DOCTORAL THESIS IN CHEMICAL ENGINEERING

Fuel Cells and Biogas

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Till familj och vänner
De jag lever genom

Till Marita och Ellen
De jag lever för
Fuel Cells and Biogas

ABSTRACT

This thesis concerns biogas-operated fuel cells. Fuel cell technology may contribute to more efficient energy use, reduce emissions and also perhaps revolutionize current energy systems. The technology is, however, still immature and has not yet been implemented as dominant in any application or niche market. Research and development is currently being carried out to investigate whether fuel cells can live up to their full potential and to further advance the technology. The research of thesis contributes by exploring the potential of using fuel cells as energy converters of biogas to electricity.

The work includes results from four different experimental test facilities and concerns experiments performed at cell, stack and fuel cell system levels. The studies on cell and stack level have focused on the influence of CO, CO2 and air bleed on the current distribution during transient operation. The dynamic response has been evaluated on a single cell, a segmented cell and at stack level. Two fuel cell systems, a 4 kW PEFC system and a 5 kW SOFC system have been operated on upgraded biogas.

A significant outcome is that the possibility of operating both PEFCs and SOFCs on biogas has been established. No interruptions or rapid performance loss could be associated with the upgraded biogas during operation. From the studies at cell and stack level, it is clear that CO causes significant changes in the current distribution in a PEFC; air bleed may recover the uneven current distribution and also the drop in cell voltage due to CO and CO2 poisoning. The recovery of cell performance during air bleed occurs evenly over the electrode surface even when the O2 partial pressure is far too low to fully recover the CO poisoning. The O2 supplied to the anode reacts on the anode catalyst and no O2 was measured at the cell outlet for air bleed levels up to 5 %.

Reformed biogas and other gases with high CO2 content are thus, from dilution and CO-poisoning perspectives, suitable for PEFC systems. The present work has enhanced our understanding of biogas-operated fuel cells and will serve as basis for future studies.

Language: English

Keywords: air bleed, biogas, carbon dioxide, carbon monoxide, current distribution, dilution, efficiency, energy conversion, energy systems, experimental, fuel cell, fuel cell systems, PEFC, poisoning, reformate, SOFC
PAPERS REFERRED TO IN THIS THESIS

The work presented in this thesis is based on the following papers, referred to in the text by their Roman numerals, and appended at the end of the thesis.

I. Key Factors in Planning a Sustainable Energy Future Including Hydrogen and Fuel Cells
Cooperation between all listed authors, it was shared responsibility for planning and execution.

II. Operating Experience and results from 3310 hours of operation of a biogas-powered 5 kW SOFC system in GlashusEtt
I was the main author and had the responsibility for planning, implementation and evaluation of the studies performed as well as writing the paper.

III. Description and modelling of the solar-hydrogen-biogas-fuel cell system in GlashusEtt
I was one of two main authors, and was responsible for planning and implementation of the experiments; together with Maria Saxe and Nicklas Holmström I evaluated and analysed the data collected from the system.

IV. Experimental results from a 5 kW PEM fuel cell stack operated on simulated reformate from highly diluted hydrocarbon fuels: Efficiency, dilution, fuel utilisation, CO poisoning and design criteria
Co-written together with Thomas Tingelöf.

V. The influence of CO₂, CO and air bleed on the current distribution of a polymer electrolyte fuel cell
Co-written together with Thomas Tingelöf. Nicklas Holmström provided indispensable assistance and guidance during the experiments.
Exploring the Possibilities of SOFC Systems Operated with Biogas - In Light of Results from Operation of a 5 kW Combined Heat and Power Unit

Operating experience and energy system analysis of the biogas-powered 5 kW SOFC system in GlashusEtt

Development of Hydrogen and Fuel Cell Technologies in a Large-Scale Lighthouse Project
A conceptual study that was commissioned by the Directorate-General for Energy and Transport and performed within a team of nine partners, coordinated by AF. Available at: www.hfpeurope.org/hfp/jti_archive, July 2006.

Analysis of the dilution and poisoning effects of high CO₂ concentrations at the anode of a PEFC
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1 INTRODUCTION

1.1 Setting the scene

It’s hard to imagine a world with no energy demand. The global energy demand has increased alongside human evolution, and even if some studies now indicate that the bond between increased GDP and energy consumption potentially may be broken, the global energy use is still increasing. Historically, increased use of energy has been followed by benefits such as improved health, longer life, increased literacy, easier travel etc., but current energy use also comes with negative effects such as emissions, environmental problems, deforestation, collapsing ecosystems, undesired climate effects etc., problems which are being addressed at all levels, all over the world. Road maps and targets are set up in unions, countries and regions. Many centres of excellence and researchers from all fields are engaged in finding solutions that will take us into a more sustainable future. Research topics include reduced use of fossil fuels, reduction of emissions, increasing energy efficiency, reducing demand, introduction of new, better, cleaner technologies and much much more. Efforts are made with the intention of enabling continued energy use with less negative external effects.

No one knows exactly how severe our current situation is, the many external effects of using fossil fuels make predictions and estimations difficult and the total extent is not easily quantifiable, see e.g. Stern (2006) or ExternE (2005). Most researchers, organizations and institutions do however agree that it would be beneficial to implement and develop less polluting technologies. Fuel cells have, for a few years now, been interesting in that perspective.

Fuel cell technology has the potential to contribute to a more efficient energy use, reduce emissions and also perhaps revolutionize current energy systems. The technology is, however, still immature and has not yet been implemented as the dominant technology in any application or niche market. Research and development is currently being performed in order to investigate whether fuel cells can live up to their full potential and to further advance the technology. This thesis should be read in that perspective, where we here explore the potential of using fuel cells as energy converters of biogas in the light of current energy trends and developments.

1.2 Objectives of the work

This main objective of this thesis is to evaluate the potential use of fuel cells as energy converter of biogas to electricity. This is done by describing arguments in favour of fuel cell research and development in the light of sustainability and alternative ideas of how to predict and prepare for the future, as well as by giving an insight into obstacles, challenges and opportunities from experience of operating fuel cells on biogas. Four different experimental test facilities (one at KTH, one at Power Cell in Gothenburg, and two placed in GlashusEtt, Stockholm) have been used in order to gain experience and a broader knowledge of fuel cells systems, and fuel cell systems operated on biogas. Experiments have been performed at cell, stack and fuel cell system level.
1.3 Research context

The content of this thesis is based on the experience, knowledge and insights gained from three different research projects. The first project commenced in 1999 and had been ongoing for four years when I started in 2003. This project included the build-up and continuous development of a research PEFC pilot plant facility. The second and third projects were third-party evaluations of a 4 kW PEFC system and a 5 kW SOFC system, respectively, installed in the Environmental Information Centre GlashusEtt in Stockholm.

In 2003, when my work was initiated, few fuel cell systems had been operated on biogas and very little data was available in the literature, thus an experimental approach was chosen in order to gain broader experience and knowledge concerning fuel cell systems, and especially on fuel cell systems operated on biogas. Data and hands-on experience were considered valuable in order to identify and investigate important issues concerning fuel cells and biogas.

My experimental research has been limited to studies of the fuel cell systems of 4 and 5 kW, to a 5 kW PEFC fuel cell stack in the test facility and PEFC single cells, 7 cm² and 54 cm² in size. The fuel cell systems used have all been pre commercial systems, the two units in GlashusEtt were also purpose built for demonstration and testing. The thesis is furthermore focussed on technical feasibility which means that e.g. public opinion, acceptance issues, implications for the energy system, life cycle assessment, etc. not has been studied in detail, instead fuel cell technology available today has been the basis of my studies as well as current energy system and infrastructure. No assumptions are made about future developments or changes in e.g. infrastructure, consumer demand or legislation. Potentials are however identified and argued for. All experiments have been done in Sweden and mainly a Swedish context influences the discussion and interest of biogas operated fuel cells.

My guiding research questions could be summarized as follows: Can fuel cell systems be operated on biogas? What does biogas do with the fuel cell system in terms of general operating characteristics, such as efficiency and dynamic responses? How do CO and CO₂ influence behaviour on stack and cell level.

1.3.1 System studies of stationary fuel cells for small-scale cogeneration applications

This programme was started within a university programme for stationary fuel cells financed by the Swedish Energy Agency and administrated by Elforsk AB. Within this project a test facility for PEFC systems was built up, including reformer, gas analysis equipment, auxiliary equipment, and an advanced control and surveillance system. The test facility was financed by the Swedish Energy Agency, Elforsk AB, ABB AB and the Swedish Defence Materiel Administration (FMV). The aim of this project was to identify possibilities for PEFC systems to act as CHP units for buildings in Sweden, the studies at system level in the test facility were complemented by experiments at single cell and segmented cell level.

1.3.2 GlashusEtt - PEFC evaluation

In order to understand and evaluate the prerequisites for sustainable and energy-saving systems, ABB and Fortum, with financial support from the Local Investment Programme (LIP) council in Stockholm and the Swedish Energy Agency, complemented the existing energy system in
GlashusEtt with an alternative energy system. The system was used to demonstrate and evaluate how a system based on fuel cells and photovoltaics could function as a complement to existing electricity and heat production. The 4 kW PEFC fuel cell system (including a reformer), supplied by H-power, was operated on upgraded biogas.

1.3.3 GlashusEtt - SOFC evaluation

This project built on the experiences of the first GlashusEtt project. The aim of the project was to gain experience of an SOFC system and to demonstrate and evaluate state-of-the-art technology. The 5 kW combined heat and power (CHP) SOFC system was supplied by Acumentrics, one of the SECA partners, and was operated on upgraded biogas.

1.3.4 Entrepreneurship

This thesis is probably also affected by the fact that I, in parallel with my PhD studies, have been active as an entrepreneur and been part of establishing and working in two companies in the area of photovoltaics and small-scale wind power. Those activities have given me useful insights and experiences of these technologies, their development, policies involved, public attitudes, etc. Useful because photovoltaics and small-scale wind power have many features in common with fuel cells, e.g. their small scale and distributed nature, grid connection issues, being relatively expensive, attracting a lot of interest and high hopes, being perceived as technologies for the future, etc. Being an entrepreneur also provided a commercial perspective on fuel cell technology.

1.4 Thesis outline

Chapter II discusses the current status of the fuel cells industry and the prognoses for 2010. The question Why fuel cells? is reviewed in the light of some ideas on how to predict and prepare for the future and applies these ideas on fuel cell research and development. The “chicken and egg” problem of hydrogen and fuel cells is also addressed and finally biogas is suggested as a fuel for fuel cells. Chapter 3 is a review of research performed on fuel cell systems and biogas and specifically the influence of CO, CO₂ and dilution on fuel cells, both at single cell as well as at stack level. Chapter 4 summarizes the results from the appended papers. Chapter 5 contains conclusions and chapter 6 some final remarks.
2 BACKGROUND

The aim of this chapter is to motivate the use of biogas-operated fuel cells. This is done by first studying the current status of the fuel cells industry and by taking a look at the predictions for 2010. Furthermore some alternative ideas of how to predict and prepare for the future are reviewed and then used in order to motivate, and give direction to, fuel cell research and development. The “chicken and egg” problem of hydrogen and fuel cells is also addressed and finally biogas is argued to be a suitable fuel for fuel cells.

2.1 Status and potential future use of fuel cell technology

2.1.1 Applications

There are three main areas in which different fuel cell applications have been considered: portable devices, stationary systems and for transportation purposes. Within these three areas, fuels cells have been tested or simulated in endless combinations. Think of any stationary application (hospitals, commercial buildings, schools, uninterruptable power supply (UPS) systems, back-up systems, banks, police stations, residential, museums, etc.) and you could find someone who has tried it with a fuel cell. Think of a portable application, and someone will have studied the feasibility of having a fuel cell in that application. The same goes for the transportation sector: scooters, buses, cars, motorbikes, bicycles, lorries, forklifts, segways, tanks, submarines, aircraft and trains, all of them have been considered and studied in combination with fuel cell systems.

The aim of most application studies mentioned above has been to investigate whether fuel cells have the potential to replace the conventional technology used in the specific application. The answer is many times yes, as long as such important factors as reliability, cost and performance reach assumed levels. Levels that many times are supposed to be reached in combination with a mass market roll out.

2.1.2 Status

The current status of the fuel cell industry is briefly discussed here from the market reports available at www.fuelcelltoday.com. The trends are clear, for stationary applications more and more fuel cell systems are shipped, reaching a total of 4000 units during 2008 (FCT 2010). There are today two dominant stationary applications: CHP applications for residential houses and UPS systems. The residential market has been created by subsidies, and three larger programmes stand out: The Danish residential programme, the German Callux programme and the Large Scale Residential programme in Japan.

In a recent report (NEF, 2009) on the largest subsidy programme, the Large Scale Residential programme in Japan, the results from a total of 3307 units were reported. A total of 21.6 million operating hours has been collected (an average of 6 350 hours per system). The safety of the system was considered validated since no fire or bodily injury occurred during the four years of operation. The electrical efficiency of the systems varies between 27-35 % (HHV), the unexpected shutdown incidents have, comparing the first year and the last year, come down from 4 to 0.29 per unit and year.
When it comes to transportation applications, two applications are dominant, APUs and material-handling vehicles which together represent more than 95% of the approximately 5000 units shipped during 2009. The main reason for the increase of material-handling equipment is the subsidy for forklift applications in the USA (as a result of the American Recovery and Reinvestment Act) of US$ 789 billion with a cap of the least of $3000 per kW or 30% of the unit cost. This has made the fuel cell forklifts shipments double each year since 2007 (FCT). Together with the APU market this spurs a rather rapid development and, according to FCT, 80% of the cumulative shipments in the transport sector since the 1960s have been shipped during the last three years.

PEFC units have more than 95% of the market share on the stationary applications and for the transportation sector PEFC had approximately 17% in 2009 with DMFC taking over 80% due to its dominance in the leisure sector.

A difference from the early years of fuel cell development (1967-2006) is that the fuel cell industry now has a mass and a momentum forward. Another difference is that the mass market role out which by many actors constantly have been targeted within 5-10 years (see e.g. Saxe 2005) for e review on articles in press from 1960-2005) now is more or less gone. Currently, when reading press releases and prognoses for some of the market leaders the numbers are actual shipments and the prognoses for the future are no longer “hockey-stick” shaped curves with extreme exponential growth, but instead rather comfortable and attainable numbers. E.g. Ballard which for many years has been a large player in the fuel cell industry has the goal of growing revenue by 35% over the 2009 level (Ballard, 2010). Plug Power which is one of the largest producers of material handling equipment has the target of 1100 units for 2010, which would be an increase of 29% over 2009 (Plug Power, 2009). The targeted growth is similar to the development of other new energy technologies, e.g. the cumulative installed PV capacity in the world has had an annual increase of 24% during 1998-2003, and of 39% during 2003-2008 (EPIA, 2009). Installed wind power capacity has grown with an average of 28% annually since 1992 (EWEA, 2009). Just because the expected growth now is similar to what has been seen in other areas does not make it certain that these levels will be reached, but it does put the expectations on fuel cell technology and its implementation on new and perhaps more reasonable levels.

2.2 Why fuel cells

Fuel cells convert fuel into electricity, heat and water trough electrochemical reactions between a fuel and an oxidant. The most common answers to the question: Why fuel cells? are its potentially high efficiency, emission-free conversion, possibly carbon-free energy conversion chain, and the fuel flexibility compared to conventional technology (most commonly the internal combustion engine). Others would however claim a rather low fuel to electricity efficiency because of all conversion steps included (reforming, gas cleaning, auxiliary equipment power consumption etc.), furthermore the emission-free conversion could also be questionable depending on how the fuel is produced and refined. This section reviews some alternative ideas of how to predict and prepare for the future and summarizes by using them to motivate, and give direction to, fuel cell research and development.
2.2.1 Difficulties in predicting the future

Smil (2003) demonstrates in his book Energy at the crossroads, that energy forecasts "No matter if they were concerned with specific inventions…or if they tried to chart broad sectoral, national, or global consumption trends” have "a manifest record of failure".

Smil has collected a large number of failed forecasts regarding energy use, conversion technologies, energy prices, electricity demand and more. Smil claims that “all long-range forecasters or energy affairs have missed every important shift of the past two generations”. Instead Smil argues in favor of “normative scenarios” which state where we would like to go, and what should happen, instead of trying to identify what is likely to happen. According to Smil normative scenarios should feature no-regret pathways which lead to “holistically defined goals that reconcile the maintenance of human dignity and a decent quality of life with the protection of the biosphere’s irreplaceable integrity”. This would then be “the best way to avoid the impact of both unpleasant and welcome surprises”.

Similar ideas are presented by Taleb in his book The Black Swan (2007); he argues that people overestimate what they know and underestimate what they do not know. Taleb’s background is economics but the ideas are general and may be applied on any area which is involved in trying to plan for the future. A Black Swan is an event that no one foresees but that everybody can explain in retrospect. Famous Black Swans are 9/11 or different market crashes. Taleb argues that Black Swans are much more common than we think, furthermore he argues that gradual change is our current paradigm but history (according to Taleb) proceeds by jumps, controlled by “the tyranny of the singular, the accidental, the unseen and the unpredictable”. According to Taleb too much emphasis is put on the odds that past events will repeat, instead, the really important events that change the course of history are rare and unpredictable.

So how should we prepare for the unpredictable? Taleb recommends what he calls ‘practical skepticism’, a readiness always to doubt the conventional wisdom and to expect our deepest assumptions to be challenged at any time. This practical skepticism should be allowed to influence both how we act and how we plan.

2.2.2 Avoiding lock-in effects

Another interesting perspective comes (mainly) from the history of technology and science. This field emphasizes the importance of our current infrastructure and how it limits us (locks us in) in our attempts at creating a more sustainable society. Scientist from this field often stress that the infrastructures of today are the results of decisions made decades ago. In the same way decisions we make today will have an impact on what we are able to do for decades to come. Furthermore they claim that we should learn from history in order to make wiser and better decisions today. And history does include many decisions to learn from.

In an interesting book about Swedish energy policy (Kaijser et al., 1988), various historic decisions and the results of those are discussed in order to find new and wiser decisions about a future energy system in Sweden. A few important points are made about bad decisions and the results of those. The authors argue that no single technology should be allowed to dominate all efforts. One should plan for the unknown or unexpected and thus a diversity of solutions should exist in order to make the system flexible and able to adapt if something unexpected occurs. As
an example Kaijser et al. (1988) review the nuclear development in Sweden, which for a time was seen as the solution to all energy-related problems, thus dominating all efforts. As time passed more and more problems with nuclear power surfaced and after a referendum in 1980 the decision was taken to shut all plants down. Arguments are also made against large natural gas pipelines, which are capital-intensive investments which make them long lasting, they might thus hinder other technical solutions that potentially could be both more efficient and environmentally friendly.

2.2.3 Remake the way we do things

In the book Cradle to Cradle MacDonough and Braungart (2003) challenge the way in which we usually regard our industrialized world and the way we make things. They want to challenge the belief that human industry must damage the natural world. Their aim is to use nature as a model in itself. The authors use the tree to give an example from a system from which we could learn and structure our targets and ambitions. “A tree produces thousands of blossoms in order to create another tree, yet we consider its abundance not wasteful but safe, beautiful, and highly effective”. As an example Braungart and MacDonough state that being less bad is in the long run equally bad. Less bad in this context means reduce emission instead of eliminating them, down cycle instead of truly recycle, limit and legislate instead of performing activities that do not need limits or legislations in order to be “less” dangerous to the human health (and the environment). This has the implication that e.g. energy efficiency is not nearly as important as substituting the energy sources we use (remaking they way we make things). The authors state that the ultimate failure of the “be less bad” approach is the belief that “poorly designed, dishonourable, destructive systems are the best humans can do”.

The authors give some examples of what a cradle to cradle design could potentially lead to. This could be “Buildings that, like trees, produce more energy than they consume and purify their own waste water”. “Factories that produce effluents that are drinking water”, “transportation that improves the quality of life while delivering goods and services”, or “Waste water treatment plants that help increase biodiversity” etc. Designed systems which all are a large step away from “simple” emission reduction and “downcycling”, and clearly energy converters in such systems have to be zero or even negative emission systems, able to provide service to ecosystems rather than being a burden.

2.2.4 Health, as important as CO$_2$ and ecological systems

The World Health Organization claims that access to commercial energy is important for both health and reduced poverty, but it should be based on renewable energy and, more specifically, the alternatives based on noncombustion processes (WHO, 2004). The combustion of coal, oil, and gas causes the most severe health effects, whereas photovoltaic and wind power are associated with fewer health effects. They refer to the work done within the ExternE project (ExternE, 2001) where, for example, coal power is estimated to have up to 100 times higher external costs than wind power. Thus, the development of noncombustion renewable technologies should be pursued according to WHO.

2.2.5 So why fuel cells?

All the above arguments are not, of course, fuel cell specific. Rather, they could be applied to any energy source or conversion technology that has potential for the future. I would then argue that
fuel cells could be a zero emission or even “negative” emission energy converter if combined with a suitable fuel. Few energy converters offer potential for an emission-free conversion chain. Fuel cells could, in the right context, constitute a no-regret pathway since the environmental impact of production and operation could be minimal. Furthermore, since fuel cells have significantly different properties and operating conditions compared to conventional technology, they might be a safeguard against the unforeseen, if e.g. conventional knowledge about the hazards with combustion technology turns out to be false. Fuel cells might even (with proper development) be able to live up to a cradle-to-cradle way of design. There are few moving parts and materials involved when producing and operating a fuel cell and thus very high levels of true recycling could probably be rather easily achieved. Furthermore, it is a non-combustion technology, which has clear positive health aspects from a WHO perspective. To summarize this chapter, it is clear that fuel cells, under the right boundary conditions and with continued development, have the potential to contribute to a desired future in a normative scenario. It is, however, closely linked to how the fuel for fuel cells is produced and refined.

2.3 Fuel cells and the (unfortunate) connection to hydrogen

Numerous studies have been directed towards the "chicken and egg" problem of fuel cells and hydrogen. Over-simplified the problem is as follows: If there is no hydrogen infrastructure available no one will develop fuel cells because it will be problematic to fuel them. On the other hand if there are no fuel cells and hence no demand for hydrogen no one will invest in hydrogen infrastructure, which puts us back where we started. This section is based on Paper I, and the argument is made that the time has come for fuel cells and hydrogen to be reviewed independently of each other. Just because we have hydrogen it might not always be the best option to use it in fuel cells. And just because we have fuel cells we might not necessarily need pure hydrogen.

One of the major disadvantages of using hydrogen as an energy carrier is the conversion losses it implies. This is emphasized in Table 1, where, reading from the left to the right, i.e. in the direction of the energy flow, the energy efficiencies for end use in vehicles or stationary applications for pure electricity and hydrogen (independently of production method) are shown.

Table 1. Estimated whole energy chain efficiencies, based on available hydrogen or electricity with end use in stationary or in tractionary (fuel cell or electric vehicle) applications

<table>
<thead>
<tr>
<th>LHV</th>
<th>First conversion</th>
<th>Packaging</th>
<th>Distr.</th>
<th>Storage</th>
<th>End-use</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>El.</td>
<td>0.8 H₂ + 0.20 Q</td>
<td>0.80 CH₂</td>
<td>0.97</td>
<td>0.85 battery</td>
<td>stationary</td>
<td>0.45 vehicle</td>
</tr>
<tr>
<td>H₂</td>
<td>0.65 el + 0.35 Q</td>
<td>0.97</td>
<td>0.85 battery</td>
<td>0.75 vehicle</td>
<td>0.40 + 0.35 Q</td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td>0.80 CH₂</td>
<td>0.97</td>
<td></td>
<td>0.45 vehicle</td>
<td></td>
<td>0.35</td>
</tr>
<tr>
<td>H₂</td>
<td>0.65 el + 0.35 Q</td>
<td>0.90 CH₂</td>
<td>0.97</td>
<td>stationary</td>
<td>0.57 el + 0.35 Q</td>
<td></td>
</tr>
</tbody>
</table>

Note: El=electricity. In the first conversion, 100 % lower heating value is assumed useful (above 100 % is losses), CH₂ denotes hydrogen compressed to a moderate pressure, Q is usable heat. All conversion efficiencies are approximated, learning towards the higher end.
Table 1 show that even if the energy source is hydrogen, it could be more efficient to convert the hydrogen into electricity and use the electricity directly in electric vehicles than to use hydrogen in fuel cell–powered electric vehicles. As exemplified in Table 1, even an energy chain with the goal of supplying fuel to vehicles could produce a large amount of heat possible to utilize in, for example, district heating networks.

The above is just one example of how important it is to be aware of losses implied by production, packaging, distribution, storage and end use of hydrogen. The strong bond between fuel cell and hydrogen might sometimes complicate and direct the focus of fuel cells in directions which at this stage might prove to be more of a detour rather than the often desired short cut. It may make us get stuck in the chicken and egg discussion instead of looking for new and interesting options. Fuel cells are fuel-flexible energy converters so which other interesting fuels are out there?

2.4 A specific fuel of interest – Biogas

Biogas has the potential of becoming a carbon dioxide-neutral fuel for any energy converter. Biogas is produced during anaerobic digestion of organic substrates, most commonly sewage sludge or manure but also from organic fractions of household and industry waste. It is also more and more common to use energy crops for biogas production. The size of biogas production facilities varies from large-scale facilities at large sewage treatment plants to small simple facilities at farms or households with suitable substrates (Petersson and Wellinger, 2009). Biogas is also produced during anaerobic degradation of landfills (sometimes referred to as landfill gas). Since biogas is produced locally it could contribute to security of supply as well as to the local economy. Today biogas is used mainly as vehicle fuel and for electricity production, however the distributed nature of biogas, and the many times small facilities could potentially also be used in combination with fuel cells in order to decrease emissions and increase efficiency.

2.4.1 Composition

The composition of biogas varies between different kinds of substrates, processes, locations and time of the year. Some average figures for biogas in general and some specific Swedish plants are given in Table 2 below.

The main difference between natural gas and biogas is the carbon dioxide content. Natural gas contains very low levels whereas biogas might have up to 50 % CO₂. Natural gas also contains a large fraction of heavier hydrocarbons. These two differences result in a lower energy content in biogas compared to natural gas. Apart from the composition illustrated in Table 2 biogas might also include many possible contaminants such as different sulphur compounds, halogens, ammonia, alkali, chlorine, phosphorous and siloxanes. Much work has been and is currently being directed towards efficient clean-up systems for the removal of these contaminants, mainly focussed on the standards for grid injection and utilization as vehicle fuel that impose restrictions and demands on gas quality. See e.g. Petersson & Wellinger (2009) for a review of biogas standards in six European countries for vehicles as well as for injection into the natural gas grid. Petersson & Wellinger also include a review of state-of-the-art cleaning and upgrading methods, both commercially available as well as ongoing research projects.
Table 2. Average compositions of biogas, landfill gas, natural gas as well as gasified biomass from large ongoing demonstration projects in Sweden

<table>
<thead>
<tr>
<th></th>
<th>Biogas (vol%)</th>
<th>Landfill gas (vol%)</th>
<th>Natural gas (Danish)</th>
<th>Värnamo gasification plant</th>
<th>Piteå black liquor gasification</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>60-70</td>
<td>35-65</td>
<td>89</td>
<td>10-12</td>
<td>0.2-1</td>
</tr>
<tr>
<td>NMHC (vol%)</td>
<td>0</td>
<td>0</td>
<td>9.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H₂ (vol%)</td>
<td>0</td>
<td>0-3</td>
<td>0</td>
<td>10-30</td>
<td>10-15</td>
</tr>
<tr>
<td>CO₂ (vol%)</td>
<td>30-40</td>
<td>15-50</td>
<td>0.67</td>
<td>20-30</td>
<td>15-17</td>
</tr>
<tr>
<td>CO (vol%)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>10-20</td>
<td>8-12</td>
</tr>
<tr>
<td>N₂ (vol%)</td>
<td>~0.2</td>
<td>5-40</td>
<td>0.28</td>
<td>-</td>
<td>55-65</td>
</tr>
<tr>
<td>O₂ (vol%)</td>
<td>0</td>
<td>0-5</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H₂S (ppm)</td>
<td>0-4000</td>
<td>0-100</td>
<td>2.9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NH₃ (ppm)</td>
<td>~100</td>
<td>~5</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>LHV (kWh/Nm³)</td>
<td>6.5</td>
<td>4.4</td>
<td>11</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

¹(Energinet.dk), ²(Chrisgas), ³(Black Liquor Gasification Program), NMHC – Non-methane hydrocarbons

2.4.2 Potential

The total amount of biogas produced in Europe in 2008 was approximately 88 TWh (EurObserv’ER, 2009). In 2008, there were 227 biogas facilities in operation in Sweden, producing 1.38 TWh (Benjaminsson & Nilsson, 2009). A major study performed on the biogas potential in Sweden was carried out by Norberg et al. (1998). Norberg concluded that the potential in Sweden was about 17 TWh. Since then the agriculture and farming has changed, a Swedish Government Official Report (SOU, 2004) has taken those changes into consideration and adjusted the potential to 14 TWh. Linné et al. (2008) have, however, adjusted the potential once again, and reach a overall biogas potential in Sweden of 10.6 TWh including all technically and economically available organic material from households, restaurants, parks, gardens, stores, industry, sewage, manure and farming.

In April 2010 the Swedish Energy Agency released a preliminary proposal for a national biogas strategy. The report suggests that there should be an increased incentive for biogas production from manure, since the environmental benefits from digestion of this substrate is the largest. With this incentive the annual amount of biogas produced in Sweden would roughly double to 2.8 TWh according to the report.

Biogas, as any other renewable fuel, has to be produced and used in a sustainable fashion, in balance with both ecosystems and competing use of the substrates in order be purely renewable and sustainable. These are also criteria which have to be fulfilled in order for fuel cells and biogas to excel according to the ideas discussed in section 2.2.

Current use of biogas and even the future potential is small compared to the energy use in e.g. the transport sector (only in Sweden the energy use in the transport sector was 129 TWh in 2008
(Swedish Energy Agency, 2009). However, keeping in mind that one of the largest actors in the fuel cell industry targets a shipment of 1100 units for 2011, both current use and future potential of biogas are very large compared to the globally installed capacity and use of fuel cell systems.

### 2.4.3 Interesting examples

Biogas is gaining more and more attention, and the installations and use of biogas are also increasing. Only in Germany, the number of biogas plants has increased from 100 in 1990 to 4000 in 2009 (Weiland, 2009), Germany produced 8318 GWh of electricity from biogas in 2009, and Great Britain was not far behind with 5322 GWh (EurObserv’ER, 2009). There is also a lot of activities in Sweden. A lot of information can be found at www.biogaspotalen.se, which is hosted by the Swedish biogas industry association (Energigas Sverige, 2010) e.g. information about all larger production facilities as well as on current R&D in Sweden. Energigas Sverige targets an annual production capacity of 3 TWh by 2012.

On a global scale, the activities are harder to quantify. Purohit et al. (2002) estimated the number of biogas plants in India to be 29 millions. In developing countries, biogas is often used for residential heating purposes and for cooking; these two uses account for a large portion of the energy demand in rural areas. However, it is also to some extent used for lighting and mechanical electricity generation.

### 2.4.4 Syngas and biofuels from biomass

Gases with compositions resembling those of biogas are also produced in different processes for gasifying biomass. This is an area with large potential that is also gaining increasing attention. Only in Sweden there are at least three larger (above 10 million € each) ongoing demonstration projects producing biofuel from biomass. The first one is the Chrissgas project (Chrissgas, 2010) where biomass is gasified to a hydrogen-rich gas. The Chrissgas project aims at producing synthesis gases with different H₂/CO ratios, and upgrading it to fuels such as dimethyl ether, methanol, Fischer-Tropsch derived diesel or hydrogen for fuel cells. The second large project is the ethanol pilot facility in Örnsköldsvik, where ethanol is produced from forest biomass in two separate processes, weak acid hydrolysis and enzymatic hydrolysis. The pilot facility produces 400 litres of ethanol a day. The aim of the project is to investigate if it is economically feasible to produce ethanol from forest biomass (Sekab, 2010). The third large ongoing project is located in Piteå where black liquor is gasified into synthesis gas. Black liquor is a by-product from paper and pulp mills, formed in the digestive process where cellulose fibres are dissolved from wood chips by the alkaline liquid called white liquor. By gasification of black liquor it is possible to increase the electricity production and to recycle the process chemicals more efficiently compared to the combustion technology used today. In 2009 the gasifier had reached 10,000 hours of operation (Chemrec, 2010)

### 2.4.5 Biogas and fuel cells

As indicated in this chapter the current production and the future potential of biogas are large compared to current fuel cell installations and fuel cell industry. Biogas could be an interesting niche that could contribute significantly to developing and testing fuel cell technology. The composition of biogas is interesting from a fuel cell perspective and biogas and fuel cells could potentially constitute the main steps in a carbon-neutral energy conversion chain.
3 FUEL CELLS AND BIOGAS

Several studies have investigated the possibility of using different fuel cell technologies with biogas. The different technologies have technology-specific criteria. Table 3 lists some important features of the different fuel cell technologies. As may be seen the low temperature fuel cells have several disadvantages such as no internal reforming, dependence on noble metal catalysts and thus a larger sensitivity to poisoning. The difference between different fuel cell systems is not as pronounced as indicated in Table 3 since all technologies have issues with durability, cost and reliability. At the same time all technologies offer interesting possibilities and have thus been studied in biogas applications. In this chapter some fundamental problems of using biogas in PEFC systems, i.e. CO and CO₂ poisoning, are studied in detail, followed by a short review of performed studies on various fuel cells systems and biogas.


<table>
<thead>
<tr>
<th>Feature</th>
<th>SOFC</th>
<th>MCFC</th>
<th>PAFC</th>
<th>PEFC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Noble metal catalysts</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>CO tolerance</td>
<td>Fuel</td>
<td>Fuel</td>
<td>Poison (&lt;0.5 %)</td>
<td>Poison (&lt;10 ppm)</td>
</tr>
<tr>
<td>Sulphur tolerance (&lt;1 ppm)</td>
<td>Poison</td>
<td>Poison</td>
<td>Poison</td>
<td>Poison</td>
</tr>
<tr>
<td>NH₃</td>
<td>Fuel</td>
<td>Fuel</td>
<td>Poison</td>
<td>Poison</td>
</tr>
<tr>
<td>Operating temperature (°C)</td>
<td>500-1000</td>
<td>~650</td>
<td>~220</td>
<td>30-100</td>
</tr>
<tr>
<td>Thermal integration potential</td>
<td>High</td>
<td>High</td>
<td>Medium</td>
<td>Low</td>
</tr>
<tr>
<td>Internal reforming</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
</tr>
</tbody>
</table>

3.1 PEFC and carbon monoxide poisoning

CO is a well known poison for PEFCs. In a stationary PEFC system the reforming unit may be operated at steady state if the inlet gas composition is fixed and the fuel cell is connected to the power grid or a battery pack to level the energy demand. If this is the case, the level of CO in the fuel may be reduced to a constant level of a few ppm. Whenever a reformer is operated with a varying fuel feed composition (and hence varying energy content in the inlet gas) or if the system is operated in a load-following mode the composition of the gas exiting the reformer will also most probably vary due to response times of the system, e.g. thermodynamic equilibrium depending on thermal masses of the system or response times of mass flow controllers, valves etc. This makes it harder to maintain a stable and low CO level, especially if the reformer is changing its point of operation. This means that at certain times the CO level will be much higher than the CO level achievable with a good preferential oxidation reactor (<10 ppm). Biogas is such a source where the gas compositions could vary from time to time. It is thus important to
have a good understanding of CO poisoning and a control strategy to keep the CO level sufficiently low.

### 3.1.1 Carbon monoxide poisoning mechanisms

It is well known that CO adsorbs onto Pt surfaces at low potentials (reaction 1) and is not electrochemically oxidized at an appreciable rate until the potential reaches about 0.7 V vs. RHE. For a review of CO adsorption and oxidation on Pt, see Marković and Ross (2002) and references therein. This means that even ppm levels of CO will cause a high surface coverage:

\[ CO + Pt \leftrightarrow Pt\cdot CO \quad (1) \]

thereby hindering the hydrogen dissociation and oxidation reactions (reactions 2 and 3):

\[ 2 \, Pt + H_2 \leftrightarrow 2Pt\cdot H \quad (2) \]

\[ Pt\cdot H \leftrightarrow Pt + H^+ + e^- \quad (3) \]

at higher potentials CO can be electrooxidized (reactions 4 and 5):

\[ Pt + H_2O \leftrightarrow Pt\cdot OH \, +H^+ + e^- \quad (4) \]

\[ Pt\cdot CO + Pt\cdot OH \leftrightarrow CO_2 + 2Pt + H^+ + e^- \quad (5) \]

The electrode potential necessary for significant electrochemical CO oxidation on Pt/C is too high for practical applications, therefore carbon-supported Pt alloys with lower overpotential for CO oxidation are used, most commonly PtRu/C.

\[ Ru + H_2O \leftrightarrow Ru\cdot OH \, +H^+ + e^- \quad (6) \]

\[ Pt\cdot CO + Ru\cdot OH \leftrightarrow CO_2 + Pt + Ru + H^+ + e^- \quad (7) \]

The alloying with ruthenium has a twofold effect. Firstly, Ru forms hydroxides (reaction 6 above) which may be utilized in the CO oxidation reaction (reaction 7) at lower potentials than for Pt (reaction 5) as suggested by Petry et al. (1965) and Watanabe and Motoo (1975). Secondly, it decreases the bond energy between Pt and CO as shown experimentally through UHV thermodesorption by Buatier et al. (1998) and predicted theoretically by Hammer et al. (1996) and by Ruban et al. (1997). Brett et al. (2004) showed, using localized CO-stripping voltammetry, that the distribution of CO in a fuel cell is anisotropic. CO adsorption/desorption and oxidation has a strong temperature dependence. For the effect of temperature on CO poisoning with different anode catalysts (in an operating low-temperature PEFC) see Lee et al. (1999).

### 3.1.2 Air bleed mechanisms

The most common strategy for dealing with CO poisoning of the fuel cell is to add a small amount of air to the fuel, a so-called air bleed, which will oxidize the CO. This method of dealing with CO poisoning was presented already in 1988 by Gottesfeld and Pafford.
From the recovery of the anode polarization due to CO poisoning it is clear that some of the oxygen (or an oxygen reduction peroxide intermediate as suggested by Eichler et al. (1999) and Schmidt et al. (2001)) reacts with the CO and it is also clear that some of the oxygen will be electrochemically reduced at anodic potentials. When oxygen is reduced on the electrode surface one of the intermediate reaction products is hydrogen peroxide. This may react further to form water, oxidize adsorbed CO, or desorb from the surface. Hence there are three competing reaction products formed by the oxygen, namely water, carbon dioxide and hydrogen peroxide.

Using experimental model system studies Stamenkovic et al. (2005) and Jusys and Behm (2004) showed that during O\textsubscript{2} reduction the H\textsubscript{2}O\textsubscript{2} yield is highly dependent on CO coverage. At high CO coverage the H\textsubscript{2}O\textsubscript{2} yield is much higher than on clean surfaces. Both studies also showed that air bleeding does not remove all adsorbed CO. This indicates that at fuel cell anode-relevant potentials oxygen reduction may occur at mass transport-limited currents even if the surface is partially covered by CO. Jusys et al. (2003) found that only 10\textsuperscript{-4} of the oxygen they supplied to the anode was consumed in the CO oxidation reaction at 60 mV vs. RHE. When O\textsubscript{2} is reduced at the carbon support the H\textsubscript{2}O\textsubscript{2} yield is likely to be high (though so will also H\textsubscript{2}O\textsubscript{2} decomposition rate at Pt be) (Paulus et al., 2002). The flow cell measurements by Schmidt et al. (2001) show that free reaction sites are necessary for heterogeneous reactions to take place between H\textsubscript{2}O\textsubscript{2} and CO on Pt. However, even at high CO coverage H\textsubscript{2}O\textsubscript{2} lowers the potential at which electrochemical CO oxidation takes place. When it comes to fuel cell measurements, Murthy et al. (2003) showed that 5 % air bleed completely recovers the performance of series 5561 PRIMEA® MEA supplied with 500 ppm CO.

If the system is operated at steady state it will be beneficial for both life-time and system efficiency reasons to minimize the amount of added air. The influence of air bleeding on the membrane degradation rate was discussed in a publication by Inaba et al. (2008): when adding air bleed possible effects on the life-time of the fuel cell and the total efficiency of the system should always be taken into account.

### 3.2 PEFC and carbon dioxide poisoning

When it comes to the effect of CO\textsubscript{2} in the anode gas of PEFCs, some have concluded that the decrease in performance in the presence of CO\textsubscript{2} may be attributed mainly to dilution (e.g. Urian et al., 2003 and Papageorgopoulos et al., 2002), whereas others have found a more negative influence than for pure inert dilution (e.g. de Bruijn et al., 2002, Bellows et al. (1998), Gu et al., 2004 and 2005, Halseid and Tunold, 2006). However, dilution also amplifies the CO-poisoning effect as a result of the lowering of the local concentration of hydrogen (Springer et al., 2001 and Bhatia and Wang, 2004).

There is some controversy as to how CO\textsubscript{2} reacts and as to the nature of the resulting adsorbed reaction products in a PEFC. The reasons for the diverging results from different model system studies are discussed by Sobkowski and Czerwinski (1985). A study by Smolinka et al. (2005) showed linearly and multiply bonded CO as the only stable reaction product. At the low potentials at which a PEFC anode is operated most studies have reported the occurrence of both linearly and bridge-bonded CO (e.g. Smolinka et al., 2005, Urian et al., 2003 and Papageorgopoulos et al., 2002 and Beden et al., 1983). The ratio between these two forms is also a function of potential (Sobkowski and Czerwinski, 1985).
There are two theories on how this CO is formed. Some (e.g. Papageorgopoulos et al., 2002, de Bruijn et al., 2002, Janssen, 2004 and Bellows et al., 1998) claim that CO₂ reacts according to the so-called reverse water-gas shift reaction (RWGS):

\[ CO_2 + 2Pt-H \leftrightarrow Pt-CO + H_2O + Pt \quad (\text{Reverse water-gas shift reaction}) \quad (8) \]

Others e.g. Ralph and Hogarth (2002) believe that CO₂ reacts in an electrochemical reduction reaction:

\[ CO_2 + 2H^+ + 2e^- + Pt \leftrightarrow Pt-CO + H_2O \quad (\text{Electro reduction}) \quad (9) \]

Thermodynamic equilibrium calculations of RWGS in a CO₂-diluted hydrogen flow results in a CO concentration ranging from 10 to 170 ppm (de Bruijn et al., 2002, Karimi and Li, 2006 and Gu et al., 2004). However, Pt/C is a poor catalyst for the RWGS below 523 K and, therefore, the RWGS reaction is kinetically hindered (Gu et al., 2005). In 2002 Ralph and Hogarth showed that CO₂ forms a CO-like poison on both Pt/C and PtRu/C and concluded that the reaction occurred predominantly by electrochemical reduction.

The factor that determines how severe the CO₂ poisoning becomes is the resulting CO coverage on the catalyst surface. Experiments performed on Pt/C electrodes in liquid electrolyte saturated with CO or CO₂ have shown that the equilibrium surface coverage is much lower for the CO₂-saturated case. This may be explained by the fact that the RWGS reaction is self-poisoning (Urian et al., 2003 and Papageorgopoulos et al., 2002), i.e. as the reaction proceeds the number of adjacent catalytic sites decreases and thereby also the reaction rate and the equilibrium surface coverage.

It is commonly accepted that air bleed has an immediate positive influence on CO poisoning, but when it comes to CO₂, fewer studies have been made. Wilson et al. (1993) indicate that air bleed has a positive effect on the CO₂ poisoning.

### 3.3 Solid oxide fuel cells and biogas

SOFC and biogas have been gaining more and more attention during the past few years. One of the concerns with biogas and solid oxide fuel cells, is that in its most common form (approximately 60 % CH₄ and 40 % CO₂), biogas composition lies above the carbon deposition boundary for dry reforming in the cell (see e.g. Farhad et al., 2010). Biogas may be moved below the boundary by adding a reforming agent such as steam, (more) CO₂ or oxygen. The biogas may also be treated in a pre-reformer or upgraded by removing the CO₂ prior to use in the fuel cell.

Other concerns with biogas are the potential contaminants, such as H₂S, chlorine, siloxanes, ammonia and odorants such as mercaptans and tetrahydrothiophen (THT). Studies have been made in order to investigate the influence of contaminants in biogas on SOFC systems, e.g. Leone et al. (2010) and Haga et al. (2008). A specific group of contaminants of interest is siloxanes; 10 ppm siloxane (D₅) has been shown to lead to fatal degradation of cell performance (Haga et al., 2008). It is however possible to clean the inlet gas from siloxanes. In a technology overview, Ajhar et al. (2010) reach the conclusion that adsorption on active carbon with a pre-
drying step is the state-of-the-art when it comes to siloxane removal (reaching levels below 0.1 mg Si/Nm³). Furthermore, Ajhar et al. point out that some siloxanes may be absorbed in water (water scrubbing), and thus, water is often used as a pre-conditioning step for subsequent adsorption.

Many of the common impurities in biogas are similar to the ones found in natural gas, Leone et al. (2010) come to the conclusion that a similar gas cleaning as suggested by Isrealson (2004) should be used for biogas purposes. That is, a double-stage desulphurization process consisting of a fixed-bed zeolite and then an active carbon reactor, which then together are able to handle all sulphur compounds present in natural gas, and thus should be suitable for cleaning of biogas.

3.3.1 Solid oxide fuel cell systems and biogas

The use of SOFC systems operated on biogas has been investigated in many studies, most are however simulations or thermodynamic studies (see e.g. Dokmaingam, 2010, Pirononlerkgul, 2009 or Farad, 2010). Earlier studies have also been done by e.g. Van herle et al. (2003, 2004a, 2004b). Van herle et al. argued that SOFC is the most suitable technology for biogas applications since it has a high operating temperature (no need for noble metal electrodes), high tolerance towards contaminants and internal reforming and thus higher system efficiency. They also argued that SOFC technology is more suitable for biogas than MCFC and PAFC because of the possibility of scaling from 1 kWel-1 MWe, i.e. covering also the smaller sites where the largest biogas potential lies. Staniforth and Kendall (1998) performed experiments on a small tubular solid oxide fuel cell and found that the power output when using biogas was similar to the power output when using hydrogen. At methane levels as low as 20 % they still had a significant power output. They suggested that SOFC and biogas could be a niche market, especially for gases which cannot be ignited because of their low methane content. Furthermore Staniforth and Kendel (2000) reported results from running an SOFC on landfill gas from the Cannock landfill in England, both with and without pre-treatment. Their main concerns were the life-time of the solid oxide fuel cell. Shiratori (2008) tested direct feeding of biogas to an SOFC (Ni-ScSZ) and obtained 50 hours of stable operation, however with some slight fluctuations which were believed to be caused by the varying composition of the biogas produced. Leone et al. (2010) studied the influence of a biogas produced in a process that inhibits the methanization step, resulting in a gas composition of 56 mol% CO₂ and 35 mol%H₂, with traces of methane, carbon monoxide and higher hydrocarbons. Only a short term test was performed but with, according to Leone et al., acceptable performance. Lanzini and Leone (2010) performed experiments on planar SOFC cells with simulated biogas with an emphasis on carbon deposition and found that there is no degradation from using conventional biogas (CH₄/CO₂) as long as the correct amount of oxidant is added to the fuel stream. Yentekakis (2008) operated a SOFC on simulated biogas for 200 hours and obtained stable performance for equimolar biogas (50 % CH₄ and 50 % CO₂). Recently Wärtsilä released a press release stating that they had successfully operated a 20 kW SOFC unit on landfill gas for 1500 hours, no data on the operation was however presented (Wärtsilä, 2010).

3.4 Molten carbonate fuel cell systems and biogas

MCFC technology has also been studied together with biogas. Trogisch et al. (2005) focussed on the advantages of using biogas as fuel for MCFCs, they demonstrated over 15 000 operating
hours and an electrical efficiency of up to 50 %, using real biogas (from land-fill, waste water, agricultural and co-fermentation) at different locations in Europe. Material analysis of six tested 300 W stacks showed that the biogas had no negative effect on stack material. Trogisch et al. pointed out that the key issue to be solved for biogas use in MCFC is gas purification (cost effective and sustainable). Bove and Lunghi (2005) studied the performance of an MCFC single cell fuelled with different gas compositions simulating biogas from different sources. The conclusion was that all investigated gases had a high potential for MCFC applications. Kivisaari et al. (2002) modelled a biomass-fuelled MCFC power plant of 60 MW size and investigated the effect of gasification pressure, temperature and influence of internal reforming on the overall system performance. They came to the conclusion that biomass may be converted into electricity through the IGCC-MCFC process with an efficiency ranging from 30 to 43 % depending on whether internal reforming is deployed or not. Cigolotti et al. (2008) made an economic comparison between internal combustion engines, gas turbines and MCFCs and came to the conclusion that MCFCs would be competitive at 3000 €/kW.

3.5 Low temperature fuel cell systems and biogas

PAFC was the first fuel cell type to be considered in connection with biogas. It has a high tolerance towards both CO and sulphur-containing compounds and it is thus an interesting option. Pandya et al. (1986) investigated the techno-economic feasibility of a PAFC coupled with biogas and found that a PAFC stack cost of <$ 1000/kW should produce electricity at a cost comparable to the cost of buying from the grid. Papers with experimental data from running a PAFC on biogas are scarce. Ascoli et al. (1988) demonstrated that a 2.5 kW stack may operate on biogas feedstock with total efficiency (reformer + stack) of 15-21 % which in their comparison is three times larger than those of engine-powered generators of the same size. Spiegel and Preston (1997, 1999, 2002) reported from a PAFC demonstration facility. The demonstration concerned both a gas cleanup system for landfill gas and field testing of a commercial PAFC. They concluded that initially there is a large potential for operating fuel cells with landfill gas in high electric cost areas and areas with average commercial rates if fuel cell waste heat may be utilized.

When it comes to PEFC much work has been done evaluating the effects of reformed natural gas, but specific information on reformed biogas is not as common. Sishtla et al. (1998) did not have biogas in mind when they performed their studies. However, they operated a PEFC with an active area of 58 cm², Nafion® 112 and Pt-catalyst with simulated reformate (80 % H₂ and 20 % CO₂) for 5000 h. The degradation was less than 1 % 1000 h⁻¹. The reversed shift reaction was shown to be slow, since thermodynamics predicted 29 ppm in the anode gas, but less than 1 ppm was detected (the detection limit of the equipment used). The conclusion was that a PEFC may be operated on carbon monoxide-free reformate even without air bleed and anode catalyst alloys such as PtRu/C. Guangwen et al. (2004) made experiments on reforming of simulated biogas and supplied the reformed gas to a 50 W PEFC stack with Pt-catalyst on both anode and cathode. They found that the performance losses were more serious at higher CO₂ fractions, especially above 20 %. This was argued to be connected to the possible poisoning effect of CO₂. Schmersahl et al. (2007) found that the reformate of biogas was sufficient for efficient and stable operation of a PEFC stack, however the lower hydrogen content compared to reformate from natural gas lead to a slightly lower efficiency and distinct lower maximum power output of the PEFC.
3.6 Summary

It is well known that CO is a poison for PEFCs. Air bleed is furthermore a common strategy to handle CO poisoning and many studies have been made on CO-poisoning and the effects of air bleed but there are few experimental data on varying CO-content and the suitable control strategies for air bleed. The impact of CO₂ is also somewhat unclear and varying results and theories may be found in the literature. Furthermore the experiments performed are often performed with lower CO₂ than found in various biogas compositions. The experiments are furthermore often carried out at single cell or on small systems, not on larger stacks or larger fuel cell systems. Solid oxide fuel cells operated on biogas have been investigated in several studies but mainly in simulation studies or experiments performed on single cell level. There are few solid oxide fuel cell systems operated on biogas, and even fewer have reported results for more than 200 hours of operation on biogas. Few PEFC systems have been operated on biogas like gas compositions, and those who have show somewhat varying results, and especially data from larger systems are scars. The next chapter deals with the results from our research which investigates these issues in detail.
4 RESULTS FROM PERFORMED STUDIES

In this chapter results from our preformed research are presented. The research reported on here has had focus on different issues of fuel cell systems operated on biogas as described in chapter III, some results are however general, and applicable to fuel cell systems, regardless of fuel.

4.1 Experience and results from biogas-operated fuel cell systems (Papers II and III)

In order to understand and evaluate the prerequisites for sustainable and energy-saving systems the existing energy system in GlashusEtt was complemented with an alternative energy system. The system was used to demonstrate and evaluate how a system based on fuel cells and photovoltaics could function as a complement to existing electricity and heat production. The 4 kW PEFC fuel cell system (including reformer), supplied by H-power was operated on upgraded biogas. The unit was later replaced with a 5 kW combined heat and power (CHP) SOFC system, supplied by Acumentrics, one of the SECA partners, and was also operated on upgraded biogas. The aim of the SOFC project was to gain experience of an SOFC system and to demonstrate and evaluate state-of-the-art SOFC technology.

4.1.1 Experimental

GlashusEtt, the environmental information centre

Hammarby Sjöstad used to be an old industrial area, but is now being transformed into a modern urban district. The environmental goals in Hammarby Sjöstad are ambitious. The achievement of those goals requires cooperation and modification in behaviour by the residents in Hammarby Sjöstad. Hence, Stockholm Vatten AB, Fortum AB and The Real Estate and Traffic Committee established the GlashusEtt project. GlashusEtt (see Figure 1), is an information centre built to inspire residents on how to achieve a more sustainable lifestyle. The idea is that GlashusEtt should serve as a natural meeting place and exhibition hall for different interest groups. The façade is made of glass as the name (Glass-house-One in English) suggests. The glass used has low thermal conductivity and should thus reduce energy losses by half, compared to a standard glass house. In order to understand and evaluate the prerequisites for sustainable and energy-saving systems, ABB and Fortum, with financial support from the Local Investment Programme (LIP) council in Stockholm, and the Swedish Energy Agency have complemented the existing energy system in GlashusEtt with an alternative energy system.

The alternative energy system (figure 2) in GlashusEtt also consists of a photovoltaic array, an electrolyzer, hydrogen storage tanks, and a separate control system. The PV array delivers electricity to the building, after being converted from dc to ac. If there is an excess of electricity (house demand is lower than produced electricity) the excess dc from the PV array may be fed to the electrolyzer. The hydrogen produced by the electrolyzer may then be stored in gas cylinders at approximately 14 bar (g), which is the delivery pressure from the electrolyzer. All components were part of the evaluation performed in Paper III, but only the fuel cell system will be discussed here.
Figure 1. Drawing of GlashusEtt

Figure 2. Schematic view of the alternative energy system in GlashusEtt.
Both fuel cell systems were operated on upgraded biogas from a sewage wastewater treatment plant, which is already available in the district gas network in the residential area where the information centre is located. The same gas is used for cooking and is also sold as vehicle fuel, therefore the methane concentration is above 95 %. The upgraded biogas composition is presented in Table 4. Due to the public use of the gas there is also a sulphur-containing odorant added to the gas.

**Table 4. Composition of the upgraded biogas**

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane (CH$_4$)</td>
<td>97 ± 2 %</td>
</tr>
<tr>
<td>Carbon dioxide (CO$_2$)</td>
<td>1.5 ± 0.5 %</td>
</tr>
<tr>
<td>Nitrogen (N$_2$)</td>
<td>&lt; 1.0 %</td>
</tr>
<tr>
<td>Oxygen (O$_2$)</td>
<td>&lt; 0.2 %</td>
</tr>
<tr>
<td>Hydrogen sulphide (H$_2$S)</td>
<td>&lt; 0.05 ppm</td>
</tr>
<tr>
<td>Tetrahydrothiophene (C$_4$H$_8$S)</td>
<td>&lt; 10 ppm</td>
</tr>
</tbody>
</table>

**4.1.2 The 4 kW H-power unit**

The first fuel cell system installed in GlashusEtt was supplied by H-power. The fuel cell system consisted of a fuel processor (reformer), including a desulphurisation unit and a CO clean-up unit, a PEFC stack, and an electrical compartment with inverters and batteries. The fuel cell system is connected to the inverter in order to convert the DC current from the stack to AC. Table 5 lists some of the physical properties of the system. The thermal energy was absorbed by a coolant loop directly connected to an accumulator tank. The principle was to use the water in the accumulator tank as a heat exchanger. The size of the accumulator tank (500 l), turned out to be inadequate. To adjust this problem the coolant water had to be cooled on the roof of the building to ensure that the fuel cell system was sufficiently cooled. The system could be operated on upgraded biogas or stored hydrogen. In the latter case, the hydrogen was fed directly to the fuel cell stack. The fuel cell system was designed to operate on natural gas or propane. However, as the upgraded biogas delivered to the building has a chemical composition close to that of natural gas, it could be operated on upgraded biogas as well. The fuel cell system was only operated at full load (hydrogen or upgraded biogas), i.e. no load-change dynamics or load-dependent behaviour has been tested.

**Table 5. Data for the PEFC system**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Delivered by</td>
<td>H Power</td>
</tr>
<tr>
<td>Working pressure</td>
<td>0.9 bar (g) from biogas, 0.35-0.7 bar (g) with hydrogen</td>
</tr>
<tr>
<td>Rated unit power output</td>
<td>4.0 kW net, 10 kW peak demand for 15 min</td>
</tr>
<tr>
<td>Rated efficiency</td>
<td>18 % electrical, 40 % total efficiency</td>
</tr>
<tr>
<td>Rated thermal output</td>
<td>6.5 kW</td>
</tr>
<tr>
<td>Volume</td>
<td>2.5 m$^3$</td>
</tr>
<tr>
<td>Weight</td>
<td>~ 1350 kg</td>
</tr>
</tbody>
</table>
The results reported here where collected during the period from January to May 2003. KTH was no longer part of the project after June 2003. The project did however continue throughout 2004. The results from the operation are summarized in a report (Rissanen, 2006) in which it is reported that hydrogen leakage from the stack was discovered in December 2003. The stack was then sent back to the supplier and was repaired, after the exchange of some faulty cells the system was operated for an additional 50 hours before a similar problem occurred. The H-power fuel cell system accumulated a total of 1800 hours.

4.1.3 The 5 kW Acumentrics Unit

The 5 kW SOFC system fuel cell system supplied by Acumentrics consists of four fuel cell stacks. Each stack contains 12 manifolds and the stacks and manifolds are coupled in series. A manifold holds six anode-supported tubular cells which are connected in parallel. The fuel processing system includes a high-temperature sulphur trap and a partial oxidation pre-reactor (POX). Air is fed to the fuel at 3:1 (Air:CH₄) volume ratio.

The cathode air supply includes a start-up burner, fuelled with upgraded biogas, which supplies extra heat to the system in order to keep the operating temperature at the desired level. Above 70 A the stack is self-sufficient on heat and the burner is turned off. The outlet of the anode is coupled to the burner and heats the cathode inlet air and prevents methane and hydrogen discharge. The heat in the exhaust gas is first recuperated by a heat exchanger coupled to the cathode inlet and thereafter in a heat exchanger where heat is transferred to a coolant which is connected to a water tank. The heat is then supplied to the heating/hot water system of the house. The system is similar to the one described and evaluated by Barrera et al. (2008) which was also delivered by Acumentrics. Table 6 lists some of the physical properties of the system.

The system was not grid-connected but powered equipment in the information centre. The load consisted of adjustable heaters of up to 3 kW plus a fluctuating load consisting of a large flat-screen TV, ranging from 0-400 W.

<table>
<thead>
<tr>
<th>Table 6. Data of the SOFC system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Delivered by:</td>
</tr>
<tr>
<td>Working pressure:</td>
</tr>
<tr>
<td>Rated unit power output:</td>
</tr>
<tr>
<td>Rated efficiency:</td>
</tr>
<tr>
<td>Rated thermal output:</td>
</tr>
<tr>
<td>Volume:</td>
</tr>
<tr>
<td>Weight:</td>
</tr>
</tbody>
</table>

Data from 78 system parameters were measured every 16 seconds. The current and power were measured as totals from the fuel cell. The voltage was measured as stack average but also on individual manifolds. In each stack the voltage from eight individual manifolds was measured. The other four manifolds were measured in pairs. The various stack temperatures were measured in 12 places in the fuel cell system: below, in the middle of and above each stack.
**Figure 3.** A picture taken during the installation of the 5 kW Acumentrics unit in GlashusEtt. The only way to get the SOFC system into the building and up to the third floor was by removing a section of the glass facade.

### 4.1.4 Results from operation

**The PEFC system**

During installation of the PEFC system issues with permits and authorities caused significant delays. The involvement of KTH was restricted in time and thus the results presented here were the results of the first six month of installation and first 200 hours of operation. These results have however good coherence with the results obtained later in the project (see Rissanen, 2006).

The electrical efficiency was calculated to 13 % and a thermal efficiency of 56 % was found for the fuel cell system using the lower heating value (LHV) of the upgraded biogas and the delivered ac power after the inverters. An approximate energy balance of the fuel cell system may be seen in Figure 4 in which 5 % of the input energy is assumed be lost through the exhaust. The waste heat (25 % of the upgraded biogas input (LHV)) delivered to the room caused the temperature to rise 8 °C.

The alternative energy system in GlashusEtt was an evaluation and demonstration facility, and as such it was not optimized for use in GlashusEtt. The rated thermal effect given was 6.5 kW according to the supplier, but the measured one was almost the double. The system has been proven to work on both upgraded biogas and hydrogen produced by electrolysis of water. The first results indicate efficiencies close to or below the rated efficiencies of the included components. The electrical efficiency of the fuel cell system was lower than rated whereas the thermal efficiency was higher.
A similar unit was reported on in Gigliucci et al. (2004), operated for 550 hours on natural gas had an electrical efficiency varying from 10 - 18 %, and a thermal efficiency varying from 25-40 %, dependent on load level. An economic evaluation was performed which showed that regardless of lifetime, investment costs and fuel infrastructure the cost structure of fuel and electricity in GlushusEtt is unfavourable for fuel cells since grid electricity is inexpensive and biogas is expensive. Even with 100 % conversion of biogas to electricity it would not make sense to produce your own electricity since it is more economic to buy electricity from the grid. This cost structure is however artificial since there is no larger market for biogas and the cost of electricity might rise in the future.

### 4.1.5 The SOFC system

In this section the operations result are presented for the 5 kW SOFC system. The system has been operated in three phases for totally 3310 hours. In Figure 5 the average stack voltage and stack current as well as the average stack temperature during all three phases are shown. The vertical lines in the figure define the time interval for the three phases. In general, a slow decaying cell voltage occurs during all phases. There are only two exceptions. Firstly, in the first part of the second phase a more rapid decaying cell voltage occur. Secondly, in the third phase just before the fuel system was shut down a faster decay of the cell voltage occurred. In both cases the faster decay could be linked to instabilities in the fuel cell system. Furthermore, at higher loads the stack temperatures will be more unstable especially before the fuel cell system was shut down in the third phase.

The operation during Phase I was stable and without interruptions, the only adjustment was of the cathode air in order to decrease the temperature gradient over the stacks. The average electrical efficiency was 33.7 %. In average 1.8 kW of heat was transferred to the building. In Phase I the average temperature difference across the stack was 54.3 ºC. The decrease in average stack voltage, within the current range 85-87 A, was 1.7 %.
In the beginning of phase II the system appeared to be unstable, the cause of instability was a combination of fluctuating loads, stack current limitations and a battery check routine, implemented in the control system. The average electrical efficiency was now 29.7% and an average of 1.5 kW of heat was delivered to the building. After 321 h of operation in phase II the fluctuating load was removed and the fluctuations stopped. The influence of the unstable periods at the beginning of phase II was probably very severe; the decrease in cell voltage was 11% after 350 h of operation in phase II. When the loads were changed and the reoccurring unstable periods were prevented the decrease slowed down.

4.1.6 Dynamics

During Phase II, after 644 hours of operation, dynamic tests were performed. Data from the dynamic tests showed that the power used for fuel cell system auxiliaries (fans, blowers, control system etc.) varied between 250 and 550 W depending on load and cooling demand. At normal operation around 3 kW DC output, the power demand for auxiliaries was 500 W. The test was performed by reducing the load gradually to zero and then back up to normal load again. The control system was however unable to handle the relatively rapid change in heat production in the stack which resulted in a forced shut down by the control system.

The system had clear problems to handle the thermal management also during minor load changes, the temperature gradient over the stack increased throughout the project, during the dynamic tests the temperature gradient in the hot module reached above 100 °C. Even under normal operation a thermal gradient across the stack of 80 °C was common.
Figure 6. Temperature distribution in the hot module during phase II, the peaks between 200 and 350 hours were caused by the fluctuating loads. The large peak after 644 hours was caused by the dynamic tests.

Figure 6 shows the temperature distribution in the hot module during phase II, the first peaks are caused by the unstable behaviour in the beginning of phase II, the large peak is a result of the dynamic tests performed after 644 hours in phase II.

During start-up of phase III it was found that one of the cells was below the shut-down voltage. After discussion with the supplier the decision was taken to continue. The shut down criteria were altered so that cell voltage was removed as criterion. During operation one manifold was clearly out of order and had a cell voltage of 0 V. In order to keep the heat balance in the system the fuel utilization had to be reduced. This in combination with the broken manifold led to an average electrical efficiency in phase III of 16.1 %.

4.1.7 Discussion
A majority of the problems during operation was not caused by the SOFC technology. During phase I the system was shut down control system failure. In phase II the control system also caused some undesired behaviour, which lead to a rapid decrease in performance. During the dynamic tests the control system was also unable to keep the temperatures on a steady level which lead to a forced shutdown of the system. During phase III the system was operated with one manifold defect which implied more stress to the system since anode gas was mixed with cathode air within the hot module. For the first 1000 hours in phase III the system was stable. After 1000 hours in phase III the load was increased and operation became more unstable. After 1700 hours of operation with a defect cell the control system was unable to keep an acceptable temperature gradient over the stacks which caused subsequent errors and a forced shutdown of the system.
The performance decrease was probably not caused by the use of biogas, i.e. the specific contaminants in biogas. E.g. siloxanes have been shown to have a fatal influence on solid oxide fuel cells. The biogas used in this study was however first upgraded using water scrubbing which according to Ajhar et al. (2010) removes some of the siloxanes. Furthermore the fuel cell system is equipped with a sulphur trap which consists of a zeolite and an active carbon reactor which both Haga et al. (2008) and Ajhar suggested to be the most effective way of removing impurities and siloxanes.

The performance decrease before operated with a low FU and a broken cell was similar to what Barrera et al. (2008) reported in their evaluation of a similar Acumentrics unit. They reported a performance decrease of 6 % during the first 700 hours of operation. For the following 650 hours they had a performance decrease of 2.7 %. This strengthens the hypothesis that the performance decrease not is caused by the use of biogas, but is instead caused by some intrinsic material or system property.

4.2 Experiments on stack and cell level (Papers IV and V)

In this section the most important results from our studies on electrochemical aspects of using biogas for PEFC are presented. The aim of the performed experiments was to analyse how a PEFC performs while operated on a wide range of biogas-like gases. Current distribution was used as tool to obtain information on the influence of CO₂, CO and air bleed on PEFC behaviour. Experiments were first performed on a single cell, then on a segmented cell and later validated on a 5 kW fuel cell stack.

Since the composition of biogas varies between different types of biogas and also between different locations where it is produced, the simplest way to investigate a wide range of fuels under controlled conditions is to mix them from pure gases.

4.2.1 Experimental

**Single and segmented cell**

The MEAs used in the single cell and segmented cell experiments were Gore PRIMEA® series 5620 and 5621. The gas diffusion layers (GDLs) were Carbel™. The MEAs were mounted in the cell with the GDLs and pressed together by the clamping pressure. After mounting the MEAs they were run with fully humidified pure H₂ and O₂ for several hours before they were activated by cutting off oxidant supply at a current density of 0.28 A cm⁻²; 10 s after the cell voltage dropped, the oxidant gas was turned back on. This procedure was repeated 5 times before each measurement. All measurements were repeated twice. In the experiments with the gas analysis equipment, the large single cell was also mounted with a Nafion® 112 membrane and Carbel™ GDLs, i.e. without catalyst layer. This was done in order to evaluate if any oxygen reacted somewhere else than on the catalyst layer. For single-cell testing a 7 cm² in-house made cell was used. The clamping pressure of the current collectors was controlled by a pneumatic piston. The graphite current collectors had a spiral flow field design. The gas on the cathode side was pure O₂ (instrument grade) at a stoichiometry of 2.4. The gases used for the anode side were H₂ (instrument grade), N₂ (detector), CO₂ (Coleman), CO in N₂ (0.125 % ± 2 % relative error) and synthetic air (20.9 % ± 2 % relative error O₂ in N₂), at a fuel stoichiometry of 1.5. The mixing of the gases was controlled by Brooks S5800 mass flow controllers. The relative humidity was held at 100 % and the cell temperature was 60 °C in all experiments. Pressures were ambient on both
anode and cathode. The load level was 1 A cm$^{-2}$ in the galvanostatic experiments. The small laboratory cell and its experimental set-up are described in more detail by Ihonen et al. (2004). In the CO$_2$ dilution experiments the fuel cell equilibrated during 1 hour at each gas composition before the data were recorded.

The segmented cell had an active area of 54 cm$^2$ and was segmented by eight rows and four columns at the anode. The segmented cathode side flow distributor had parallel channels and the anode side had an un-segmented stainless steel net. The currents through the individual segments were calculated from potential differences over shunt resistances. The gases, temperature, pressure and relative humidity were the same as for the single cell testing. The gas flow was co-flow in all experiments. The segmented cell and its experimental set-up have been outlined by Noponen et al. (2004). Before CO or air was introduced to the anode, the cell was always operated for 1 hour with pure H$_2$/O$_2$ and thereafter for 1 hour at the experimental design point without CO. The preferred mode of operation during the segmented experiments was galvanostatic as it enables easy control of the stoichiometry using manual gas mixing. However, the CO experiments on the PtRu/C anode were also conducted in a potentiostatic mode to avoid the oscillating cell voltage that otherwise occurs. The galvanostatic current density in the experiments with CO had to be limited to 0.5 A cm$^{-2}$ since the power output of the cell otherwise was too low to drive the resistances in the circuit connecting the load due to the drop in cell voltage by CO poisoning.

The large single cell had an active area of 54 cm$^2$ and both flow distributors were stainless steel nets. It was identical to the segmented cell used except for the flow field on the cathode side which in this case was a stainless steel net. The dry gas composition in the large single cell experiments was analysed continuously. The sample gas passed through heated tubes via humidity sensors and gas cooler to the gas analysis system. The hydrogen content was measured with a thermal conductivity module. Carbon monoxide, carbon dioxide and higher hydrocarbons were measured by an infrared module and the oxygen content was measured by a magnet mechanical module. The gas analysis equipment has been described in more detail by Wallmark et al. (2006).

**Fuel cell stack**

A Powercell Mark 1.0 5 kW reformate stack was supplied by Powercell AB. The stack design is based on the one developed within the Mistra fuel cell programme which was optimized for good performance. The stack consists of 40 cells and is water-cooled. Both bipolar plates and the end plates are made of stainless steel. The MEAs used are Gore PRIMEA® series 5561 (Pt cathode 0.4 mg cm$^{-2}$ and PtRu anode 0.45 mg cm$^{-2}$, membrane thickness 25 μm) and the gas diffusion layers are Carbel™. The temperature in all experiments was 60 °C. The stoichiometries were always 2.0 at cathode and 1.5 at anode. Air was used as oxidant in all experiments. The cooling water flow for the stack was 30 dm$^3$ minute$^{-1}$. The stack was operated for at least 1 h on pure gases before measuring to ensure that it had reached a stable point of operation. During the dilution experiments with CO$_2$ and N$_2$ the pressures were held at 0.5 bar gauge pressure at both anode and cathode outlets. The stack was equilibrated for 1 h at each dilution level when CO$_2$ was used, and for 20 minutes at each dilution level when N$_2$ was used, before the cell voltage was recorded. Pressures were held at 1 bar gauge pressure at both anode and cathode in all experiments with reformate-like mixtures. The polarization curves were taken at a galvanostatic sweep rate of 0.1 A cm$^{-2}$ minute$^{-1}$, or approximately 0.55 mV s$^{-1}$ cell$^{-1}$. Two kinds of CO-
poisoning transients were tested. During the experiments with different CO levels at constant air bleed level the CO level was ramped upwards from 40 ppm by 20 ppm every 15 minutes. When CO peaks were investigated 1 minute-long pulses at different CO levels were introduced at constant air bleed into the anode fuel streams until the lowest cell voltage was below 400 mV. After all poisoning transient experiments the stack was allowed to stabilize at the cell voltage it had before the transient, always with at least 10 minutes at a sufficient air bleed level though the recovery of the voltage was much faster. The composition of the simulated reformate from non-upgraded biogas containing 40, 60 and 80 % methane, respectively, in carbon dioxide was calculated using a steady-state, isothermal model of the combinatorial biogas reformer in the KTH fuel cell test facility, for more details see the master thesis of Lundin (2006).

4.2.2 Dilution and fuel utilization

Theoretically, dilution has very small impact. At 30 % hydrogen and 60 °C the thermodynamic loss due to dilution is approximately 17 mV. The three polarization curves at the top in Figure 7 show the 5 kW fuel cell stack operated on simulated reformate from non-upgraded biogas containing 40, 60 and 80 % methane, respectively, in carbon dioxide (these are common biogas compositions, see Table 2). As may be seen the efficiency of the fuel cell stack (efficiency defined as cell voltage over reversible cell voltage multiplied by fuel utilization) drops by less than 1 %, at an average current density of 0.7 A cm$^{-2}$, when going from 80 to 40 % methane in the biogas. The two lower polarization curves in Figure 7 are included to show that even further dilution of the fuel, resulting in lower hydrogen content in the fuel cell stack, will not be a problem in a PEFC. As may be seen the performance is still stable, though of course the efficiency of the process continues to drop. For the largest dilution case the polarization curve stops at a current density of 0.85 A cm$^{-2}$ since the mass flow controllers could not supply more inert gas to the fuel cell stack.

![Figure 7](image)

Figure 7. Polarization curves from a 40 cell 5 kW PEFC stack. The top three are simulated reformate mixtures from autothermal reforming of 80, 60 or 40 % CH$_4$ in CO$_2$. The lower two demonstrate reformate from more diluted fuels. Efficiency is defined as electrochemical efficiency multiplied by fuel utilization. Stoichiometry cathode 2.0, anode 1.5. Pressure 2 bar$_{abs}$. Cell temperature 60 °C. Relative humidity 100 %.
It may also be noticed that even at high fuel utilization the cell voltages are very stable. In Figure 8 the normalized voltage is shown as a function of fuel utilization for various fuel compositions. The results from the experiments with the high H₂ partial pressure (above 40 % H₂) show the same dependence on fuel utilization, but as the H₂ partial pressure is reduced to 30 and then 20 % the normalized cell voltage decreases more and more rapidly. This is due to the H₂ partial pressure at the cell outlet being very low (in the most dilute and highest fuel utilization case the H₂ content will be 4.6 % at the outlet).

**Figure 8.** Normalized average cell voltages in a 5 kW PEFC fuel cell stack when varying the fuel utilization at different degrees of dilution. Stoichiometry cathode 2.0. Pressure 2 bar abs. Cell temperature 60 °C. Relative humidity 100 %.

### 4.2.3 Influence of carbon dioxide

The dilution of hydrogen with carbon dioxide as compared to dilution with nitrogen causes a clear deterioration in cell voltage on a Pt/C electrode and a small deterioration on a PtRu/C electrode in the single cell set-up seen in Figure 9. We can see that the anode is poisoned by CO₂ and that the PtRu/C electrode is better at handling this poisoning than the Pt/C catalyst. This indicates that the poisoning is similar to the CO poisoning for which the PtRu/C catalysts are developed and thus supports the theory that the reaction product is a CO-like compound. Whether this compound is formed through the RWGS reaction (reaction 8), or the electroreduction reaction (reaction 9) is not possible to distinguish in our experimental set-up, but its influence on cell voltage is clear. It is also clear that no matter how high the CO₂ concentration in the anode feed the resulting poisoning is not nearly as severe as the poisoning induced by a small fraction of CO. This indicates that the CO₂ poisoning results in a lower surface coverage than poisoning by CO in a PEFC. This supports the works of Smolinka et al. (2005) and Papageorgopoulos et al. (2002) and demonstrates that the conclusions they drew based on their model experiments about a self-poisoning reaction are likely to be valid for the present experimental PEFC set-up.
Figure 9. Galvanostatic (average current density 1 A cm⁻²) single cell testing of H₂ dilution by N₂ or CO₂ for Pt/C and PtRu/C anodes, Pt/C cathode. Stoichiometry cathode 2.4, anode 1.5. Cell temperature 60 °C. RH 100 %. Pressure ambient.

The difference between dilution with N₂ or CO₂ was also tested in the segmented cell set-up with a Pt/C catalyst up to a dilution degree of 20 % H₂. In all current distribution plots the average current density per row is plotted vs. the number of the row, where the gas inlet is located at row number 1 and the gas outlet is located at row number 8, as shown in Figure 10.

The changes in current distribution from dilution with CO₂ or N₂ are plotted in Figure 11. Both dilution cases follow the same trend and the change in current distribution may be attributed to an additional dilution of the anode gas due to consumption of H₂ in the flow direction. There is a good coherence between the decrease in performance seen in Figure 11 between the inlet (20 % H₂ diluted with N₂ or CO₂) and the outlet (7.7 % H₂ in N₂ or CO₂) and the results in Figure 9. That is to say, the difference between the N₂ dilution case and the CO₂ dilution case is also here small. The cell voltage of the segmented cell when diluted with N₂ or CO₂ follows the same trend as in Figure 9. This implies an even poisoning of the electrode surface. The current distribution results from diluting the anode gas over a PtRu/C catalyst with N₂/CO₂ do not deviate from the Pt/C results to any large extent and the same conclusions are valid.

In Figure 12 the dilution effects of CO₂ and N₂ is shown for the fuel cell stack. As may be seen the losses with CO₂ dilution are also here somewhat larger than for the case with N₂ dilution due to a slight poisoning of the anode catalyst.
Figure 10. Model for plots of current distribution. The average current density ($i_{AVG}$) is plotted on the y-axis vs. the number of the row on the x-axis. The gas flow is co-current (inlet at 1 and outlet at 8) in all experiments.

Figure 11. Galvanostatic (average current density 1 A cm$^{-2}$) current distribution over a Pt/C anode catalyst at 20 % and 100 % H$_2$ in N$_2$ and CO$_2$. Stoichiometry cathode 2.4, anode 1.5. Cell temperature 60 °C. RH 100 %. Pressure ambient.
Figure 12. Dilution of H₂ at anode with N₂ or CO₂ in a 5 kW PEFC stack. Average current density 0.5 A cm⁻². Stoichiometry cathode 2.0, anode 1.5. Pressure 2 bar abs. Cell temperature 60 °C. Relative humidity 100 %.

Figure 12 also shows that the electrical efficiency of the fuel cell stack is not significantly diminished when the fuel is diluted with CO₂. The electrical efficiency at 0.5 A cm⁻² is reduced from 39 % to 37 % when the CO₂ content in the gas is doubled from 23 to 50 %. No other measures had to be taken when the gas composition was changed, and the performance, as shown, was stable even for the lower partial pressures of H₂.

4.2.4 Influence of carbon monoxide

In our first series of experiments with CO we investigated current distribution over a PtRu/C catalyst exposed to ppm levels of CO in a mixture of 50 % H₂, 40 % CO₂ and 10 % N₂ (This gas mixture is hence forth called reformate mix) when operating the cell in a galvanostatic mode. As may be seen in Figures 13 and 14, introducing ppm levels of CO will not cause any major transient behaviour with respect to current density on a PtRu/C catalyst, as long as the current density is constant. There are small deviations, but no trend may be distinguished. However, the situation is quite different when the cell is operated potentiostatically at 680 mV (Figures 15 and 16).

As may be seen in Figure 15 the adsorption of CO (reaction 1) is fast and decreases the available surface area for hydrogen dissociation and oxidation (reactions 2 and 3) at the inlet faster than at the outlet. As the CO coverage at the inlet increases the CO may be transported further and further along the flow direction, eventually giving rise to an even current distribution, at a total current much lower than for the non-poisoned case. After 1 hour the current density distribution is fairly stable for the 10 ppm case (Figure 15), whereas 10 minutes is enough for 80 ppm CO (Figure 16).
Figure 13. Galvanostatic (average current density 0.5 A cm\(^{-2}\)) current distribution transient behaviour of PtRu/C during 1.5 hours when introducing 10 ppm CO in 50 % H\(_2\), 40 % CO\(_2\) and 10 % N\(_2\) (reformate mix). Stoichiometry cathode 2.4, anode 1.5. Cell temperature 60 °C. RH 100 %. Pressure ambient.

Figure 14. Galvanostatic (average current density 0.5 A cm\(^{-2}\)) current distribution transient behaviour for PtRu/C during 1 hour when introducing 80 ppm CO in 50 % H\(_2\), 40 % CO\(_2\) and 10 % N\(_2\) (reformate mix). Stoichiometry cathode 2.4, anode 1.5. Cell temperature 60 °C. RH 100 %. Pressure ambient.
Figure 15. Potentiostatic (680 mV) current distribution transient behaviour of PtRu/C during 2 hours current distribution when introducing 10 ppm CO in 50 % H₂, 40 % CO₂ and 10 % N₂ (reformate mix). Stoichiometry cathode 2.4, anode 1.5. Cell temperature 60 °C. RH 100 %. Pressure ambient.

Figure 16. Potentiostatic (680 mV) current distribution transient behaviour of PtRu/C when introducing 80 ppm CO in 50 % H₂, 40 % CO₂ and 10 % N₂ (reformate mix). Stoichiometry cathode 2.4, anode 1.5. Cell temperature 60 °C. RH 100 %. Pressure ambient.
The reason for the discrepancy between the two modes of operation lies in the anodic polarization. In the galvanostatic experiment the cell voltage fluctuates (see small figure in Figure 14), this means that as the CO coverage increases, the anodic potential will also increase. As the potential increases, hydroxides form at the Ru sites of the catalyst (reaction 6). The hydroxides will be utilized in the carbon monoxide oxidation reaction (reaction 7) according to the so-called bi-functional mechanism. These oxidation pulses occur evenly over the catalyst surface and thereby lower the surface coverage and make the current distribution more even. As soon as the CO coverage drops, the anodic polarization will also drop and the adsorption/oxidation cycle may start over again. For the potentiostatic case the potential of the anode is locked below that of any substantial CO oxidation (OCV – operating voltage – iR-drop – contact resistance – cathodic polarisation), which means that adsorbed CO stays on the surface.

As may be seen in Figures 17 and 18, steady-state current distribution profiles are developed when introducing CO into a Pt/C anode run in a galvanostatic mode. The current at the inlet of the cell is lower than the current at the outlet at a cell voltage of around 400 mV for 10 ppm and at 300 mV for 80 ppm of CO. The reason for this uneven current distribution profile might be that as the surface coverage at the inlet increases, the anodic polarization also increases enough to cause small pulses of electrochemical CO oxidation. These pulses might oxidize the CO that is being continuously transferred to the surface, thus maintaining the steady-state profile. The oxidizing current pulses in this case would not be as high as in the PtRu/C case, where they have a much more predominant effect on current distribution. The same behaviour is observed for the 80 ppm case as for the 10 ppm case, even though the process is much faster for the 80 ppm case.

![Figure 17. Galvanostatic (average current density 0.5 A cm⁻²) current distribution transient behaviour of Pt/C during 1 hour when introducing 10 ppm CO in 50 % H₂, 40 % CO₂ and 10 % N₂ (reformate mix). Stoichiometry cathode 2.4, anode 1.5. Cell temperature 60 °C. RH 100 %. Pressure ambient.](image-url)
Figure 18. Galvanostatic (average current density 0.5 A cm\(^{-2}\)) current distribution transient behaviour of Pt/C during 1 hour when introducing 80 ppm CO in 50 % H\(_2\), 40 % CO\(_2\) and 10 % N\(_2\) (reformate mix). Stoichiometry cathode 2.4, anode 1.5. Cell temperature 60 °C. RH 100 %. Pressure ambient

4.2.5 Influence of air bleed

The influence of air bleed on current distribution was tested both for CO and CO\(_2\) poisoning. The recovery of cell performance from CO\(_2\) poisoning for a Pt/C anode by air bleed was very fast; an air bleed level of 0.5 % was enough to give a cell voltage of the same magnitude as when diluting to the same degree with N\(_2\).

When CO was added to the fuel stream more air bleed was needed. As may be seen in Figure 19 the cell performance of a PtRu/C anode with 80 ppm CO in the anode gas starts to improve already at low air bleed levels, but is not recovered until the air bleed level is 4 %. It was found that approximately 0.5 % air bleed is needed for each 10 ppm CO. This was also true for the Pt/C anode, when operated in galvanostatic mode. An air bleed level of 0.5 % per 10 ppm CO means that a maximum of 0.5 % of the added oxygen reacts with CO. As previously mentioned Jusys and Behm (2004) found that 10\(^{-4}\) of the oxygen supplied in their flow cell study reacted with CO. This might be attributed to different flow conditions. Whenever PtRu/C was operated under galvanostatic conditions with CO, the air bleed stabilized the otherwise very unstable cell voltage.

About 2/3 of the poisoning at the largest dilution was however recovered by adding a 1 % air bleed. This would not be absolutely necessary, especially at low dilution. However, over long operating periods the CO\(_2\) poisoning might be worsened.
Figure 19. Potentiostatic (680 mV) current distribution steady-state of PtRu/C for different levels of air in 80 ppm CO, 50 % H₂, 40 % CO₂ and 10 % N₂ (reformate mix). Stoichiometry cathode 2.4, anode 1.5. Cell temperature 60 °C. RH 100 %. Pressure ambient.

Figure 20. Potentiostatic (680 mV) current distribution of PtRu/C when introducing 3 % air in 80 ppm CO, 50 % H₂, 40 % CO₂ and 10 % N₂ (reformate mix). Stoichiometry cathode 2.4, anode 1.5. Cell temperature 60 °C. RH 100 %. Pressure ambient.
As seen in Figures 15 and 17 the dynamics of the poisoning is relatively slow when 10 ppm CO is introduced into the fuel stream. In the Pt/C case (figure 17) the cell voltage starts to drop slowly, and reaches a steady-state value after approximately 60 min. For the potentiostatic PtRu/C case (figure 15) the current distribution also reaches a steady-state value after approximately 60 minutes. Even when introducing 80 ppm (figure 13) it takes approximately 8 minutes for the current distribution to reach steady-state. This implies that at a steady-state CO level of 10 ppm and an air bleed level of 2 %, short CO peaks as high as 100 ppm would probably not need any additional air bleed. From a poisoning perspective, these peaks could then be allowed, for example, during load change of a reformer.

As seen in Figure 20, it takes approximately 4 minutes for the PtRu/C to reach steady-state when 3 % air bleed is introduced. This is half the time it takes for the poisoning effect of 80 ppm to reach steady state (figure 16). During the recovery of an electrode poisoned by 80 ppm CO in the potentiostatic mode, there is no dependence on air bleed level (figure 19) or time of air bleed (figure 20) on current distribution.

This implies that oxygen reacts evenly over the surface also in the cases where there is not enough oxygen present to recover all of the current, in spite of the extreme overpotential with reference to oxygen reduction. However, if this would be the case there would have to be some oxygen present at the anode outlet of the cell, especially at high air bleed levels. As may be seen in Table 7 there is no O₂ present at the anode outlet if there is a catalyst layer present. If the cell is mounted with only a Nafion® membrane instead of a MEA the O₂ is present at the outlet of the cell at the same partial pressure as at the inlet.

**Table 7. Results from gas analysis with and without catalyst in a 54 cm² PEFC single cell**

<table>
<thead>
<tr>
<th></th>
<th>O₂ % Cell inlet</th>
<th>CO ppm Cell inlet</th>
<th>O₂ % Cell outlet</th>
<th>CO ppm Cell outlet</th>
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<tr>
<td>Gore PRIMEA® series 5621, Carbel™</td>
<td>0.00</td>
<td>100</td>
<td>0.00</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>0.13</td>
<td>100</td>
<td>0.00</td>
<td>0.00</td>
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<tr>
<td></td>
<td>0.26</td>
<td>100</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>0.53</td>
<td>100</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Nafion® 112, Carbel™</td>
<td>0.00</td>
<td>9.93</td>
<td>0.00</td>
<td>9.99</td>
</tr>
<tr>
<td></td>
<td>0.11</td>
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<td>9.95</td>
</tr>
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<td></td>
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<td>9.89</td>
<td>0.20</td>
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<tr>
<td></td>
<td>0.40</td>
<td>9.86</td>
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<td>9.73</td>
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<td></td>
<td>0.85</td>
<td>9.52</td>
<td>0.83</td>
<td>9.35</td>
</tr>
<tr>
<td></td>
<td>1.57</td>
<td>9.12</td>
<td>1.53</td>
<td>8.97</td>
</tr>
</tbody>
</table>

This means that only an amount lower than the detection limit of our measuring equipment for O₂ could react, for instance, on the carbon in the GDL. Since no O₂ was detected at the anode outlet when operating the cell with a Gore PRIMEA® series 5621 MEA, at an air bleed level of 2.5 % (0.53 % O₂), most of the O₂ probably reacts at the anode inlet. The reason could be that
the anode inlet simply acts as a preferential oxidation reactor, cutting the supply of CO to the catalyst further downstream. The increase in available surface area for hydrogen oxidation towards the end of the cell would thus not be a result of O₂ reaching the end of the cell, but of the local concentration of CO at the outlet being lowered by O₂ oxidation at the anode inlet. Alternatively, the O₂ could be reduced to H₂O₂ at the inlet, which would then react with CO as it is transported towards the cell outlet. In Table 7 the CO partial pressure is also accounted for. As may be seen the CO level at the anode outlet reaches zero already at a very low air bleed. However, the cell performance is not recovered until the air bleed level is much higher, as may be seen for instance in Figure 19. The performance of the cell is of course not recovered until there is no electrochemical CO oxidation and this is not related to the CO level at the anode.

As seen in Figure 21 the air bleed level does not have any influence on the current distribution with fully humidified gases. As mentioned above a maximum of 0.5 % of the oxygen in the air bleed is actually utilized for oxidizing CO. If the remaining oxygen were to react with hydrogen and form water it would produce heat, since the enthalpy of that reaction is approximately -240 kJ mol⁻¹. When adding 4 % air bleed the heat production in the cell could potentially increase by 25 % (at 0.5 A cm⁻² and 0.6 V) in the cell and potentially dry out the membrane at the inlet. This is however not the case when operating the cell with well humidified gases since no shift in current distribution could be measured. When operating the fuel cell galvanostatically during air bleeding the cell voltage is reduced by a few mV due to the mixed potential at the anode.

As mentioned above air bleeding does not remove all adsorbed CO even if the cell voltage does not indicate poisoning. This is emphasized in Figure 22. As may be seen an anode catalyst that is completely clean will need a few minutes (195 s for 50 ppm and 135 s for 100 ppm CO) before the surface coverage is so high that the potential starts to decrease, giving the control system some time to take action. If the air bleed is turned off while having a constant CO level of 50 ppm the potential of the cell starts to decrease after approximately 85 seconds, which then is even worse than a 100 ppm CO pulse on a clean catalyst (the supply of CO to the cell is almost instantaneous). This indicates that the surface coverage by CO is quite high already with air bleed in the case where the air bleed is turned off. Thus, the air bleed does not remove all CO adsorbed onto the anode surface. This has also been measured in experimental model studies (Jusys et al., 2003 and Stamenkovic et al., 2005).
Figure 21. Galvanostatic (average current density 0.5 A cm$^{-2}$) current distribution of PtRu/C when introducing air into pure H$_2$. Stoichiometry cathode 2.4, anode 1.5. Cell temperature 60°C. RH 100 %. Pressure ambient.

Figure 22. 50 - 100 ppm CO poisoning transients in a 5 kW PEFC fuel cell stack. Fuel 50 % H$_2$, 40 % CO$_2$, 10 % N$_2$, varying CO and air bleed levels. In the first case a 4 % air bleed is turned off while the 50 ppm CO level is left constant. In the second case the CO level is stepped from 0 to 50 ppm. In the third case the CO level is stepped from 0 to 100 ppm. As the lowest cell potential goes below 400 mV a 4 % air bleed is turned on. Stoichiometry cathode 2.0, anode 1.5. Pressure 2 bar abs. Cell temperature 60°C. Relative humidity 100 %.
4.2.6 CO peaks

Peaks of higher levels of CO were investigated at stack level. In Figure 23, CO peaks lasting a minute at different concentrations are shown for an air bleed level of 2 %. The 50 ppm CO present in the gas before the peaks is close to the concentration where the potential starts to drop due to CO poisoning. A peak of 200 ppm will cause a potential drop of 50 mV. A peak of 400 ppm will cause a rapid decrease resulting in the cell voltage oscillating at around 450 mV. At this point only a small amount of the CO is oxidized by the air bleed, since most is oxidized in the electrochemical reaction at the anode (the anode potential at this point being approximately 250 – 300 mV).

![Figure 23](image.png)

**Figure 23.** CO pulses lasting 1 minute in a 5 kW PEFC 50 % H₂, 40 % CO₂, 10 % N₂ and 50 ppm CO (before peaks) at a constant air bleed level of 2 %. Stoichiometry cathode 2.0, anode 1.5. Pressure 2 bar abs. Cell temperature 60 °C. Relative humidity 100 %.

If the fuel cell is operated with a reformer that gives CO peaks higher than 200 ppm, an air bleed level of 2 % would not be sufficient. One way of dealing with these pulses would be to increase the air bleed level. In Figure 24, one minute long CO pulses of 300 ppm are shown for different cases. As may be seen for the first case with 2 % air bleed and 50 ppm CO in the gas before the peak, a 300 ppm CO pulse decreases the average cell voltage to approximately 475 mV in less than a minute.

If the air bleed level is increased to 4 % while keeping the CO level before the peak at 50 ppm the voltage loss during one minute is approximately 15 mV. For the third case in Figure 18 the air bleed was held at 4 % while increasing the CO level before the peak to 100 ppm. This resulted in a potential drop of approximately 25 mV. This shows that CO peaks of 300 ppm during a single minute are not fatal for the system. If no measures are taken the power output is temporarily reduced (0.36 W cm⁻² to 0.22 W cm⁻²), but the system is fully recovered after a few minutes of normal operation (50 ppm CO in the gas before peak, 2 % air bleed). This indicates the delays allowable for the control systems of the air bleed as well as the control system of the potential reformer or gasification unit in order to still achieve a stable power output from the fuel cell system.
Figure 24. Pulses of 300 ppm CO lasting 1 minute in a 5 kW PEFC 50 % H₂, 40 % CO₂, 10 % N₂, at a) an air bleed level of 2 % with a CO level of 50 ppm (before peak) and b) an air bleed level of 4 % with CO levels of 50 and 100 ppm (before peaks). Stoichiometry cathode 2.0, anode 1.5. Pressure 2 barₐbs. Cell temperature 60 °C. Relative humidity 100 %. 
5 CONCLUSIONS

5.1 System level
A significant outcome of this study is that the possibility of operating both PEFC systems as well as SOFC systems on biogas has been established. No interruptions or rapid performance loss could be associated with the operation on upgraded biogas. The SOFC system was operated for a total of 3310 hours. The performance decrease during period before the broken cell was similar to other studies of systems from the same supplier operated on natural gas. The same is true for the H-power system. The SOFC system was unable to handle thermal management during load change. During dynamic tests the temperature gradient over the stack increased to unsustainable levels which reached even above 100 °C.

The results from the 4 kW H-power unit in GlashusEtt showed a system with low electrical efficiency (13%) and a comparably high thermal efficiency (56 %). The heat was supplied to the building both as waste heat from the system as well as through the heat recovery system.

The SOFC system was operated for 1700 hours with a broken cell indicating that shutdown conditions, which of course are good for identifying problems, might not always be necessary for the safety and operability of the SOFC systems.

An absolute majority of the problems during operation of both the PEFC unit as well as the SOFC unit was not caused by the fuel cell technology but rather the control systems or other components in the units.

5.2 Stack and cell
The 5 kW PEFC stack supplied with simulated reformate with a hydrogen content as low as 25 % showed stable operating conditions for all experiments performed. The efficiency of the fuel cell stack is not significantly changed when diluted fuel streams are used. The efficiency at 0.5 A cm⁻² is reduced from 39 % to 37.2 % when the CO₂ content in the gas is doubled from 23 to 50 %. CO₂ has a more negative effect on the cell voltage of a PEFC compared to N₂ and the effect is enhanced by increased dilution. The poisoning effect is small; it depends on the anode catalyst used and may be recovered with small air bleed, which means that it is catalytic.

Poisoning effects are unevenly distributed throughout the cell which makes current distribution measurement a good tool for evaluating poisoning phenomena in a full-size PEFC. Air bleed may recover the uneven current distribution caused by CO. In the experimental set-up used in this study an air bleed level of approximately 0.5 % was needed for each 10 ppm of CO, which means that a maximum of 0.5 % of the added oxygen reacted with CO. The recovery of cell performance during air bleed occurs evenly over the electrode surface even when the O₂ partial pressure is far too low to fully recover the CO poisoning.

CO-poisoning transients for the investigated CO concentrations are fast, but the air bleeding recovery transients are faster. The current distribution reaches steady state after approximately 8 minutes following addition of 80 ppm CO to the feed stream, by adding 3 % air bleed the current distribution is recovered in 3 minutes. The O₂ that is supplied to the anode reacts on the anode
catalyst and no O$_2$ is measured at the cell outlet. The amount of CO at the anode outlet reaches zero already at a very low air bleed. However, the cell performance is not recovered until the air bleed level is much higher since the performance of the cell is related to the surface area available for H$_2$ oxidation and the rate of electrochemical CO oxidation. At a non-poisoned PtRu/C electrode, air bleeding does not influence the current distribution at all.

When running a fuel cell on gas from a load-following reformer it is recommended to have slightly more air bleed than needed at steady state in order to facilitate a faster recovery from peaks. CO peaks of 300 ppm during a minute are not fatal to the system. If no measures are taken the power output is temporarily reduced from 0.36 W cm$^{-2}$ to 0.22 W cm$^{-2}$, but the system is fully recovered after a few minutes of normal operation (50 ppm CO in the gas before peak, 2 % air bleed).

Reformed biogas and other gases with high CO$_2$ content are, from dilution and CO-poisoning perspectives, suitable for PEFCs. Biogas-specific challenges that remain are connected to the gas composition and cleaning the biogas from different possible contaminants. These results do however indicate that upgrading of biogas is not necessary for the use of biogas in PEFC systems, which could be a significant system simplification compared to the use of biogas in combustion technologies. The work presented in this thesis has enhanced our understanding of biogas-operated fuel cells and will serve as basis for future studies.
6 Final Remarks

If the negative effect on climate, environment and eco systems continues it is probable that there will be an increased pressure on policy makers, politicians and society as a whole to implement more sustainable lifestyles and consumption patterns. I would argue that it has been shown in this thesis that one path (out of many) to pursue on such a mission should be fuel cells operated on biogas.

Fuel cells and biogas constitute an interesting option for local decentralized electricity production with the use of locally produced biogas, as well as an interesting niche which might further help develop fuel cells and provide, in terms of installed units in 2010, a substantial market for fuel cells. Together fuel cells and biogas might fit into a normative scenario constituting a no-regret pathway and a safeguard against the unforeseen.

Infrastructural change is often subsidized and helped. The progress made in wind power and photovoltaics is not mainly a merit of the technologies’ competitiveness but rather the result of political decisions that have created markets and incentives to develop and improve the technologies. The mass and momentum that the fuel cell industry has today could be further significantly supported if fuel cells and biogas were to receive directed support similar to the subsidy programme in the US for forklifts or the NEDO large-scale demonstration programme in Japan. Support and efforts directed towards fuel cells and biogas could take us one step closer to revealing the true potential of fuel cells, no matter what it turns out to be.

Fuel cells and the possibly carbon-free conversion chain that they potentially could be part of is of course from many perspectives an attractive solution for all kinds of applications. When discussed in the light of today’s energy system the concept is at first sight very appealing, but then when the effects of production, packaging, distribution, storage and end use of hydrogen are included one might end up with a total energy chain with implies more emissions than for conventional technology and simultaneously being less efficient than the existing systems.

It is however hard it to predict the future and the potential of fuel cells as energy converters in an emission-free conversion chain stands out from conventional combustion technology. It is far too early to say if fuel cells will live up to their potential or not and at the same time it is impossible to know how we will be able to produce hydrogen in the future.
7 ACKNOWLEDGEMENTS

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Marita, I love you. Thank you for all support and for putting up with my sometimes slightly time optimistic approach to life. You really help me be the best I can be and you support my sometimes too many undertakings. And last but not least (except in size), Ellen, 8 months and already a strong and charming personality. I love you and I will do my best to be the best parent ever.
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AC</td>
<td>Alternating current</td>
</tr>
<tr>
<td>APU</td>
<td>Auxiliary power unit</td>
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<tr>
<td>CH₂</td>
<td>Compressed hydrogen</td>
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<td>CHP</td>
<td>Combined heat and power</td>
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<td>DC</td>
<td>Direct current</td>
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<td>Direct methanol fuel cell</td>
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<td>DOE</td>
<td>Department of Energy (US)</td>
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<tr>
<td>El</td>
<td>Electricity</td>
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<tr>
<td>FU</td>
<td>Fuel utilization</td>
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<tr>
<td>GDL</td>
<td>Gas diffusion layer</td>
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<tr>
<td>GDP</td>
<td>Gross domestic product</td>
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<td>GH₁</td>
<td>GlasiusEtt (The environmental information centre in Hammarby)</td>
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<tr>
<td>HHV</td>
<td>Higher heating value</td>
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<tr>
<td>HT-PEFC</td>
<td>High-temperature polymer electrolyte fuel cell</td>
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<tr>
<td>i&lt;sub&gt;avg&lt;/sub&gt;</td>
<td>Average current density</td>
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<td>International Energy Agency</td>
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<tr>
<td>IGCC</td>
<td>Integrated gasification combined cycle</td>
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<td>LHV</td>
<td>Lower heating value</td>
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<td>Molten carbonate fuel cell</td>
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<td>MEA</td>
<td>Membrane electrode assembly</td>
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<td>Open circuit voltage</td>
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<td>Phosphoric acid fuel cell</td>
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<td>Proton exchange membrane</td>
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<td>Partial oxidation</td>
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<td>Reference hydrogen electrode</td>
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<td>Reverse water gas shift</td>
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<td>SECA</td>
<td>Solid state Energy Conversion Alliance</td>
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<tr>
<td>SOFC</td>
<td>Solid oxide fuel cell</td>
</tr>
<tr>
<td>UPS</td>
<td>Uninterruptible power supply</td>
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REFERENCES

Ajhar M, Travesset M, Yüce S and Melin T, Siloxane removal from landfill and digester gas – A technology overview, Bioresource Technology 2010;101(9): 2913-2923

Ascoli A, Pandya J D and Redaelli G, Electrical characterization of a 2.5 kW phosphoric acid fuel cell stack operating on simulated reformed biogas, Energy 1989;14(12):875-878


Dokmaingam P, Assabumrungrat S, Soottitantawat A and Laosiripojana N, Modelling of tubular-designed solid oxide fuel cell with indirect internal reforming operation fed by different primary fuels, J Power Sources 2010;195: 69-78

Eichler A and Hafner J, Reaction channels for the catalytic oxidation of CO on Pt(111), Phys Rev B 1999;59(8): 5960-5967


EUR 20719 EN - Final report of the High Level Group (2003), European Commission: Hydrogen energy and fuel cells—A vision of our future, European Commission, Luxembourg, Belgium


Farhad S, Yoo Y and Hamdullahpur F, Effects of fuel processing methods on industrial scale biogas-fuelled solid oxide fuel cell system for operating in wastewater treatment plants, J Power Sources 2010;195(5): 1446-1453


Hultman M, and Saxe M, Full gas mot en renare miljö– Om hur bränsleceller framställs av media och experter, Arbetsnotat Nr 31, Program Energisystem, Linköpings Universitet, 2005 (In Swedish)


Israelson G, Results of testing various natural gas desulphurisation adsorbents, J Mater Eng Perform 2004;13(3): 282–286


Kivisaari T, Björnbom P and Sylwan C, Studies of biomass fuelled MCFC systems, J Power Sources 2002;104: 115-124


NEF –New Energy Foundation (2009), FY 2008 Interim Annual Report – Progress Report on The Large-Scale Stationary Fuel Cell Demonstration Project in Japan. Available from okuda@nef.or.jp


Staniforth J and Kendall K, Cannock landfill gas powering a small tubular solid oxide fuel cell – A case study, J Power Sources 2000;86(1-2): 401-403


Trogisch S, Hoffmann J and Bertrand I D, Operation of molten carbonate fuel cells with different biogas sources: A challenging approach for field trials, J Power Sources 2005;145(2): 632-638


Van herle J, Membrez Y and Bucheli O, Biogas as a fuel source for SOFC co-generators, J Power Sources 2004;127(1-2): 300-312


Wärtsilä Corporation, Wärtsilä has been highly successful in operating its groundbreaking fuel cell unit. Retrieved from www.wartsila.com, May 1, 2010
