oversized, but the larger capacity is practical during testing.

The supercapacitor needs to have a rated voltage high enough and be able to balance power peaks in the system, so the fuel cell can work with steady loads. If the fuel cell is connected directly in parallel with the supercapacitor current limitation needs to be used if the fuel cell cannot provide currents above 3 A. The current limitation must be dimensioned so that the current from the fuel cell is possibly high without being too high, since higher current charges the supercapacitor faster, which is more convenient if one wants to get power to the load quickly.

If the supercapacitor is used as a temporary source of energy that is charged by the fuel cell and then discharged into the load, the capacitance of the supercapacitor has to be high enough to give a high enough current so the load battery gets charged. This is required since the backlight of the phone is lit for a few seconds to indicate that the phone is being charged and this consumes quite a lot of energy. To actually charge the phone, i.e. make the power input to the phone larger than the power that the phone backlight uses, the charging must last long enough, which requires a large enough capacitance.

In the prototype system a supercapacitor with a rated voltage of 2.1 V and a 210 F capacitance is used. The supercapacitor is built from three 70 F supercapacitors, which also can be used separately if needed, i.e. capacitances of 70, 140 and 210 F can be achieved. This is beneficial for prototyping purposes, but in this work the 210 F supercapacitor has been used in all tests. The large capacitance is needed when charging the phone battery since around 10 W of power is lost when the backlight is lit at the end of the charging as a notification to the user. A discharging efficiency test was conducted with the previous 10 F version of the supercapacitor, but it proved that the energy transferred from the supercapacitor to the phone battery was 24,4 W of which 10,2 W was lost when the backlight was lit at the end of the charging. This means that almost half the energy was lost to the backlight, which renders the system very inefficient. The new supercapacitor with a twenty times larger capacitance makes it possible charge the load much longer, which makes the energy transfer much more effective. Though a supercapacitor with an

even larger capacitance would be beneficial from the energy transfer efficiency point of view, it was concluded that a capacitance of 210 F was better, since it would take very long to charge a supercapacitor with a higher capacitance and the size would be too large.

The requirement for the DC/DC converter is that they perform the needed voltage conversion, which is from 1.6 V to 5 V in the prototype system. High efficiency and small size of the converters is also important. For the prototype system four NCP1402SN50T1 DC/DC converters have been chosen since they were readily available, small size, and are capable of the needed voltage conversion with efficiency around 75%. Higher efficiency could possibly be achieved with converters specially designed for the system, but for a prototype the availability was more important than the efficiency, also since the main purpose of this work is to develop the fuel cell – electrolyser part of the system and the DC/DC converters are of secondary interest.

The pumps need to be able to pump the required amount of air and water-methanol solution and also have low power consumption and small size. Usually double the required amount of air is pumped to the fuel cell to ensure steady function (Larminie and Dicks, 2003, p. 397). For the prototype system with 1 A of current in the fuel cell, this means that 66 ml air needs to be pumped every minute, see appendix D. If we want to keep the methanol concentration at 94% of the starting value when it comes out of the last electrolyser, see appendix D, then a flow of 2.5 ml/min is required for the liquid pump. In the prototype system we have chosen to use small diaphragm pumps from Xavitech since they are spark-free, which is important in case of a hydrogen leak, efficient, and small size, only 37x21x21 millimetres. The maximum flows of the pumps are 340 ml/min for the air pump and 21.5 ml/min for the liquid pump. As the pumping efficiency is highest at maximum flow for the air pump and at 15.6 ml/min of flow for the liquid pump when using a 5 V supply, see section 4.2, the pumps need to run at 20 and 16% duty cycles, respectively, to save as much power as possible. These values are valid when the fuel cell current is 1 A and the electrolyser current is 0.6 A. For a commercial product it could be more beneficial to have smaller pumps and use them continuously, but the chosen ones are small enough for the prototype system.

For a commercial system the minimal size that fills the requirements with some margin should be chosen for all components. This way the overall size of the system will also be minimised, which is desirable in a mobile extender application.

3.2 Mechanical components

3.2.1 Methanol and air system

The hydrogen for the fuel cell is produced through electrolysis of methanol, due to the benefits of methanol electrolysis described in sections 2.1.3 and 2.4.1, especially the high energy density and easy handling of liquid methanol. The high energy density makes it possible to use the system for very long times, e.g. more than 33 hours using 100 ml of aqueous methanol solution with 5 per cent methanol of the volume and a constant 0.6 A current in the fuel cell. The calculations can be found in appendix D. The liquid state of methanol at room temperature allows the use of

conventional tubing and liquid pumps for methanol transportation. Five per cent water – methanol solution is used in the electrolysis, and a liquid pump, i.e. V200-LIQ-5V from Xavitech, is used for circulating the solution via the methanol container to keep the methanol concentration in the electrolyser as high as in the rest of the solution, as can be seen in figure 3.3. If no circulation is used the methanol concentration in the electrolyser slowly drops as the methanol is consumed. Another problem is that the carbon dioxide that is produced in the electrolysis might block the electrolyser channels especially if they are very thin. Even if the channels are not thin, the carbon dioxide created in the electrolyser during electrolysis reduces the active area of the electrolyser by obstructing the methanol. When circulation is used the active area is kept maximal since the carbon dioxide bubbles are forced out of the electrolyser into the methanol container from which the carbon dioxide evaporates into the air.

The water-methanol solution does not need to be circulated fast since it takes more than one and a half hour with a current of 0.6 A to use all methanol in 5 ml of solution, which is the approximate internal volume of a single electrolyser. Even if the methanol concentration is kept at a high level it should be sufficient to replace the solution in the electrolyser every 5-10 minutes. However, since the same solution is transported through all electrolysers before returning to the solution container, the time it stays in a single electrolyser has to be three times shorter, as three electrolysers are used.

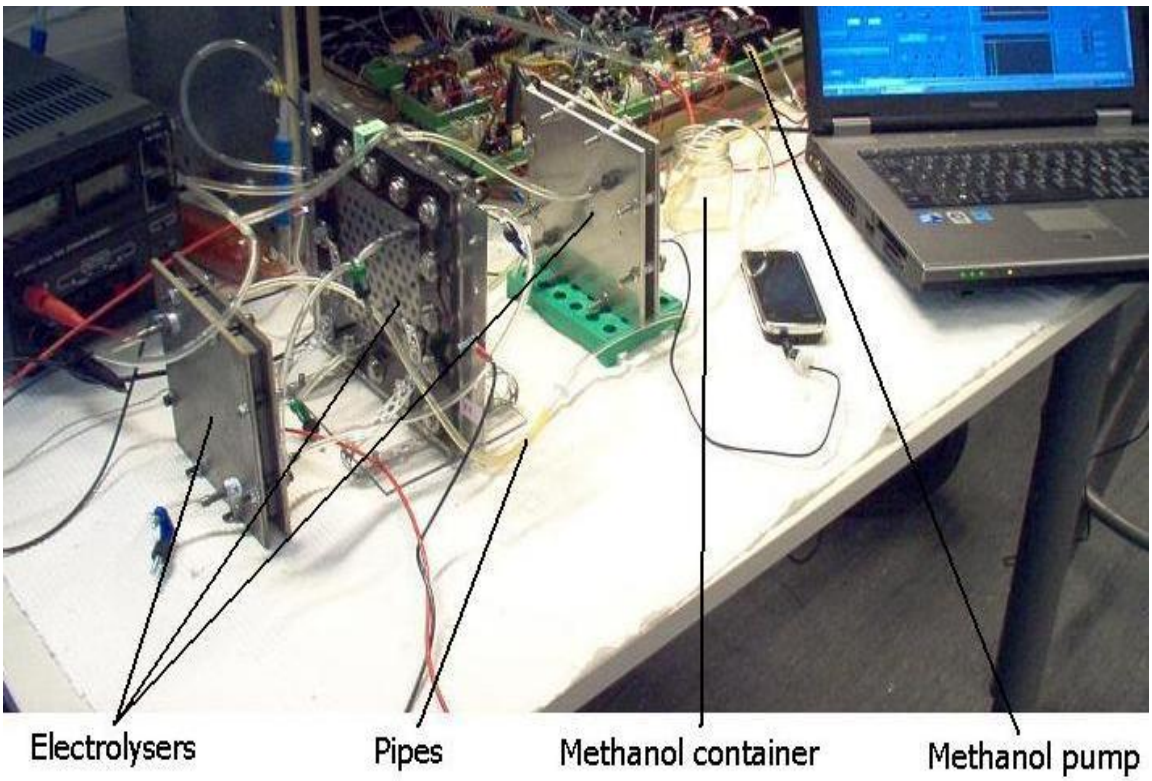

Figure 3.3: The methanol system used in the prototype system.

The air pump is compulsory in this system, since the fuel cell is not free breathing and the oxygen runs out after some time, which stops the fuel cell reaction. Another reason is that nitrogen from

the supplied air might obstruct the oxygen from reaching the active sites in the fuel cell if the air supply is not well circulated (Larminie and Dicks 2003, p. 59). The circulation also assists in removing water that builds up at the cathode. In one of the system tests, where the fuel cell was used at very light loads, the air pump was off, which caused the fuel cell voltage to drop after around 30 minutes. The time would be clearly shorter if a fuel cell with a smaller internal volume would be used or the load would be higher.

In the prototype system the pumping is done using a P200-GAS-5V gas pump from Xavitech. Calculations on the exact amount of air that is needed can be found in appendix D. If using a small fuel cell it could be beneficial to use a free-breathing structure instead of the now used where the air is fed from one inlet through thin channels.

3.2.2 Hydrogen system

The hydrogen system has been improved by removing the hydrogen storage tank and replacing the fuel cell. The removal of the hydrogen storage tank makes it possible to make the system very much smaller. The only problem is that the electrolysers produce some liquid, possibly water or methanol that has leaked through the membrane, and it should not enter the fuel cell. This is fixed by adding a small container between the electrolysers and the fuel cell that collects the liquid. The fuel cell leakage was partly fixed by replacing the fuel cell with a better one. However, there is still a hydrogen leak present in the system, most probably in the fuel cell.

The matter of membrane drying in the fuel cell has not been investigated in this work. It is assumed that the hydrogen from the electrolysers contains some water that has permeated the electrolyser membrane. This water humidifies the hydrogen so that membrane drying should not be any problem. The fuel cell used in this work is open-ended with a manual purge valve. In one of the system tests the inlet of an additional fuel cell was connected to the outlet of the primary cell to observe if hydrogen is present in the outlet stream of the primary cell. Since the voltage of the secondary fuel cell did not rise at all it was concluded that no or very little hydrogen is present in the primary fuel cell hydrogen outlet. The probable cause is that the active area of the fuel cell is so large that all hydrogen is used up at all tested loads. However, as was noticed in another test the purge valve needs to be closed if the fuel cell load is close to zero and the electrolyser current is low. Otherwise the small amount of produced hydrogen leaks out. This means that the purge valve has to be closed at least during start-up, while it should be opened shortly every now and then during high fuel cell loads to let water vapour exit the cell. In the prototype system the purge valve was implemented by manually opening and closing the purge valve.

3.2.3 Future improvements

Future improvements that could be done to the mechanical system is primarily minimising all components and possibly removing components that can be replaced with better solutions. One of these components is the methanol pump, which could be replaced e.g. with the solution proposed by Meng and Kim (2009), in which they use the carbon dioxide bubbles created in a micro DMFC to create a methanol flow as well as to remove the carbon dioxide. Their solution

involves a hydrophobic nanoporous membrane, impermeable to the methanol solution, through which the carbon dioxide is vented thus creating a suction that creates a flow. Their system was used with a DMFC, but it should be possible to use it with a methanol electrolyser also as long as the channels are thin enough for the needed micro capillary effects to take place. The main benefits of their solution are that no methanol pump is needed, which saves energy, the methanol flow is proportional to the current, since more carbon dioxide is created at larger currents thus creating a larger suction, and the solution is orientation independent.

Another clear improvement would be to use pure or high concentration methanol in a separate container, and mix it with the water solution going to the electrolysers as the methanol in the solution is used, the same way as oil is mixed with gasoline in modern boat engines. This would allow for a very much smaller methanol container to be used since the amount of water would not need to be as large. Since the methanol electrolysis reaction, see equation (4), uses one mole of water for each mole of methanol, there has to be some water for the electrolysers to work. If all water is supplied from the separate container, the maximal concentration can be close to 69 vol-%. The percentage can be calculated from the molar masses and densities of water and methanol knowing that there should be one mole of water for each mole of methanol. However, the hydrogen fuel cell reaction produces water that could be used in the electrolysers. Since every mole of hydrogen produces one mole of water, see equation (1), and methanol electrolysis produces three moles of hydrogen for every mole of water, there is a lot of surplus water if all water could be recycled to the electrolysers. This would allow for a 100 per cent methanol solution to be used, if a good method for recycling the water was invented.

One possible solution that would give a very compact system design would be to integrate the electrolyser and the fuel cell stack into one stack. This could be done if the electrolyser cells and fuel cells MEAs would all be the same size and the amount of cells would be of the right proportions so the fuel cell and the electrolyser part could be directly connected. The main problem with this solution is that the electrolysers are not yet functioning well when stacked, and one would have to find a solution to how to remove the liquid that leaks through the electrolyser membrane onto the hydrogen side as it poisons the fuel cell if it contains methanol.

3.3 Control system

The purpose of the control system is to start, run and shutdown the system in a controlled way. This is done by controlling which electrical components are interconnected, and when the pumps are active. The control system also has an interface for controlling when the purge valve is opened, though a purge valve is not used in this system. However, if another fuel cell would be used with the system, then the purge valve would be needed. Thus the purge valve control was included in the control system. The aim of the design was to make the control system as simple as possible while being able to control the system satisfactorily.

3.3.1 Implemented design

The control system is a state machine with six modes; startup, reload startup source, charge temporary, charge load, shutdown – reloading startup source, and shutdown successful. Each mode completes its own functions and the transitions between the modes are triggered by certain events, e.g. a value exceeding a threshold, as can be seen in figure 3.4. The modes are marked with blue boxes with the mode name in the box and the transition conditions are written in the ellipses. Observe that if the stop button is pressed then the mode is changed from any mode to the shutdown successful mode.

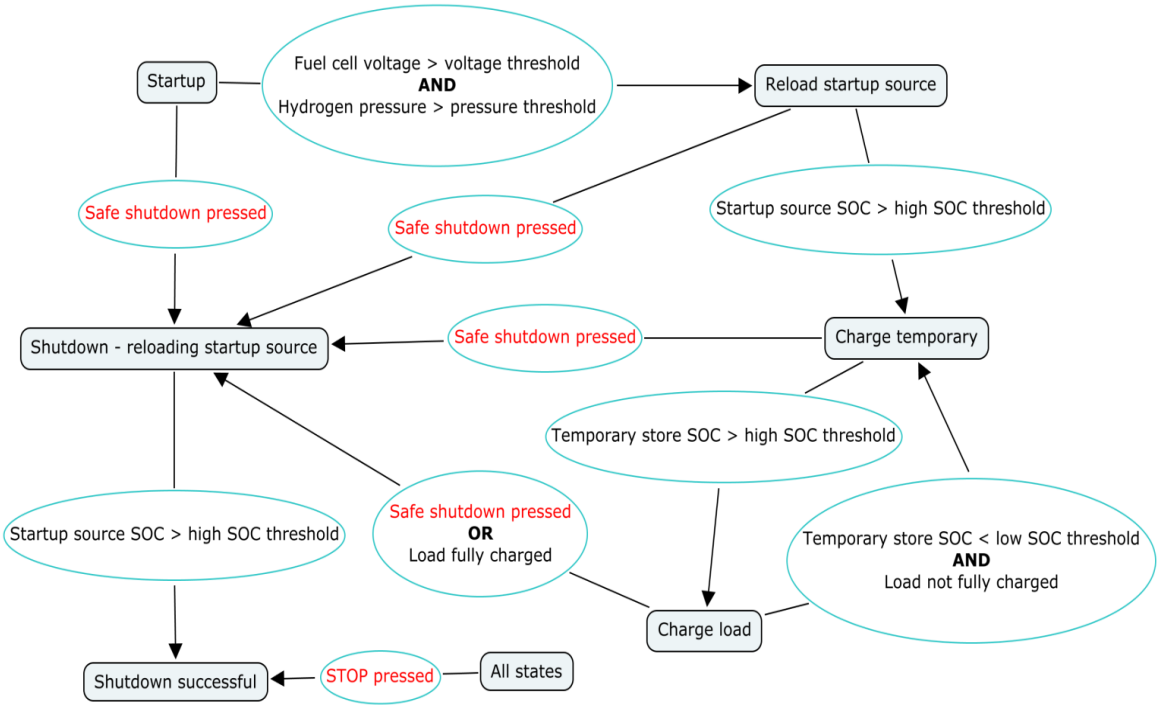

Figure 3.4: Mode transition diagram of the designed control system.

The main mode function is setting which components are interconnected, but also some other functionality is implemented in the modes. An overview of when the components are connected electrically can be found in table 4. It should be noted that the electrolyser is connected all the time, but since all the other components are disconnected in the shutdown successful mode, then also the electrolyser is effectively disconnected.

The *startup* mode sets checks which start-up source is chosen and stores the value into memory for use in the other modes. Then the start-up source is connected to the electrolyser while the other components are disconnected. When the electrolyser has produced enough hydrogen and the voltage of the fuel cell has risen to the right value, the state changes to *reload startup source*. In this mode the start-up source chosen in the *startup* mode is recharged. Practically it means that the start-up source, the electrolyser, and the fuel cell are interconnected.

Table 4: The electrical components that are connected in the different modes. The minus sign indicates that the component is not connected.

Component\ Mode	*Startup*	*Reload startup source*	*Charge temporary*	*Charge load*	*Shutdown - reloading startup source*	*Shutdown successful*
Start-up source	yes	yes	-**	-	yes	-
Temporary source	-	-	yes*	yes*	-	-
Fuel cell	-	yes	yes	-	yes	-
Load	-	-	-	yes	-	-
Electrolyser	yes	yes	yes	yes	yes	yes
	**not if the "no temporary store" option is chosen.*					
	*** The battery is connected when the capacitor is charged*					

One of the selectable start-up sources is a rechargeable battery that requires some extra logic to get a reliable voltage measurement. The measurement logic is needed since the terminal voltage of a battery rises higher during recharging than it actually is when the charger is disconnected. Therefore the start-up source is disconnected every now and then for a certain time, during which the terminal voltage stabilises to its real value and is measured. The measurement interval and the time of the measurement can be changed from the user interface of the control system. The measurement logic is implemented in the *reload startup source* mode and is used if the chosen start-up source is the rechargeable battery.

In the *charge temporary* mode the control system connects and charges the chosen temporary source, which can be a rechargeable battery or a capacitor. One can also chose not to use a temporary store. In that case the system assumes that the system is capable of charging the load without using a temporary store. Practically this means that neither the battery nor the capacitor is connected in the *charge temporary* mode, and the mode immediately changes to charge load mode. The *charge load* mode connects the temporary source in the same way as in the charge temporary mode, and additionally also the load is connected by activation of the DC/DC converters.

The *shutdown – reloading startup source* mode does the same as the *reloading startup source* mode, i.e. connects the fuel cell, the electrolyser and the start-up source. It keeps them connected until the state of charge (SOC) of the start-up source is so high that the system can be started using the energy in the start-up source the next time it is turned on.

The *shutdown successful* mode is for ensuring that all outputs are off and all electrical components are disconnected. In a final version of a product using this control system it would power the device off, but in this development version it only turns all outputs off and continues monitoring the voltages and currents in the system. Additionally, in all modes the inputs are measured, calculations are made, e.g. powers and SOCs are calculated, the graphs on the user interface are updated and the data is logged to disk.

3.3.2 Alternative designs

There are very clear modes in the action of the prototype system, e.g. start-up of the fuel cell, running the system, and shutting the system down. This means that a state machine needs to be implemented, as has been done. The control in the different states on the other hand could be made active, i.e. the system could be controlled by controlling the currents to and from the electrical components, not only by switching devices on and off as is done now. This would allow more freedom for the control as is explained in section 2.5.1. This would however require that the fuel cell, the electrolyser, the battery and the supercapacitor currents could be controlled using e.g. DC/DC converters. In this case the control system would have to calculate the needed currents and control the DC/DC converters according to them.

For our prototype system, where efficiency should be kept as high as possible since all power is produced by the fuel cell that has limited resource, it was decided that the benefits gained by using an active system are less important than the efficiency gained when not using multiple DC/DC converters. Additionally an active control system would be more complex, thus requiring more computational power, thus increasing the power consumption.

3.3.3 Microcontroller

3.3.3.1 Implemented

The heart of the implemented control system is a National Instruments sbRIO-9631 microcontroller containing a real-time microprocessor, an FPGA, and IO (National Instruments, 2011). The microprocessor is a 266 MHz industrial processor, and the FPGA a Xilinx Spartan with 1 M gates. The IO contains 110 digital IO lines, 32 single-ended 16-bit analog input channels, which also can be used as 16 differential input channels, and four 16-bit analog output channels. The IO can be expanded since three NI C-series modules can be added. Peripheral devices can be connected using the RS 232 serial port. The microcontroller also contains 64 MB of DRAM for embedded operation and 128 MB of non-volatile memory for data logging and program storage.

The communication between the microcontroller and the host computer used for programming or data transfer is done through a 10/100 Mb/s Ethernet connection. Programming of the microprocessor and the FPGA is done on a host computer using the NI LabVIEW software.

The benefits with the current microprocessor is that is very powerful and LabVIEW has many pre-programmed control modules which easily can be added to the control software, e.g. PID-control or fuzzy logic. This makes the developing of a control system rather fast. The main problem for a small, embedded system is the power consumption of the current microcontroller which is 7.75 W when no outputs are driven. The consumption is way too high for a future embedded small size system where every milliwatt used by the control and auxiliary systems has to be produced by the fuel cell – electrolyser system. Another problem is the rather large size, 20.8 x 14.2 centimetres, which partly is caused since the microcontroller contains a lot of components, e.g. IO, that we do not use in the prototype system. Both problems can however be solved by using optimised

components, and integrating the microcontroller on the same circuit board as all the other needed electronics, e.g. the switch and the current measurements.

3.3.3.2 Future requirements

The most important improvements that need to be done to the control system before a commercial fuel cell – electrolyser system can be implemented, is reducing the power consumption and the size, while keeping the needed functionalities. In an embedded system also e.g. heat production needs to be evaluated.

With the current control system the microcontroller needs to have at least eight digital IO lines and five analog input lines. Additionally seven more analog input lines are used in the prototype system to be able to completely monitor the system. This is clearly less than the IO available on the sbRIO-9631 board used in the prototype system, which means that the next system version could be made much smaller.

The computational power of the microprocessor could also be reduced, which would reduce the power consumption. This is possible since the processor CPU usage stays below 18% all the time when the program is executed at a typical rate, i.e. every 250 ms. This means that a four to five times less powerful microprocessor could be used with the current control system. For most situations the control does not need to be even so fast, e.g. program execution every 500 ms could be used, which uses only 11% of the CPUs resources if LabVIEW generated code would be used. The computational power needed when using another programming language is hard to estimate.

Since it is not totally clear if the control system will be similar to the one now used or if it will be more complex, it is beneficial to leave some computational power overhead when choosing the next generation microcontroller. Leaving computational overhead and saving power could be achieved at the same time if dynamic voltage and frequency scaling technology, see section 2.7.1, would be used in the microcontroller. Another alternative is putting the microcontroller to sleep between the cycles. The 64 MB DRAM memory of the device cannot be very much reduced, since almost 60% of the memory, i.e. 35.5 MB, is allocated during program execution. However, the code is in LabVIEW format, and the size would probably be greatly reduced if the control system would be programmed in e.g. C.

The next microcontroller should also have communication abilities, e.g. through Ethernet or serial port, to enable easy programming. The programming language affects the ease of programming and reusability of the control system code, so a standard language, e.g. C is recommended. One has also to consider if other subsystem or special features such as A/D or D/A-conversion or fuzzy logic needs to be available in the microcontroller. If the system is to be produced in larger quantities, the microcontroller should also be easily available and replaceable. A list of some possible microcontroller alternatives can be found in appendix F.

4 Tests and results

4.1 Laptop and mobile phone power measurements

The design of a hybrid system, especially the component sizing, is dependent on the average power consumption and the load profile. Therefore current measurements on two possible application devices, an Asus EEE PC laptop computer, and a Nokia 5230 Navi mobile phone, have been conducted. Only the current was measured, but since the voltages are stable and known, the used power can easily be calculated.

4.1.1 Laptop computer power consumption

The measurements were done by connecting a current measuring digital Fluke 189-multimeter in series with the device and the charger. The laptop measurements were conducted both for light and heavy processor and memory loads. At idle the current was around 0.5 A, at light loads 0.6-0.7 A, and at heavy loads peaking up to 0.85 A. The heavy load measurements were done using HeavyLoad, a program that maximises the computer load. The heavy load tests were conducted at 100% CPU load and 75-85% memory used.

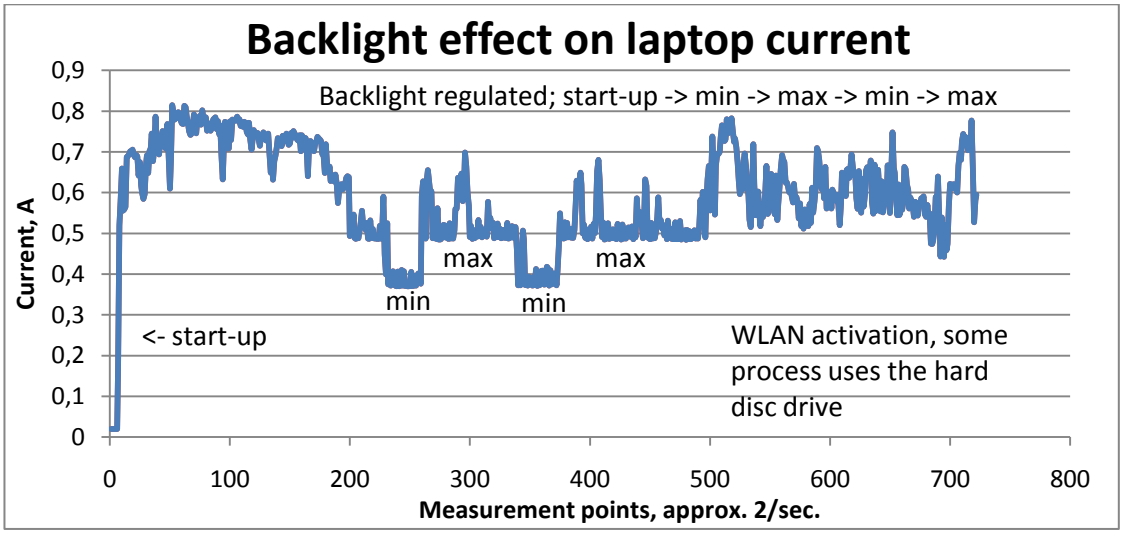

Figure 4.1: Backlight effect on the current used by the laptop. Data from the other laptop measurements can be found in appendix E.

Also a battery recharge test was conducted, in which the laptop battery was charged using a laboratory power supply. It was noticed that a current of 1.9 A was needed before recharging of the battery started, see figure e-2 and figure e-3. The current did not change when the laptop was started, only small additional ripple was noticed. It should be noted that dimming the backlight from the maximal brightness to no backlight reduced the current by around 0.1 A, as can be seen in figure 4.1, in all situations but when the battery was being recharged. The other graphs can be found in appendix E. To summarise this gives a minimal current of 0.4 A in idle state without backlight, 0.6-0.7 A at “normal” consumption, with backlight and light load, peaks up to 0.85 A at

heavy loads, and 1.9 A when recharging. As the voltage stayed near 19 V all the time, this corresponds to 7.6 W, 11.4-13.3 W, 15.2 W and 36.1 W, respectively.

As the hybrid system in our case is intended only to extend the time one can use the device without access to the grid, the hybrid system does not need to be able to produce the 1.9 A recharge current. This can be provided by an external charger as usually is done with laptop computers. This means that the system should be able to handle currents from zero to around 0.85 A, which corresponds to powers from zero to around 16 W. It should however be remembered that a mobile time extender does not have to provide all power that the device uses as long as it provides enough to increase the mobile usage time significantly. Additionally, the laptop battery has a nominal voltage of 11.25 V, so 19 V is not needed for mobile time extension. Providing power to the laptop computer using 11.25 V would naturally require that a hardware modification would be made, which would allow for connecting the mobile time extender directly to the battery instead of using the existing charging connector. This approach would however make it impossible or at least harder to use the same mobile time extender system with different laptop computers.

For the laptop computer the transients are quite fast and large so a hybrid system is needed so the fuel cell can work at more optimal steady loads, as described in section 2.5.1. Using a supercapacitor in the hybrid system would probably increase the lifetime of the battery, since the fast variations at normal consumption are around 0.1-0.2 A, which already is rather large for small size batteries.

4.1.2 Mobile phone power consumption

Also for the mobile phone measurements with different loads were conducted, as well as a recharging test. These tests were conducted by Sami Kielosto. A Fluke 189-multimeter was connected in series with the phone and the charger and the currents were measured, from which the powers were calculated. The results can be found in figure 4.2. The Nokia 5230 Navi mobile phone used around 44 µA when it was shut off, 3 mA when keys were locked and backlight was off, 130 mA for idle in active mode with the backlight off, 350-450 mA during call, with backlight off and on, respectively, 200 mA when listening to music, and 640 mA for watching videos using the 3.5G modem. As the nominal battery voltage was 3.7 V this corresponds to 0.16 mW, 0.01 W, 0.48 W, 1.3-1.7 W, 0.74 W, and 2.37 W, respectively. Recharging required almost 0.9 A, which corresponds to 3.3 W. The mobile phone can however also be recharged already with a charging current of around 90 mA.

As for the laptop, the transients for the mobile phone are large and fast, which means an electrical system is needed to smoothen the power peaks for the fuel cell. On the other hand, for the mobile phone, the power used is varying more depending on what is done with the phone than with the laptop computer. The hybrid system should be able to support up to 2.4 W peaks, which might be long, as videos usually last at least a few minutes. For calls the power needed is lower, around 1.5 W, but calls might be even hours long. When the phone is not used, i.e. keys locked and backlight is off, the power consumption is very low. Mobile phones are usually is in low power state for long

periods, which makes the average consumption low. However, the higher power peaks might also be very long.

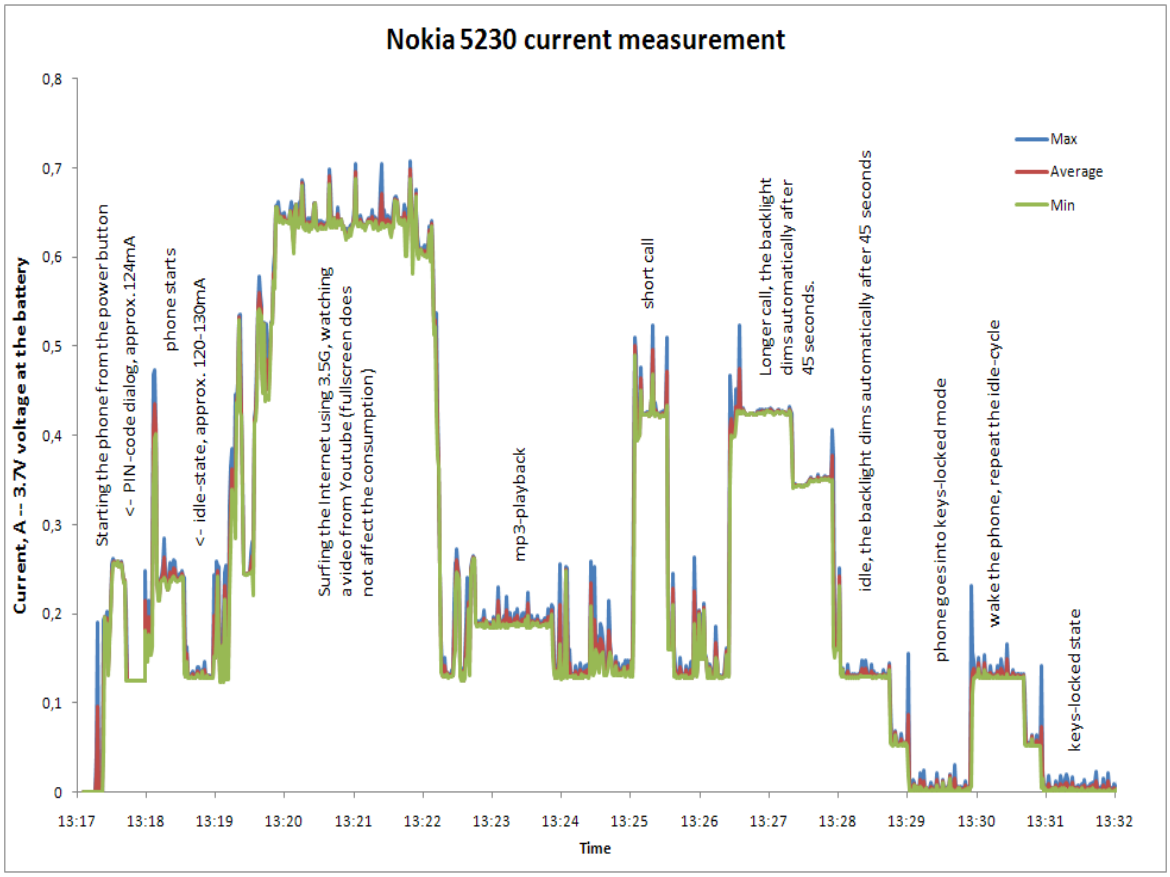

Figure 4.2: Current consumption of a Nokia 5230 Navi during some typical use of a mobile phone.

This would imply, that the optimal sizing of the hybrid system, would involve a small fuel cell and a relatively large battery. The fuel cell would provide more than the average power, to be able to recharge the battery under low loads. The battery in turn should be able to provide hours of mobile time together with the fuel cell. As the fuel cell would be relatively small, the battery would have to provide most of the peak powers on its own. Another approach would be to make the fuel cell adapt to different load levels. That is, the fuel cell would provide slightly more than average power for low consumption, and start to provide higher powers e.g. during calls or when surfing the Internet. The second approach would need a larger fuel cell and some logic to decide when the load is high and long enough to use the fuel cell at higher power. The advantage would be that a possibly much smaller battery could be used. For the mobile phone, the currents are quite small, which might render the use of a supercapacitor unnecessary. However, a supercapacitor might increase the battery lifetime significantly by reducing large transients for the battery, and in that case it would be beneficial to use one.

4.2 Pump power consumption tests

4.2.1 Air pump

To be able to find the optimal pumping parameters the flows caused by the pumps were measured at different currents and input voltages and the powers used by the pumps were calculated. The flow through the air pump, a Xavitech P200-GAS-5V pump, was measured using a Honeywell AWM 700 mass flow sensor that was attached to the output of the air pump. The air pump was fed with an external supply voltage of 3.3 V or 5 V and it was controller using a potentiometer. The current used by the pump at different potentiometer positions was measured using a Fluke 189 current meter connected in series with the power supply. The 3.3 V was made from the 5 V fed by the external source using a built-in regulator on the circuit board.

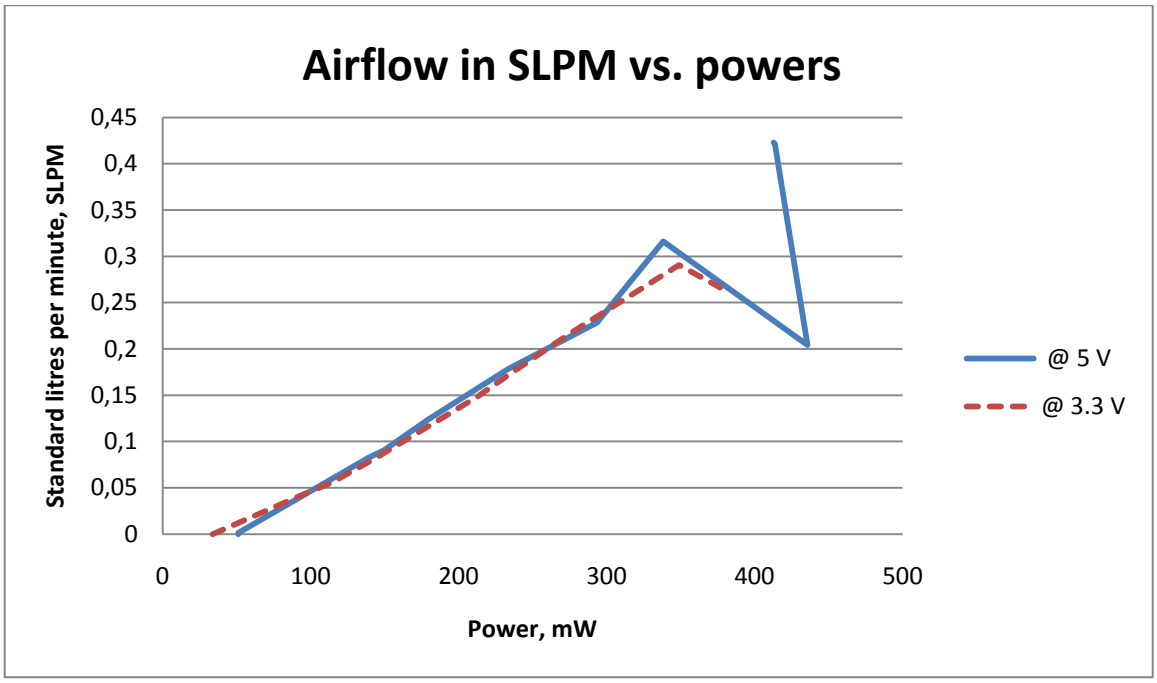

Figure 4.3: The amount of airflow, expressed in standard litres per minute, compared to the power fed into the air pump.

From figure 4.3 we can see that the flow increases almost linearly when the power fed to the pump is increased. The main difference between the 5 and 3.3 V supply voltages is that the total power that can be fed into the pump is smaller in the 3.3 V case while the currents needed to produce the same powers are larger. The jump in SLPM at 450 mW is caused since the pump does not work so efficiently when at almost full throttle. After this range the pump enters factory setting mode, which uses maximal stroke frequency and is factory optimised so it is efficient, causing the current and therefore the power to decrease, while the flow increases.

Since the flow measured with the mass flow sensor, i.e. 420 ml per minute, is higher than the maximal flow according to the specifications of the pump, i.e. 300 ml per minute, the air flow was also measured by measuring the time for the pump to fill an 80 ml volume in an air-water tank.

This measurement was done only for the lowest and the highest pump speeds. According to these measurements the flow at full speed was 343 ml per minute, which still is higher than the specifications. It might however be that the value in the specifications is a value that is promised for the whole lifetime of the pump, and if so it would be probable that the flow is higher when the pump is new. The measurement of the flow at the lowest and the highest pump speeds showed that the mass flow sensor probably shows around 1.1 to 1.2 times too large flows across the whole measured range.

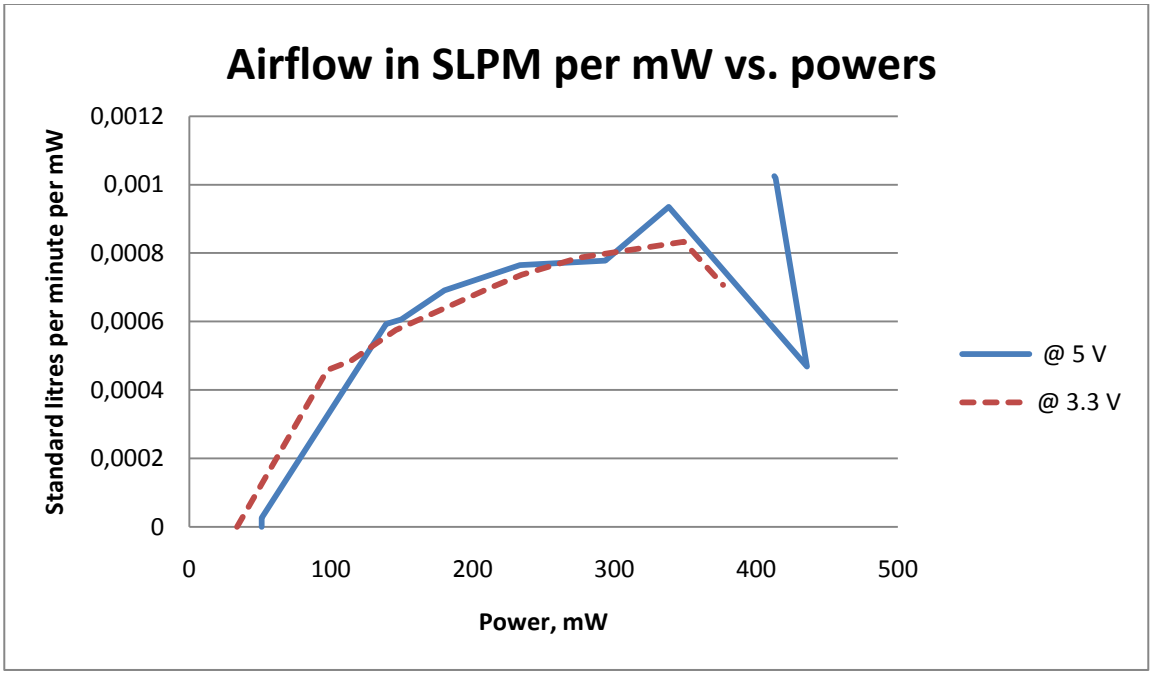

Figure 4.4: The amount of airflow per mW of power, expressed in standard litres per minute, as a function of the power.

From figure 4.4 we can see that it is most efficient, considering litres of air pumped per mW used, to pump air using the pump at full speed. However, to keep the fuel cell reaction going with an oxygen stoichiometry of two, i.e. supply twice as much oxygen as the fuel cell reaction needs, only around 66 ml air per minute is required at a current of 1 A when using a fuel cell stack with two cells, as is calculated in appendix D. This means that since the pump pumps around 340 ml per minute on full speed, a duty cycle of almost 20% gives the wanted stoichiometry at this current. As the power consumption is 413 mW at full pumping speed and 30 mW at stop the duty cycle of 20% gives an average power consumption of 107 mW. As the amount of air is directly proportional to the amount of current used, i.e. every 300 mA of current requires 20 ml of air per minute with a two cell fuel cell stack, the required duty cycle for the pump when using other fuel cell currents can easily be calculated.

The real flows might differ slightly from the measured ones since the counterpressure when feeding air into the fuel cell is larger than the counterpressure of the mass flow sensor due to the thin capillaries in the fuel cell. In the measurement of filling air into the air-water tank on the other hand, the counterpressure is a function of the amount of air that has been pumped, since the

hydrostatic pressure resisting the pumping of air increases as more air is pumped into the tank. This was clearly noted when filling the tank slowly. Inaccuracies may also be caused since the mass flow sensor is designed for large flows, i.e. zero to 200 standard litres per minute (SLPM), while the flows we are measuring are below 0.5 SLPM. Even when combined these inaccuracies are not so important, since a stoichiometry of two is used and the expense of slightly increasing the duty cycle for the pump is counted in milliwatts.

4.2.2 Methanol pump

The flow through the methanol pump, a Xavitech V200-LIQ-5V pump, and the currents used by the pump were measured to find the optimal drive parameters. The flow was calculated from the time it took for the pump to pump 20 ml solution from one container to another. The final solution that will be used is probably a 5 vol-% aqueous methanol solution, which has almost the same properties as water considering how it flows, so the tests were conducted using distilled water. The pump was started with the first container, the pump, and the pipes filled with solution and the second container empty. The time from when the surface of the liquid passed the 5 ml marking in the container to when it reached the 25 ml marking was measured. The pump was controlled using a potentiometer on the circuit board and the current at the different potentiometer positions was measured using the averaging function of a Fluke 189 current meter connected in series with a 5 V power supply. In the test the pump was fed with both the 5 V from the external supply and with 3.3 V made by a built-in regulator on the circuit board. The test was repeated at least two times for each pump speed.

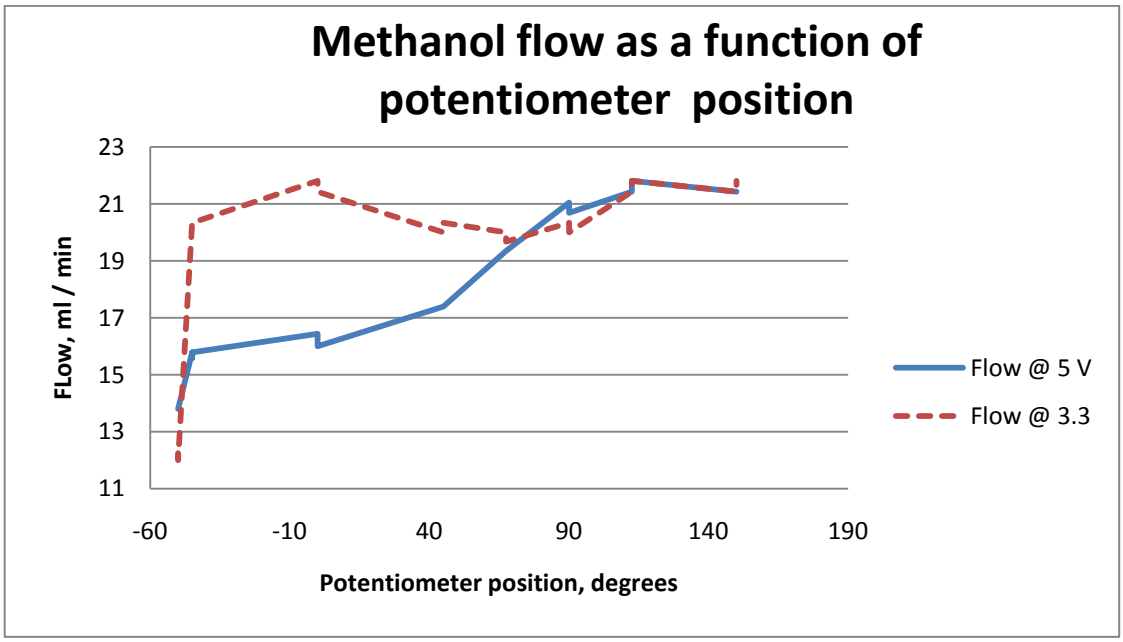

Figure 4.5: Flow as a function of potentiometer position for both 5 and 3.3 V feed to the pump.

As can be seen from figure 4.5 the flows are in the range of 13.8-21.4 ml/min at 5 V, and 12.2-21.8 ml/min at 3.3 V, which agrees with the specifications, i.e. max flow of 22 ml/min. The flow at 5 V increases with increasing current while at 3.3 V the flow and the current are small at minimum drive, but after it the current increases while the flow stays at roughly the same level.

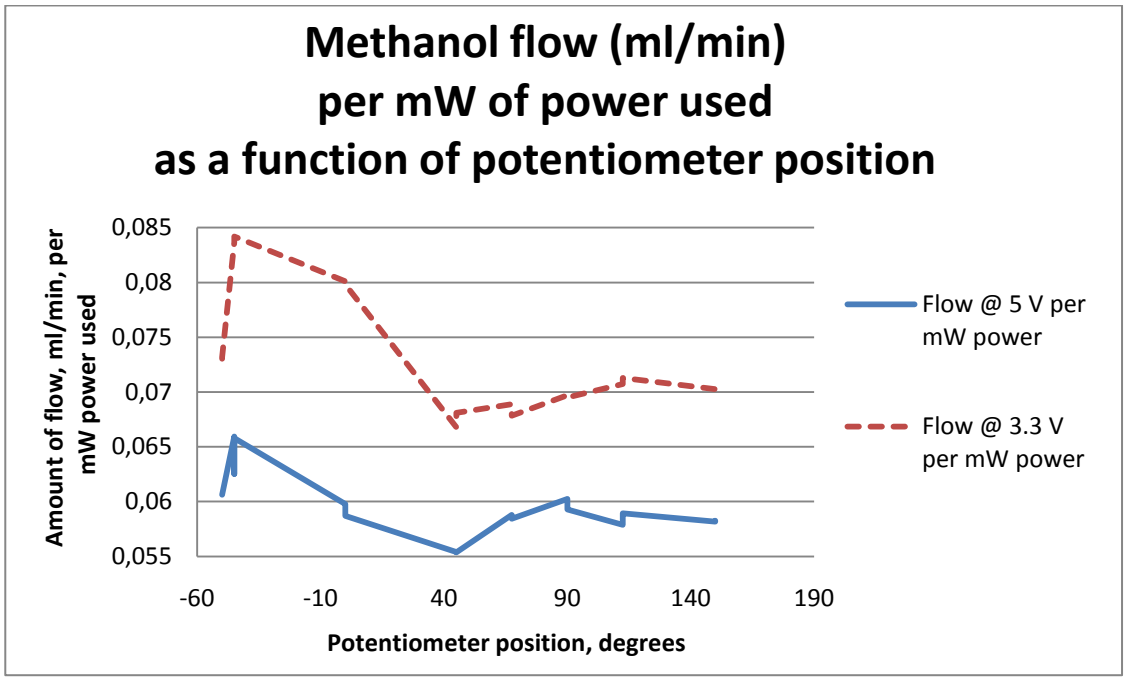

Figure 4.6: Amount of flow, ml/min, per mW of power used as a function of potentiometer position.

From figure 4.6 we can see that the pump is most effective considering amount of flow per mW of power used when the potentiometer is at position -45 degrees. This corresponds to next to the lowest stroke frequency possible with the pump. At this point the flow is 20.3 ml/min and the power usage around 240 mW when using 3.3 V. From figure 4.6 we can also see that feeding the pump with 3.3 V is clearly more efficient than using 5 V. However, as can be seen in figure 4.5, the flow cannot really be controlled at 3.3 V since it jumps to almost maximal flow directly, while it is easier to control at 5 V. In our case this is no problem, since as is calculated in appendix D, the needed flow with our electrolysers are around 2.5 ml/min if the internal volume of the electrolysers are 5 ml each, the current is 0.6 A, the aqueous methanol solution strength is 5% and we allow a drop in methanol concentration of at most 6 per cent units between the input solution to the first electrolyser and the output solution of the third one. A flow of 2.5 ml/min is very much lower than the flow at the slowest setting if the pumps are on constantly, and since we want to use as little energy as possible for the auxiliary systems, we want to use the pumps at the highest efficiency with the lowest duty cycle that gives the required flow. As we nonetheless vary the flow by adjusting the duty cycle, while adjusting the flow using the potentiometer is not very exact, the higher amount of control gained by using the pump at 5 V is not necessary.

In the prototype system the pumps are on the same circuit board, which has only 5 V available so here we will use the 5 V, with a duty cycle of 16% thus giving an average pumping power of 81

mW, though the efficiency is lower than when using 3.3 V, which would give a duty cycle of 12.3% and an average power of 59 mW. On the other hand the efficiency is higher for the air pump when using 5 V.

Since no new methanol is added during operation of the system the total amount of methanol slowly decreases in the system as the methanol is consumed in the electrolysis. This causes the methanol concentration to slowly decrease. The methanol pump only keeps the local concentrations of methanol in the electrolysers close to the overall methanol concentration in the system. Without a pump a large amount of the methanol would not be used, as the diffusion, which slowly balances the methanol concentrations, is slower than the consumption of methanol in the electrolysers.

A somewhat too high methanol concentration at the beginning might be the solution to the problem, since the current density in an electrolyser is relatively stable in a region with somewhat higher methanol concentration, as can be seen in figure 4.7. Higher methanol concentration however increases the risk for catalyst poisoning, so the optimal concentration has to be evaluated separately for each system. The matter will not be investigated in the scope of this work. Another possible solution would be using close to 100 vol-% methanol in a separate container and mix it with water before it enters the electrolysers. This option is more thoroughly explained in section 3.2.3.

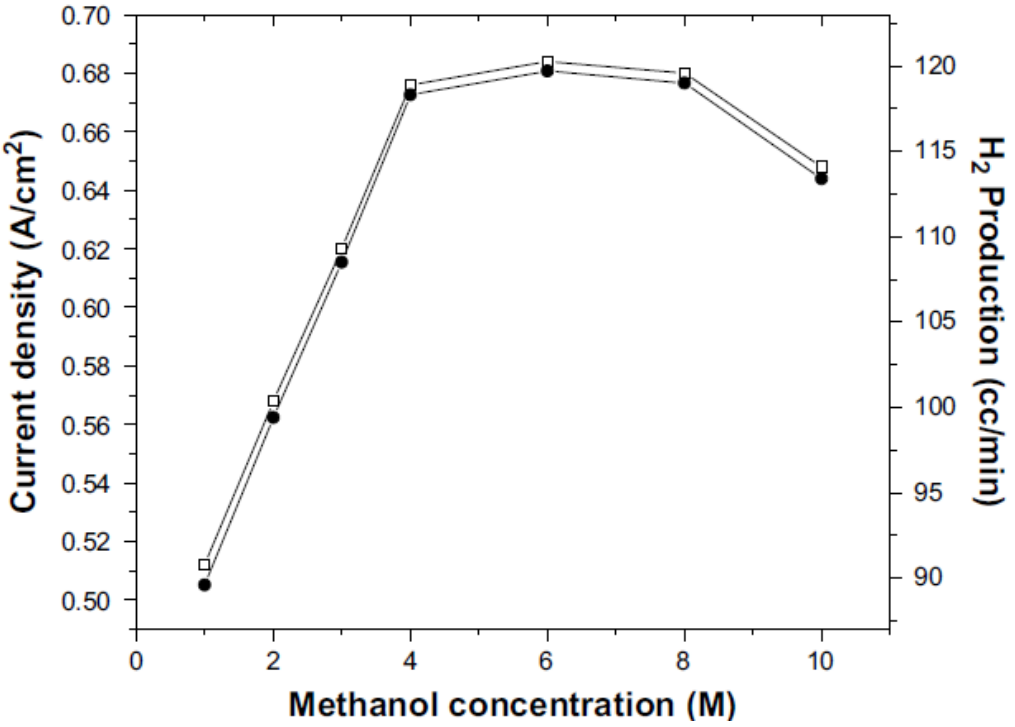

Figure 4.7: Current density and hydrogen production of an aqueous methanol electrolyser with different methanol concentrations at 1.0 V and 30°C with Nafion-117 membrane. (□ = current density, ●= hydrogen production) (Adopted from Sasikumar et al. p. 5907, fig. 2)

The results from the test contain some inaccuracies. Firstly, the counterpressure in the test was probably quite low compared to the counterpressure of three electrolysers connected in series. Secondly, the average current rose slowly, e.g. 0.3 mA, during the filling of the secondary container when using all but the smallest currents. This might have been caused since the liquid level of the container from where the liquid was pumped subsided during the test, which lowered the hydrostatic pressure that was helping the pump. While the inaccuracies cause some uncertainty in the absolute flows produced by the pump, the results that the highest efficiency is achieved at the next to lowest stroke frequency, and that the pump can be controlled at 3.3 V only by varying the duty cycle, are very likely to hold also when the pumps are used in the prototype system.

4.3 System tests

4.3.1 Control system

The control system was tested by completing a full system test run consisting of start-up, recharging the start-up source, three charge – discharge cycles with the temporary source, and safe shutdown. The whole test run was performed automatically but for minor changes in parameters and giving the system the command to shut down. During the test a 3.88% methanol solution was used and the methanol pump was used with a duty cycle of 15%, while the air pump was on continuously. The battery voltage was 1.334 V and the supercapacitor voltage was 1.194 V before the test. The battery was used as start-up source and the supercapacitor as temporary source. A silica gel column was used to dry the hydrogen gas.

In these system tests the battery measurement logic described in section 3.3.1 was turned off, since preliminary tests had showed that disconnecting the battery causes a current peak for the fuel cell, which would shorten the lifetime of the fuel cell if this logic would be used. Turning off the battery measurement logic however makes it impossible to determine the real voltage of the battery, but it was not considered too important in this test. A better solution would be to disconnect also the fuel cell during the measurement or to keep a supercapacitor connected to the fuel cell to smoothen the current peaks. The second approach would require an extra supercapacitor to be connected to the fuel cell all the time so it is at the same voltage as the fuel cell. Otherwise the peak caused by connecting a supercapacitor with a different voltage might be larger than the peak caused by simply disconnecting the battery. The requirement of having the supercapacitor at the same voltage as the fuel cell all the time inhibits the use of the supercapacitor already present in the system for this. Adding a secondary supercapacitor in parallel with the fuel cell would however be easy.

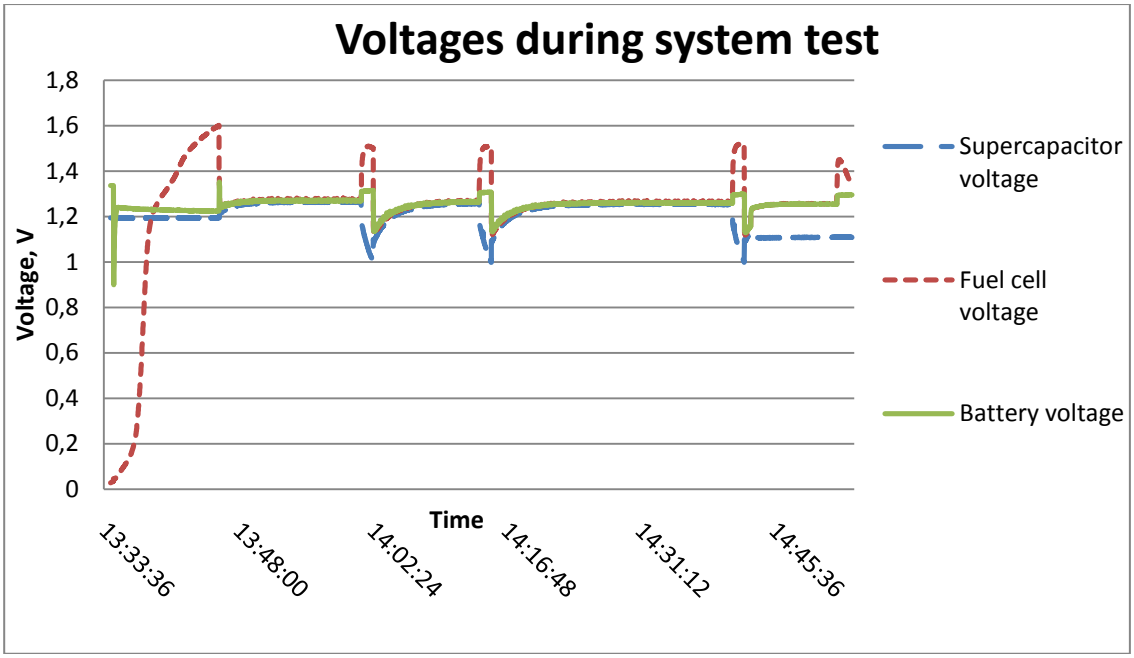

Figure 4.8: The voltages during the control system test.

The voltages and currents during the test run are found in figure 4.8, figure 4.9, and Figure 4.10. From figure 4.8 we can see that the fuel cell voltage rose from zero to 1.6 V in approximately 10 minutes after which it was connected to the rest of the system causing the fuel cell voltage to drop. The *recharge start-up source* mode is not visible in this test since the start-up source voltage was so high that it did not have to be recharged. Therefore the control system proceeded to the *charge temporary source* mode immediately. After this voltage drop caused by the connecting of the fuel cell and the supercapacitor, the voltages of the fuel cell, the battery, and the supercapacitor began to rise slowly until they reached the state-of-charge threshold defined for the supercapacitor. When this threshold was reached the battery and the fuel cell were disconnected, which is seen as a jump to a higher voltage, while the supercapacitor voltage started to drop as it was discharged through the DC/DC converters into the load. This charge – discharge cycle for the temporary store was repeated three times as can be seen from figure 4.8. The length of the third charge-cycle was longer since the system did rise to a slightly lower voltage every time the cycle was repeated. Since the voltage rose quickly at first, but then more slowly, it naturally took longer and longer for the system to reach the defined limit. In the last cycle we even had to lower the limit slightly for the system to proceed to the *load charge* mode. During the fourth recharging cycle the safe shutdown button was pressed, which disconnected the supercapacitor from the system and recharged the start-up source to ensure a successful start-up the next time the system is started. This caused the supercapacitor voltage to remain at a low level, while the voltages of the fuel cell and the battery rose to the voltage threshold defined to ensure a safe start-up. Finally the limit was reached and the system disconnected all components, which is seen as a sudden increase in the fuel cell and the battery voltage. This sudden increase was caused since the fuel cell and the battery did not longer feed power into the electrolysers.

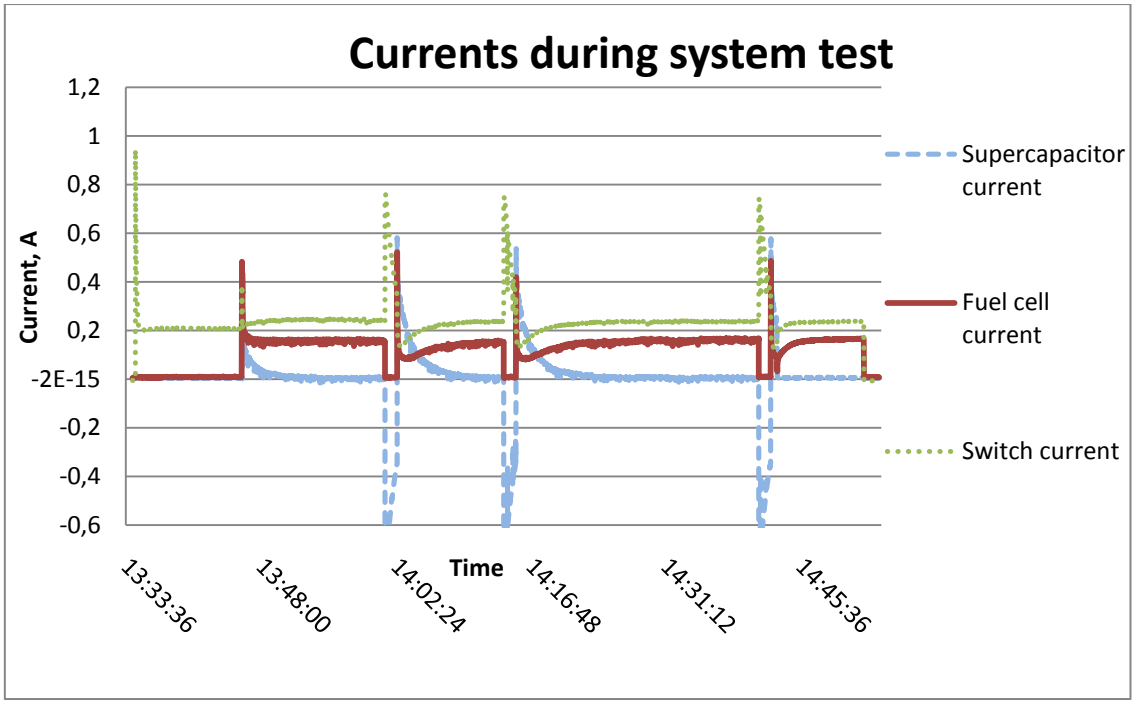

Figure 4.9: The fuel cell, supercapacitor and switch currents during the control system test. The rest of the currents are found in figure 4.10.

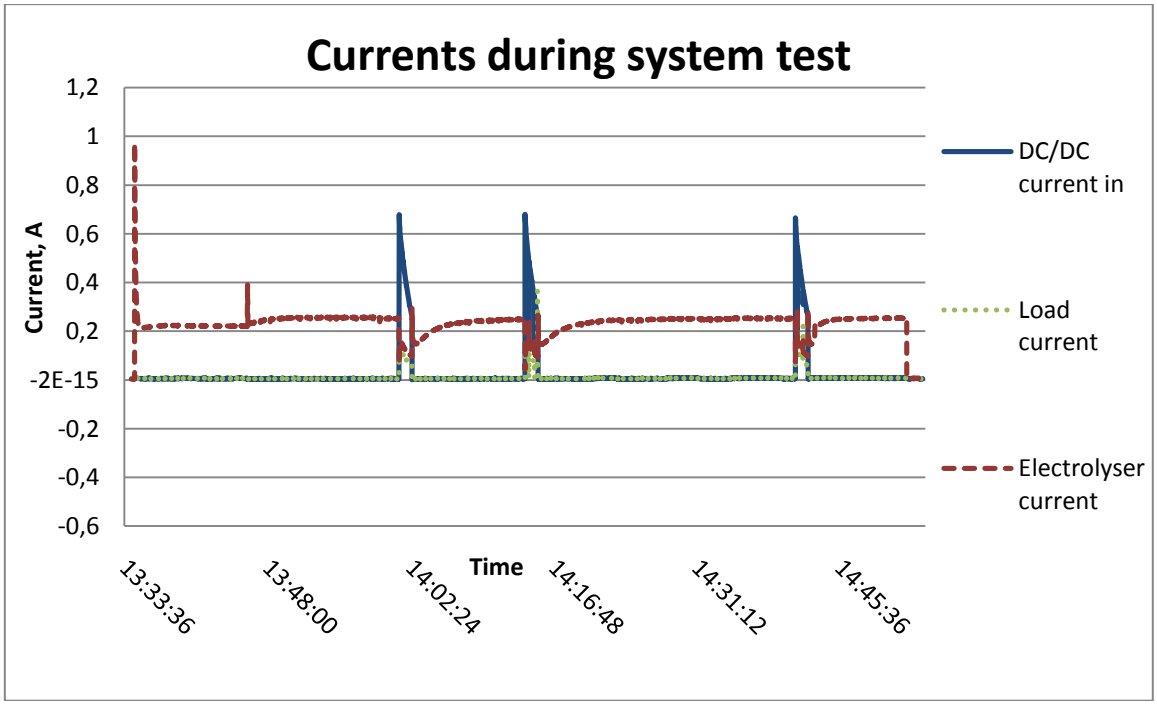

Figure 4.10: The DC/DC input current, load current, and the current of the electrolysers during the control system test. The rest of the currents are found in figure 4.9.

From figure 4.9 and Figure 4.10 on the other hand we can see the same test run, but from the current point of view. The battery current was not directly measured in the test but it can be

deduced from the switch current, which is the sum of the fuel cell, the battery, the supercapacitor, the electrolyser and the DC/DC input current, when the other currents are known. From the figure we can see that the electrolyser and the switch currents initially are the same, which means that the battery provides all power to the electrolysers, since no other components are connected. When the fuel cell and the supercapacitor have been connected we can see that the fuel cell starts providing power, but the battery also provides some. The supercapacitor provides power only for a short while after it has been connected. When the system enters the *charge load* mode the fuel cell and the battery are disconnected, while the electrolyser current drops somewhat and the DC/DC current peaks and then slowly decreases as the supercapacitor is discharged into the load. This cycle is then repeated three times and then the battery is recharged after which the system is shut down.

From the aforementioned figures we can see that the control system works as it should and is capable of controlling the state transitions as designed. However, the fuel cell – electrolyser system is not producing enough power to actually recharge the battery and the supercapacitor. As can be deduced from the currents in figure 4.9 and Figure 4.10 the battery provides a portion of the current all the time. This is not seen in the voltage graph in figure 4.8, since the battery voltage remains the same with many different states-of-charge. The probable reason to the low fuel cell power is that the hydrogen system has a small leak, probably in the fuel cell. This leak was noticed since the fuel cell voltage did not rise to its highest possible value though the fuel cell purge valve was closed. Higher fuel cell voltages were achieved when more hydrogen was produced per time unit in another test. When a low hydrogen production was used as in this test the leak however became significant. Another reason to suspect a leak is that the hydrogen pressure, which was monitored using a Honeywell ASDX series pressure sensor, was only approximately 1 mbar.

Due to the inefficiency in the system the fuel cell is not capable of staying at a certain voltage when it is connected directly in parallel with the electrolysers, though it should be able to do that. However, if the battery is connected in parallel with the fuel cell then the voltage of both the battery and the fuel cell rises. Due to this the logic of the control system had to be modified to connect also the battery if the supercapacitor was used as the temporary source. Additionally, to be able to run the system, all the electronics components, such as the microcontroller, the sensors, and the switch, were powered using mains current.

4.3.2 Conduction losses

During the system tests also losses in the electrical connections were measured. All losses were not measured, only the most important, i.e. the loop between the battery, the electrolyser and the fuel cell. These measurements are only indicative since they are not complete and because they were conducted only at a certain current during operation, as the voltage drop depends on the current according to Ohm's law. The current, around 300 mA, was probably realistic for the case of the battery and the electrolyser losses, since the battery was feeding the electrolysers when the voltage drop was measured. This was probably not the case with the fuel cell, which produced a current of approximately 200 mA, since the hydrogen leak made the fuel cell current

approximately four to five times lower than it will be in a final system without leaks. It can however be seen from table 5 that the largest losses occur in the battery connector, the switch, and the electrolysers. A battery holder making a tighter contact with the battery would probably reduce the voltage drop at the battery. A part of the voltage drop in the electrolysers is caused since there is a voltage drop in the electrolyser itself between the supporting outer plate and the electrodes due to a non-ideal contact. This voltage drop was between 2 mV and 9 mV for the different electrolysers. Improving the structure of the electrolysers could decrease the voltage drop somewhat. The voltage drop in the switch and the wires is harder to remove. Using shorter wires, as would be done in an embedded system, would naturally reduce the losses in the wires if the same wire thicknesses were used.

If we could reduce the battery holder loss to around 10 mV and estimate that the part of the system that was not measured contains around 50-100 mV of losses, then the total losses would be around 150-200 mV. This would be no problem in a system using a high voltage, but it is very significant as the voltage is below 2 V.

Table 5: Some of the voltage losses in the system during system operation.

Voltage losses:	
mV	
4	Electrolyser manual switch
5	Electrolyser switch to electrolyser current measurement
3	Electrolyser current measurement
3	Electrolyser current measurement to switch
14	Switch
6	Switch to battery positive
63	Battery negative to ground split 1
3	Ground split 1 to ground split 2
3	Ground split 2 to old electrolyser cathode
10	Old electrolyser anode to iron electrolyser cathode
14	Iron electrolyser anode to stainless electrolyser cathode
7	Stainless steel electrolyser anode to electrolyser manual switch
13	Fuel cell positive to current measurement
3	Fuel cell current measurement
3	Fuel cell current measurement to switch
154	**Total (mV)**

4.3.3 Energy transfer from the supercapacitor to the load

As the supercapacitor is used as a temporary energy store in the prototype system, it was important to assess the energy transfer from the supercapacitor to the load. When we know the energy that is transferred to the load during one charge-discharge cycle and the time one discharge cycle takes, we can calculate the average power the system can provide to the load device.

The energy in a supercapacitor depends on the capacitance and the voltage according to equation (5)

$$E = \frac{1}{2} C U^2 \tag{5}$$

, where *E* is the energy, *C* is the capacitance and *U* is the voltage difference. The energy transferred from the supercapacitor to the load is found by using the voltage difference in the supercapacitor between the start and the end of the discharging. Since we want to find out the average power we divide the energy with the time of a single charge – discharge cycle for the supercapacitor according to equation (6)

$$P = \frac{E}{\Delta t} \tag{6}$$

, where *P* is the power, *E* is the energy, and Δt is the time. During the test two charge – discharge cycles were completed with the supercapacitor voltage dropping from 1.251 V to 0.996 V and 1.25 V to 1.02 V. These cycles took 11 minutes, i.e. 660 seconds, and 9 minutes and 2 seconds, i.e. 542 seconds, respectively. The cycle length was measured as the time it took for the system to recharge the supercapacitor to a voltage 20 mV lower than the voltage before the load was connected. The voltage was chosen to be 20 mV lower than the starting voltage, since it takes clearly longer, i.e. at least ten minutes more, for the supercapacitor to reach exactly the starting value due to the hydrogen leak. We used equation (5) to calculate the energy in the supercapacitor at the starting voltages and the energy at the ending voltages. The energy differences, i.e. 60.2 W and 54.6 W, were then divided by the total cycle time using equation (6) and thus we get the average powers of 91.2 mW and 100.7 mW power out from the supercapacitor during the two test cycles. Assuming that the DC/DC converter works at an efficiency of 75%, see section 4.3.4, we get an average power of approximately 70 mW out of the DC/DC converter. As the phone battery has a nominal voltage of 3.7 volts the average current to the phone is close to 19 mA.

This average current is lower than the 80 mA average current goal set in section 3.1.3. An average charging current of 80 mA is however needed to reach the five-hour target only if the current consumption of the phone stays at an average level of 190 mA. This happens if the phone is used for calls, surfing the Internet and listening to music approximately one third to half of the time, depending on what the user is using the phone for. If the phone has the keys locked and the backlight off for most of the time, the average current is much lower and the mobile time extension target will be reached.

One way of increasing the average current would be to change the electrical connection scheme so that two temporary stores, preferably supercapacitors, could be used. That is, the fuel cell would always charge one of the temporary stores, while the other is discharged into the load. An electric connection scheme that would allow for this is seen in figure 4.11. Depending on the charge and discharge times this could at best double the average current supplied to the load by

the system. This would however require that one supercapacitor could be charged in the same time as the other one is discharged, which probably is not possible using a low power fuel cell. On the other hand the energy transfer efficiency could also be improved when using two temporary stores because the discharge can be allowed to take as long as the charging. This would lower the load charging current, which would imply lower ohmic losses. It should however be remembered that the mobile phone needs at least 100 mA for charging, which means that a current of at least 500 mA would be needed from the temporary store as the DC/DC conversion is from approximately 1.5 V to 5 V and the conversion efficiency is 75%. A current of 500 mA discharges the supercapacitor rather quickly.

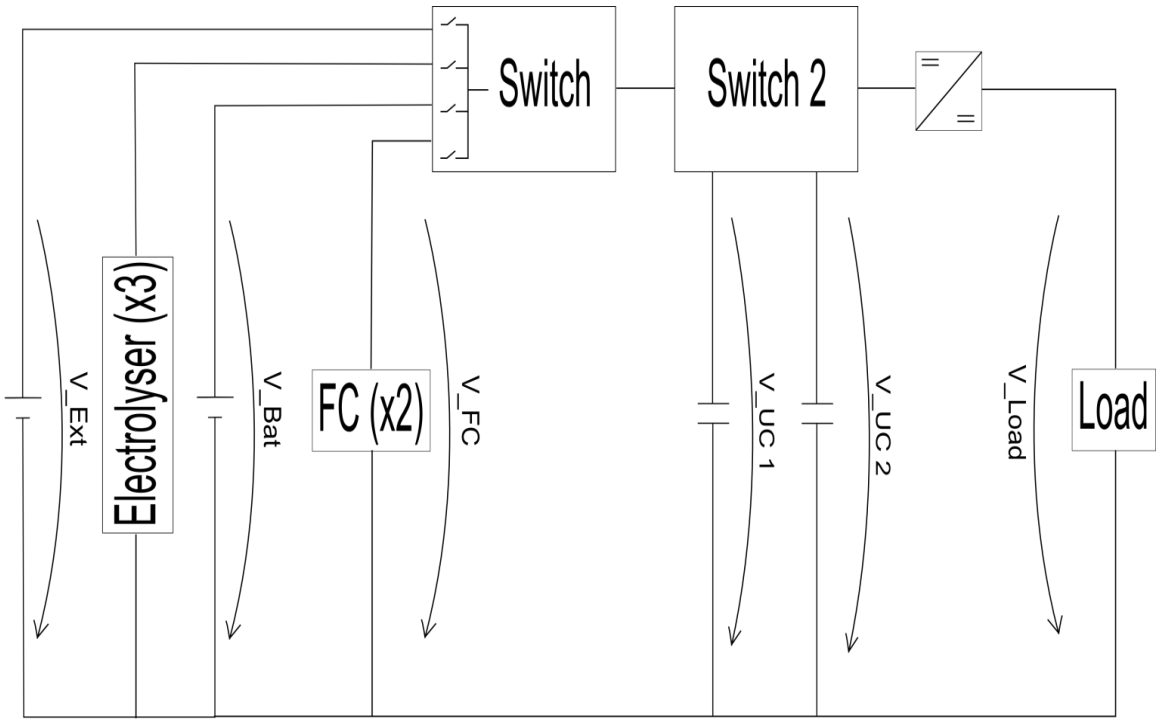

Figure 4.11: Alternative electric connection scheme. Switch 2 represents a switch which can be used to connect either supercapacitor one (UC 1) or supercapacitor two (UC 2) to the load, while the other one is connected to the rest of the system.

In the test it was also noticed that a separate current limitation for the supercapacitor was not needed. This is probably caused by the FET-transistors used in the supercapacitor circuit. The transistors were designed for voltages from 4 V upwards and the power supply for the transistors produced only around 7 V. With a driving voltage of 7 V the FET is not fully opened, which causes it so have some resistance, which in turn limits the output current.

4.3.4 DC/DC converter efficiency

The prototype system allows for one to four DC/DC converters to be used in parallel for the voltage conversion from 1.6 to 5 V. The used DC/DC converters are all of the NCP1402SN50T1-type with a 5 V regulated output. In the test the voltage of 1.6 V was supplied with an external power source, i.e. a Farnell L30C power supply, and the current was limited to different values with the

current limit in the power supply. The mobile phone that is used as load in the prototype system, i.e. a Nokia 5230 Navi, was used as load also in this test to get a maximally real test situation. The phone battery was at around 50% charge during the test, according to the battery state display on the phone. Additionally, the phone was powered off, which causes the power used by the phone during charging to be higher than if the phone is on and in the state were the keys are locked and the backlight is off. However, no other effects from having the phone turned off have been noticed so this should not affect the DC/DC conversion efficiency. The conversion efficiency was calculated as the power out from the DC/DC converter divided by the power into the DC/DC converter. The input and output voltages and currents were measured using a National Instruments sbRIO-9631 embedded control and acquisition device and the load powers as well as the conversion efficiency were calculated using LabVIEW. The data acquisition device is the same as in the prototype system as described in section 2.6. Also the effect of using different amounts of DC/DC converters was tested. The results from the test can be found in table 6.

Table 6: DC/DC conversion efficiencies, calculated as the power out of the DC/DC converters divided by the power into the DC/DC converters, in different current ranges and with different amounts of DC/DC converters. With lower currents than the ones marked at the maximum efficiency values the efficiency of the DC/DC converters decreases, but the converters are capable of conversion e.g. with more than 65% efficiency down to 80 mA for the case with 3 DC/DC converters and down to 100 mA with 4 DC/DC converters.

		Current (A) I-DC/DC-in					
		(Input current at maximum efficiency)	**0.3-0.5 A**	**0.5-0.75 A**	**0.75-1 A**	**1 A -**	**Maximum current to load (I-DC/DC-out)**
Amount of DC/DC converters	**4 DC/DC converters**	0.78 (@ 260 mA)	0.78 - 0.77	0.77-0.745	0.75-0.71	0.7-0.65 (max 1.4 A)	295 mA
	3 DC/DC converters	0.775 (@ 260 mA)	0.77-0.74	0.74-0.7	0.7-0.65	0.65-0.615 (max 1.23 A)	255 mA
	2 DC/DC converters	0.75 (@ 220 mA)	0.74-0.7	0.7-0.64	0.64-0.58	0.575 (max 1.02 A)	180 mA
	1 DC/DC converter	0.7 (@ 130 mA)	0.65-0.57	0.57-0.59 (max 0.53A)	-	-	115 mA

According to the specifications of the DC/DC converters the efficiency should be above 80% as best with an input voltage of 1.6 V and output currents between 10 and 60 mA per converter. The results however show that the efficiency achieved in the test is around 5% lower for most values.

From table 6 we can clearly see that it is more efficient to use a larger amount of DC/DC converters as long as the current is higher than 260 mA. If the current to the DC/DC converter is

very low and does not have high current peaks, as might be the case when it is supplied by a fuel cell, it might be more efficient to use a smaller amount of DC/DC converters.

During the test it was noticed that the phone indicates that charging starts with 30-35 mA of current to the DC/DC converter. This is however not true, since the power out of the converter is practically zero if not negative with this current. This would imply that the phone battery actually is discharged if one tries to charge the phone with a current this low. The current to the load is positive when at least 60 mA of current is fed to the converter. Since the phone draws around 50 mA of current when it is off and charged using 1.6 V, the power into the phone, i.e. out of the DC/DC converter, has to be at least 50 mA to give more power than the phone consumes. If the phone is on and the keys are locked the phone draws a current of only 15-18 mA when charged, so charging of the phone battery occurs already at lower currents when the phone is on. The currents drawn by the phone in on and off state are independent of the charging current.

4.3.5 Required start-up energy

The required start-up energy was calculated from a test in which the system was started using only a battery charged to around 1.32 volts, i.e. the battery was feeding power to the electrolysers, which in turn were feeding hydrogen to the fuel cell. In figure 4.12, which is showing the first part of the conducted test, we can see that the fuel cell voltage rises rather quickly at first and then somewhat slower. At 9:40 the second part of the test was started, i.e. the fuel cell was connected in parallel with the battery and started producing power for the electrolysers. This is seen as a drop in the fuel cell voltage.

The currents and powers that were drawn from the battery were calculated from the average current and voltage values during the measurement intervals and the cumulative values were found by summing all these values. The start-up energy is defined here as the energy in mWh needed before the fuel cell reaches a certain voltage, which in turn indicates that the fuel cell can be connected to the rest of the system. If we choose this voltage to be 1.6 volts, which the system reaches at 9:25:25 in this test, i.e. 17.5 minutes after starting the system, the cumulative power used for start-up is 66.6 mWh. If we choose this voltage to be 1.7 volts, which the system reaches at 9:28:07, i.e. 20 minutes after start, the cumulative power usage is 81.8 mWh. These values correspond to 58.3 and 70.2 mAh respectively, which is very low compared to the 2700 mAh capacity of the standard AA battery used. This is also much lower than the estimate of 200 mAh needed for start-up as presented in section 3.1.3. The main cause for this is that the electrolyser current during start-up was estimated to be around 600 mA, while the tests showed that it was 230 mA on average. This means that a much smaller battery could be used in the final system as long as the voltage is kept the same. If the battery voltage is increased the electrolyser current also increases, which might increase the needed energy. On the other hand the system starts faster if more hydrogen is produced so the needed energy might remain almost the same. A small increase in needed energy should be noted, since electrolysers are more efficient at lower current densities. For a certain answer the matter would require further investigation, which is not done in this work.

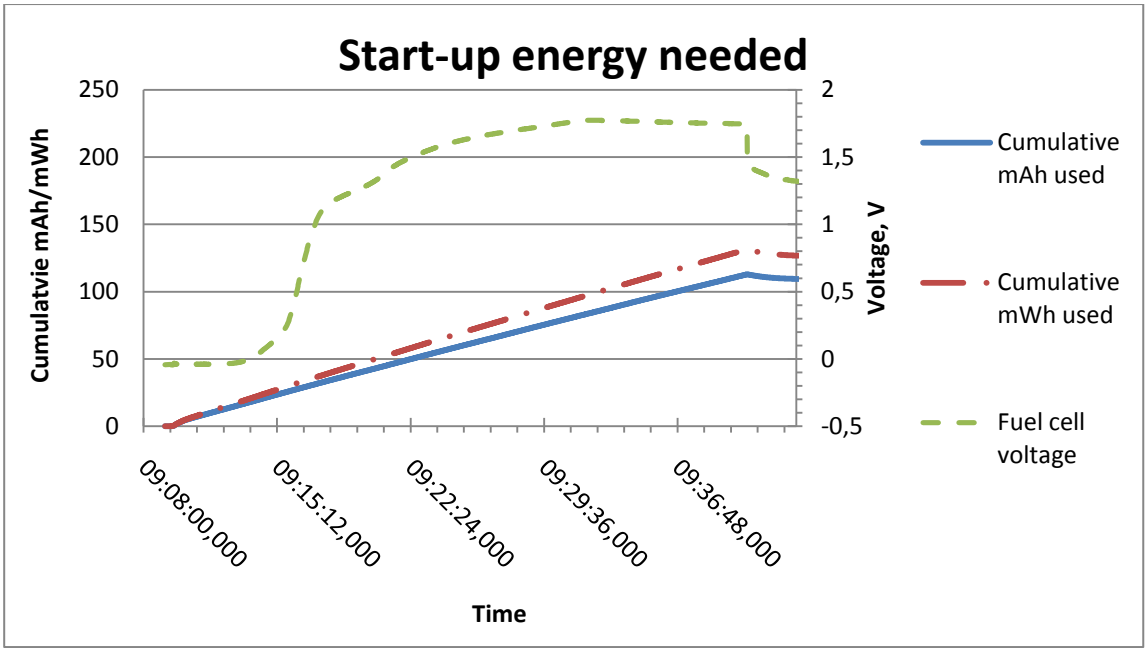

Figure 4.12: The mAh and mWh, which were taken from the battery as well as the fuel cell voltage when starting the system. The mAh and mWh values are seen on the axis to the left of the figure and the fuel cell voltage is seen on the axis to the right of the figure. The fuel cell was disconnected from all loads until 9:40, where a clear voltage drop is visible in the figure.

5 Conclusions concerning the experimental results

This section gathers the most important results and conclusions of the experiments presented in section 4. The flows of the Xavitech pumps followed the specifications with flows of roughly 300 ml/min for the air pump, and 22 ml/min for the methanol pump. The flows could be controlled by potentiometers as well as by changing the voltage. It was concluded that the highest efficiency for the air pump was at 5V and full throttle. The methanol pump on the other hand was most effective at 3.3 V and next to the lowest stroke frequency. As the flows at maximal pumping efficiency were much higher than the required flows with the current system, and maximal efficiency was desired, duty cycles of 20% for the air pump and 11% for the methanol pump were chosen, as they should have provided the needed flows.

In the final tests it was however noted that the fuel cell voltage did not rise properly when the air pump was used in pulses. On the other hand, the methanol circulation worked as it was supposed to. The problem was overcome when the air pump was run continuously. As the air pump is equipped with a backpressure valve, which obstructs the air from flowing backwards, there always is a flow through the fuel cell when the air pump is used and the flow cannot reverse when the pump is off. This means that the reason for the poor performance cannot be a lack of flow. However, the channels in the fuel cell are narrow, and especially the holes from the edge of the bipolar plates into the flow channels are very narrow to make the flow as even as possible in the parallel serpentine channels. The narrow holes probably cause a high flow resistance, especially at the moment when the air pump is turned on. Therefore the amount of air that flows into the fuel cell through the holes is very small when a pulsing flow is used, which causes oxygen starvation in the fuel cell, which reduces the performance.

With a duty cycle of 15% the methanol pump used 81 mW on average, while the continuously used air pump required 413 mW. The consumption is almost tolerable for the methanol pump, but the air pump consumption would need to be reduced. A possible solution for the air pump that was not tried would have been to make the pump draw air from the outlet of the fuel cell instead of blowing air into the inlet. This could have worked better also with a pulsed pump action. Pulsed pump action would in turn have reduced the power consumption greatly. Another solution would be to use smaller size pumps that would give the desired flows also at continuous use. This would also make the pumps smaller, which is desirable. This would however require that pumps would be available that effectively could produce flows of approximately zero to 70 ml/min for the air pump and zero to 20 ml/min for the methanol pump.

Having an air pump controller, which adjusts the airflow according to the fuel cell current, i.e. around 20 ml of air per 300 mA of fuel cell current, and a methanol pump controller, which adjusts the methanol flow according to the electrolyser current, would also reduce the current consumption of the pumps. Another option is to remove the air pump and use a free-breathing fuel cell structure. The free-breathing structure is better if feasible, since the air pump naturally consumes power and the total power consumption would be lower if the pump could be omitted.

On the other hand an air pump will be needed if the system is put into a small size mobile time extension device, where free air circulation might be hard to achieve.

The Asus EEE PC laptop computer charging voltage is 19 V, and the power consumption is 8-36 W, which is very high compared to the 1.5 W power target of the prototype system. Therefore a decent mobile time extension cannot be provided with the current fuel cell – electrolyser system. The designed control system on the other hand is capable of recharging also the laptop or other higher power load devices with only minor changes to the parameters if the hardware would be replaced to provide a higher power or at least a higher voltage. A higher voltage, and thus a possibility to charge the laptop, could be achieved with the current system. This could be done using a secondary temporary source, e.g. a supercapacitor that would be charged by the current system and a secondary DC/DC converter after this supercapacitor, which would lift the voltage from 5 V to the 19 V required to charge the laptop. Nineteen volts is however required only if one needs to charge the laptop battery using the normal charging connector. The laptop battery itself has a nominal voltage of 11.25 V, so mobile time extension could be achieved already at this voltage. A hardware modification would however be needed to allow for connecting the mobile time extender system directly to the battery. This approach would also make it impossible or at least hard to use the same mobile extender with other laptop computers. Additionally, since the power of the current system is low a better solution would be to build a fuel cell – electrolyser system with a higher net power and use the same control system to control it.

The target device for the designed system, i.e. a Nokia Navi 5230 mobile phone, has a nominal voltage of 3.7 V and the power consumption is between 0.16 mW and 2.37 W. The average power is somewhere between these values depending on how the mobile phone is used. As the purpose of the system is to extend the mobile usage time, the average power provided by the fuel cell – electrolyser system does not need to be very high.

According to the system tests the average current output of the system is 20 mA at 3.7 V, i.e. 70 mW. Depending on how the user uses the phone this might be lower or higher than the average consumption of the mobile phone. If the phone is used a lot in high power modes, e.g. talking and surfing the Internet, the mobile time extension will not be so long. If we assume an average consumption of 190 mA, which is the case if the phone is used for talking approximately half of the time, then the mobile time will be increased only from seven to eight hours, i.e. the mobile time extension is one hour of seven, or 14%. On the other hand, if the phone mostly has keys locked and backlight off, then the mobile time extension can even be as long as there is methanol left in the system, assuming that the power consumption of the mobile phone is distributed evenly enough.

The DC/DC conversion efficiency was rather high in the system, around 75%. It was noticed that it is more efficient to use a larger amount of DC/DC converters as long as the current is higher than 260 mA. If the current to the DC/DC converter is very low and does not have high current peaks, as might be the case when it is supplied only by a fuel cell, it might be more efficient to use a smaller amount of DC/DC converters. As the voltage losses in the system are something around 10-15%

the total electrical system efficiency is between 60% and 70%. Using a higher voltage on the voltage bus to reduce the conduction losses in a low voltage system would however not be beneficial according to the calculations done in appendix C.

In the tests the needed start-up energy was found to be below 100 mAh, which was less than expected, since the electrolyser current was smaller than expected. This was probably caused by the internal resistance of the battery, which did not allow for a faster discharge rate. The small start-up energy requirement means that a very small capacity rechargeable battery could be used in as start-up source in future systems even when self-discharge, aging effects, etc. are taken into consideration.

In this prototype system the purge valve was manually controlled, but for a commercial system it should be controlled by the control system. One good option would be opening the purge valve according to the integrative amount of current drawn from the fuel cell. This would cause the purge valve to be closed at start-up, when the fuel cell is not under load, and open the purge valve increasingly often at higher loads when there actually is water that needs to be removed.

The measurement accuracy of the prototype system could be improved around 5 mV if differential measurements would be used instead of single ended measurements. This would however require that double the amount of analog input channels would be used, which might not be possible if a smaller prototype is built.

The question of how small the hydrogen store between the electrolysers and the fuel cell could be was never answered in the tests, since the size of the prototype electrolysers and the fuel cell required rather long pipes between the electrolysers and the fuel cell. The volume of the hydrogen pipes and the silica gel column and the large internal volume of the fuel cell created a large enough hydrogen buffer for any hydrogen shortage phenomena to be visible.

The size of the prototype system could be made smaller with different improvements. The most important one is choosing all components to be of the minimum size that fills the requirements for the power output of the system. This involves all the electrical components, the microcontroller used for the control system, as well as the pumps. The size of the methanol system could be greatly reduced if one could use 100% methanol that would be mixed with water in the system to provide the needed 4-8% aqueous methanol solution to the electrolysers. This would require a good method for mixing the methanol with the right amount of water. Additionally, water created in the fuel cell would have to be recycled to the methanol system. Otherwise there is not enough water for the electrolysis reaction. If this cannot be done a maximally 69% methanol solution can be used, since it contains enough water in itself. The methanol pump could be omitted if a system as the one by Meng and Kim (2009) could be implemented, in which a hydrophobic nanoporous membrane and carbon dioxide bubbles created in the electrolysis are used to create a methanol flow, which is proportional to the electrolysis current. Their solution is orientation independent, which is beneficial, but requires that the channels are thin enough for micro capillary effects to take place. On the other hand, if the electrolysers and the fuel cell could be stacked into a single

stack, then their volume would also be much less. This might however require an innovative solution for removing liquid coming from the electrolysers before it enters the fuel cell.

6 Summary

In this work a test bench for a fuel cell – electrolyser system was further developed and a control system was designed on the basis of the experience gathered during the construction and testing of the previously built system. The designed system is unique in the sense that no system using a methanol electrolyser with a hydrogen fuel cell was found in literature. The main problems with the previous system were the low efficiency of the DC/DC converters, the leakage of hydrogen from the fuel cell, and the modular electrical system, which caused larger conduction losses than an integrated system would have (Viitanen, 2010). There were also some problems with drying of the fuel cell membrane at higher loads.

Firstly, the new system improves the electrical efficiency by making the fuel cell – electrolyser part of the system passive and using the converters only to lift the voltage to the level required by the load. The used DC/DC converters have a higher efficiency than the ones used in the previous prototype. The fuel cell – electrolyser system could be made passive since the amount of electrolyser cells is one and a half times the amount of cells in the fuel cell stack, while the active areas of the single cells are roughly the same, which makes the voltages directly compatible. This also means that one cannot control the hydrogen production or the fuel cell voltage directly, but higher system efficiency compensates for the lack of control.

Secondly, the fuel cell has been replaced which effectively reduces the hydrogen leakage. It was however noted in the tests that there is a small hydrogen leak also in the new fuel cell or somewhere in the modular hydrogen system. This was observed since the maximal pressure that was measured with the pressure sensor was only around 1 mbar. Another indicator is that though the fuel cell purge valve was closed and there was no load connected to the fuel cell, the fuel cell voltage did not rise as high when using a low electrolyser current, as when using a higher electrolyser current. The drying of the membrane with the new fuel cell has not yet been investigated. The minimum size of the hydrogen buffer between the electrolysers and the fuel cell proved impossible to evaluate with the prototype system. This was due to the large buffering volume of all hydrogen pipes in the system, as well as the large internal volumes of the silica gel column and the fuel cell.

Thirdly, the electrical system has been kept modular despite the higher conducting losses, since a modular system is clearly easier to test and modify. The electrical efficiency of the system was now around 60-70%, since the DC/DC conversion efficiency was around 75% and the conduction losses were around 10-15%. Using a higher voltage on the voltage bus to reduce the conduction losses was also considered, but according to the calculations done in appendix C this would not be beneficial. The conduction losses would be clearly less in an embedded system due to shorter wire lengths and no need to use screw terminals and other connectors with a rather high resistance. An embedded control system could easily be constructed on the basis of the now implemented control system and the modules built.

According to the system tests the designed control system is capable of automatically performing start-up, mobile time extension duties, and controlled shutdown. The now designed system is low

power, but the control system could also be used to control mobile time extension duties of a higher power fuel cell – electrolyser system. This would require only minor changes to parameters and allow e.g. for charging the battery of a laptop computer or other higher power mobile device.

The average current output of the system is 20 mA at 3.7 V according to the tests. This might be lower or higher than the average consumption of the mobile phone depending on how the user uses the phone. The mobile time extension will not be so long if the phone is used a lot in high power modes, e.g. talking and surfing the Internet. For example if the phone is used for talking approximately half of the time this gives an average consumption of 190 mA, which would cause the mobile time to increase only from seven to eight hours, i.e. the mobile time extension is one hour of seven, or 14%. On the other hand, the mobile time extension can even be as long as there is methanol left in the system, assuming that the power consumption of the mobile phone is distributed evenly enough. This can be the case if the phone mostly has keys locked and backlight off. It should also be remembered that the mobile time extension will be longer when the leak in the hydrogen fuel cell has been fixed, as the average power produced by the system will be higher.

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8 Appendices

A. Basic fuel cell types

Alkaline fuel cells (AFCs) have been historically important as they have powered and provided drinking water for the Apollo and Shuttle spacecrafts. They operate at 50-200°C, sometimes at high pressures, mainly use potassium hydroxide as the electrolyte, have porous electrodes and can achieve efficiencies up to 70%. (Ortiz-Rivera et al. 2007, p. 120) Additional advantages are quick start-up, no corrosion problems, low weight and volume as well as lower cost because of the small amount of catalyst needed (Andújar and Segura 2009, p. 2318). The main problem is that they are very sensitive to carbon dioxide and therefore need to use pure oxygen and hydrogen as fuels (Ortiz-Rivera et al. 2007, p. 120). Other problems are a relatively short lifetime and the liquid electrolyte that causes handling problems (Andújar and Segura 2009, p. 2318).

Phosphoric acid fuel cells (PAFCs) have developed more slowly than other acid electrolyte fuel cells since the conductivity of phosphoric acid is low. The electrolyte in use is liquid phosphoric acid and the temperature is around 230°C to boost the reaction. The advantages over sulphuric acid fuel cells are that phosphoric acid is not electrochemically reduced when the cell is operating, and the PAFCs can run on air, instead of oxygen. The efficiency of PAFCs is more than 40%, and if also the heat is collected as in combined heat and power (CHP) systems, the efficiency can be almost 85%. Another advantage is that this type of fuel cell tolerates carbon monoxide concentrations up to 1.5% and therefore it can use impure hydrogen as fuel. (Ortiz-Rivera et al. 2007, p. 120) According to Larminie and Dicks (2003, p. 15) the fuel can be produced by reforming natural gas, e.g. methane, though it increases the size, cost and complexity of the fuel cell system. Disadvantages with PAFC are that they use a liquid electrolyte, causing handling and safety problems, are big and heavy, and have a longer start-up time than e.g. PEM fuel cells because of the higher operation temperature. (Andújar and Segura 2009, p. 2320) However, Larminie and Dicks (2003, p. 15) as well as Ortiz-Rivera et al. (2007, p. 120) point out that phosphoric acid fuel cells are one of the few widely commercially available fuel cell technologies today, and that hundreds of PAFC systems are in use around the world. According to Larminie and Dicks many PAFC systems in use are producing 200kW of electric power, and some additionally 200kW as heat energy.

The electrolyte in **molten carbonate fuel cells** (MCFCs) is a molten carbonate salt mixture that is retained in a chemically inert porous material. The MCFCs operate at temperatures around 650°C and require carbon dioxide and oxygen to work. Since they use carbon dioxide they can use various fuels, e.g. hydrogen, carbon monoxide, natural gas, propane, landfill gas and marine diesel. (Ortiz-Rivera et al. 2007, p. 119) Advantages with MCFCs are that nickel, a relatively low-cost catalyst, can be used since the temperature is high, and the fuel can be internally reformed. (Larminie and Dicks 2003, p. 16) Other advantages caused by the high temperature are high-speed reactions and heat generation, the latter which can be used in combined heat and power systems. On the other hand preheating is needed before the system can work. Additionally, the electrolyte is highly corrosive which puts demands on the materials used, increasing the cost. Though the

MCFCs can use various fuels, sulphur intolerance is a major problem. In spite of the disadvantages, high efficiency can be achieved using molten carbonate fuel cells. (Andújar and Segura 2009, pp. 2316-2317)

Solid oxide fuel cells operate at temperatures around 1000°C and use a solid ceramic non-porous compound as electrolyte. They are used e.g. in stationary applications and vehicles to provide auxiliary power. (Ortiz-Rivera et al. 2007, p. 120) The very high temperature eliminates the need for external fuel reformers and expensive metal catalysts, and provides high reaction rates giving high efficiency, especially in combined heat and power systems, as well as higher current densities than with molten carbonate fuel cells (Andújar and Segura 2009, pp. 2317-2318). Because of the high temperature the start-up is slow, pre-heaters for fuel and air are needed, and the cooling system is complex. Additionally the ceramic electrolyte is fragile and expensive to manufacture. As Larminie and Dicks (2003, p. 16) state: “each fuel cell type solves some problems, but brings new difficulties of its own”.

Other promising fuel cell types are **protons ceramic fuel cells** (PCFCs) and **direct borohydride fuel cells** (DBFCs). Protons ceramic fuel cells use fossil fuels, a ceramic electrolyte and high temperatures, which give the same benefits as other high temperature fuel cells. On the other hand, direct borohydride fuel cells use highly alkaline sodium borohydride as a fuel and sodium borate as an additive, which makes the fuel cell more resistant to carbon dioxide. (Andújar and Segura 2009, p. 2321) However, according to Larminie and Dicks (2003, p. 300) the cost of producing hydrogen using sodium borohydride is approximately 470€ per kilogram of hydrogen. Therefore, both protons ceramic and direct borohydride fuel cells give certain benefits, but only time will tell if they will succeed or not.

In this section basic fuel cell types have been introduced. All of them have their own advantages and disadvantages, making some of them more useful for certain applications. High temperature fuel cells are typically large and are used in stationary applications to provide both electric power and heat. The smaller, low temperature fuel cells are mostly developed for mobile applications since they are relatively small and light, while possessing a higher energy density than e.g. batteries.

B. Virtual instruments and variables in the LabVIEW control system

In this section short descriptions of the LabVIEW virtual instruments (Vis) used in the designed control system are presented.

Windows side virtual instruments

Controller.vi:

Controller.vi is the main program of the control system. The control system is used through its user interface. Controller.vi is running on the windows operating system on the personal computer and is used for changing parameters, controlling execution, e.g. loop timing, logging data to disk, and monitoring the system through graphs, LED indicators and displayed numerical values.

DataLogging.vi

Used to log the data onto disk by writing the data from LabVIEW into .tdms-files. Also used for displaying the dialog asking the user to give a filename for the logged data, and for giving names to the logged data channels. The tdms-files can be opened with Microsoft Excel using the TDM Excel Add-in. The plugin is available at http://zone.ni.com/devzone/cda/epd/p/id/2944. With the add-in installed right-click the .tdms file and choose: “Open with: Excel importer”.

ShowHide*.vi:s

Used for making the user interface more intuitive by disabling controls that cannot be used in the current state. The control system is not dependent on them to work.

Virtual instruments running on the microprocessor

AnalogInput.vi

Used for fetching the data from the analog inputs on the FPGA to the microprocessor. It also converts the data from the fixed-point format used by the FPGA into the double format used by the microprocessor.

BatteryVoltage-Measurement-TimingLogic.vi

This is currently switched off since the fuel cell load varied too much when the battery was disconnected. One solution would be to disconnect also the FC when the battery voltage is measured. The terminal voltage of a battery being charged is higher than the terminal voltage will be when the battery is disconnected from the power source. Therefore this virtual instrument calculates when to charge and when to measure the voltage of the battery given the period, the off time, the measuring time, and the measurement interval. The measuring interval has to be during the off time for this logic to work.

ConverterEfficiency.vi

Calculates the efficiency of the DC/DC converter.

DC-DC-Power.vi

Calculates the power input to the DC/DC converter.

Digital output.vi

It writes the values given by the control system to the digital outputs. It also contains logic that checks that all the digital outputs are turned off before the control system is shut off when the stop-button is pressed and the system is shutdown quickly.

ElectrolyserPower.vi

Calculates the power of the electrolyser.

ExternalSourceSafetyLogic.vi

The logic disconnects the external source from the rest of the system if it is connected and its voltage rises higher than the threshold value, i.e. the “External source disconnect voltage” defined in the user interface, and keeps it disconnected until the voltage has dropped 0.1 V below the threshold value. Also, the red “External source voltage too high” LED on the user interface is lit when the voltage of the external source is too high.

IsLoadCurrentZeroForMoreThan10s.vi

Sub virtual instrument to the ModeSelect.vi. Is a timer used to check if the load current is zero for more than ten seconds, or any other time that is set for the timer. The real time is a bit longer, since there is an approximately two second long delay when the timer is restarted for some unknown reason. The timer starts in when the load current falls below zero, e.g. when the load is full and turns off charging or the charging cable is disconnected for some reason. The timer is reset when the current is greater than zero or the mode is changed to any other mode than the charge load mode. When the timer runs out it displays a message to the user of what happened.

IsTheFuelCellCurrentNegative.vi

Checks if the fuel cell current is flowing in the wrong direction.

LoadPower.vi

Calculates the load power. The load power is negated as the load consumes the power.

ManualModeSwitching.vi

If manual mode is on this block reads the manual switches and outputs the values to the DigitalOutput.vi. If manual switching is off it only forwards the existing values.

ModeActions.vi

Handles which outputs and indicators are set in the different modes. A thorough description can be found in section 3.3.1.

ModeSelect.vi

Implements the logic for the transitions between the different modes of the control system. A thorough description can be found in section 3.3.1.

PressureSensorVoltage-To-Pressure.vi

Converts the voltage signal from the pressure sensor into a pressure value in pounds per square inch (psi).

PumpTiming.vi

Calculates when the pump is one given the period and the active time. If the active time is longer than the period, then the pump is continuously on.

PurgeControl.vi

Calculates when the purge valve is open given the period and the active time. If the active time is longer than the period, then the purge valve is open continuously. Also contains logic for manually controlling the purge valve.

RealTimeController.vi

The main software component on the microprocessor side. Inherits the user interface from the Controller.vi. Uses the sub-vi:s to read from inputs and write to outputs, perform calculations and switch between modes.

RechargeStartupSource.vi

Sets different outputs depending on the start-up source used. The BatteryVoltageMeasurementTimingLogic.vi is a sub-vi to this virtual instrument.

RechargeTemporarySource.vi

Same as RechargeStartupSource.vi, but for the temporary source.

SignalMergeAndGraphing.vi

Collects and merges the voltage, current, power, DC/DC converter efficiency, and pressure sensor signals that are displayed on the user interface and logged. However, the digital output indicators are not merged here since they are logged separately in the DataLogging.vi.

SOC-Mapping.vi

Takes the current voltage of the battery or capacitor as well as the defined voltage limits for when the battery or capacitor is empty and fully charged, and maps the current value into a state of charge value, i.e. a value between zero and one, where zero is empty and one is fully charged. The mapping is done using linear interpolation and values outside the range are mapped to the end of the range, i.e. voltages lower than the empty voltage are mapped to the value zero and voltages higher than the full voltage are mapped to the value one.

StackPower.vi

Calculates the power produced by the fuel cell stack.

StartupSource-SOC.vi

Returns the state of charge of the current start-up source. If the external source was the start-up source, then the returned state of charge is one, which corresponds to fully charged, since external sources cannot be recharged, otherwise it is the value returned by the SOC-Mapping.vi.

TemporaryStore-SOC.vi

Same as StartupSource-SOC.vi, but returns the state of charge for the temporary store.

Virtual instruments running on the FPGA

FPGAIO.vi

FPGAIO.vi handles all the data reading and writing to and from the microprocessor as well as to and from the FPGA. Contains two loops, one for analog input and output, and another for digital input and output. The separate loops make it possible to use different data writing and acquisition rates for the digital and analog signals.

Variables used

Current mode

Keeps track of the current mode of the control system. Is needed for resetting the timer (IsLoadCurrentZeroForeMoreThan10s) checking if the load current has been zero for ten seconds.3

External voltage too high

If the voltage of the external source gets too high the variable is set and the red “External source voltage too high” LED is lit on the user interface, until the voltage drops 0.1 V below the threshold value.

ShutdownFast

Boolean variable that is set when the stop button is pressed. The setting of ShutdownFast makes the system quickly turn off all outputs and then stop the LabVIEW software.

Sleeping

Boolean variable that is set when the FPGA is put to sleep, and reset when the FPGA is awakened.

C. Wire resistance calculations

In this section power losses caused by wire resistances are calculated. The resistance in a wire can be calculated using equation (C.1)

$$R = \rho * \frac{l}{A} \quad \textbf{(C.1)}$$

, where *R* is the resistance, *ρ* is the resistivity of the conductor material, *l* is the length and *A* is the cross-sectional area of the conductor. The electrical power can be calculated from equation (C.2)

$$P = U * I \quad \textbf{(C.2)}$$

, where *P* is the power, *U* is the voltage, and *I* is the current. The voltage can be calculated using equation (C.3)

$$U = R * I \quad \textbf{(C.3)}$$

, where *U* is the voltage, *R* is the resistance, and *I* is the current. Since we want to estimate the change caused by using different voltages we calculate the current from the total power using equation (C.2). Combining equations (C.1), (C.2) and (C.3) we get the power loss in a wire due to the resistance. This can be expressed as equation (C.4)

$$P_{loss} = \rho * \frac{l}{A} * \frac{{P_{tot}}^2}{U} \quad \textbf{(C.4)}$$

, where P_{loss} is the total loss caused by the resistance and P_{tot} is the power throughput of the system. The resistivity of copper at 20°C is $1.68*10^{-8}$. Assuming total wire lengths of 10 meters for the test system and 2 meters for the embedded system, as well as the voltages and powers seen in table c.1, we get the results seen in the table. The losses above 20% are marked with red text and underlined, the losses between 10 and 5% are marked with light green text, and the losses below 5% are marked with dark green text and green fill. The values corresponding most closely to the values of the prototype system are inside the box in the table. On these rows we can see that thick enough wire, preferably with an area of 2 mm^2 or more, compensates even for large currents, while increasing the voltage would clearly decrease the current and thus also the losses.

Even for the cases with a voltage of 1.6 V the losses are below 10% or close to it, when not using the thinnest wire, which means that a very effective voltage conversion would have to be achieved for it to be beneficial. The use of a lower voltage and thicker wires is also motivated by the simplicity of the system. One should remember that the prototype system also has conduction losses caused by the connections at the screw and spring terminals. These would however not be

present in an embedded system, while their magnitude is very hard to predict for the prototype system.

It should be pointed out that the cross-sectional area of the wire in a real embedded system would be one or two orders of magnitude smaller than normal thin wire used for prototyping. The power loss using these very thin wires is calculated on the two last rows of table c.1, and it can be seen that the losses are large if wire of this thickness is used. However, the total wire lengths might be shorter for the real systems. Since the embedded system is planned to be on one circuit board, the total wire length might be as short as one meter or even shorter, which effectively would at least halve the losses. Additionally thicker wires could be used where it is known that the currents are larger, and thinner wires e.g. for the measurements wires, where the currents are very small. The benefits of boosting the voltage in the embedded system have to be reassessed when precise specifications for the system are available.

Table C.1: Power losses due to wire resistances. Power losses above 20% are marked with red text and underlined, the losses between 10 and 5% are marked with light green text, and the losses below 5% are marked with dark green text and green fill. The rows most important for the prototype system, which has a power of around 1.5 W, are inside the box. The two last rows represent circuit board wire, which is 0.61 mm wide and 35 µm thick.

Wire area (mm^2)	Wire area (m^2)	Voltage (V)	Power (W)	Current (A)	Total power loss test system (W)	Total power loss embedded system (W)	Percentual loss test system	Percentual loss embedded system
0,22	2,20E-07	1,6	1	0,625	0,2983	0,0597	29,83	5,97
0,40	4,00E-07	1,6	1	0,625	0,1641	0,0328	16,41	3,28
0,40	4,00E-07	3,3	1	0,303	0,0386	0,0077	3,86	0,77
0,22	2,20E-07	3,3	1	0,303	0,0701	0,0140	7,01	1,40
0,22	2,20E-07	1,6	0,5	0,3125	0,0746	0,0149	14,91	2,98
0,40	4,00E-07	1,6	0,5	0,3125	0,0410	0,0082	8,20	1,64
0,40	4,00E-07	3,3	0,5	0,1515	0,0096	0,0019	1,93	0,39
0,22	2,20E-07	3,3	0,5	0,1515	0,0175	0,0035	3,51	0,70
1,00	0,00	1,60	1,50	0,94	0,15	0,00	9,84	0,00
2,00	0,00	1,60	1,50	0,94	0,07	0,01	4,92	0,98
4,00	0,00	1,60	1,50	0,94	0,04	0,01	2,46	0,49
4,00	0,00	3,30	1,50	0,45	0,01	0,00	0,58	0,12
0,02135	2,14E-08	1,6	0,5	0,3125	0,7684	0,1537	153,69	30,74
0,02135	2,14E-08	3,3	0,5	0,1515	0,1806	0,0361	36,13	7,23

D. Pumping requirement calculations

The amount of air and methanol that needs to be pumped can be calculated using basic formulas, when the currents in the fuel cell and the electrolyser are known.

Methanol pump

The time it takes to use the methanol in an aqueous methanol solution can be calculated from the physical quantities. The formula for aqueous methanol electrolysis can be found in equation (D.1).

$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2 \quad \textbf{(D.1)}$$

What can be observed from the equation is that every mole of methanol produces three moles of hydrogen. The mass of pure methanol in the aqueous methanol solution can be calculated using equation (D.2)

$$m_{CH_3OH} = \rho_{CH_3OH} * V_{tot} * \alpha \quad \textbf{(D.2)}$$

, where m_{CH_3OH} is the methanol mass, ρ_{CH_3OH} is the density of methanol, V_{tot} is the total volume of the solution, and α is the volume fraction of methanol in the solution. The amount of substance can be calculated from the mass using equation (D.3), where *n* is the amount of substance, *m* is the mass and *M* is the molar mass.

$$n = \frac{m}{M} \quad \textbf{(D.3)}$$

The hydrogen amount of substance is three times the methanol amount of substance as previously explained. Also, as can be seen in equation (D.4) every mole of hydrogen releases two moles of electrons.

$$2\mathrm{H2} \rightarrow 4\mathrm{H} + + 4\mathrm{e}^- \quad \textbf{(D.4)}$$

As every mole contains 6.0221367E+23 electrons and the elementary charge is 1,6021773E-19 Coulombs, the total charge, *Q*, can be calculated according to equation (D.5), where N_A is the amount of electrons per mole, n_{CH_3OH} is the substance amount of methanol, *e* is the elementary charge, and the constants 3 and 2 are how many moles of hydrogen are produced per mole of methanol and how many electrons are produced per mole of hydrogen, respectively.

$$Q = N_A * n_{CH_3OH} * e * 3 * 2 \quad \textbf{(D.5)}$$

Assuming a constant current, *I,* one can calculate the time it takes for the fuel cell to use all the hydrogen that is produced if all methanol is electrolysed using equation (D.6), where *t* is the time, *I* is the current, and *Q* is the total charge.

$$t = \frac{Q}{I} \tag{D.6}$$

Combining equations (D.1) to (D.6) we get an expression, see equation (D.7), for the time in seconds it takes to use all methanol in the solution.

$$t = \frac{N_A * e * \rho_{CH_3OH} * V_{tot} * \ \alpha * 6}{I * M_{CH_3OH}} \tag{D.7}$$

Using e.g. a 100 ml (= 100cm^3) solution of 5 volume-% of methanol and a current of 0.6 amperes:

$$t = \frac{6.0221367 * 10^{23}\ mol^{-1} * 1.602173 * 10^{-19} C * 0.79 \frac{g}{cm^3} * 100\ cm^3 * 0.05 * 6}{0.6\ A * 32.04 \frac{g}{mol}}$$

, we get a time of more than 33 hours. When using three electrolysers with a current of 0.6 A, as is done in the prototype system, 100 ml methanol will last for more than 11 hours.

To approximate the pumping requirements we assume that the internal volume of a single electrolyser is around 5 ml, the current is 0.6 A, and the methanol concentration is 5 vol-%. According to equation (D.7) the methanol in this solution should last for 1.65 hours, which equals roughly 100 minutes. However, since the electrolysers are connected in series, to be able to use only one pump, the total internal volume of the electrolysers and the tubes between them is larger, while the total current used for electrolysis is three times larger. The first electrolyser gets fresh aqueous methanol solution, while the second gets used solution and the third two times used solution. Since all electrolysers should be supplied with strong enough aqueous methanol solution the flow has to be larger than for a single electrolyser.

For example, if we let the methanol be only 2 minutes in a single electrolyser the amount of methanol drops close to 2 percentage units per electrolyser, giving at least 94% of the amount of methanol at the output of the third electrolyser compared to the input amount to the first electrolyser. To achieve this all aqueous methanol solution in the first electrolyser has to be replaced in two minutes. If we assume an internal volume of 5 ml the flow has to be at least 2.5 ml/min. According to the methanol pump test, see section 4.2.2, this can be most effectively achieved using a supply voltage of 5 V with a flow of 15.6 ml/min and a duty cycle of 16%, or with a supply voltage of 3.3 V with a flow of 20.34 ml/min and a duty cycle of 12.3%.

With these duty cycles and a current consumption of 10 mA when the pump is not working, we get an average power consumption is 59 mW using 3.3 V and 80.7 mW using 5 V. Since the measurements were done with a circuit board that has a higher current consumption in off state than the one that will be used for the prototype system, the average power consumption of the

methanol pump will be somewhat less. On the other hand, the currents and powers in the prototype system might be higher than according to this test, since the counterpressure caused by the three electrolysers is probably higher than the counterpressure in the test and the pump might have to work harder.

Air pump

The needed amount of air can be calculated from the basic equations. We know that the total charge is calculated as the current multiplied with the time according to equation (D.6) and that the charge also can be expressed as in equation (D.8)

$$Q = x * e \tag{D.8}$$

, where *Q* is the charge, *x* is the number of electrons and *e* is the elementary charge. Expressing the amount of electrons in moles we get equation (D.9)

$$Q = y * N_A * e \tag{D.9}$$

, where *y* is the amount of electrons in moles and N_A is Avogadro's constant, i.e. 6.0221367E+23. The fuel cell reaction of a H2-PEM fuel cell can be found in equation (D.10) and shows that we need 4 moles of electrons for each mole of oxygen.

$$O_2 + 4e^- + 4\mathrm{H} \rightarrow 4\mathrm{e}^- \tag{D.10}$$

If we use many cells in the stack the air usage is multiplied with the amount of cells. If we combine this fact with equations (D.6), (D.9) and (D.10), we get an expression, see equation (D.11), for the amount of oxygen needed

$$z = \frac{I * t * n}{e * 4 * N_A} \tag{D.11}$$

, where z is the amount of oxygen needed counted in moles, *I* is the used current, *t* is the time in seconds, *n* is the amount of cells in the fuel cells stack, *e* is the elementary charge, $1.6*10^{-19}$ Coulombs, *4* is the amount of electron moles we need for each oxygen mole, and N_A is Avogadro's constant, $6.02*10^{23}$, i.e. how many particles there are in a mole of substance. Since there is 20.946% of oxygen in the atmosphere we must use roughly five times more air than oxygen. If we add this to the formula we get equation (D.12).

$$w = \frac{I * t * n * \frac{100}{20.946}}{e * 4 * N_A} \quad \textbf{(D.12)}$$

Since we want to know the volume of air we need we combine equation (D.12) with equations (D.2) and (D.3) and get equation (D.13)

$$V = \frac{M}{\rho} * \frac{I * t * n * \frac{100}{20.946}}{e * 4 * N_A} \quad \textbf{(D.13)}$$

, where *V* is the air volume needed, *M* is the molar mass, and *ρ* is the density of air. Using e.g. a current of 1 A, a two cell fuel cell stack, and a time of one minute, we get V = 33.26 ml/min. This is the absolute minimum amount of air required for the fuel cell to work. Usually at least twice the amount of air is used (Larminie and Dicks, 2003, p. 397). Twice the amount would be 66.52 ml/min. It should be remembered that higher currents or using more cells in the fuel cell stack increases the amount of air needed.

E. Additional graphs

This section contains additional graphs for the reader who wants to examine the test results more carefully.

Laptop tests

The additional results of the laptop charging and current consumption tests will be presented here.

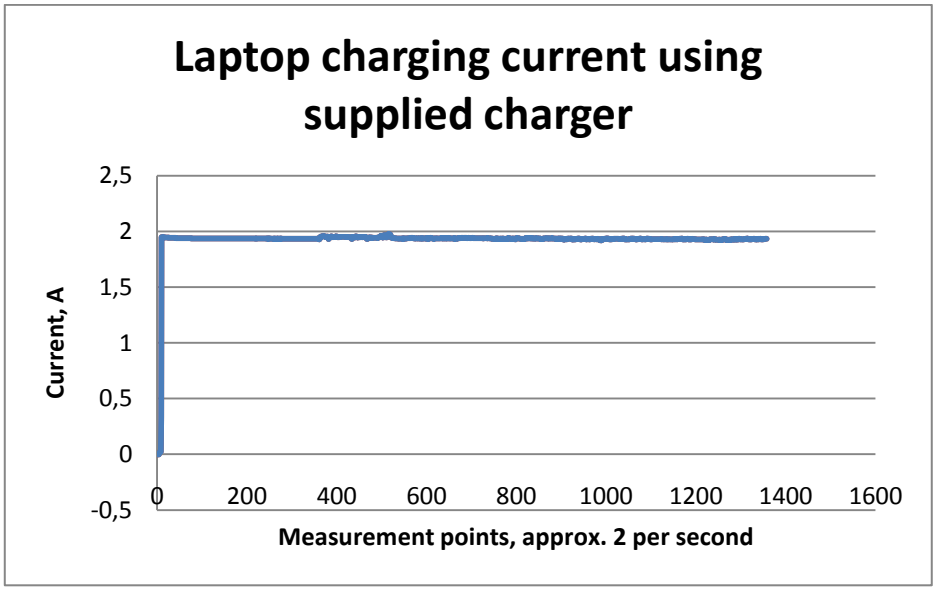

Figure E-1: Charging current using charger supplied with the Asus EEE PC laptop computer.

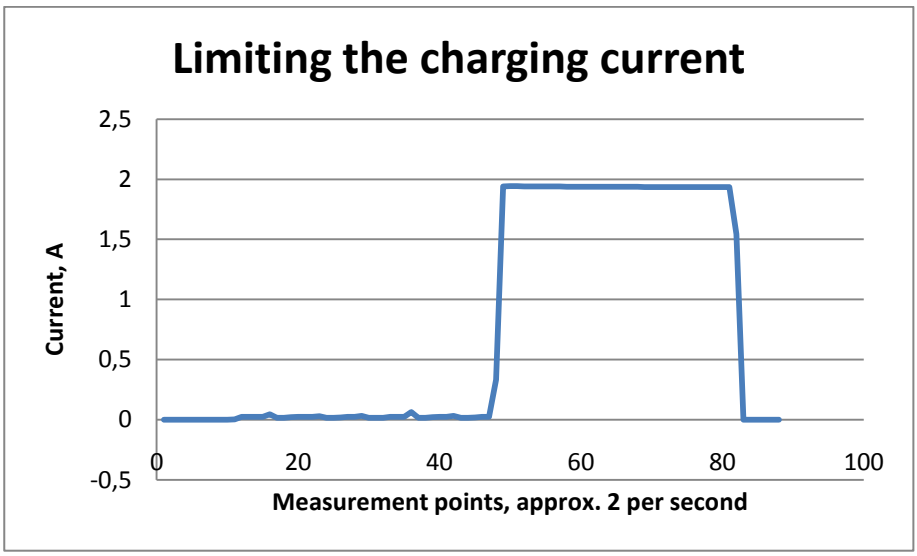

Figure E-2: Charging the laptop battery while limiting the current is not possible.

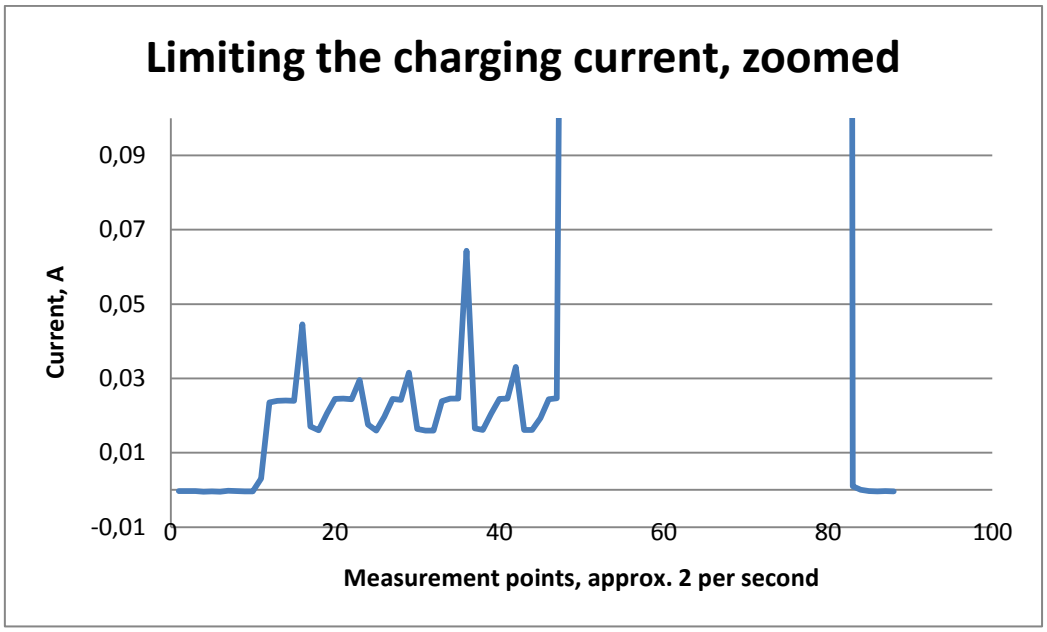

Figure E-3: A zoomed version of the test where the charging current was limited. It can be clearly noted that the device tries to charge, but the charging does not start until the current limit on the power supply is high enough.

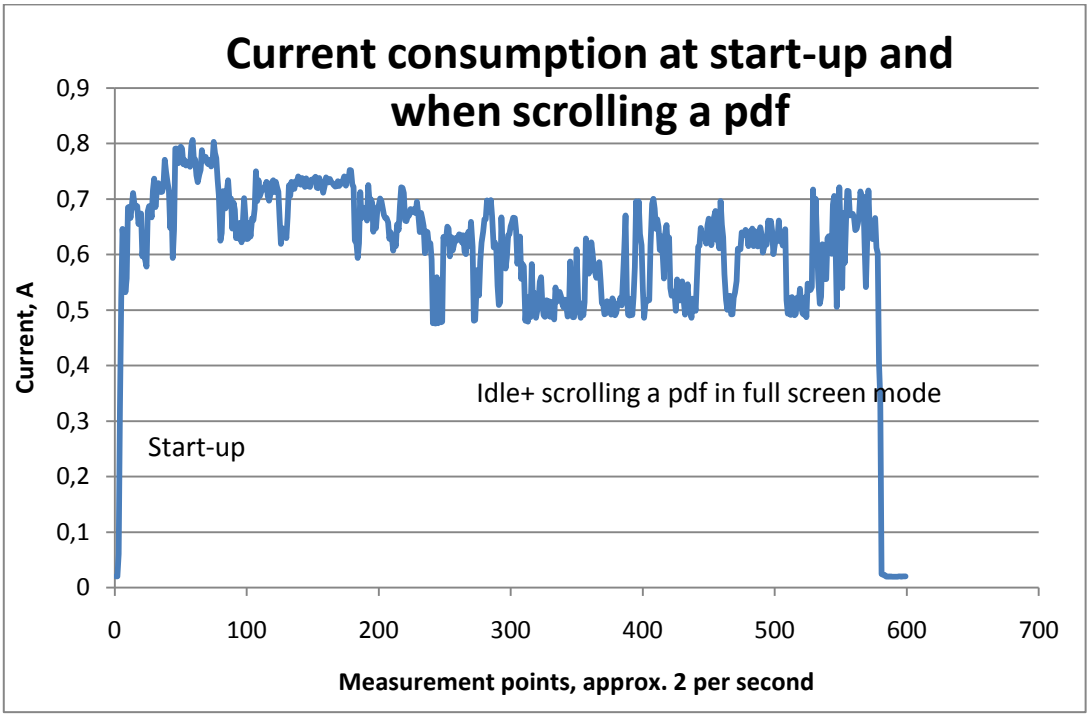

Figure E-4: Current consumption when at start-up of the laptop computer and when scrolling a pdf file in full screen mode.

Mobile phone tests

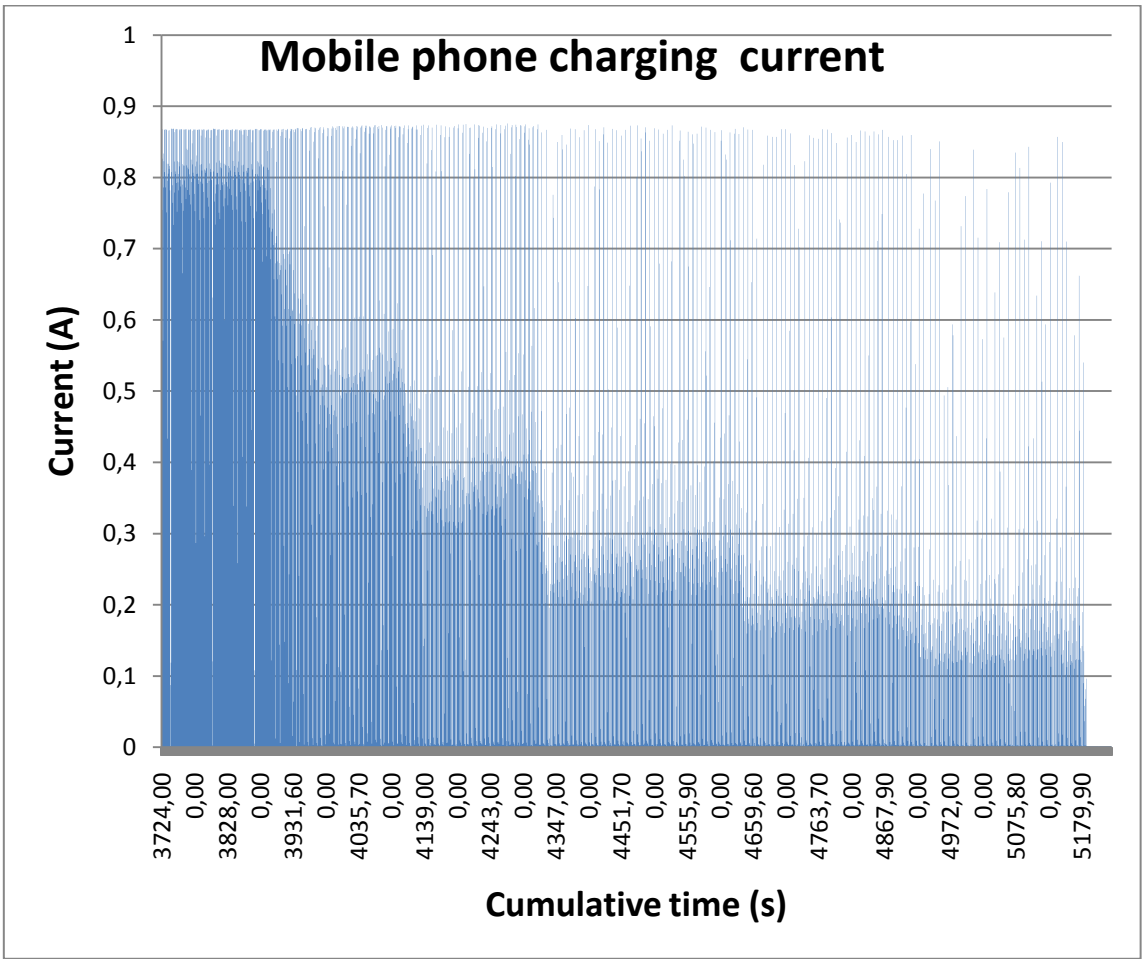

Figure E-5: Mobile phone charging current when the phone was charged for the first time. Toward the end of the charging the current is pulsing, which indicates that the battery in the mobile phone is approaching fully charged state.

F. Microcontrollers alternatives

This section presents some microcontrollers that could be used in the next iteration of the control system. It should be noted that the list is very limited and the microcontroller development is fast, which might render the list unusable after some time.

Arduino

- Programmed in wiring based language (syntax+ libraries), similar to C++ with some simplifications and modifications and a Processing-based IDE
- Idle current 20 mA at 16 MHz before sleep without external devices (http://www.arduino.cc/playground/Learning/ArduinoSpecs)
- Power supply 5V USB or 7-35 VDC external
- 2.1 x 2.95 inches (5.3x7.5 cm)
- Features:
    - Open-source electronics prototyping platform
    - 8-bit Atmel AVR processor and on-board IO
- Accessory hardware
    - Ethernet
    - ZigBee
    - TouchScreen
    - Datalog
    - USBHost
    - WiFI
    - etc.

C stamp

- Programmed in C
- Current draw 19mA at 5V and 40 MHz, 0.7uA at sleep, without external devices (http://www.c-stamp.com/CS110000.htm)
- Power supply, 5-24 VDC external
- Size 2.4x1.1x0.4 inches (6.1x2.8x1cm)
- Features:
    - 41 pins + 2 dedicated serial
    - PWM
    - Serial communication
    - I2C-communication
    - Hobby servo pulse trains
    - Pseudo-sine wave frequencies
    - Clock
    - I/O pins 41 + 2 dedicated serial (More than any BASIC stamp)
    - Programming interface, MPLAB IDE (v7.22 and up), Serial (57600 baud)

  - EEPROM data size 1 Kb, 2Kb RAM, scratch pad RAM 2Kb.
  - Program memory size 32Kb
  - 2 D/A converters (10 bits), 12 A/D converters (10 bits)
  - Floating point numbers support

PICAXE

- Programming done using Programming Editor or AXEpad editor, which is a free software supporting all operating systems.
- Programming Editor software includes a comprehensive line by line on-screen simulation, which can be used for debugging, of the BASIC like program
- Current draw 18-153uA (PIC12F629 model) without external devices
- Power supply 1.8-5V VDC (M2 series)
- Features:
  - 8-40 pins
  - 128-4096 byte EEPROM program memory (40-1000 lines of code)
  - Programs downloaded to device using USB or RS-232 serial connection
  - Can be connected to LCDs serially as long as baud rate is supported
  - Digital outputs for each sink/source can be around 20mA (up to 200mA for some chips)
  - Analog inputs (amount and resolution depending on type)
- Accessory hardware
  - ZigBee
  - I2C-bus
- To observe
  - Analog outputs not available directly
  - Can however be generated using PWM and external circuitry

PIC microcontroller

- Programmed in C
- Current draw 75-275 µA/MHz in run mode depending on model, 20-30 nA during sleep. (http://www.microchip.com/en_us/technology/xlp/products.html)
- Features
  - Floating point numbers support