Hydrogen supply in proton exchange membrane fuel cell systems

Kaj Nikiforow
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A doctoral dissertation completed for the degree of Doctor of Science (Technology) to be defended, with the permission of the Aalto University School of Chemical Engineering, at a public examination held at the lecture hall Ke2 of the school on 8th June 2018 at 12.

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Abstract
Proton exchange membrane fuel cells (PEMFCs) are a fuel cell type that operate at low temperature and are commonly fueled with hydrogen gas. A PEMFC is seen as a promising power source for various applications including road vehicles, marine vessels, backup power, and grid balancing. Commercial PEMFC products are already available. The main factors limiting their widespread use are the lack of an extensive hydrogen distribution network, their price, and their durability.

To work efficiently, a PEMFC requires a set of components for fuel supply, oxidant supply, and cooling. This set of components is called the balance of plant (BoP). The PEMFC and the BoP together form a PEMFC system. The BoP contributes to a substantial fraction of the total system price and considerably affects system performance and durability.

This thesis examines the hydrogen supply in PEMFC systems with electrical power in the range 5 to 50 kW. In particular, components and methods for realizing hydrogen purge, hydrogen humidification, and hydrogen recirculation are evaluated theoretically and experimentally. Effort is put on examining solutions that improve system efficiency and durability while decreasing cost.

Hydrogen purge is a widely used approach for removing impurities and liquid water from a dead-end anode. In this work, methods for determining PEMFC membrane permeability, fuel purity, as well as the amount and composition of purged gas are developed and demonstrated. These methods can be used as indicators of fuel supply or PEMFC system malfunctioning. Further, the effects of hydrogen purge on an 8 kW PEMFC system performance are studied by varying the cathode inlet humidity. Results show that PEMFC stack efficiency improves by 0.7% when increasing cathode inlet dew point temperature from 52 °C to 58 °C. The role of the purge shifts at these high-humidity conditions from impurity removal towards liquid water removal.

A humidifier can be employed to increase the anode inlet gas humidity and, consequently, to increase the PEMFC efficiency and durability. In this work, a bubble humidifier for a 50 kW PEMFC pilot plant using PEMFC stack waste heat is modelled and characterized. One commonly cited disadvantage of a bubble humidifier is the high hydrostatic pressure drop. The modelling results suggest that efficient humidification is achieved with only 5 mbar hydrostatic pressure drop.

Hydrogen recirculation is commonly applied to increase the gas flow velocity in a PEMFC. Ejectors have attracted attention because of their low price and high durability compared to mechanical pumps. However, ejector sizing and control still lack established methods. In this work, a 2-dimensional (2D) computational fluid dynamics (CFD) modelling approach for ejectors is validated against experimental data using three different turbulence models. In addition, a discrete control system for ejector is developed. Finally, the low-price and robust combination of a single fixed geometry ejector and a discrete control system is tested with a 5 kW PEMFC system by performing load transients from 2 kW to 4 kW within a fraction of a second.

Keywords PEMFC, hydrogen purge, hydrogen humidification, hydrogen recirculation
Tekijä
Kaj Nikiforow

Väitöskirjan nimi
Vedensyöttö protoninvaihtopolttokennojärjestelmää

Julkaisija
Kemian teknikan korkeakoulu

Yksikkö
Kemian teknikan ja metallurgian laitos

Sarja
Aalto University publication series DOCTORAL DISSERTATIONS 110/2018

Tutkimusala
Kemian laitetekniikka

Käsikirjoituksen pvm
01.02.2018

Väitöspäivä
08.06.2018

Julkaisuluvan myöntämispäivä
24.04.2018

Kieli
Englanti

Monografia

Artikkeliväitöskirja

Esseeväitöskirja

Tiivistelmä

Toimikseen tehokkaasti, PEMFC tarvitsee joukon komponentteja polttoaineensyöttöön, hapetimensyöttöön ja jähdytykseen. Näistä komponentteista käytetään englanninkielistä nimitystä "balance of plant" (BoP). Yhdessä PEMFC:n kanssa BoP-komponentit muodostavat PEMFC-järjestelmän. BoP-komponentit muodostavat merkittävän osan PEMFC-järjestelmän hinnasta ja ne vaikuttavat keskeisesti PEMFC-järjestelmän suorituskykyyn ja kestävyyteen.

Tässä väitöskirjassa tarkastellaan vedyn syöttöä 5-50 kW PEMFC-järjestelmöissä. Erityisesti arvioidaan teoreettisesti ja kokeellisesti komponentteja ja menetelmiä vetyhuutelun, vedyn kostutuksen ja vedyn kerrityksen toteutamiseksi. Pyrkimyksenä on tarkastella ratkaisuja, jotka parantavat järjestelmän hyötysuhtetta ja kestävyyttä mutta laskevat sen hintaa.


Avainsanat
PEMFC, vetyhuutelu, vedyn kostutus, vedyn kerritys

ISBN (painettu) 978-952-60-8029-1

ISBN (pdf) 978-952-60-8030-7

ISSN (painettu) 1799-4934

ISSN (pdf) 1799-4942

Julkaisupaikka Helsingin

Painopaikka Helsingin

Vuosi 2018

Sivumäärä 192

Preface

The work presented in this thesis was conducted at VTT Technical Research Centre of Finland Ltd during the years 2011-2013 and 2016-2018 and at Aalto University during the years 2013-2016. The work at VTT was conducted under the TopDrive and DuraDemo projects that were funded by Tekes (the Finnish Funding Agency for Innovation), the PEMBeyond project that was funded by the European Union’s Seventh Framework Programme for research, technological development and demonstration, and the EL-TRAN project that was funded by the Academy of Finland. I would like to acknowledge the Graduate School of Chemical Engineering (GSCE), VTT, and the Walter Ahlström foundation for financial support, which has allowed me to concentrate on this thesis.

This thesis would not have been possible without the help of many people that I have had the opportunity to work with during the past seven years. For this, I would like to acknowledge them all.

Especially, I want to thank my supervisor, Professor Ville Alopaeus and my instructor, Dr. Jari Ihonen. Ville Alopaeus, with his proficiency in chemical engineering and his attention to details, has guided me through the process of thesis writing. Jari Ihonen’s expertise in the field of proton exchange membrane fuel cells and his never-ending innovation of new ideas and solutions has provided me with an inspiring working environment.

I also want to thank my co-authors, technicians at VTT, and other colleagues both at VTT and at Aalto University, who have made this work possible.

Last but not least, I want to thank my family – my wife, my two sons, and my yet unborn daughter – for being there and counterbalancing my work.

Espoo, Finland, January 2, 2018

Kaj Nikiforow
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**Publications I-VI**
This doctoral dissertation consists of a summary and the following publications, which are referred to in the text by Roman numerals.


Author’s Contribution

I: The use of on-line hydrogen sensor for studying inert gas effects and nitrogen crossover in PEMFC system

H. Karimäki took part in designing and building the PEMFC system, conducted system characterization, took part in inert buildup measurements, and was the main writer of the manuscript. L.C. Pérez took part in measurements and in writing the manuscript. K. Nikiforow took part in building the PEMFC system, in inert buildup measurements, and in reviewing the manuscript. T.M. Keränen, J. Viitakangas, and J. Ihonen took part in designing the PEMFC system and the experiments and reviewed the manuscript.

II: Optimization study of purge cycle in proton exchange membrane fuel cell system

K. Nikiforow took part in designing and modifying the PEMFC system, conducted the measurements, compiled and interpreted the results, and was the main writer of the manuscript. H. Karimäki took part in designing and modifying the PEMFC system, interpreting the results, and writing the manuscript. T.M. Keränen and J. Ihonen took part in designing the PEMFC system, interpreting the results, and reviewing the manuscript.

III: Modeling and experimental validation of H₂ gas bubble humidifier for a 50 kW stationary PEMFC system

K. Nikiforow was responsible for designing, characterizing, and modelling the bubble humidifier. K. Nikiforow also compiled and interpreted the results and was the main writer of the manuscript. J. Ihonen took part in designing the bubble humidifier, designing the experiments, interpreting the results, and reviewing the manuscript. T. Keränen and H. Karimäki took part in designing and characterizing the bubble humidifier, interpreting the results, and reviewing the manuscript. V. Alopaeus took part in interpreting the results and reviewing the manuscript.

IV: Designing a hydrogen gas ejector for 5 kW stationary PEMFC system – CFD-modeling and experimental validation

K. Nikiforow designed the ejector inner dimensions, participated in building the test setup, conducted the experiments, performed the CFD simulations, compiled the data, and was the main writer of the manuscript. P. Koski was responsible for ejector manufacturing and participated also in building the test setup,
in interpreting the results, and reviewing the manuscript. H. Karimäki, J. Ihonen, and V. Alopaeus took part in interpreting the results and reviewing the manuscript.

V: Discrete ejector control solution design, characterization, and verification in a 5 kW PEMFC system

K. Nikiforow designed the PEMFC system, took part in designing the ejector primary flow control solution (EPC), sized and tested the EPC, conducted the measurements, compiled the results, and was the main writer of the manuscript. P. Koski took part in the experimental work and in designing the EPC, in interpreting the results, and in reviewing the manuscript. J. Ihonen took part in designing the EPC and the experiments, in interpreting the results, and in reviewing the manuscript.

VI: Power ramp rate capabilities of a 5 kW proton exchange membrane fuel cell system with discrete ejector control

K. Nikiforow made the modifications to the PEMFC system and to the control software, conducted the experiments, compiled the experimental data, and was the main writer of the paper. J. Pennanen implemented the model, conducted the simulations, and compiled the simulation results. J. Ihonen took part in designing the experiments, in interpreting the results, and in writing the paper. S. Uski participated in writing the manuscript. P. Koski reviewed the manuscript.
# List of Abbreviations and Symbols

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<th>Latin symbol</th>
<th>Explanation</th>
<th>Value/unit</th>
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<tr>
<td>$A$</td>
<td>Area</td>
<td>m$^2$</td>
</tr>
<tr>
<td>$a_i$</td>
<td>Activity of species $i$</td>
<td>-</td>
</tr>
<tr>
<td>$b$</td>
<td>Cell pressure drop coefficient</td>
<td>bar/(kg/s)</td>
</tr>
<tr>
<td>$C_p$</td>
<td>Isobaric heat capacity</td>
<td>J/(mol·K)</td>
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<td>$C_i$</td>
<td>Specific heat capacity of $i$</td>
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<td>$c$</td>
<td>Concentration</td>
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<tr>
<td>$d$</td>
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<td>$e$</td>
<td>Elementary charge</td>
<td>1.6022·10$^{-19}$ C [1]</td>
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<td>$F_o$</td>
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<td>$\Delta G$</td>
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<td>Power</td>
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<td>$T$</td>
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<td>$h$</td>
<td>Heating water</td>
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<td>Ejector secondary inlet</td>
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<tr>
<td>sim</td>
<td>Simulated</td>
</tr>
<tr>
<td>tot</td>
<td>Total</td>
</tr>
</tbody>
</table>

### Superscript Explanation

<table>
<thead>
<tr>
<th>Superscript</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>*</td>
<td>Ideal gas</td>
</tr>
<tr>
<td>0</td>
<td>Standard conditions ($T = 25^\circ C$, $p = 1$ bar)</td>
</tr>
</tbody>
</table>

### Abbreviation Explanation

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1D</td>
<td>One-dimensional</td>
</tr>
<tr>
<td>2D</td>
<td>Two-dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>Three-dimensional</td>
</tr>
<tr>
<td>AC</td>
<td>Alternating current</td>
</tr>
<tr>
<td>AD</td>
<td>Mean absolute deviation (see Eq. 64)</td>
</tr>
<tr>
<td>BD</td>
<td>(Water) back-diffusion</td>
</tr>
<tr>
<td>BoP</td>
<td>Balance of plant</td>
</tr>
<tr>
<td>CFD</td>
<td>Computational fluid dynamics</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>DEA</td>
<td>Dead-end anode</td>
</tr>
<tr>
<td>DEFC</td>
<td>Direct ethanol fuel cell</td>
</tr>
<tr>
<td>DMFC</td>
<td>Direct methanol fuel cell</td>
</tr>
<tr>
<td>EOD</td>
<td>Electro-osmotic drag</td>
</tr>
<tr>
<td>EPC</td>
<td>Ejector-primary-gas-control-system</td>
</tr>
<tr>
<td>EVM</td>
<td>Eddy viscosity model</td>
</tr>
<tr>
<td>GDL</td>
<td>Gas diffusion layer</td>
</tr>
<tr>
<td>HOR</td>
<td>Hydrogen oxidation reaction</td>
</tr>
<tr>
<td>ICE</td>
<td>Internal combustion engine</td>
</tr>
<tr>
<td>LHV</td>
<td>Lower heating value</td>
</tr>
<tr>
<td>MEA</td>
<td>Membrane electrode assembly</td>
</tr>
<tr>
<td>NTP</td>
<td>Normal temperature ($273.15$ K) and pressure ($1.01325$ bar)</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Explanation</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>OCV</td>
<td>Open circuit voltage</td>
</tr>
<tr>
<td>ORR</td>
<td>Oxygen reduction reaction</td>
</tr>
<tr>
<td>PEMFC</td>
<td>Proton exchange membrane fuel cell (the single cell unless otherwise noted)</td>
</tr>
<tr>
<td>PFSA</td>
<td>Perfluorosulfonic acid</td>
</tr>
<tr>
<td>PV</td>
<td>Photovoltaic</td>
</tr>
<tr>
<td>RANS</td>
<td>Reynolds-averaged Navier–Stokes</td>
</tr>
<tr>
<td>RD</td>
<td>Mean relative deviation (see Eq. 65)</td>
</tr>
</tbody>
</table>
1. Introduction

Modern society relies on energy being available for transportation, industry and residential heating or cooling, among others. Along with increasing population and growing personal income, the energy demand is expected to increase [2].

Fossil fuels have fulfilled a large portion of our energy demand for several decades. The use of fossil fuels is, however, not sustainable because of their limited reserves and the emissions associated with them.

Interest in renewable and sustainable energy has increased in the past decades. The total renewable power capacity has increased by 150% from 800 GW in year 2004 to 2017 GW in year 2016. In the same period of time, the sum of solar (photovoltaic, PV) and wind power capacity increased more than 15 times from 50.6 GW to 790 GW. [3,4]

The power output of both PV and wind power plants depends on prevailing weather conditions. For this reason, power generation from these sources is unpredictable in the long term and is likely to mismatch with the demand for power. In addition, the electric grid is unevenly loaded from these sources, and, therefore, energy storage is needed. [2]

The concept of the Hydrogen economy was first published in 1972 [5]. The idea behind this concept is to found the energy infrastructure on hydrogen as energy storage [2]. The excessive energy from PV and wind power can be stored as hydrogen by splitting water with electrolysis, for example.

Fuel cells are devices that can convert the energy stored in hydrogen back to electricity while emitting only water and heat. Fuel cells have no moving parts in contrast to combustion engines, which makes their operation efficient and silent [6].

Proton exchange membrane fuel cells (PEMFCs) are one type of fuel cells especially suited for applications where rapid load changes are expected (e.g. automotive, grid balancing, backup power) [7]. PEMFCs are, however, still too expensive for large-scale commercialization, but research is ongoing to reduce their price [8].

PEMFCs, like other fuel cell types, require a set of system components for fuel supply, oxidant supply, and cooling, for example. This set of components is called the balance of plant (BoP), and it makes up a substantial fraction of the total system cost [9]. The purpose of the BoP is to ensure optimal operating conditions for the PEMFC. Thus, careful design of the BoP is a key to cost efficient and durable PEMFC systems.
1.1 Thesis objective

The primary task of a hydrogen supply system in a PEMFC is to deliver hydrogen to a fuel cell. Without a hydrogen supply, the PEMFC cannot operate. The hydrogen supply system also has secondary tasks, such as preventing the buildup of impurities (contaminants and inert gases), removing liquid water, humidifying the hydrogen, and recirculating hydrogen. These tasks are important for efficient and long lasting PEMFC operation. The objective of this thesis is to study devices and methods for hydrogen supply that could improve PEMFC system performance and durability.

Hydrogen purge is an efficient way of removing inert gases and other impurities as well as liquid water from an anode. However, it has not been clear how the anode inert gas content, system humidity level, and hydrogen purge parameters affect the PEMFC and fuel efficiencies. Methods for measuring the required quantities were developed, and the aforementioned questions were studied in publications [I] and [II].

Although hydrogen humidification adds system complexity and cost, it is often employed because it improves PEMFC efficiency. A bubble humidifier has a simple design and working principle and is, thus, a good humidifier candidate for PEMFC systems. However, downsides such as hydrostatic pressure drop and the lack of controllability are factors often considered to outweigh the benefits. In publication [III], a bubble humidifier was designed, characterized, and modelled, and improvements on its design and control were discussed.

Hydrogen recirculation is typically employed in PEMFC systems because it improves PEMFC performance. Mechanical pumps often employed for hydrogen recirculation have been proven too unreliable. Ejectors, on the other hand, are seen as promising devices for this application. However, the limited working range of ejectors and the challenges in ejector primary flow control are seen as factors limiting their usability. Publications [IV]-[VI] examined the possibility of using the simplest thinkable approach to hydrogen recirculation – a single ejector with discrete primary flow control.

1.2 Thesis structure

The thesis first gives a brief introduction to PEMFC technology and PEMFC systems in Chapter 2. Chapter 3 provides an overview of hydrogen supply in PEMFC systems and describes the three secondary tasks of the hydrogen supply system: hydrogen purge, hydrogen humidification, and hydrogen recirculation.

Chapters 4-6 discuss the three secondary tasks of hydrogen supply in more detail and present the methods employed and results obtained in publications [I]-[VI]. Chapter 4 focuses on inert buildup and hydrogen purge, which was studied experimentally in publications [I] and [II]. Chapter 5 presents design, characterization, and modelling of a bubble humidifier for hydrogen humidification based on publication [III]. Chapter 6 presents methods and results of the work done in publications [IV]-[VI], which targeted hydrogen recirculation with a single, fixed geometry ejector and a discrete primary flow control.

A summary of the results is given in Chapter 7. The publications that thesis is based on are attached at the end.
2. Background

This chapter introduces proton exchange membrane fuel cell (PEMFC) technology. The PEMFC itself is introduced in Section 2.1, and the auxiliary components needed for successful operation of a PEMFC, i.e. the PEMFC system, are introduced in Section 2.2.

2.1 Proton exchange membrane fuel cell

A PEMFC, like other types of fuel cells, is an electrochemical cell; it converts the chemical energy of a fuel to electricity. Its function, therefore, resembles that of a battery. The main difference between fuel cells and batteries is, however, that fuel and oxidant are continuously supplied to fuel cells whereas batteries are closed systems. Therefore, fuel cells can, in principle, output electrical energy as long as fuel and oxidant are supplied. In this sense, the function of fuel cells closely resembles that of internal combustion engines (ICEs). The main difference between ICEs and fuel cells is, however, that fuel cells do not output mechanical energy like ICEs but electrical energy.

This work focuses solely on PEMFCs although a number of other fuel cell types exist. An introduction to PEMFC structure, its working principle, and factors that affect PEMFC voltage, power, and efficiency follow. A key factor in PEMFC technology, namely water management, is introduced in Section 2.1.3.

2.1.1 Structure and working principle

The basic structure of a PEMFC is shown in Figure 1. It consists of a membrane electrode assembly (MEA), gas diffusion layers (GDLs), gaskets, and end plates sandwiched together. The MEA is a polymer membrane (electrolyte) with catalyst layers (electrodes) attached to both sides. To enable normal PEMFC operation, the polymer membrane should be 1) proton conductive, 2) impermeable to gases, and 3) an electrical insulator [10]. The purposes of the GDLs is to enable the transport of 1) reactant gases to the catalyst, 2) water away from the catalyst, and 3) heat and electrons from the catalyst to the end plate, and 4) to give mechanical support to the MEA [6]. The end plates provide mechanical support, function as electron conductors, and contain gas channels for distributing the reactants over the entire cell [10].
Several PEMFCs can be connected electrically in series to form a PEMFC stack. The end plates between two adjacent cells then serve as both anodic and cathodic end plates and are called bipolar plates. Stacking cells together enables higher output voltages, as in batteries.

PEMFCs use pure hydrogen gas as the fuel. Hydrogen rich reformate gas can also be used as the fuel but, in that case, special attention is required because of the fuel’s higher impurity content. Reformate gas typically contains at least the impurities CO₂ and CO but might also contain significant amounts of N₂, H₂O, and CH₄ depending on the fuel and production process [12–15]. Liquid fuels, such as methanol or ethanol, can also be used. However, in such a case, the fuel cell is called a direct methanol fuel cell (DMFC) or a direct ethanol fuel cell (DEFC).

Hydrogen is fed to the PEMFC on the anode side, where it transfers from the gas channels through the GDL to the anode catalyst sites (see Figure 2). The catalyst splits hydrogen into protons and electrons. The protons pass through the membrane to the cathode, and the electrons pass through an external circuit, thus producing an electrical current.

The oxidant used in PEMFCs is commonly air, but pure oxygen can also be used. Either way, the oxidant is fed to the cathode, and the oxygen transfers through the GDL to the cathode catalyst sites. At these sites, oxygen reacts with the protons and the electrons and water is produced. Depending on operating conditions, the water produced may transfer to the anode side or leave the cell with the oxidant stream as shown in Figure 2.
2.1.2 Current, voltage, power, and efficiency

The voltage of a PEMFC is a function of current drawn. Consequently, the output power is not a linear function of current, and the cell efficiency is not constant. This section briefly explains how cell current, voltage, power, and efficiency are interrelated.

The half-cell reactions (hydrogen oxidation reaction, HOR, and oxygen reduction reaction, ORR), the overall reaction, and the Gibbs energy changes at standard state ($\Delta G^0$) per mole of water formed [16] are:

\[
\begin{aligned}
\text{HOR:} & \quad \text{H}_2(\text{gas}) \rightarrow 2\text{H}^+(\text{aq}) + 2e^- \quad \Delta G^0 = 0 \frac{\text{J}}{\text{mol}} \quad (1) \\
\text{ORR:} & \quad \frac{1}{2}\text{O}_2(\text{gas}) + 2\text{H}^+(\text{aq}) + 2e^- \rightarrow \text{H}_2\text{O}(\text{liq}) \quad \Delta G^0 = -237140 \frac{\text{J}}{\text{mol}} \quad (2) \\
\text{Overall:} & \quad \text{H}_2(\text{gas}) + \frac{1}{2}\text{O}_2(\text{gas}) \rightarrow \text{H}_2\text{O}(\text{liq}) \quad \Delta G^0 = -237140 \frac{\text{J}}{\text{mol}} \quad (3)
\end{aligned}
\]

The Gibbs energy change ($\Delta G$) for a chemical reaction is [6]:

\[
\Delta G = \Delta G^0 + R \cdot T \cdot \ln \prod a_i^{\nu_i} \quad (4)
\]

where $a_i$ is the activity and $\nu_i$ is the stoichiometric coefficient of species $i$. For an ideal gas (denoted by superscript *) [6]:

\[
a_i^* = \frac{p_i^*}{p^*} \quad (5)
\]

The Gibbs energy change equals the maximum attainable work per mole ($W_e$) in a reaction. The electrical work ($W_e$) is obtained by multiplying the charge ($q$) by the voltage ($E$) [6]:

\[W_e = q \cdot E \]

---

*Figure 2. The reactions occurring and the transport of reactants and products in a PEMFC (single cell) when one oxygen molecule reacts with two hydrogen molecules and forms two molecules of water.*
\[ \Delta G = \frac{W_e}{n} = \frac{qE}{n} \]  

(6)

The number of electrons transferred per molecule of water produced (according to Eq. 3) is 2. Thus, the charge transferred per mole water produced is:

\[ \frac{q}{n} = 2 \cdot N_A \cdot (-e) = -2 \cdot F \]  

(7)

where \( N_A \) is the Avogadro constant, \( e \) is the elementary charge, and \( F \) is the Faraday constant. Combining Eqs. 6 and 7 gives an equation for the reversible open circuit voltage (OCV) for a hydrogen fuel cell:

\[ E = \frac{\Delta G}{-2F} \]  

(8)

Further, combining Eqs. 4 and 8 gives the Nernst equation:

\[ E = E^0 - \frac{RT}{2F} \ln \frac{a_{H_2}^{1/2}}{a_{H_2O}^{1/2}} \]  

(9)

which relates the reversible OCV to the standard state reversible OCV \( (E^0) \), the temperature \( (T) \), and the activities \( (a_i) \).

The standard state reversible OCV can be calculated from the reaction Gibbs energy change at standard state \( (\Delta G^0 = -237140 \text{ J/mol}) \): \( E^0 = 1.229 \text{ V} \). The actual OCV is notably lower (typically around 1.0 V) mainly because of hydrogen crossover [17] and internal currents [6]. Also the temperature and the reactant activities affect the reversible OCV, as seen in Eq. 9.

When current is drawn from a cell, the voltage drops further. This is called voltage polarization and is mainly caused by three types of irreversibilities or losses: activation losses, ohmic losses, and concentration losses [6]. Other commonly used terms for these irreversibilities include overpotential, overvoltage, or voltage drop. The aforementioned irreversibilities have their most pronounced influence on cell voltage at different current levels (Sections I, II, and III), which gives the cell voltage polarization curve its characteristic shape (Figure 3 a).
The activation losses in Section I cause a notable drop in cell voltage with increasing current. The activation losses are caused by reaction kinetic limitations. The activation loss of HOR is negligible compared to the activation loss of ORR in PEMFCs. [6]

The ohmic losses in Section II cause a nearly linear voltage drop with increasing current. The ohmic losses arise from the resistance of the electrolyte and the current carrying parts of the cell [6]. These resistances follow Ohm’s law and, for that reason, have a linear relationship with current.

The mass transfer starts to limit the achievable current in Section III. The cell current-voltage behavior starts to deviate from the linear relationship, and, at some current, the cell voltage suddenly drops. This is the current that corresponds to the maximum mass transfer rate.

The PEMFC power output is:

$$ P = I \cdot E $$ (10)

A typical PEMFC current-power ($I$-$P$) curve is shown in Figure 3 b. The power increases typically almost linearly with current in Sections I and II and is roughly half of the maximum power. In other words, the other half is converted into heat. In Section III, the mass transfer limited current is reached, and the power collapses.
Fuel cell efficiency \( (\eta_{cell}) \) is commonly related to the lower heating value (LHV) of hydrogen combustion at standard state:

\[
\text{H}_2(\text{gas}) + \frac{1}{2}\text{O}_2(\text{gas}) \rightarrow \text{H}_2\text{O}(\text{gas}) \quad \Delta H^0 = -241830 \frac{\text{J}}{\text{mol}} \quad [16]
\]

and is defined as follows:

\[
\eta_{cell} = \frac{\Delta \bar{U}}{\Delta H^0} = -\frac{E}{1.253 \text{ V}} \tag{12}
\]

Consequently, the shape of the current-efficiency curve is identical with the current-voltage \((I-E)\) curve shown in Figure 3 a. At zero current, the maximum efficiency is obtained, but the power is zero.

### 2.1.3 Water management

Water management is a key factor for operating a PEMFC successfully. This is because the polymer membrane must be hydrated in order to be proton conductive. Water is formed in the cathode reaction, which, in principle, would suffice to keep the membrane hydrated. In practice, however, the water formed at the cathode is distributed unevenly within the cell.

The membrane in PEMFCs is most commonly made of perfluorosulfonic acid (PFSA) polymer [18,19]. In PFSA, sulphonated side chains form hydrophilic clusters, which absorb water. Within these hydrated regions and between them, protons are able to move, thus giving rise to proton conductivity. [6] Therefore, the membrane needs to be hydrated to be proton conductive. The higher the water content, the higher the membrane proton conductivity [6,20]. Dehydration decreases membrane conductivity, increases ohmic losses, and, subsequently, decreases PEMFC performance. [21]

When water is produced at the cathode, the membrane absorbs part of it while the rest of it eventually leaves the fuel cell with the cathode gas. Ideally the water formed in the reaction would suffice to maintain the membrane hydrated as the water absorbed by the membrane is not consumed. However, various water transport mechanisms cause the water to distribute unevenly within the cell.

The most important water transport mechanisms are electro-osmotic drag (EOD), back-diffusion (BD), and convection. Pressure and temperature differences also cause water transport. [19]

EOD is a result of protons moving from the anode towards the cathode and dragging along water molecules [19]. Thus, the EOD is always in the direction away from the anode towards the cathode. As a result of EOD and water generation, water builds up at the cathode while the anode remains drier. The concentration difference tends naturally to even out by diffusion. This form of water transport is called back-diffusion [19].

Convective water transport act along cell in contrast to the other water transport mechanisms. Dry reactant gases fed to the cell will dry out the cell inlet. Water will condense at the end of the cell when the reactant gas flow has
become saturated. [6] If the liquid water is not removed, it will buildup and prevent reactant gases from reaching the reaction site — a condition called flooding [21,22].

Water generation at the cathode and the various water transport mechanisms (mainly EOD and convective water transport) result in uneven water distribution within the cell unless care is taken. One part of the cell may suffer from dehydration while another part floods. Particularly at high current density levels, the cathode water concentration will increase due to water generation, and the anode may be dehydrated due to the EOD [21].

Both flooding and membrane dehydration should be avoided throughout the cell. Flooding prevents reactants from reaching the reaction sites and, therefore, causes a performance decrease and possibly permanent damage to the PEMFC [23]. As a consequence of water generation, the EOD, and the reactant gas flows, flooding is more likely to occur at the cathode close to cell outlet, but anode flooding is also possible [I,II]. Membrane dehydration, on the other hand, besides decreasing PEMFC performance through decreased proton conductivity, also speeds up membrane aging [23].

Theory and practice have shown that membrane dehydration in PEMFCs cannot be avoided at operating temperatures above approximately 60°C without external humidification. Because of this and because more humid operating conditions result in better performance, external humidification is commonly employed. [6,24] Reactant gas inlet humidities should, however, be controlled to avoid flooding in the cell.

### 2.2 Proton exchange membrane fuel cell system

PEMFC stacks in operation consume reactants and produce heat. The reactants typically need to be humidified before entering the PEMFC stack. Therefore, equipment for preparing and feeding the reactants and for removing heat is needed. This equipment together with the PEMFC stack forms a PEMFC system.

PEMFC systems can be classified according to their reactant pressure level, operating temperature level, fuel supply method, and oxidant supply method (see Table 1). Pressurizing reactants not only improves PEMFC performance (see Nernst equation, Eq. 9) but also consumes energy and adds system complexity [25]. This work focuses on non-pressurized systems.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating pressure</td>
<td>Non-pressurized (~0-0.3 barg) / Pressurized (~0.5-2 barg)</td>
</tr>
<tr>
<td>Operating temperature</td>
<td>Low (&lt; 50°C) / Moderate (50-80°C) / High (&gt; 80°C)</td>
</tr>
<tr>
<td>Fuel supply</td>
<td>Open anode / Dead-end anode (with or without recirculation)</td>
</tr>
<tr>
<td>Oxidant supply</td>
<td>Free-breathing / Forced convection</td>
</tr>
</tbody>
</table>

PEMFC stack performance improves with increasing temperature through the improved reaction kinetics [6,26]. However, maintaining the electrolyte suffi-
ciently hydrated at elevated temperatures is challenging [6], and a PEMFC performance decrease associated with dehydration is possible. The focus of this work is on PEMFC systems operating at moderate (50-80 °C) temperatures.

Fuel can be supplied to a PEMFC stack in open anode mode or in dead-end anode (DEA) mode. In open anode mode, the fuel is fed in excess and the not utilized fuel is vented out. This mode is employed mainly in test setups and when reformate gas is used as fuel. In the DEA mode, the anode outlet is closed with a valve, and the PEMFC stack is fed with the amount fuel that is utilized. With time, impurities enrich in the anode, and a hydrogen purge (also called anode purge) must be performed (i.e. the anode outlet valve is opened) to remove the impurities. Alternatively, a bleed valve can be employed to pass a small bleed stream that prevents impurities from enriching. Conceptually, the bleed valve does not differ from open anode operation. Hydrogen recirculation can be employed in both open anode and DEA modes to increase the flow rate through the stack although hydrogen recirculation in open anode systems is uncommon. This work focuses on systems with DEA and occasional hydrogen purges and with hydrogen recirculation.

When system simplicity or energy density [J/m²] is crucial (e.g. in portable applications), the cathode can be made free-breathing. In this case, the air enters the cathode by free convection and no blower is needed. The relatively slow air supply rate, however, limits fuel cell power output [10]. Therefore, if high power density [W/m³] is needed, forced convection with an air blower or compressor must be employed. The PEMFC stack air supply in this work is realized with blowers.

Figure 4 shows a typical but simplified schematic of a non-pressurized PEMFC system with DEA and using ambient air as the oxidant and pressurized hydrogen as fuel. This system consists of three subsystems: 1) fuel supply, 2) oxidant supply, and 3) cooling. The oxidant supply and cooling subsystems are briefly discussed below. The fuel supply subsystem is discussed in more detail in Section 3.

![Figure 4. Simplified schematic of the PEMFC system. B: blower, EV: expansion vessel, F: filter, H: humidifier, HE: heat exchanger, L: electrical load, P: pump, PR: pressure reducer, PU: purge valve.](image)

When using ambient air as the oxidant, the oxidant supply subsystem typically contains at least an air filter, a blower, and a humidifier, as shown in Figure 4.
Recirculation is not a viable option to humidify the air because of the high inert content (~79%) in air. Instead, a humidifier – typically a membrane humidifier [27] or a spray tower [28] – is employed. Operation without an air humidifier has also been demonstrated [24] but with a notable performance decrease compared to a humidified system. Pure oxygen can be used as the oxidant in applications where air is not available [29,30].

The cooling subsystem consists of at least a cooling water recirculation pump, a heat exchanger, and an expansion vessel. The operating temperature range focused on in this work is 60–70 °C. The low operating temperature necessitates using a larger heat exchanger because of the low temperature difference. In stationary applications, the size of the heat exchanger is not a problem [27,28], but in e.g. transport applications, the size of the system is a critical factor.

Details of the electrical subsystem do not fall within the scope of this thesis. However, some general characteristics are worth mentioning. The maximum stack output current is typically ca 1 A/cm² cell area in non-pressurized systems and ca 2 A/cm² cell area in pressurized systems. The maximum stack output voltage is relative to the number of cells in the stack, which might range from a few to a few hundred, depending on the application. Because the voltage varies with load current, a DC/DC converter is usually employed to maintain constant output voltage. Additionally, the electrical subsystem can be hybridized to limit the required PEMFC stack size.
3. Hydrogen Supply in a PEMFC System

The main purposes of the hydrogen supply system in a PEMFC system are: 1) to maintain a suitable pressure level at the anode, 2) to maintain a sufficient fuel flow rate through the stack, 3) to guarantee a sufficient fuel inlet humidity level, and 4) to prevent excessive hydrogen discharge to the surrounding air. In its simplest form, the hydrogen supply can simply comprise a pressure reducer that reduces the pressure of hydrogen in the storage tank to a suitable level. In practice, however, the hydrogen supply comprises many components that deal with the aforementioned tasks. This chapter introduces the principles of hydrogen supply in PEMFC systems.

3.1 Overview

The hydrogen fed to the PEMFC stack is not 100% hydrogen but contains impurities that are either inert or poisonous to the PEMFC. In addition, some nitrogen and carbon dioxide will permeate through the membrane to the anode when air is employed as the oxidant. The impurities are not consumed, unlike fuel, and are, therefore, enriched in the anode. The enriched impurities decrease PEMFC performance either by decreasing fuel concentration (Nernst equation) or by poisoning the PEMFC [31]. This thesis focuses on inert impurities that are not poisonous to the PEMFC, such as nitrogen (N₂), and their effect on fuel cell performance.

The performance decrease associated with inert gas buildup can be mitigated by allowing fresh fuel to flush out the impurities either intermittently (hydrogen purge) or continuously (bleed). The fraction of hydrogen purged is termed the purge fraction \( f_p \). The higher the purge fraction, the more hydrogen is lost but the lower the impurity concentration will be in the anode.

Anode gas recirculation is often applied in multi-kW PEMFC systems. The recirculation serves the purpose of increasing the gas flow rate, thus enhancing convective mass transfer and preventing water droplet formation due to water BD (back-diffusion) from the cathode. Water droplet formation occurs especially close to the cell outlet, where the anode gas is also hydrogen depleted. Recirculation also humidifies the anode inlet gas, which is completely dry unless a humidification is employed.

The effects of the purge fraction and recirculation rate are best visualized by solving the balance equations. This is done in the next section.
3.2 Anode material balances

Figure 5 shows the anode side streams for which the steady state material and species balance equations are solved. The stream denoted by subscript $ff$ represents fresh fuel from storage. Subscript $in$ denotes the anode inlet stream, which is a combination of the fresh fuel stream and the recirculated stream denoted by $r$. Subscript $out$ denotes the anode outlet stream, which is split into the recirculated stream and the purged stream, denoted by $p$. Subscript $s$ refers to species consumption or transport inside the stack.

![Figure 5. Streams in a PEMFC fuel supply system.](image)

The molar flow rate is denoted by $\dot{n}_j$ where the subscript $j$ refers to the stream. The hydrogen consumption rate ($\dot{n}_{H_2,s}$), the nitrogen permeation rate ($\dot{n}_{N_2,s}$), and the water transport rate ($\dot{n}_{H_2O,s}$) are all assumed to occur away from the anode. Normally nitrogen permeation and water transport occur towards the anode and, therefore, they might take negative values. In contrast, the hydrogen consumption rate is always positive, and it is calculated, based on Eq. 7, as follows:

$$\dot{n}_{H_2,s} = \frac{i \cdot N_{cell}}{Z \cdot F}$$  \hspace{1cm} (13)

where $i$ is the current applied, $N_{cell}$ is the number of cells in the PEMFC stack, and $F$ is the Faraday constant.

The mole fractions are denoted by $z_{i,j}$ where the subscript $i$ refers to species (H$_2$, N$_2$, or H$_2$O) and the subscript $j$ refers to the stream. For simplicity, N$_2$ represents all inert compounds entering the anode with the fuel or diffusing from the cathode through the membrane. The diffusion of hydrogen to the cathode or hydrogen consumption in the reaction with oxygen diffused from the cathode is not considered.

The total material balance equations are:

$$\dot{n}_{ff} + \dot{n}_r = \dot{n}_{in}$$  \hspace{1cm} (14)

$$\dot{n}_{in} = \dot{n}_s + \dot{n}_{out} = (\dot{n}_{H_2,s} + \dot{n}_{N_2,s} + \dot{n}_{H_2O,s}) + \dot{n}_{out}$$  \hspace{1cm} (15)

$$\dot{n}_{out} = \dot{n}_r + \dot{n}_p$$  \hspace{1cm} (16)

and the species balance equations are:

$$\dot{n}_{ff} \cdot z_{i,ff} + \dot{n}_r \cdot z_{i,r} = \dot{n}_{in} \cdot z_{i,in}$$  \hspace{1cm} (17)
\[ \dot{n}_{\text{in}} \cdot z_{\text{in}} = \dot{n}_{\text{in},s} + \dot{n}_{\text{out}} \cdot z_{\text{out}} \]  \hspace{1cm} (18)

\[ \dot{n}_{\text{out}} \cdot z_{\text{out}} = \dot{n}_{r} \cdot z_{\text{r}} + \dot{n}_{p} \cdot z_{\text{p}} \]  \hspace{1cm} (19)

Purged gas and recirculated gas are recognized to have the same composition as the anode outlet gas (i.e. \( z_{\text{r}} = z_{\text{p}} \)). Combining these equations yields the total material and species balance equations for the entire fuel supply system:

\[ \dot{n}_{\text{ff}} = \dot{n}_{s} + \dot{n}_{p} \]  \hspace{1cm} (20)

\[ \dot{n}_{\text{ff}} \cdot z_{\text{ff}} = \dot{n}_{l,s} + \dot{n}_{p} \cdot z_{\text{p}} \]  \hspace{1cm} (21)

With this notation, the purge fraction \((f_p)\) is defined as follows:

\[ f_p = \frac{\dot{n}_{H_2,p}}{\dot{n}_{\text{ff}} \cdot z_{H_2,ff}} = 1 - \frac{\dot{n}_{H_2,s}}{\dot{n}_{\text{ff}} \cdot z_{H_2,ff}} \]  \hspace{1cm} (22)

and it is related to the fuel efficiency \((\eta_f)\) – also known as the total fuel utilization \((u_{f,\text{tot}})\) – as follows:

\[ u_{f,\text{tot}} = \eta_f = \frac{\dot{n}_{H_2,s}}{\dot{n}_{\text{ff}} \cdot z_{H_2,ff}} = 1 - f_p \]  \hspace{1cm} (23)

The fuel utilization per pass \((u_{f,\text{pp}})\), which is a measure of the recirculation rate, is defined as follows:

\[ u_{f,\text{pp}} = \frac{\dot{n}_{H_2,s}}{\dot{n}_{\text{in}} \cdot z_{H_2,\text{in}}} = \frac{1}{\lambda_f} \]  \hspace{1cm} (24)

where \(\lambda_f\) is the fuel stoichiometric ratio at inlet. The steady state balance equations can be solved by assuming 1) the stack pressure drop is a linear function of the inlet mass flow rate:

\[ \Delta p_s = p_{\text{in}} - p_{\text{out}} = b \cdot \dot{m}_{\text{in}}, \]  \hspace{1cm} (25)

2) the anode outlet gas is saturated at stack temperature:

\[ z_{H_2,\text{out}} = \frac{p_{\text{out}}^{\text{aq}}(T_s) \cdot \dot{H}_{\text{out}}}{p_{\text{out}}}, \]  \hspace{1cm} (26)

and 3) continuous purging (i.e. bleed). For operation with intermittent purges and the same purge fraction, the results would be similar except that the concentrations would vary around those with continuous purging.

The results are plotted in gas phase mole fractions \((\gamma_{\text{ij}})\) to visualize possible water condensation and because the gas phase mole fractions are typically measured, not the total mole fractions. The gas phase mole fractions are computed by limiting water gas phase mole fraction according to Eq. 26 and keeping the ratio of hydrogen and nitrogen mole fractions constant.

The parameters in Table 2 are used for example calculations (unless otherwise noted) in Section 3 to illustrate the effect of the purge fraction, anode gas recirc-
calculation rate, fuel purity, and nitrogen permeation rate on the anode gas composition. For simplicity, the anode outlet humidity and the nitrogen permeation rate are assumed constant.

Table 2. Parameters for the model. The parameters are chosen based on the PEMFC systems studied in this work (see sections 4.2.1 and 6.5).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_s$</td>
<td>60 °C</td>
<td>Cell temperature</td>
</tr>
<tr>
<td>$p_{H_2}(T_s)$</td>
<td>0.199 bar [32]</td>
<td>Water vapor pressure at cell temperature</td>
</tr>
<tr>
<td>$RH_{out}$</td>
<td>100%</td>
<td>Cell outlet relative humidity</td>
</tr>
<tr>
<td>$l$</td>
<td>120 A</td>
<td>Cell current</td>
</tr>
<tr>
<td>$N_{cell}$</td>
<td>1</td>
<td>Number of cells in stack</td>
</tr>
<tr>
<td>$y_{H_2,ff}$</td>
<td>0.9999</td>
<td>Hydrogen mole fraction in fuel</td>
</tr>
<tr>
<td>$y_{N_2,ff}$</td>
<td>0.0001 (= 100 ppm)</td>
<td>Nitrogen mole fraction in fuel</td>
</tr>
<tr>
<td>$y_{H_2O,ff}$</td>
<td>0.0000</td>
<td>Water mole fraction in fuel</td>
</tr>
<tr>
<td>$u_{f,tot}$</td>
<td>0.99</td>
<td>Total fuel utilization</td>
</tr>
<tr>
<td>$u_{f,pp}$</td>
<td>0.60</td>
<td>Fuel utilization per pass</td>
</tr>
<tr>
<td>$p_{in}$</td>
<td>0.25 barg</td>
<td>Cell inlet pressure</td>
</tr>
<tr>
<td>$b$</td>
<td>$1.5 \cdot 10^4 \text{ bar} \cdot \text{(kg} \cdot \text{s}^{-1})^{-1}$</td>
<td>Cell pressure drop coefficient</td>
</tr>
<tr>
<td>$\dot{n}_{N_2,s}$</td>
<td>$-3.7 \cdot 10^{-7} \text{ mol/s (*)}$</td>
<td>Nitrogen permeation rate (anode to cathode)</td>
</tr>
</tbody>
</table>

(*) For a fully hydrated membrane at 60 °C, with 25 μm thickness, with 200 cm² area, and exposed to 0.9 bar N₂ partial pressure difference [33,34].

Despite the simplified approach employed here, some generally valid observations about the effects of purge fraction and recirculation rate can be made. First, decreasing the purge fraction (i.e. increasing total fuel utilization) increases anode impurity (represented here by N₂) concentration and decreases fuel concentration, as discussed is Section 3.1. Employing a low purge fraction can result in impurity concentrations that are several orders of magnitude higher in the fuel cell than in the fuel, as seen in Figure 6 a. For example, a purge fraction of $f_p = 10^{-3}$ results in 1933 times higher N₂ mole fraction in the anode inlet stream compared to the fuel. With a zero purge fraction, the N₂ partial pressure on the anode side approaches that on the cathode side. This would result in an excessive decrease in performance especially in non-pressurized PEMFC systems. The water concentration, which depends on the fixed outlet relative humidity, changes only a little with purge fraction; the observed change is due to a change in pressure drop.
Second, an increase in the recirculation rate (i.e. a decrease in fuel utilization per pass) causes inlet concentrations to approach the outlet concentrations (Figure 6 b). Therefore, increasing the recirculation rate theoretically (but not in practice) decreases PEMFC performance. The outlet concentrations remain nearly unchanged over most of the recirculation rate range. The change in outlet concentrations observed at high recirculation rates is due to an increased water outlet mole fraction as a consequence of the increased pressure drop. In reality, the outlet concentrations also depend on water transport and the N₂ permeation rate, both of which are functions of the recirculation rate.

Third, the anode gas recirculation humidifies the anode inlet (Figure 7 b). Without recirculation, the anode inlet gas equals the dry hydrogen supply from the storage unless a humidifier is employed. The anode inlet humidity increases with increasing recirculation rate. For example, a roughly 35% (i.e. a relatively low) fuel utilization per pass is required to achieve a 55 °C dew point temperature (corresponding to a 80% relative humidity) at the anode inlet even though the anode outlet is assumed saturated with water. In practice, the recirculation rate is limited by the power consumption, when employing a mechanical pump, or the achieved recirculation rate, when employing an ejector.
The anode inlet dew point temperature exceeds that of the anode outlet at approximately 25% fuel utilization per pass. This is possible because of the increase in pressure difference between the inlet and the outlet while the anode outlet partial pressure remains constant. The effect of the purge fraction on inlet humidity is minor (Figure 7 a).

The effects of fuel impurity concentration and the $N_2$ permeation rate are shown in Figure 8 a and b. The relative effect of fuel concentration at the simulated conditions (Table 2) is minor ($0.6 \cdot 10^{-7}$ mol/s) compared to the $N_2$ permeation rate ($3.7 \cdot 10^{-7}$ mol/s); decreasing the concentration of impurity in fuel by an order of magnitude does not significantly decrease the concentrations in the fuel cell, as seen in Figure 8 a. Instead, the $N_2$ permeation rate accounts for most of the impurity buildup at these conditions. An increase either in fuel impurity concentration or in the membrane permeation rate results in a higher recirculated stream impurity content and, subsequently, necessitates an increase in purge frequency or bleed rate.

![Figure 8. Gas phase mole fractions at anode inlet and outlet at varying a) $N_2$ mole fraction in fuel ($y_{N_2,f}$) and b) $N_2$ permeation rate ($\dot{n}_{N_2,e}$). Solved from material balance equations. The dashed line indicates conditions shown in Table 2.](image)

It is important to distinguish between steady state and dynamic behavior. The above discussion solely considers steady state. The time required for concentrations to reach a steady state (or pseudo steady-state with intermittent purges) depends mainly on anode volume and current level. Based on experience from PEMFC systems presented in sections 4.2.1 and 6.5, the steady state is typically reached in tens of minutes, the temperatures and, consequently, the water concentrations taking the longest time to stabilize. Steady state is likely never reached in applications with load changes several times within a minute. In applications with long periods (thousands of hours) of constant operation, the steady state is of primary importance, and the way steady state is reached (i.e. system dynamics) is of minor importance.

### 3.3 Hydrogen purge

One purpose of the hydrogen purge is to remove accumulated impurities. A purge fraction that is too high results in poor fuel efficiency. A purge fraction that is too low results in high concentration polarization and reduced fuel cell
Hydrogen Supply in a PEMFC System

efficiency. The Nernst equation (Eq. 9) can be used for estimating the effect of a decrease in hydrogen partial pressure on cell voltage [6]:

$$\Delta E_{\text{Nernst}} = E - E_{\text{ref}}$$

$$= \left( E^0 - \frac{RT}{2F} \cdot \ln \left[ \frac{p_{H_2}^0}{p_{H_2}^0} \right] \right)$$

$$- \left( E^0 - \frac{RT}{2F} \cdot \ln \left[ \frac{p_{H_2}^0}{p_{H_2}^0} \left( \frac{p_{O_2}^0}{p_{O_2}^0} \right)^{1/2} \right] \right)_{\text{ref}}$$

$$= \frac{RT}{2F} \cdot \ln \frac{p_{H_2}}{p_{H_2,\text{ref}}}$$

(27)

where the hydrogen partial pressure ($p_{H_2}$) is averaged over the cell, and the reference hydrogen partial pressure ($p_{H_2,\text{ref}}$) corresponds to the reference cell voltage ($E_{\text{ref}}$). The power decrease per cell due to concentration polarization is:

$$\Delta P_{\text{Nernst}} = I \cdot \Delta E_{\text{Nernst}}$$

(28)

On the other hand, the power lost per cell due to hydrogen vented out in purges (at an average rate of $\bar{n}_{H_2,\text{P}}$) is computed by applying Faraday’s law of electrolysis:

$$\Delta P_{\text{fuel}} = \frac{\bar{i}_p}{N_{\text{cell}}} \cdot E_{\text{ref}} = \frac{\bar{n}_{H_2,\text{P}} \cdot z \cdot F}{N_{\text{cell}}} \cdot E_{\text{ref}}$$

(29)

where $\bar{i}_p$ is the average rate of hydrogen lost in purges converted to electrical current, and $E_{\text{ref}}$ is a reference cell voltage (same as above). $\Delta P_{\text{Nernst}}$ and $\Delta P_{\text{fuel}}$ are plotted in Figure 9 as a function of purge fraction and fuel utilization per pass.

![Figure 9. Change in cell power output due to concentration polarization and hydrogen lost in purges at varying a) purge fraction ($f_p$) and b) fuel utilization per pass ($u_{f,pp}$). Solved from material balance equations. The values are relative to the dashed line indicating conditions shown in Table 2. $E_{\text{ref}} = 650 \text{ mV}$ is assumed.](image)
As seen in Figure 9a, the cell net output power is much more sensitive to total fuel utilization than to concentration polarization at the simulated conditions. One could draw the conclusion that the optimal purge fraction is very low (<0.001). However, in publication [II], it is shown that the measured concentration polarization can be notably higher than the theoretical one. In addition, these simulations (like numerous others, e.g. [35–38]) do not account for the effects of water transport and condensation.

Water condenses when water vapor partial pressure exceeds water vapor pressure. Liquid water in anode gas channels is harmful in two ways; it 1) restricts the gas flow in gas channels and 2) prevents hydrogen from reaching the catalyst sites. The uneven flow distribution between cells that occurs from the water droplets plugging the gas channels induces further growth of existing droplets.

Fuel starvation is a condition in which hydrogen cannot reach the reaction site, either locally because of water droplets blocking them or globally because of no hydrogen present. When local fuel starvation occurs, the cell regions suffering from hydrogen shortage adapt their electrode potentials to a higher level. The potential difference between the anode and the cathode remains constant because of the highly conductive bipolar plates. The elevated electrode potentials enable unwanted reactions (water splitting and corrosion of the carbon support on the cathode and oxygen reduction at the anode) and a reversed current. Local fuel starvation has, therefore, negative effect on cell lifetime, but it is difficult to detect before irreversible damage to the PEMFC has occurred because of the unchanged cell voltage. [23,39]

The other main purpose of the hydrogen purge is, thus, to remove liquid water from the gas channels and guarantee stable performance even when operating at very humid conditions, i.e. at conditions where the reactant gases are close to saturated or even oversaturated with water. A PEMFC typically achieves maximum performance at such high-humidity conditions. The effect of humidity level on the optimal purge parameters is difficult to study by modelling, but some experimental studies about the subject have been conducted (e.g. [40,41]). This is also the main topic in publication [II].

A hydrogen purge can be triggered based on various criteria: a predefined voltage drop [42], [II], time-based [43], the applied load current [37,44], the anode pressure [V], or a predefined impurity concentration [35,37], for example. The choice of triggering criterion is governed by the expected drive cycle and by the operating conditions. The primary purpose of a hydrogen purge at dry operating conditions is to remove inert gases and, for this reason, either a time-based or a coulomb counter-based purge trigger would be suitable. Flooding can be expected at humid operating conditions, and cell voltage deviation is one of the best indicators of that.

The liquid water is removed most efficiently with a high-flow-rate purge. Therefore, the purge valve should have a sufficiently low flow resistance, i.e. a high $K_v$-value. An excessively high $K_v$-value, however, depressurizes the anode
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rapidly as soon as the valve is opened. This results in a pressure difference between the anode and cathode and causes unnecessary stresses on the polymer membrane [23].

While a high flow rate efficiently removes liquid water, it also results in a large amount of hydrogen being vented out. Therefore, the purge length (i.e. the time the valve is kept open) should be relatively short, typically few hundred milliseconds. The typical response time of a solenoid valve is a few tens of milliseconds. In other words, the valve may not have time to fully open before it is closed during very short purges.

An alternative to a hydrogen purge is a hydrogen bleed [36,45], i.e. to continuously vent out a fraction of the anode outlet gas. Hydrogen bleed can also be employed in parallel with hydrogen purge. This might be necessary when using low grade hydrogen to avoid excess buildup of impurities in the anode loop. A correctly sized and fast reacting proportional valve can also be employed both as a bleed valve and as a purge valve.

The main difference between a hydrogen purge and a bleed is the maximum flow rate encountered through the stack during operation. During a hydrogen purge, the flow rate is normally multiplied whereas a continuous bleed adds typically at most a few percent (depends on total fuel utilization) to the flow rate. Because of this, the purge is often preferred as it efficiently removes liquid water, thus stabilizing PEMFC operation.

Another difference between a hydrogen purge and a bleed is the rapid pressure decrease during a purge. This easily leads to an excessive pressure difference between the anode and cathode, especially in pressurized systems, and, subsequently, complicates pressure management.

### 3.4 Hydrogen humidifiers

As seen in Figure 7 b, the anode inlet humidity (expressed in dew point temperature) is relatively low even with hydrogen recirculation unless high recirculation rate is applied. For example, a typical fuel utilization per pass of 0.6 results in an anode inlet dew point temperature of 45 °C which corresponds to a relative humidity of only 48% at the cell operating temperature (60 °C). For best PEMFC performance, the anode inlet relative humidity should be close to 100%.

The anode inlet is further dehydrated at high power levels because of the EOD (electro-osmotic drag) prevailing over BD (back-diffusion) and because the fuel that is fed is drier (unless the recirculation rate is increased in the same proportion). Anode inlet dehydration can be mitigated by feeding air and fuel to the cell in counterflow mode because water is then transported from the humid cathode outlet stream to the dry anode inlet stream. Despite the advances in polymer technology that enable the use of thinner membranes (18 μm membranes were available in 2007), which in turn facilitates membrane hydration [25], inlet gas humidification is often applied to increase PEMFC performance and durability [21]. Gas humidifiers are commonly employed not only on the cathode side but also often on the anode side in addition to hydrogen recirculation [27,28].
Humidifiers typically employed for anode gas humidification can be classified as either a gas-to-gas type or a liquid-to-gas type. From a system complexity point of view, the gas-to-gas type humidifiers are more attractive since liquid water is not needed. Liquid water must either be refilled or condensed from PEMFC stack outlet gas streams. A gas-to-gas type humidifier can be placed between the streams where a transfer of humidity is required without the need for any additional system components.

Possible humidifier types and their advantages and disadvantages are listed in Table 3. An example of a gas-to-gas humidifier is the enthalpy wheel [46,47]. Examples of liquid-to-gas humidifiers are the water atomizer [48–50], spray tower [28], and bubble humidifier [51,52]. A membrane humidifier can be operated both in gas-to-gas [53,54] and in liquid-to-gas [55] modes.

Table 3. A summary of the advantages and disadvantages of humidifiers with respect to hydrogen gas humidification based on references [6,28,46–55] and the author’s own experience.

<table>
<thead>
<tr>
<th>Gas-to-gas</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Humidifier type</strong></td>
<td><strong>Advantages</strong></td>
<td><strong>Disadvantages</strong></td>
</tr>
<tr>
<td><strong>Enthalpy wheel</strong></td>
<td>- Compact size</td>
<td>- Gas leakages</td>
</tr>
<tr>
<td></td>
<td>- Low gas pressure drop</td>
<td>- Power consumption</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Require maintenance</td>
</tr>
<tr>
<td><strong>Membrane humidifier</strong></td>
<td>- No power consumption</td>
<td>- Gas leakages</td>
</tr>
<tr>
<td></td>
<td>- Compact size</td>
<td>- Moderate gas pressure drop</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(20-50 mbar [47], times two)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- High price</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Liquid-to-gas</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Humidifier type</strong></td>
<td><strong>Advantages</strong></td>
<td><strong>Disadvantages</strong></td>
</tr>
<tr>
<td><strong>Water atomizer</strong></td>
<td>- Gas tight</td>
<td>- Inefficient heat transfer</td>
</tr>
<tr>
<td></td>
<td>- Low gas pressure drop</td>
<td>- Sensitive to control (oversatura-</td>
</tr>
<tr>
<td></td>
<td>- Controllable humidity</td>
<td>tion possible)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Power consumption</td>
</tr>
<tr>
<td><strong>Membrane humidifier</strong></td>
<td>- Compact size</td>
<td>- Gas leakages possible</td>
</tr>
<tr>
<td></td>
<td>- No power consumption</td>
<td>- High price</td>
</tr>
<tr>
<td><strong>Spray tower</strong></td>
<td>- Gas tight</td>
<td>- Large size (several times that</td>
</tr>
<tr>
<td></td>
<td>- Low gas pressure drop</td>
<td>of a membrane humidifier)</td>
</tr>
<tr>
<td></td>
<td>- Low power consumption</td>
<td></td>
</tr>
<tr>
<td><strong>Bubble humidifier</strong></td>
<td>- Gas tight</td>
<td>- Large size (several times that</td>
</tr>
<tr>
<td></td>
<td>- Low power consumption</td>
<td>of a membrane humidifier)</td>
</tr>
</tbody>
</table>

A characteristic feature of gas-to-gas humidifiers is that the mass transfer is not limited to water – other gases are also transferred between the two streams [47]. This introduces a safety risk through possible leakages when humidifying hydrogen since the cathode outlet air is the only possible humidity source. Therefore, gas-to-gas type humidifiers are not considered here for hydrogen humidification.

The water atomizer humidifiers have the advantages of being small, enabling humidity control with short delay, and having practically no gas pressure drop [48–50]. However, unless the humidified gas requires cooling (e.g. after compression), a heat exchanger is needed [48,49] since water evaporation is a heat-intensive process. A heat exchanger causes a drop in gas pressure and adds to the humidifier size, especially if the available temperature difference is low (e.g.
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PEMFC stack coolant). Heating with electricity reduces size and weight but adds parasitic power consumption. In addition, a liquid water flow control mechanism is required for water atomizers [48,49]. Finally, water-atomizing humidifiers permit over-saturating the gas, which can lead to PEMFC flooding.

Liquid-to-gas membrane humidifiers are compact in size, they require no power to operate, and they can easily make use of the waste heat rejected from a PEMFC stack through the cooling circuit. However, as with the gas-to-gas membrane humidifier, gas leakages might occur in the liquid-to-gas version, which introduces a safety risk when humidifying hydrogen. Further, impurities in the heating water have been reported to plug the humidifier [50], thus limiting its lifetime. In addition, the price of membrane humidifiers is high [47,48]. For example, the price of the two membrane humidifiers used for humidifying the cathode inlet air in the 50 kW PEMFC pilot plant [27] was thousands of euros per piece. On the other hand, the membrane humidifier for a mass-produced 80 kW PEMFC system was estimated to cost approximately $100 in 2010 [25].

The spray tower (with a packed bed [28]) and the bubble humidifier both bring the heated water and the gas in direct contact with each other. Although these humidifiers are relatively large and heavy, the good contact between phases ensures efficient heat and mass transport. For example, the approach dew point temperatures achieved with the bubble humidifier studied in publication [III] were notably lower compared to those achieved with water atomizing humidifiers [48,49]. The achieved humidification performance depends, however, on humidifier sizing and, therefore, direct comparison cannot be made. Both the spray tower and the bubble humidifier are gas tight and consume little power but the gas pressure drop in a bubble humidifier is higher than in a spray tower due to the water bed.

3.5 Hydrogen recirculation

As shown in Figure 6 b, an increase in recirculation rate results in a higher average N₂ concentration in the anode gas channels. Therefore, a decrease in PEMFC performance with an increase in the recirculation rate could be expected (Figure 9 b). However, a higher average N₂ concentration decreases the N₂ permeation rate, thus partly cancelling out the increase in the average N₂ concentration caused by the increase in recirculation rate. In addition, an increase in recirculation rate enhances convective mass transfer and prevents water droplet formation inside the PEMFC, as mentioned in Section 3.1. In general, the higher the recirculation rate, the better and more stable the PEMFC performance, especially at high-humidity conditions.

The recirculation rate in systems with a mechanical pump (Figure 4) is limited by pump power consumption (given a pump with high enough performance). At some point, the added recirculation rate does not pay off. The power consumption of recirculation will typically be low (depends on recirculation rate and system flow resistance) relative to the power consumption of the cathode blower. Furthermore, the recirculation can be varied with a variable rotating speed pump to meet the requirements of the prevailing operating conditions. Therefore, the sizing and operation of a mechanical hydrogen recirculation pump is simple.
Mechanical pumps for hydrogen recirculation are relatively expensive. Experience has also shown that the operating conditions in PEMFC systems can be too demanding for mechanical pumps to meet the system lifetime requirements [27]. These qualities have resulted in a greater interest in other hydrogen recirculation solutions.

### 3.5.1 Hydrogen recirculation with ejectors

Ejectors are a valid alternative to mechanical pumps in PEMFC systems for anode gas recirculation. Their operation relies on transferring momentum directly from a primary gas to a secondary gas. A high-pressure primary gas is supplied to the primary inlet port after which it enters the nozzle (Figure 10). In the nozzle, the primary gas is accelerated to high velocity (up to several Mach) and its pressure is reduced. The high-velocity primary gas meets the almost stagnant secondary gas downstream of the nozzle, and the transfer of momentum equalizes the velocities of the two gases as they mix. The gas mixture decelerates in the ejector diffuser, and, as a result, the pressure increases. The primary gas in PEMFC applications equals the fresh hydrogen feed from storage, the secondary gas equals the recirculated gas, and the ejector outlet gas equals the anode inlet gas (Figure 11).

Figure 10. Ejector main parts.

![Figure 10. Ejector main parts.](image)

Figure 11. Simplified schematic of the PEMFC fuel supply system with an ejector. PR: pressure reducer, PU: purge valve, E: ejector.

Ejectors are more durable and less expensive than mechanical pumps because they have no moving parts. These are the main reasons why ejectors have received growing interest recently. In addition, the solid construction of ejectors makes it easy to seal them. Ejectors also make use of the hydrogen storage pressure energy – an energy source otherwise lost – which makes them more energy efficient than mechanical pumps.

Ejectors, however, have qualities that make their usage more challenging than mechanical pumps. First, the primary gas flow rate of an ejector is proportional to the primary inlet pressure. Therefore, the primary gas pressure (or flow rate) of an ejector must be controlled to match the hydrogen consumption rate. Otherwise, the anode pressure will vary in a DEA (dead-end anode) setup. Second,
the recirculation rate achieved with an ejector varies with the primary gas flow rate (i.e. the hydrogen consumption rate) and cannot be controlled. Therefore, the ejector must be sized carefully to achieve an adequate flow rate when needed. Third, the hydrogen purge with an ejector is not as efficient as in systems with hydrogen fed passively through a pressure reducer since the ejector nozzle limits the flow rate of the primary gas. Instead, either the primary pressure of the ejector must be increased during a purge or a hydrogen supply line bypassing the ejector must be implemented.

3.5.2 Model-based ejector sizing

Ejector sizing is conducted with models that predict the effect of ejector dimensions and boundary conditions on ejector performance. Ejectors have been modelled with various approaches ranging from simplified 1D models [56–58] to complex CFD models in 3D [59–61].

The 1D models are based on isentropic flow relations and the balance equations of mass, energy, and momentum. These models consider only the main ejector dimensions, such as the diameters of the nozzle and mixing section. The computation is inherently relatively light. While satisfactory accuracy has been obtained with the 1D models, their accuracy is usually limited to specific operating conditions or a range of operating conditions. Further, their accuracy relies largely on experimental parameters [62] applied to account for non-idealities in ejector operation.

At the other end of the model spectrum, CFD models are based on actual ejector geometry. The modelling domain is spatially discretized, and the balance equations are solved in every discretized portion, “cell”, separately. Consequently, CFD models in 3D can provide more accurate predictions of ejector performance for a wider range of conditions [60]. However, the number of degrees of freedom in a 3D model (millions) is considerably higher than in a 1D model (dozens), and more time and computational resources (memory and CPU) is required to both setup the model and solve it.

A 2D CFD model is lighter than a 3D CFD model both computationally and in model setup, and it provides more accurate predictions of ejector performance than a 1D model. A 2D CFD model does not require parameter tuning like 1D models do. Moreover, 2D modelling conducted with CFD can be employed for checking the effects of various ejector dimensions, which are neglected in 1D models. However, a 2D CFD model is limited to the axisymmetric part of an ejector and, therefore, cannot capture the phenomena resulting from the non-axisymmetric parts. The degree to which the non-axisymmetry affect ejector performance depends on the ejector design.

The flow in ejectors is typically turbulent, which adds modelling complexity. In CFD, turbulence is typically modelled by employing Reynolds-averaged Navier–Stokes (RANS) equations. In practice, this means that the flow (pressure and velocity) is decomposed into a mean part and a fluctuating part. The fluctuating part (the Reynolds stress term) can be modelled with an eddy viscosity model (EVM), which relates the Reynolds stress term to mean velocities. Examples of EVMs are the k-ε and the k-ω models. Many alternative approaches for
turbulence modelling exist but the RANS equations coupled with EVMs are usually a good compromise between accuracy and computational cost.

Because of the trade-off between accuracy and effort, the ejector is, in many cases, best designed by stepwise increasing the modelling complexity (Figure 12). The initial screening of possible ejector designs is conducted with simple models. The modelling complexity can be increased with a limited number of designs once some estimate of the ejector performance in the intended system is obtained. Ultimately, the final adjustments of the design (before manufacturing) are made with a complex model.

Figure 12. Ejector design approach.
4. Hydrogen Purge

Impurities enter the anode both with the fuel and through the membrane. The impurities will build up in a DEA setup to a high level and will impair fuel cell stack performance unless hydrogen purges or a bleed is applied. In addition, a fraction of the water formed at the cathode is transported to the anode. At high-humidity conditions, water might condense and cause an uneven flow between anode gas channels. The high flow velocity achieved during a hydrogen purge flushes out condensed water and maintains stable PEMFC performance.

The impaired stack performance resulting both from impurity buildup and from anode gas channel flooding is possible to detect by monitoring the cell voltages. However, even though cell voltages would decrease at these conditions, the cause for the decrease in voltages may be difficult to track down. Possible causes for decreased cell voltages include a decrease in anode gas recirculation rate and an increase in impurity content. A decrease in recirculation rate might be a result of liquid water plugging the gas channels, for example. An increase in impurity content might be a result of an increased rate of inert gas permeation through the membrane, a variation in fuel purity level, or inefficient hydrogen purges.

A better view of the prevailing conditions can be obtained with additional measurements, and the operating parameters can be optimized. For example, by measuring the anode gas composition, the purge frequency and length can be optimized to result in stable operation without purging hydrogen in excess. In addition, added instrumentation in a fuel cell system can, at best, aid in detecting the malfunction of a component and help in choosing the best strategy for continued operation. On the other hand, extra transmitters are usually avoided to keep the system cost as low as possible and to avoid potentially failing components that the system operation depends on.

In publications [I] and [II], methods for determining some key figures of hydrogen supply and recirculation were developed. In publication [I], a method for determining fresh fuel purity and the membrane inert gas permeation rate in a fuel cell system was developed. In publication [II], the same but updated fuel cell system was used to develop methods for determining the purged gas volume and composition.
4.1 Inert buildup and hydrogen purge calculations

The calculations used to determine some key figures of hydrogen supply and recirculation are presented below.

4.1.1 Fuel quality and inert gas membrane permeability

In a system with DEA, the concentration of inert gases (mainly nitrogen) in the anode gas increases between hydrogen purges due to fuel impurities and membrane permeability. The rate of increase in inert concentration can be used to estimate the inert concentration in the fuel and the membrane permeability. Using the notation in Section 3.2 and assuming ideal gas \((\gamma_i,j = z_i,j)\) at constant pressure and temperature, the inert gas (here represented by nitrogen, \(N_2\)) buildup rate \((\bar{\dot{n}}_{N_2,an})\) is:

\[
\bar{\dot{n}}_{N_2,an} = \dot{n}_{an} \cdot \frac{dy_{N_2,an}}{R T_{an}} = \frac{p_{an} V_{an}}{R T_{an}} \cdot \frac{dy_{N_2,an}}{dt} = \bar{\dot{n}}_{N_2,ff} - \bar{\dot{n}}_{N_2,S}
\]

(30)

where \(\bar{\dot{n}}_{N_2,ff}\) is the rate of inert gas entering with fuel:

\[
\bar{\dot{n}}_{N_2,ff} = y_{N_2,ff} \cdot \bar{\dot{n}}_{N_2,S} = y_{N_2,ff} \cdot \frac{i_{N_{cell}}}{2F}
\]

(31)

and \(-\bar{\dot{n}}_{N_2,S}\) is the molar flow rate of inert gases entering the anode through the membrane. Combining Eqs. 30 and 31 gives:

\[
\bar{\dot{n}}_{N_2,an} = y_{N_2,ff} \cdot \frac{i_{N_{cell}}}{2F} - \bar{\dot{n}}_{N_2,S}
\]

(32)

Differentiating \(\bar{\dot{n}}_{N_2,an}\) with respect to \(I\) and assuming that membrane permeability, anode pressure, and temperature are independent of the load current \((\frac{d\bar{\dot{n}}_{N_2,S}}{dt} = \frac{dp_{an}}{dt} = \frac{d\frac{1}{T_{an}}}{dt} = 0)\) gives the following expression for the inert gas mole fraction in fuel:

\[
y_{N_2,ff} = \frac{2F}{N_{cell}} \cdot \frac{dy_{N_2,an}}{dt} = \frac{2F}{N_{cell}} \cdot \frac{p_{an} V_{an}}{R T_{an}} \cdot \frac{d}{dt}(\frac{dy_{N_2,an}}{dt})
\]

(33)

Substituting Eq. 33 into Eq 32 gives an expression for the rate of inert gases entering the anode through the membrane:

\[
-\bar{\dot{n}}_{N_2,S} = \bar{\dot{n}}_{N_2,an} - y_{N_2,ff} \cdot \frac{i_{N_{cell}}}{2F} = \bar{\dot{n}}_{N_2,an}\{I = 0\}
\]

(34)

As mentioned above, Eqs. 33 and 34 are valid when the membrane permeability can be assumed independent of the load current. This is not exactly true since membrane permeability is known to be a function of at least the membrane pressure difference, humidity, and temperature [34,63]; all of which depend, at least to some degree, on the load current. Further, current density affects membrane permeability [63], and the fuel and oxygen crossovers (both of which consume fuel) have been neglected in this analysis. Neglecting gas crossover might not be a valid assumption in the future as new PEMFCs employ thinner membranes with higher gas crossover rates.
The error associated with using gas phase mole fractions \( y_{i,j} \) instead of total mole fractions \( z_{i,j} \) is related to the anode gas volume \( v_{an} \). Therefore, the use of gas phase mole fractions, which usually are measured, can be used even though some water condensation occurs.

Eqs. 33 and 34 can be used to detect variations in fuel purity and membrane permeability, especially in applications with a repeated load cycle. Even though the results are only approximations and might deviate from actual ones, the measurements give the overall trends and help detect a change in the determined quantities.

### 4.1.2 Purge gas amount and composition

The hydrogen purge serves two purposes. First, it removes condensed water from the channels, thus stabilizing fuel cell performance under humid operating conditions. Second, it removes inert gases from the anode, which, when accumulated, decrease fuel cell performance. Knowledge of the purged amount and composition gas give an indication of purge efficiency and aids in choosing the correct purge parameters for the prevailing operating conditions.

The total fuel utilization \( u_{f,tot} \), i.e. the fuel efficiency \( \eta_f \), of a fuel cell is the ratio of the hydrogen consumption rate to the hydrogen supply rate. The difference between supply and consumption rates equal the rate at which hydrogen is lost, mainly in hydrogen purges. Thus, dividing the average hydrogen lost rate by the purge frequency gives the average of hydrogen lost during one purge. However, this does not give the total amount of purged anode gas vented during a purge, which typically also contains water and nitrogen. Even if fuel efficiency is corrected with measured water and nitrogen concentrations, the amount of purged gas determined this way is not very accurate because the purged gas composition depends on purge length, as will be shown in Section 4.3.2.

The approach to determining the purged gas amount depends on how the system is operated. In systems where the hydrogen supply rate is kept constant during a purge, the amount of gas purged \( n_p \) can be determined from the anode pressure difference before (1) and after (2) the purge:

\[
 n_p = \left( p_{an,1} - p_{an,2} \right) \cdot \frac{v_{an}}{R \cdot T_{an}} \quad (35)
\]

In systems where the anode pressure is kept constant by supplying hydrogen through a pressure reducer, the amount of purged gas \( n_p \) can be determined by numerically integrating the difference between the fuel supply rate \( \dot{n}_f \) and the hydrogen consumption rate \( \dot{n}_{H_2,s} \) during a purge:

\[
 n_p = \int (\dot{n}_f - \dot{n}_{H_2,s}) dt \quad (36)
\]

This requires measuring the fuel supply rate with a transmitter that has a short response time. Figure 13 shows an example of a measured hydrogen flow rate profile during a hydrogen purge in a system with the anode pressure maintained constant with a pressure regulator.
In both of the above cases, the change in anode gas temperature (hydrogen supply is usually colder than anode gas) might introduce an error. However, unless the temperature change during the purge is significant, the error should be small. In addition, the pressure change in the case of constant hydrogen supply rate might not be uniform due to hydrogen recirculation. Therefore, computing the amount of purged gas separately in different parts of the anode might give results that are more accurate.

The composition of purged gas can be determined based on the hydrogen balance. The gas phase mole fractions \( y_{k,j} \) are again used because they are measured whereas the total mole fractions \( z_{k,j} \) are not (for reasoning, see section 4.1.1). The amount of hydrogen supplied during a purge is:

\[
   n_{\text{H}_2,ff} = y_{\text{H}_2,ff} \cdot n_p
\]

where \( y_{\text{H}_2,ff} \) is the hydrogen mole fraction in fuel. The amount of hydrogen in the anode before \((n_{\text{H}_2,an,0})\) the purge is:

\[
   n_{\text{H}_2,an,0} = y_{\text{H}_2,an,0} \cdot n_{an}
\]

and the amount of hydrogen in the anode after \((n_{\text{H}_2,an,1})\) the purge is:

\[
   n_{\text{H}_2,an,1} = y_{\text{H}_2,an,1} \cdot n_{an}
\]

It is assumed that the total amount of anode gas remains unchanged \((n_{an,0} = n_{an,1})\). This implies that the same amount of gas \((n_p)\), but with a different composition, exits the anode during the purge. The amount of hydrogen in the purged gas is the difference between the amount of hydrogen supplied \((n_{\text{H}_2,ff})\) and the amount of hydrogen accumulated in the anode \((y_{\text{H}_2,an,1} \cdot n_{an} - y_{\text{H}_2,an,0} \cdot n_{an})\) during the purge. The purged gas hydrogen mole fraction is, therefore:

\[
   y_{\text{H}_2,p} = \frac{y_{\text{H}_2,ff} n_p - (y_{\text{H}_2,an,1} - y_{\text{H}_2,an,0}) n_{an}}{n_p} = y_{\text{H}_2,ff} - (y_{\text{H}_2,an,1} - y_{\text{H}_2,an,0}) \cdot \frac{n_{an}}{n_p}
\]
which is the same result that is obtained when a perfectly mixed anode is assumed (see Appendix A). Similar equations can be obtained for the other gas components.

As the gas concentrations in the anode loop are non-uniform, volume-based averaging is necessary before applying Eq. 40. An example of a change in the hydrogen mole fraction at the anode inlet during a hydrogen purge measured in publication [II] is shown in Figure 13.

As discussed earlier in this section, the purged gas composition does not necessarily equal anode outlet gas composition before the purge. This is because the anode outlet gas concentration changes as the purge process proceeds. Immediately after opening the purge valve, the gas close to the purge valve vents out. Simultaneously, the flow rate from other parts of the anode starts gradually to increase – first upstream of the anode gas recirculation pump and through the stack. Ultimately, with a high enough pressure difference between the anode inlet and purge valve, the gas flow in the recirculation pump might even reverse.

If the purge valve is open long enough, the purged gas hydrogen content gradually increases as the hydrogen depleted gas flows out and fresh fuel enters the anode. The purged gas hydrogen content increases as the flow rate through the stack increases, thus decreasing the fuel utilization per pass. When the fresh fuel front reaches the purge valve, the hydrogen content in the purged gas increases further. When the purged gas hydrogen content increases from the initial one, the purged gas can be thought of as being a mixture of fresh fuel \( n_{p,ff} \) and anode outlet gas \( n_{p} - n_{p,ff} \), as concluded in Appendix A:

\[
y_{H_2,p} \cdot n_p = y_{H_2,ff} \cdot n_{p,ff} + y_{H_2,\text{out},0} \cdot (n_p - n_{p,ff})
\]

Thus, the fraction of fresh fuel in purged gas can be expressed as follows:

\[
\frac{n_{p,ff}}{n_p} = \frac{y_{H_2,p} - y_{H_2,\text{out},0}}{y_{H_2,ff} - y_{H_2,\text{out},0}}
\]

This quantity can be used as a measure to determine a suitable purge length for the system. If \( n_{p,ff}/n_p = 0 \), the purged gas has the same \( H_2 \) mole fraction as the anode outlet gas before the purge. This might be an indication of a too short purge resulting in inefficient for water removal. From fuel efficiency point of view, the case of \( n_{p,ff}/n_p = 0 \) is optimal because minimum amount of \( H_2 \) is lost relative to total purged gas volume. The value of \( n_{p,ff}/n_p \) cannot be less than zero. On the other hand, if \( n_{p,ff}/n_p \gg 0 \), the purged gas contains much hydrogen as a result of a too long purge. This results in poor fuel efficiency. The optimal \( n_{p,ff}/n_p \) naturally depends on the system and the operating conditions.

The purged gas amount could, in principle, also be determined from the change in measured anode gas composition. However, this is possible only if the purge is sufficiently short and the purged gas composition is the same as the anode gas composition before the purge (see Eq. 40).
4.1.3 Recirculation rate

The hydrogen recirculation rate is challenging to measure as the anode gas typically consists of at least hydrogen, nitrogen, and both gaseous and condensed water. The total mass or volume flow rate can be determined with standard devices but usually not without introducing a significant flow resistance, which decreases the recirculation rate or adds power consumption. Gas composition transmitters are needed to be able to determine the composition of the recirculated gas and the fuel utilization per pass (or alternatively the stoichiometric ratio of hydrogen at the anode inlet).

The recirculation rate can be determined from the material balances if gas composition transmitters are available and the fuel feed composition is known. Using the notation introduced in Section 3 but again, gas phase mole fractions \( y_{i,j} \) instead of total mole fractions \( z_{i,j} \), the anode inlet molar flow rate is (Eq. 14 and Eq. 17):

\[
\dot{n}_{in} = \dot{n}_{ff} + \dot{n}_r = \frac{\dot{n}_{ff} y_{i,ff} + \dot{n}_r y_{i,r}}{y_{i,in}}
\]

or

\[
\dot{n}_r = \frac{\dot{n}_{ff} y_{i,ff} - y_{i,in}}{y_{i,in} - y_{i,r}}
\]

The recirculation rate can thus be computed when the molar feed rate and the mole fractions of one component are known in the feed, at the anode inlet, and in the recirculated gas (or in the anode outlet gas, \( y_{i,r} = y_{i,out} \)). The feed rate in a DEA setup equals the hydrogen consumption rate (\( \dot{n}_{ff} = \dot{n}_{H_2,S} = \frac{t \cdot N_{cell}}{2 \cdot F} \)), and the feed is typically almost pure (>99.9%) hydrogen. Therefore, the recirculation rate can be approximated based on load current and, e.g. the humidity measurements, as in publication [I]:

\[
\dot{n}_r = \frac{t \cdot N_{cell}}{2 \cdot F} \cdot \frac{y_{H_2,0,in}}{y_{H_2,0,out} - y_{H_2,0,in}}
\]

The accuracy of Eq. 45 depends mainly on the accuracy of the humidity measurements. This accuracy decreases with an increase in recirculation rate because of the decrease in the water mole fraction difference in the nominator, as pointed out by Koski et al. [45]. Furthermore, humidity measurements close to the dew point decrease accuracy because of possible water condensation.

Assuming only three gas components (the three main components are usually hydrogen, water, and nitrogen), the anode gas composition at any point can be determined by one additional measurement of the concentration of either hydrogen or nitrogen at the anode inlet, at the anode outlet, or in the recirculation line. The remaining gas compositions are calculated using Eqs. 14-19 and recalling that \( z_{i,out} = z_{i,r} = z_{i,p} \).

Alternatively, if a mass flow transmitter (e.g. a coriolis flow meter) is employed instead of a concentration transmitter, the composition in the recirculation line can be computed by solving the following set of equations:

\[
\dot{n}_r = \sum \dot{m}_{i,r} = \sum (M_{w,i} \cdot \dot{n}_{i,r}) = \dot{n}_r \cdot \sum (M_{w,i} \cdot y_{i,r})
\]
\[
\sum y_{i,r} = 1
\]

(47)

where \( \dot{m} \) is the mass flow rate, \( M_w \) is the molar mass, and the summation is carried for all species \( i = H_2, H_2O, N_2 \). Again, only three components must be assumed.

If neither a hydrogen concentration transmitter nor a mass flow transmitter is employed, the mass flow rate at the anode inlet or outlet can be estimated from the stack pressure drop, although with limited accuracy. Water condensation in gas channels might drastically change the flow resistance inside the stack. In addition, the pressure drop is not only a function of the mass flow rate but also of the gas composition and the temperature.

With knowledge of the molar flow rate of the recirculated gas and the gas composition, the fuel utilization per pass (or alternatively the anode inlet hydrogen stoichiometry) can be computed with Eq. 24.

### 4.2 Experimental setup and measurements

#### 4.2.1 Test bench [I,II]

The test bench used in inert buildup and hydrogen purge measurements is shown in Figure 14. Hydrogen was fed through a pressure reducer and hydrogen recirculation was realized with a diaphragm pump (GD Thomas 118ZC20/24). Air was fed with a 24 VDC blower (Domel 497.3.265) and humidified using a membrane humidifier (PermaPure FC300-1660-10HP). The deionized cooling water was pumped (Johnson Pump, CM30P7-1) through a liquid-to-liquid heat exchanger (SWEP, B5Hx20/1PSC-S) with tap water flowing through the cold side.

In the initial (1st generation) test bench, used for inert buildup measurements, an aged Nedstack P8 64-cell stack with a 200 cm² active single cell area was employed. The anode inlet \( H_2 \) concentration was measured with a concentration transmitter (H2scan, HY-OPTIMA 740) placed in a slipstream. The slipstream was dried with an ice bath because the \( H_2 \) concentration transmitter did not tolerate condensed water.
In the 2nd generation test bench, used for hydrogen purge measurements, the aged stack was replaced with a new Nedstack P8 64-cell stack with a 200 cm² active single cell area. In addition, new H₂ concentration transmitters (Applied Sensor HPS-100) were used. The new transmitters tolerated water condensation, and they could be placed directly in the recirculation stream. The slipstream was removed. In the 2nd generation test bench, a setup for controlling the cathode inlet humidity was implemented with a humidifier bypass line and two manual valves, as shown in Figure 14.

4.2.2 Inert buildup measurements [I]

The measurements were conducted by operating the PEMFC system at constant load current levels ranging from 25 A to 175 A at 25 A steps, without hydrogen purges, and with a constant air flow rate corresponding to the air stoichiometry of 2.5 at 175 A current level. Each current level was maintained for several minutes, and the decrease in the H₂ mole fraction was recorded. The slipstream setup used for measuring the H₂ mole fraction caused a short (in the order of seconds) delay in mole fraction readings, which was negligible with the long measurement times employed.

4.2.3 Hydrogen purge measurements [II]

The objective of the hydrogen purge measurements was to find out how various purge parameters and system humidity levels affect purge efficiency (the removal of liquid water and inert gases) and system efficiency. The varied parameters were the purge length ($t_p$), the cathode inlet humidity ($T_{dew,cat,in}$), the criteria triggering a purge ($\Delta E_{trigger}$), and the purge type (single or double). $\Delta E_{trigger}$ is defined as the measured change in average cell voltage since the last purge.

The measurements were performed by first allowing the system to stabilize at operating conditions (120 A load current, 200 mbar anode pressure, 2.5 air stoichiometry, and 60-60.5 °C coolant inlet temperature). After stabilization, 10 consecutive purge cycles were performed. The results were averaged from the successful purge cycles recorded.

4.3 Results and discussion

4.3.1 Inert buildup [I]

Figure 15 a shows the inert gas buildup at various stack load current levels as a function of time. The amount of inert gas ($n_{N_2,an}$) was calculated from measured hydrogen mole fractions using the ideal gas law. The solid straight lines show the linear fits made to the measurements.

The inert buildup rates calculated from the linear fits, few of which are shown in Figure 15 a, were plotted as a function of the stack current in Figure 15 b. As shown in the figure, the inert buildup rate is linearly proportional to the current. Assuming that membrane permeability is independent of the load current, the
The inert concentration in fuel can be calculated using Eq. 33 and the slope \( \frac{dn_{N_2,an}}{dt} \) in Figure 15 b:

\[
\gamma_{N_2,F} = \frac{2 \cdot 96 \cdot 485 \cdot \frac{C}{mol} \cdot 1.622 \cdot 10^{-7}}{64} = 5 \cdot 10^{-4}
\]  

(48)

In other words, according to measurements, the fuel used was 99.95% pure hydrogen. The measurements were conducted with grade 2.5 hydrogen (purity ≥ 99.5%).

The anode outlet humidity readings fluctuated during the inert buildup measurements presumably due to water condensation. This made the determination of water concentration unreliable. Therefore, water concentrations averaging between the anode inlet and outlet was employed in the calculations.

The partial volumes of anode inlet gas and anode outlet gas were not measured. The results presented here are based on estimated partial volumes (40% anode inlet and 60% anode outlet of the total anode volume 2.6 dm³). In contrast, the results presented in publication [I] were based on the assumption that the entire anode loop had the same \( H_2 \) concentration. The partial anode volumes
clearly affected the results, and, for precise measurements, the partial anode volumes should be determined.

4.3.2 Purge gas volume and composition [II]

Figure 16 shows the averaged flow rate profiles measured with three different hydrogen purge strategies: a) a double purge with $t_p = 200 \text{ ms}$, b) a single purge with $t_p = 200 \text{ ms}$, and c) a single purge with $t_p = 400 \text{ ms}$. The purges were performed with a $\Delta E_{\text{trigger}} = -3 \text{ mV}$ trigger criteria and at three levels of cathode inlet humidity: $T_{\text{dew,cat,in}} = 52, 55, 58 \degree \text{C}$.

![Figure 16. Fuel (hydrogen) feed flow rate profiles during a) double purge ($t_p = 200 \text{ ms}$), b) single purge ($t_p = 200 \text{ ms}$) and c) single purge ($t_p = 400 \text{ ms}$) performed with varying cathode inlet humidities ($T_{\text{dew,cat,in}} = 52, 55, 58 \degree \text{C}$) and with purge triggering criteria $E_{\text{trigger}} = -3 \text{ mV}$. The dashed lines show the control signal of the purge valve (on/off). The averaged flow profiles are based on 6-9 (*) consecutive purge cycles (each plotted in lighter color) at each condition (see publication [II]). *The experiments with $T_{\text{dew,cat,in}} = 58 \degree \text{C}$ in a)-figure were repeated only 2 times.

The effect of cathode inlet humidity on purge efficiency is clearly seen from the higher flow rates achieved at drier conditions. When a double purge is performed (Figure 16 a), the second flow rate peak is almost independent of the
cathode inlet humidity, which indicates that the first purge had flushed the liquid water from the gas channels. The double purge can be used to indicate purge efficiency [64].

Following the approach presented in Section 4.1.2, the amount and the composition of the purged gas can be determined based on hydrogen flow rate profile measurements (Figure 16) and changes in the hydrogen mole fraction. The results are shown in Figure 17.

As expected, the amount of purged gas decreased with an increase in cathode inlet humidity (Figure 17 a) due to a greater amount of condensed water and, consequently, an increase in flow resistance. Simultaneously, the composition of the purged gas approached that of the anode outlet before the purge (Figure 17 b), especially with $t_p = 200$ ms. This indicates that the change in flow rate during the purge became too sluggish for the temporary increase in fuel utilization per pass to affect the composition of the purged gas.

Figure 18 shows the fraction of fresh fuel in the purged gas ($n_{p,ff}/n_p$) as a function of cathode inlet humidity. At the most humid conditions ($T_{dew,cat,in} = 58 \, ^\circ C$) and with a short purge $t_p = 200$ ms, $n_{p,ff}/n_p$ essentially dropped to zero (Figure 18 a), which from a fuel efficiency point of view is optimal. Figure 18 b shows the amount of purged gas at this condition, $V_p = 0.26 \, \text{dm}^3 \, @ \, \text{NTP}$. This corresponds to the maximum volume that could be purged in this system with
minimum hydrogen concentration in the purged gas. For comparison, the total anode volume was ca 2.6 dm$^3$.

![Figure 18](image)

Figure 18. Fraction of fresh hydrogen in purged gas ($n_{\text{p,f}}/n_p$) as a function of a) cathode inlet humidity ($T_{\text{dew,cat,in}}$) and b) purged volume ($V_p$). Operating parameters: $\Delta E_{\text{trigger}} = -3$ mV; $t_p = 200, 400$ ms. The error bars show the standard deviation of the measured values. Figure modified from publication [II]. The results are based on 6-9 consecutive purge cycles at each condition (see publication [II]).

4.3.3 Effect of inert buildup on concentration polarization [II]

The voltage drop that triggered the hydrogen purge ($\Delta E_{\text{trigger}} = -3, -6, -9$ mV) is related to the decrease in reactant concentration at catalyst sites. The Nernst equation (Eq. 9) relates reactant concentrations to cell voltage. Therefore, the theoretical voltage drop can be calculated with Eq. 27, which relates the measured hydrogen partial pressures at the anode ($p_{H_2,an}$) and the expected voltage drop. As the hydrogen partial pressure varies inside the cell, the hydrogen partial pressure is averaged between the cell inlet and outlet:

$$p_{H_2,an} = \frac{p_{an,in}Y_{H_2,in} + p_{an,out}Y_{H_2,out}}{2}$$  \hspace{1cm} (49)

The temperature ($T$) in Eq. 27 is the anode outlet temperature and is believed to represent well the conditions inside the stack.

Figure 19 shows the results. As seen, the calculated voltage drop as a result of dilution of the anode gas by the inert gases is roughly half of the measured voltage drop. This implies that the hydrogen partial pressure in the gas channel deviates remarkably from the catalyst site hydrogen partial pressure. In other words, the mass transfer resistance between the anode gas channels and the catalyst sites (i.e. in the GDL) can be notable and should be taken into account when designing the hydrogen supply and recirculation in PEMFC system.

The cathode inlet humidity does not seem to affect the ratio of theoretical to measured voltage drop even though the changes in water activity were disregarded when calculating the theoretical voltage drop. This can be due to the low operating temperature and that liquid water was present. The activity of liquid water is close to one and is independent of pressure.
4.3.4 Effect of hydrogen purge on fuel and stack efficiencies [II]

The amount of hydrogen lost during hydrogen purges affects the total efficiency of the system through fuel efficiency. Figure 20 shows the measured fuel efficiency ($\eta_f$), stack efficiency ($\eta_s$), and their combined efficiency ($\eta_c$), all as a function of purge-triggering voltage and as a function of the cathode inlet humidity. The efficiencies are computed as follows:

$$\eta_f = \frac{n_{H_2,s}}{n_{H_2,s} + n_{H_2,p}} = \frac{n_{H_2,s}}{n_f Y_{H_2,f}} = 1 - f_p \quad (50)$$

$$\eta_s = \frac{\eta_{cell}}{E_{cell,avg}} = \frac{2F \cdot E_{cell,avg}}{\Delta H^0} \quad (51)$$

$$\eta_c = \eta_f \cdot \eta_s = \frac{n_{H_2,s}}{n_{H_2,s} + n_{H_2,p}} \cdot \frac{2F \cdot E_{cell,avg}}{\Delta H^0} = \frac{P_s}{(n_{H_2,s} + n_{H_2,p}) \Delta H^0} \quad (52)$$

where it has been recognized that stack efficiency equals average cell efficiency ($\eta_{cell}$). The stack efficiency is calculated based on the LHV of hydrogen at standard conditions, $\Delta H^0 = -241830 \text{ J/mol}$ [16].

As shown in Figure 20 a, frequent purges ($\Delta E_{trigger} = -3 \text{ mV}$) result in poorer fuel efficiency because more hydrogen is vented out. Nonetheless, the highest combined efficiency was achieved at these same conditions with the two tested purge lengths and with two different cathode inlet humidities (Figure 20 c). This underlines the importance of one of the main purposes of the hydrogen purge:
to prevent concentration polarization through the removal of impurities. In addition, a close to 100% fuel efficiency increases the risk of (local) fuel starvation, thus compromising stack lifetime.

The combined efficiency also increased with an increase in cathode inlet humidity, as shown in Figure 20 f. This is partly due to higher fuel efficiency (Figure 20 d) and partly due to higher stack efficiency (Figure 20 e). Compared to the short purge ($t_p = 200$ ms), the long purge ($t_p = 400$ ms) appears to improve stack efficiency and the combined efficiency at high-humidity conditions despite poorer fuel efficiency (Figure 20 f). This underlines the importance of the second main purpose of the hydrogen purge: to guarantee stable stack operation by the removal of condensed water from the gas channels.
5. Hydrogen Humidification

Even with hydrogen recirculation, the anode inlet humidity may be inadequate, as was discussed in Section 3. The work presented in publication [III] targeted designing and manufacturing a hydrogen humidifier for a 50 kW PEMFC system [27,65], which is shown in the schematic diagram in Figure 21. A bubble humidifier was regarded as most suitable for this purpose mainly because of its simple, gastight construction and its continued humidification after power failure.

![Simplified schematic diagram of the 50 kW PEMFC pilot plant](image)

With a lack of references, the bubble humidifier was designed in-house with safe tolerances. Effort was put into characterizing the humidifier and validating the implemented model. The validated model was then employed for studying bubble humidifier control and for suggesting improvements in bubble humidifier design.

5.1 Bubble humidifier design and construction [III]

The design of the bubble humidifier is shown in Figure 22. The bubble column was a 1.525 m high DN 400 pipe. Both ends of the column were made of pipe caps; the bottom was welded to the pipe and the cover was removable and fastened with a flange fitting.

The gas inlet and outlet were located in the cover of the bubble column. The gas inlet was connected with a pipe to the sparger that was located at the bottom of the column. Two spargers were manufactured, one with 486 pieces of 1 mm
diameter laser-cut holes and the other with 65 pieces of 2 mm diameter holes. The sparger holes were sized to cause a gas pressure drop large enough to overcome the hydrostatic pressure inside the sparger and to push the water out through a hole drilled at the bottom. This enabled an even distribution of gas flow through the sparger holes. The humidifier gas outlet was open to the gas volume in the top part of the column.

![Bubble humidifier design and test setup](image)

Figure 22. Bubble humidifier design and test setup. C: compressor, FI: flow rate indicator, FT: flow rate transmitter, HT: humidity transmitter, LI: level indicator, PD: differential pressure transmitter, PT: gauge pressure transmitter, TT: temperature transmitter. Dimensions are in mm. Figure from publication [III].

The heating water inlet and outlet were also located in the cover, and they were connected in a closed loop with the heat exchanger. The heat exchanger was made of 6 m long DN 15 finned pipe turned into a coil, and it had a total heat exchange area of ca 3.9 m². A fraction of the PEMFC system coolant water was circulated through the bubble column (controlled by a throttle) to supply the heat needed.

The water needed to replace the humidity leaving with the gas was supplied from the bottom of the column. The water supplied was condensed from the PEMFC stack cathode outlet and filtered through deionization filters. Therefore, the PEMFC system was completely self-contained with respect to water and heat.
needed by the bubble humidifier. The water level was visible through a transparent tube located on side of the column. When operated in the power plant, capacitive water level sensors were mounted onto the transparent pipe to allow for automated water level control [27].

All bubble humidifier metal parts were made of corrosion-resistant steel (EN 1.4404), and the welds in contact with the water-gas mixture were passivated by pickling. In addition, the entire bubble humidifier was insulated with foamed plastic to minimize heat losses.

5.2 Bubble humidifier characterization [III]

The bubble humidifier was characterized using the setup illustrated in Figure 22. Ambient air was used instead of hydrogen, and it was supplied with a roots compressor (Ogura, TX12) at flow rates of 275, 550, and 840 nlpm. These flow rates correspond approximately to the hydrogen flow rates at low power (75 A), nominal power (150 A), and full power (230 A). The temperature and humidity of the humidifier outlet gas were measured with a Vaisala HMM-211 transmitter.

The heating water was supplied employing three heaters with a combined maximum heating power of 5.8 kW. The heating water was supplied at two flow rates (ca 8 lpm and 13.5 lpm) and three humidifier inlet temperatures (55 °C, 60 °C, and 65 °C). Both the heating water inlet and outlet temperatures were measured with K-type thermocouples.

During humidifier characterization, the water level was maintained at a constant 0.86 m above the sparger. Both of the spargers (the one with 1 mm holes and the one with 2 mm holes) were tested.

5.3 Bubble humidifier modelling [III]

The bubble humidifier model developed and presented in publication [III] can be divided into two parts: 1) heat transfer from heating water to bubble column, and 2) mass transfer of water (evaporation) from bubble column to bubbles. The principle is illustrated in Figure 23.

The heat transfer from heating water (subscript $h$) to bubble column media (subscript $l$) was modelled by solving the energy balance equations for two control volumes: 1) the bubble column (subscript $bc$) with all content including the gas (subscript $g$) and the heat exchanger with the exclusion of heating water, and 2) the heating water. The energy balances for these control volumes are:

\[
\left( V_{liq} \cdot \rho_{liq} / M_{w,liq} \cdot C_{p,liq} + m_{bc} \cdot C_{p,pc} \right) \cdot dT_{liq}/dt = \dot{Q} - \dot{n}_{gas} \cdot \int_{T_{gas,in}}^{T_{gas,out}} C_{p,gas} dT_{gas} - \dot{n}_{liq} \cdot \Delta H_{vap}(T_{liq}) \tag{53}
\]

\[
0 = \dot{Q} + \dot{n}_{h} \cdot \int_{T_{h,in}}^{T_{h,out}} C_{p,h} dT_{h} \tag{54}
\]
On the left hand side of Eq. 53, \( V_{liq} \) is the volume of (liquid) water in bubble column, \( \rho_{liq} \) is the density of (liquid) water in bubble column, \( M_{w,liq} \) is the molar mass of water, \( C_{p,liq} \) is the heat capacity of (liquid) water in bubble column, and \( T_{liq} \) is the temperature of bubble column content. On the right hand side of Eq. 53, \( \dot{Q} \) is the heat transfer rate, \( \dot{n}_{gas} \) is the molar flow rate of gas, \( T_{gas} \) is the gas temperature, \( \dot{n}_{liq} \) is the molar evaporation rate of water in the bubble column, and \( \Delta H_{vap} \) is the latent heat of water. In Eq. 54, \( \dot{n}_h \) is the molar flow rate of heating water, \( C_{p,h} \) is the heat capacity of heating water, and \( T_h \) is the temperature of heating water. The heat transfer rate (\( \dot{Q} \)) depends on the heat transfer resistance inside the heat exchanger pipe (\( R_{in} \)), through the pipe (\( R_{wall} \)), and outside the pipe (\( R_{out} \)):

\[
\dot{Q} = \Delta T_{im}/R_{tot} = \Delta T_{im}/(R_{in} + R_{wall} + R_{out}) \tag{55}
\]

where the logarithmic mean temperature difference (\( \Delta T_{im} \)) is computed from heating water inlet and outlet temperatures (\( T_{h,in}, T_{h,out} \)) and the temperature of bubble column content as follows:

\[
\Delta T_{im} = (T_{h,in} - T_{h,out})/\ln\left\{T_{h,in} - T_{liq}/T_{h,out} - T_{liq}\right\}, \tag{56}
\]
the heat transfer resistance inside the heat exchanger pipe depends on the convectional heat transfer coefficient inside the heat exchanger \( (h_{in}) \) and the pipe inside area \( (A_{in}) \) as follows:

\[
R_{in} = 1/(h_{in} \cdot A_{in}), \tag{57}
\]

the heat transfer resistance through the pipe depends on the pipe inner and outer radius \( (r_{in}, r_{out}) \), the pipe inside area, and the thermal conductivity of heat exchanger wall \( (k_w) \) as follows:

\[
R_{wall} = r_{in} \cdot \ln(r_{out}/r_{in})/(A_{in} \cdot k_w), \tag{58}
\]

and the heat transfer resistance outside the pipe depends on the convective heat transfer coefficient outside the heat exchanger \( (h_{out}) \), the heat exchanger pipe outside area \( (A_{out}) \), the fin efficiency \( (\eta_{fin}) \), and the fin area \( (A_{fin}) \) as follows:

\[
R_{out} = 1/(h_{out} \cdot (A_{out} + \eta_{fin} \cdot A_{fin})). \tag{59}
\]

In the bubble column energy balance equation (Eq. 53) and in calculating the logarithmic mean temperature difference (Eq. 56), uniform bubble column temperature was assumed.

The convective heat transfer coefficients \( (h_{in} \text{ and } h_{out}) \) were calculated using correlations found in literature \([66,67]\text{ and } [68,69]\), respectively. The fin efficiency in Eq. 59 accounts for a decline in fin temperature when approaching its tip, and is calculated as suggested in reference \([70]\).

The mass transfer of water to the gas bubbles was assumed to occur solely by diffusion and can be thought to represent a worst-case scenario. First, the bubble surface was assumed to be saturated with water vapor at the temperature of the bubble column media. Assuming ideal gas behavior, the saturated water concentration is:

\[
\xi_0 = \frac{p_{sat}(T_{liq})}{RT_{liq}}. \tag{60}
\]

The volume-average water concentration inside the bubble \( (\bar{c}) \) was calculated as follows \([71]\):

\[
\bar{c} = 1 - \exp\{-1.5 \cdot Fo \cdot \bar{Sh}\} \tag{61}
\]

where the time averaged Sherwood number \( (\bar{Sh}) \) and the Fourier number \( (Fo) \) are defined as follows:

\[
\bar{Sh} = 4/\sqrt{\pi \cdot Fo} + \frac{63.237 \cdot \sqrt{Fo} + 71.892 \cdot Fo + 1.5 \cdot 116.673 \cdot Fo^{1.5}}{1 + 33.616 \cdot \sqrt{Fo} + 45.628 \cdot Fo + 116.673 \cdot Fo^{1.5}}, \tag{62}
\]

\[
Fo = \frac{D_{H_2O} \Delta t}{r_b^2}, \tag{63}
\]

where \( D_{H_2O} \) is the water diffusion coefficient, \( \Delta t \) is the bubble retention time, and \( r_b \) is the bubble radius. The radius of bubbles formed in the sparger was
calculated using correlations suggested by Bhavaraju et al. [72]. The bubble retention time was calculated based on the water level and the rise velocity, of which the latter was calculated using a correlation by Grace et al. [73].

5.4 Results and discussion [III]

A comparison of simulated and measured bubble column temperatures during characterization tests is shown in Figure 24. As can be seen, the match is good: the average deviation of bubble column temperature \( T_{liq} \) was less than 0.3 °C at all tested conditions.

The measured approach dew point temperatures relative to heating water inlet temperatures were in the range of 1.8 to 8.7 °C. The corresponding relative humidities \( (RH) \) were in the range of 67% to 92% at heating water inlet temperature. At a gas flow rate corresponding to low system power, the approach dew point temperature was 3.1 °C when heating water was supplied at 65 °C and at a 13.5 lpm flow rate. At a gas flow rate corresponding to nominal and full power, the approach dew point increased to 5.9 °C and 8.5 °C, respectively.

The measurements with a 13.5 lpm heating water flow rate resulted in a 0.6-2.3 °C lower approach dew point temperature (2.4 to 7.7% higher \( (RH) \)) compared to measurements conducted with an 8 lpm heating water flow rate. The effect of heating water flow rate increased with increasing gas flow rate.

Using the sparger with larger holes resulted in a lower approach dew point temperature in most cases. However, the differences were small.

The approach dew point temperatures above were calculated from the heating water inlet temperature and the surface temperature of the bubble column water – not the gas outlet dew point temperature. This was due to the assumed condensation of water vapor from the gas phase during characterization tests and a resulting drop in dew point temperature.
Figure 25 shows the results of water mass transfer simulations when the mass transfer rate is assumed to be limited by the diffusion rate in the gas bubbles. In reality, some convection also occurs and, thus, the simulated mass transfer rates were interpreted as worst-case scenarios. The results show that bubbles with a ca 1 cm diameter (as in the present study) require roughly a 5 cm water bed to reach saturation. In practice, fitting a large enough heat exchanger in such a low water bed is challenging. Therefore, it is safe to say that the mass transfer rate does not limit the performance of the humidifier but the heat transfer rate does. In addition, it is justified to use the surface temperature of the bubble column water in calculating the approach dew point temperatures of the humidified gas.

![Figure 25. a) Time (Δt) and b) water bed height (ΔZ_{w}) needed for water vapor to reach 99.9% of equilibrium concentration (c_{eq}) in spherical hydrogen bubbles due to pure diffusion at T_{eq} = 60 °C as a function of hydrogen bubble diameter (d_{b} = 2 \cdot r_{s}). Figure modified from publication [III].](image)

The high gas pressure drop is one of the most cited disadvantages of a bubble humidifier (e.g. [47,49]). The results shown in Figure 25 suggest that this is not necessarily true. The 5 cm water bed height required to reach saturation is equivalent to a 5 mbar hydrostatic pressure drop. With the pressure drop introduced in the spargers (≤ 15 mbar [65]), the total pressure drop would be approximately 20 mbar – a figure comparable to many other humidifier types. However, as pointed out above, the heat exchanger needs careful design to accomplish this if placed inside a bubble humidifier. Another option is to heat the humidifier water in an external heat exchanger.

Since humidifier performance is not mass transfer limited according to the simulations, it must be heat transfer limited. Thus, humidifier performance can be improved by improving heat transfer. In practice, the means to improve humidifier performance are limited to increasing the heating water flow rate and the heat exchange area. The heat transfer rate also depends on the gas flow rate (through heat consumption and a change in temperature difference) and the heating water inlet temperature. However, these parameters are typically fixed by system design.
Figure 26 shows the simulated effect of the heating water flow rate and heat exchange area on the humidifier outlet dew point temperature reached. According to simulations, a 5.7 °C approach dew point temperature is reached at nominal system power (i.e. with 558 nlpm hydrogen gas flow rate), with 13.5 lpm heating water flow rate, and with 3.9 m² heat exchange area. Doubling the heating water flow rate to 27 lpm decreases the approach dew point temperature to 4.3 °C, whereas, doubling the heat exchange area to 7.8 m², decreases the approach dew point temperature to 4.1 °C. However, a high heating water flow rate translates into a high pressure drop and additional power consumption of the coolant pump. A large heat exchanger, on the other hand, is more expensive. Thus, sizing the bubble humidifier is a compromise between performance and cost.

![Figure 26. Simulated steady state bubble humidifier outlet dew point temperature ($T_{\text{dew, out}}$) as a function of heating water flow rate ($V_h$) and heat exchange area ($A_{\text{out}} + A_{\text{in}}$). Hydrogen gas flow rate ($V_{\text{gas}}$) is 558 nlpm (left) and 856 nlpm (right). Heating water inlet temperature is $T_{\text{h,in}} = 65^\circ\text{C}$. The dew point temperature attained with 3.9 m² heat exchanger and 13.5 lpm heating water flow rate is marked in the figures. Figure modified from publication [III].](image)

The membrane’s proton conductivity, and, consequently, fuel cell performance, improves with increasing humidity level. However, operating conditions that are too humid cause unstable fuel cell performance because of water condensation in the gas channels. The water generation rate and, consequently, the humidity level in the fuel cell is proportional to the load current. Therefore, controlling the inlet gas humidity may be desired. With a bubble humidifier, the humidification can be controlled either by varying the heating water flow rate or by varying the heat transfer area, as shown in Figure 26. The heating water flow rate can be varied with a (proportional) valve or a pump. The heat transfer area can be varied, for example, by passing heating water either through one or several parallel heat exchangers all submerged in the bubble column.

### 5.5 Bubble humidifier in 50 kW power plant

The bubble humidifier was successfully operated for 4,400 hours and it provided sufficient humidification for the 50 kW PEMFC pilot plant [27]. The only problem encountered was the too efficient humidification at low gas flow rates, which caused stack flooding during system startup. In addition, minor corrosion
was observed in the heat exchanger welds after characterization experiments conducted with air.

A solution to the too efficient humidification at low gas flow rates could be a humidifier bypass [27] or controllable heat transfer, as discussed in Section 5.4. The rather slow humidifier control discussed in publication [III] could be speeded up with a decrease in the amount of water in the humidifier. This would allow more rapid changes in humidification, but it would also place more strict requirements on the humidifier control. The amount of water used in publication [III] was excessive due to the rapid mass transfer in evaporation.
6. Hydrogen Recirculation

One of the main challenges of mechanical hydrogen recirculation pumps is their wear and, ultimately, breakdown [27]. One option for a mechanical hydrogen recirculation pump is to use a single fixed geometry ejector and its discrete control in a PEMFC system. This hydrogen recirculation scheme operates without any moving parts apart from the solenoid valves for hydrogen supply and hydrogen purge. Thus, it provides a hydrogen supply and recirculation setup with ultimate simplicity and at a potentially very low price compared to mechanical hydrogen recirculation pumps. The downside of employing a single fixed geometry ejector with discrete control is, however, a more challenging system operation since the ejector operation is limited to discrete points.

This chapter discusses the application of a single, fixed geometry ejector and discrete flow control in PEMFC system. First, a 2D CFD modelling approach to the ejector is introduced and the modelling accuracy is discussed (publication [IV]). Second, the discrete control approach, its challenges, and management strategies are discussed (publication [V]). Finally, the capabilities of a system employing the ejector and discrete control method for rapid load changes are studied (publication [VI]).

6.1 Ejector design and manufacturing [IV]

The work presented in publications [IV-VI] is based on the same ejector, the design of which is shown in Figure 27. The primary nozzle was sized based on isentropic flow relations, assuming critical flow and ideal gas behavior. The rest of the ejector dimensions were chosen based on previous work found in the literature [74–76]. The ejector design targeted a wide operating range in a 5 kW PEMFC system.

The ejector was manufactured by 3D printing at AM Finland Oy with the direct metal laser-sintering technique. The critical ejector surfaces were polished at the Finnish School of Watchmaking.
6.2 Ejector modelling [IV]

Modelling always involves assumptions and simplifications. Therefore, the modelling approach must be validated against experimental data before any conclusions are drawn based on the results.

The modelling work in publication [IV] aimed at validating a 2D axisymmetric CFD modelling approach. The differences in the accuracies of three turbulence models (SST k-ω, RNG k-ε, and Realizable k-ε) in predicting ejector performance were studied in particular.

The modelling was conducted with ANSYS Fluent v16.0 software installed on workstation with an 8-core CPU and 16 GB RAM. The flow was assumed compressible and steady. The fluid was treated as an ideal gas, and both gravity and phase transitions were neglected. The modelled domain (shaded area in Figure 27) was spatially discretized with structured quadrilateral meshes. Mesh-independence tests were conducted. The smallest mesh tested had ca 48,000 cells and the finest had ca 753,000 cells. The balance equations were solved with a pressure-based solver. Second-order interpolation and upwind schemes were employed for the pressure and the balance equations, respectively. The ejector walls were assumed smooth and adiabatic, and the no-slip condition was applied.

6.3 Ejector characterization [IV]

Publication [IV] presents the characterization of two ejectors; the custom-made ejector and a commercially available ejector (SMC, ZH05S-X267) sold mainly for vacuum generation.

The characterization was conducted with the test setup shown in Figure 28. In the setup, the ejector primary and secondary inlets were fed with either air or
Hydrogen recirculation

The pressure of both inlets could be varied independently with manual pressure regulators. The secondary inlet gas passed through a liquid-to-gas membrane humidifier before being fed to the ejector. The secondary inlet gas humidity could be controlled by varying the liquid temperature and flow rate. Ejector outlet pressure was controlled with a manual backpressure regulator.

Figure 28. Ejector characterization test setup. TT: temperature transmitter, FT: flow rate transmitter, PT: gauge pressure transmitter, HT: humidity transmitter. Figure from publication [IV].

6.4 Ejector discrete control [V]

In publication [V], a discrete ejector-primary-gas-control system (EPC) based on three solenoid valves and flow restrictions was designed and implemented.

The principle of the discrete EPC is to fluidically connect two or more (in this case three) flow restrictions in parallel. By allowing flow either through one or several of these flow restrictions, discrete flow rate levels (corresponding to PEMFC stack load current levels) is achieved. The solenoid valves used for enabling/disabling flow through a restrictor can also act as the restrictors if suitable sizes are available. The principle of the discrete EPC is shown in Figure 29.

Figure 29. Principle of the discrete EPC. Figure from publication [V].

The sizing of flow restrictions can be done in various ways. One approach that results in evenly spaced flow rate levels is obtained when the smallest flow restrictor (or valve) is sized to pass a flow rate that equals the desired flow rate difference between two levels. The next restrictors should be sized to pass a flow
rate twice that of the previous restrictor. This sizing approach was employed in publication [V]. However, because of a hydrogen supply pressure that was too low (ca 16 barg was required while only ca 9 barg was applied), the evenly spaced flow rate levels could not be achieved throughout the operating range. Table 4 shows the stack currents achieved with the EPC sizing employed in the present work.

Table 4. Measured 50-cell stack load current levels achieved with the current fuel supply system operated at 8.5-8.7 barg restrictor inlet pressure and 0.05 to 0.1 barg anode pressure. Table reproduced from publication [V].

<table>
<thead>
<tr>
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<td>22</td>
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<tr>
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<td>5.7</td>
<td>149</td>
<td>16</td>
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<tr>
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<td>1, 2, 3</td>
<td>8.5 (**)</td>
<td>6.3</td>
<td>162</td>
<td>14</td>
</tr>
</tbody>
</table>

(*) Flow in ejector primary nozzle is subcritical, i.e. the primary flow rate (and the achievable stack current) depends on both ejector primary and outlet pressure.

(**) Flow in restrictors is subcritical, i.e. the current step increment size decreases.

One drawback of the discrete EPC is that the hydrogen supply rate cannot be adjusted from the levels fixed in the design stage. If the supply rate deviates from the consumption rate, anode pressure will vary. The rate of variation in anode pressure due to a mismatch between hydrogen supply and consumption rate is inversely proportional to the anode volume. Consequently, in anode volume-optimized systems, the anode pressure changes can be very fast (several bars per second).

During normal operation, a mismatch between hydrogen supply rates and the consumption rate can occur due to a load change, a hydrogen purge, or a variation in hydrogen supply pressure (e.g. because of temperature variation in a spring-loaded pressure reducer). When such a mismatch occurs, some action must be taken to prevent over- or under-pressure. A possible action in hybridized systems, for example, is variation of the load current.

If variation of the load current is not possible, the EPC can be sized and the PEMFC system can be operated in such a way that hydrogen is always delivered in excess. The excess hydrogen can be vented out with periodic or pressure triggered purges, continuous purge (=bleed), or by employing a backpressure regulator. In the work described in publication [V], both periodic purging and variation of load current were proven to work well.
6.5 Ejector-based system testing [V]

The characterized custom-made ejector and the discrete EPC were tested in a 5 kW PEMFC system with a 50-cell S2 stack by PowerCell Sweden AB. Other main components in the system were an air blower (Ametek Inc., Windjammer, 230 VAC), a cathode gas-to-gas membrane humidifier (Perma Pure LLC, FC300-1600-10HP), a coolant pump (EMP Inc., WP29), a coolant deionization filter (Spectrapure Inc., DI-MBHT-RT3-10L-25), and a liquid-to-liquid heat exchanger (Swep International AB, B5Hx20/1P-SC-S). The anode inlet was humidified only with the hydrogen recirculation achieved with the single ejector. A simplified system scheme is shown in Figure 30.


A buffer volume of roughly 11 dm$^3$ was applied at the anode inlet, as shown in Figure 30. This was a safety precaution targeted at slower pressure changes that result from the mismatch between the hydrogen supply rate and consumption rate. The use of a buffer volume turned out to be useful in preventing an excessive pressure rise or drop and, thus, possible system damage, especially during the system testing phase. Later, with experience on system behavior, the buffer volume was disconnected from the anode loop with a manual valve.

After initial system testing, two sets of measurements were conducted. First, a polarization curve was measured to validate system and ejector performance at steady state operation. The polarization curve was measured by operating the system at load current levels 1 A to 3.5 A below those dictated by EPC sizing. Excessive anode pressure was avoided by periodic hydrogen purges. The system was operated at the load current levels shown in Table 4 in the following order: starting from load level 4, increasing the load up to level 7, then decreasing down to level 0, and finally increasing the load back to level 4. Each load current level (except load level zero) was maintained for 15 minutes.

Second, the effect of inert content on the recirculation rate was measured. The measurements were conducted by operating the system at constant load current and anode pressure levels with long purge cycles to allow inert gas buildup in the anode. The measurements were conducted with varying anode inlet pressure levels (20, 60, 150 mbarg) at load level 4 (each measurement repeated 2-5 times) and with varying load levels (1, 4, 7) and constant anode inlet pressure of 60 mbarg (each measurement repeated 5 times).
6.6 Load changes with discrete ejector control [VI]

During a load change, the fuel supply and consumption rates temporarily mismatch when discrete ejector control is used. This is because the load current changes almost instantaneously while the fuel supply rate develops more slowly. The mismatch can cause over- or under-pressure at the anode or, at worst, fuel starvation. One method to manage the mismatch is to optimize the timing of fuel supply with respect to the load change.

The effect of fuel supply timing was studied with the 5 kW PEMFC system. For these experiments, the control software was modified as follows. First, the data acquisition routine was improved to achieve continuous a 100 Hz data recording rate. Second, the timing of the hydrogen supply valve, air blower, and electronic load control was improved. In addition, mechanical relays employed for controlling the hydrogen supply valve were found unreliable during fast control sequences, and they were replaced with solid-state relays.

The experiments were conducted by letting the system stabilize on load level 2 (see Table 4), which resulted in ca 2 kW stack power. The anode pressure was maintained at 100 mbarg, air stoichiometry was maintained at 2.5, and the coolant inlet temperature was maintained at 70 °C. The buffer volume employed during system testing was disabled, and the anode pressure was controlled by fine-tuning the load current with a PI controller.

Prior to ramping up the power, the airflow rate was increased (ca 2 seconds before power ramp), and fine-tuning of the load current was disabled (ca 1 second before the power ramp). In addition, the data recording rate was increased to 100 Hz.

The power ramp-up was performed by ramping up the fuel supply and the load current to level 7 (≈ 4 kW). The load ramp-up timing \( \Delta t_{trf} \) was relative to the fuel supply initiation. Five load ramp-up timings were tested: -50 ms, 0 ms, +50 ms, +100 ms, and +200 ms. The experiments with each load ramp-up timing were repeated at least six times. Approximately 1 second after the power ramp-up, load current fine-tuning was again enabled, and, approximately after 10 seconds, the recording rate was set to normal.

The anode pressure was observed to be a critical parameter in the initial tests because a pressure that is too high or low could damage the stack. Therefore, a model for predicting anode pressure during load changes was implemented. The simulation results were used for determining the safe load ramp-up timings listed in the previous paragraph. A description of the model can be found in publication [VI].

6.7 Results and discussion

6.7.1 Ejector modelling [IV]

The measured ejector entrainment ratios and those obtained with 2D CFD modelling were compared by calculating both the mean absolute deviation (AD) and the mean relative deviations (RD). The ADs and RDs were computed as follows:
\[
AD = \frac{1}{N_{tot}} \cdot \sum_{i=1}^{N_{tot}} \left| \Omega_{meas,i} - \Omega_{sim,i} \right|
\]

(64)

\[
RD = \frac{1}{N_{tot}} \cdot \sum_{i=1}^{N_{tot}} \left| 1 - \frac{\Omega_{sim,i}}{\Omega_{meas,i}} \right|
\]

(65)

where \(\Omega_{meas,i}\) is the measured entrainment ratio, \(\Omega_{sim,i}\) is the simulated entrainment ratio, \(i\) is the index of measurement, and \(N_{tot}\) is the total number of measurements. The entrainment ratio is the ratio of the ejector secondary inlet mass flow rate (\(m_{s,in}\)) to the ejector primary inlet mass flow rate (\(m_{p,in}\)):

\[
\Omega = \frac{m_{s,in}}{m_{p,in}}
\]

(66)

The ADs and RDs of modelled entrainment ratios compared to the measured entrainment ratio are shown in Table 5.

<table>
<thead>
<tr>
<th>Model</th>
<th>(\Omega_{meas} &lt; 1)</th>
<th>(\Omega_{meas} &gt; 1)</th>
<th>All</th>
<th>(\Omega_{meas} &lt; 1)</th>
<th>(\Omega_{meas} &gt; 1)</th>
<th>All</th>
</tr>
</thead>
<tbody>
<tr>
<td>SST k-(\omega)</td>
<td>0.78</td>
<td>0.72</td>
<td>0.73</td>
<td>227.2%</td>
<td>31.5%</td>
<td>68.2%</td>
</tr>
<tr>
<td>RNG k-(\varepsilon)</td>
<td>0.47</td>
<td>1.08</td>
<td>0.97</td>
<td>144.6%</td>
<td>41.5%</td>
<td>60.9%</td>
</tr>
<tr>
<td>Realizable k-(\varepsilon)</td>
<td>0.48</td>
<td>1.17</td>
<td>1.04</td>
<td>146.2%</td>
<td>44.5%</td>
<td>63.6%</td>
</tr>
</tbody>
</table>

Overall, the 2D axisymmetric CFD modelling gave relatively good predictions of the performance of the ejector considering the substantially lighter computation compared to 3D modelling. The 2D modelling overestimated the performance of the ejector for all turbulence models at nearly all conditions. The mean absolute deviations (ADs) of simulated ejector entrainment ratios were in the range 0.73 to 1.04 and the mean relative deviations (RDs) were in the range 60.9% to 68.2%, as shown in Table 5.

Simulations conducted with the SST k-\(\omega\) model had the lowest AD while simulations conducted with the RNG k-\(\varepsilon\) model had the lowest RD. There was, however, notable variation in the accuracies of the turbulence models depending on the conditions, as seen in Figure 31. In a system with a low flow resistance (\(\leq 51.7\) mbar, \(\Delta p_z\): “low”), the SST k-\(\omega\) model gave more accurate predictions of the ejector performance at high primary gas flow rates while the two k-\(\varepsilon\) models gave better predictions at low primary gas flow rates. In a system with a high flow resistance (\(\leq 206.9\) mbar, \(\Delta p_z\): “high”), all three turbulence models gave similar predictions, the maximum deviation in the predicted entrainment ratio being less than 9%. 
Figure 31. Comparison of a) fuel utilization per pass and b) entrainment ratio predictions obtained with the different turbulence models along the low-flow-resistance operating curve ($\Delta p_s$: "low") and the high-flow-resistance ($\Delta p_s$: "high") operating curve. Working gas = $\text{H}_2$, $T_{dew,in} = 60$ °C, $p_{ej, out} = 250$ mbarg. Figure modified from publication [IV].

Figure 32 shows the ejector exergetic efficiency as a function of stack pressure drop measured and modelled at three primary pressure levels. It can be seen that the maximum efficiency occurred at stack pressure drops close to half of their maximum at all primary pressure levels.

The ejector should operate at maximum efficiency for highest recirculation rate. The observation that maximum efficiency is reached at stack pressure drops half of their maximum can be useful in the first stage of dimensioning an ejector for a specified system because, in principle, only the maximum pressure difference for an ejector must be known for optimal sizing. However, the maximum efficiency of a certain ejector geometry does not necessarily mean that that ejector geometry, of all possible ejector geometries, gives the best performance.
Therefore, this method can only be used as a first approximation in the search for optimal ejector dimensions.

A comparison of the simulation results of the three models in Figure 32 shows that the two $k$-$\varepsilon$ models accurately predict the position of maximum efficiency. Therefore, these models would be more useful in ejector optimization than the $k$-$\omega$ model, which tends to predict maximum efficiency at a pressure drop that is too high. None of the models predicted the value of the efficiency accurately.

### 6.7.2 Ejector characterization [IV]

The entrainment ratio and efficiency maps of the two ejectors measured with humid air and a 500 mbarg ejector outlet pressure are shown in Figure 33. The operating lines plotted on the maps represent the path along which an ejector operates when used in systems with low ($\leq 51.7$ mbar, $\Delta P_s$: “low”), moderate ($\leq 103.4$ mbar, $\Delta P_s$: “moderate”), or high flow resistance ($\leq 206.9$ mbar, $\Delta P_s$: “high”). The maximum efficiency curve, i.e. the curve along which maximum efficiency is achieved, is also plotted on the efficiency maps.

![Figure 33. Custom-made ejector operating curves plotted on a) entrainment ratio map and b) efficiency map, and commercial ejector operating curves plotted on c) entrainment ratio map and d) efficiency map. Working gas = air, $T_{dew,s,in} = 60$ °C, $p_{ej,out} = 500$ mbarg. Figure modified from publication [IV].](image)

The ejector operating maps in Figure 33 show that the recirculation rate achieved with the ejectors declined when system flow resistance increased, as expected. For the custom-made ejector, the best efficiency was achieved close to the high-flow-resistance operating curve. The commercial ejector operated mostly far from its maximum efficiency and, therefore, achieved a poor recirculation rate compared to the custom-made ejector.

Optimally, the ejector would operate close to maximum efficiency throughout its operating range. However, the ejector operating curve and the maximum efficiency curve might not be possible to match over the entire range. Either a
variable geometry ejector can be employed [74] or several differently sized ejectors can be operated in parallel [75] to address this issue.

Figure 34 shows the custom-made ejector operating curves plotted on the efficiency and fuel utilization per pass maps measured with humid hydrogen and a 250 mbarg outlet pressure. Again, the highest efficiency was mostly achieved in the high-flow-resistance system. Nonetheless, the highest recirculation rate was achieved in a system with low flow resistance for which the fuel utilization per pass was almost 50% at a primary pressure as high as 5 barg. This highlights the significance of anode subsystem flow resistance in the achieved recirculation rate, especially when ejectors are employed.

![Figure 34. Custom-made ejector operating curves plotted on a) exergetic efficiency ($\eta_{ex}$) map and b) fuel utilization per pass ($u_{FP}$) map. Working gas = H$_2$, $T_{de:w,in} = 60$ °C, $p_{ej, out} = 250$ mbarg. Figure modified from publication [IV].]

6.7.3 **System testing [V]**

The measured ejector performance in the actual PEMFC system is shown in Figure 35. The time-averaged fuel utilization per pass ($u_{FP}$) varied between 40% (±7%) at 25 A stack current and 64% at 160 A stack current. Correspondingly, the time-averaged anode inlet hydrogen stoichiometry ($\lambda_f$) varied from 2.6 (±0.4) to 1.6 within the same stack current range.

![Figure 35. Ejector performance as function of stack current: fuel utilization per pass ($u_{FP}$), ejector secondary gas pressure lift ($\Delta p_{ej}$), entrainment ratio ($\Omega$), and ejector primary pressure ($p_{p,in}$). The error bars show the variation in time-averaged values between upward and downward polarization curve measurements. *Only data from downward curve is available. Figure modified from publication [V].]

60
The recirculation rate was lower than what could be expected from Figure 34. Possible reasons for this include the inert content of the recirculated gas (characterization was conducted with pure hydrogen) and the lower anode pressure. Both of these factors were found to affect the recirculation rate, and their effect will be addressed below. An additional cause for the observed lower recirculation rate is the poor efficiency of the ejector at these conditions. Because of the low efficiency, the effect of flow resistance of the system on the achieved recirculation rate is minor.

The effects of recirculated gas inert content and anode pressure are shown in Figure 36. The fuel utilization per pass, the ejector entrainment ratio, the ejector secondary inlet dew point temperature (which is close to the anode outlet dew point temperature), the ejector outlet dew point temperature (i.e. the anode inlet dew point temperature), and the ejector secondary gas pressure increase are plotted as functions of the inert mole fraction of the ejector secondary gas calculated on dry basis ($y_{N_2, dry, s, in}$).

![Figure 36. Effect of anode gas inert content on dry basis ($y_{N_2, dry, s, in}$) on fuel utilization per pass ($u_{f, pp}$), entrainment ratio ($\Omega$), ejector secondary inlet dew point temperature ($T_{dew, s, in}$), ejector outlet dew point temperature ($T_{dew, s, out}$), and ejector secondary gas pressure lift ($\Delta p_{e,j}$) at load levels 1, 4, and 7 (a-e) and at anode pressure levels 20, 60, and 150 mbarg (f-j). Each experiment was repeated 2-5 times. Figure is a combination of two figures in publication [V].](image-url)
The increase in the anode gas inert content reduced the anode inlet dew point temperature ($T_{dew\_e\_out}$) roughly by 2 to 3 °C when the inert content of dry recirculated gas ($y_{N_2,\_dry\_S\_in}$) increased by 0.1 (Figure 36 d and i). The decrease in anode inlet humidity (Figure 36 c and h) was a result of the decrease in molar recirculation rate (increased fuel utilization per pass, Figure 36 a and f), which was a result of hydrogen being replaced with the heavier nitrogen. At the same time, the mass-based recirculation rate (i.e. the entrainment ratio) increased (Figure 36 b and g). The magnitude of the effect depended on the load level. These observations can explained with the added molar mass of recirculated gas, which leads to a lower recirculation rate since the ejector operation is based on momentum transfer.

The effect of the anode gas inert content on water management is twofold. On one hand, the added inert concentration decreases the recirculation rate (as noted in the previous paragraph) thus, depressing the removal of water droplets from gas channels. On the other hand, the added inert concentration increases both the mass flow rate and the anode gas viscosity, both of which enhance the removal of water droplets. Therefore, the net effect of added inert concentration on water management deserves additional study.

The increase of anode pressure level caused both the molar recirculation and the mass-based recirculation rate to increase, as seen in Figure 36 f and g. This can be explained by a higher gas density that allowed a higher flow rate through the fixed geometry ejector.

The anode inlet humidity appeared to be independent of the anode pressure level despite the greater recirculation rate (Figure 36 i). Instead, the anode outlet humidity decreased 1.4-1.7 °C with a 130 mbar (20 mbarg to 150 mbarg) increase in the anode pressure level. A possible explanation for this observation is a decreased water transport rate from cathode to anode as a result of the higher anode pressure. Another explanation is the drier operating conditions at higher anode pressures, which are a result of more efficient hydrogen purges.

### 6.7.4 Load changes with discrete ejector control [VI]

During rapid load changes with a PEMFC system, one of the main concerns is sufficient fuel supply and prevention of fuel starvation. In addition, the anode pressure variation is a concern in systems where the anode pressure is not autoregulated (e.g. by a pressure regulator). Figure 37 shows ejector primary pressure (which is proportional to the hydrogen supply rate), anode pressure, as well as stack current, voltage, and power measured during the experiments described in Section 6.6.

The hydrogen flow developed relative slowly; the final primary pressure level and, consequently, the final hydrogen flow rate was reached in ca 350 milliseconds, as seen in Figure 37 a. The time is proportional to the volume between the EPC and the ejector. Thus, by minimizing this volume, the time required to reach the final flow rate can be reduced. The opening times of the fuel supply valve also affect the time required to reach the final flow rate.
Figure 37. a) Ejector primary pressure ($p_{p,in}$), b) anode inlet pressure relative to set point ($p_{an,rel.} = p_{an,in} - 100$ mbar), c) stack load current ($I_s$), d) stack voltage ($E_s$), and e) stack output power ($P_o$) as function of time relative to hydrogen supply ramp-up for five load ramp-up timings relative to fuel supply ramp-up ($t_{trf} = -50, 0, +50, +100, +200$ ms). The experiments with each load ramp-up timing were repeated at least six times. The thin lines show the measurement variation. Figure modified from publication [VI].

The stack voltages (Figure 37 d) showed no depression, i.e. no sign of fuel shortage on the reaction sites despite the slowly developing fuel supply rate. In one case (i.e. $t_{trf} = -50$ ms), the load current was increased even before the initiation of fuel supply, and still the stack voltage showed no depression. This can be explained by a sufficiently large hydrogen buffer in the anode volume. Therefore, this behavior might be different in anode-volume-optimized systems.

The pressure at the anode inlet (Figure 37 b) shows relatively modest variations, which supports the notion that the hydrogen buffer was sufficient. The measured variations in anode pressure are in line with the simulated ones (Figure 38 a) with the exception of the effect of load control, which was disabled in the measurements. Figure 38 b shows minimum and maximum anode pressures as functions of load ramp-up timing.
Figure 38. Simulated a) relative anode inlet pressure \( P_{\text{an,rel}} = P_{\text{an,in}} - 100 \text{ mbar} \) as function of time relative to hydrogen supply ramp-up for four load ramp-up timings \( (t_{\text{trf}} = -100, 0, +100, +200 \text{ ms}) \) and b) maximum and minimum anode pressure as a function of load ramp-up timing. Figure modified from publication [VI].

Optimally, the load ramp-up timing would be chosen to result in minimal variation in anode pressure. In publication [VI] it was found that minimal variation in pressure does not occur when the hydrogen supply is ramped up simultaneously with the load current (i.e. at \( t_{\text{trf}} = 0 \text{ ms} \)). Instead, variation in pressure depends on the time that the hydrogen flow requires to fully develop, and the optimal load ramp-up timing is, therefore, always positive (assuming that the load change occurs instantaneously). In the current case, it was ca 100 milliseconds and the resulting pressure variation was 20-25 mbar, as shown in Figure 39.

Figure 39. Simulated and measured anode pressure variation \( (P_{\text{an,max}} - P_{\text{an,min}}) \) during a power ramp-up as function of load ramp-up timings relative to fuel supply ramp-up \( (t_{\text{trf}}) \). The error bars show measurement variations.

In the present system, where the anode volume was rather large (~1.5 dm³ or ~0.3 dm³/kW), the variation in anode pressure was only little higher than 100 mbar even when the load ramp-up time deviated 200 milliseconds from the optimum. Since the pressure variation is inversely proportional to the anode volume, the rate of pressure changes in anode-volume-optimized systems can be notably higher.
7. Summary and Conclusions

This work studied devices and methods for the hydrogen supply system in PEMFC systems both through modelling and experimental work. The studies concentrated on 1) inert buildup and hydrogen purge, 2) hydrogen humidification, and 3) hydrogen recirculation. A summary of key findings follows.

7.1 Hydrogen purge

Inert gas buildup and hydrogen purges were studied with a close to commercial PEMFC system with advanced instrumentation. Methods for determining membrane permeability, fuel purity, as well as the amount and composition of purged gas were developed. The effects of hydrogen purge on system performance were studied by varying the purge triggering criteria (average cell voltage drop 3 mV, 6 mV, or 9 mV), purge length (200 ms or 400 ms), purge type (single or double), and cathode inlet dew point temperature (52 °C, 55 °C, or 58 °C).

It was found that, even though fuel efficiency decreased with more frequent purging, the overall system efficiency increased. In other words, while very high fuel efficiencies (>99.9%) were easily attainable, the buildup of inert gases caused voltage polarization that outweighed the benefits of improved fuel efficiency.

At increasingly humid conditions, the primary function of a hydrogen purge shifted from the removal of inert gas towards the removal of water. While increasing the humidity level improved PEMFC performance, the operation also became more unstable because of accumulated liquid water in the gas channels. At high-humidity conditions, relatively long (400 ms) and frequent hydrogen purges resulted in the highest combined fuel and stack efficiency.

A double purge (two consecutive purges performed with a short interval) was also tested. The second purge resulted in higher flow rates because the first purge had flushed part of the liquid water from the gas channels. Thus, the second purge could serve as an indicator of the suitability of the purge parameters (length, frequency) employed. The double purge was not found to improve the removal of water compared to a longer single purge.

Finally, the concentration polarization measured between consecutive purges was compared to the voltage polarization predicted by the Nernst equation calculated with gas concentrations in anode gas channels. The measured voltage polarization was observed to be roughly twice that of the theoretical one. Thus,
it is important to account for mass transfer resistance when designing the PEMFC hydrogen supply system.

7.2 Hydrogen humidification

A bubble humidifier for a 50 kW$_e$ PEMFC pilot plant was designed and characterized. The humidifier was powered with waste heat from the PEMFC system and supplied with water condensed from the cathode outlet gas.

The humidifier was characterized by supplying air at flow rates corresponding to hydrogen consumption rates at PEMFC system low (75 A), nominal (150 A), and full (230 A) power. The approach dew point temperatures achieved were 3.1 °C at low power, 5.9 °C at nominal power, and 8.5 °C at full power when the humidifier was supplied with heating water at 65 °C at a 13.5 lpm flow rate.

The bubble humidifier was modelled with correlations for heat and mass transfer found in literature. A comparison of experimental data and simulation results showed good agreement. Simulations revealed that the humidifier performance was heat transfer limited. According to the simulations, the approach dew point could be decreased from 5.7 °C to 4.3 °C or 4.1 °C at nominal power by doubling the heating water flow rate or the heat transfer area, respectively.

The bubble humidifier was successfully operated for 4,400 hours in a 50 kW$_e$ pilot plant in Äetsä, Finland. During operation at low power, the bubble humidifier was found to provide humidification that was too efficient. Thus, humidification control would be needed. The easiest control methods would be letting part of the gas bypass the humidifier or letting part of the heating water bypass the humidifier.

7.3 Hydrogen recirculation

An ejector for a 5 kW PEMFC system was characterized, modelled, and verified in a PEMFC system. Moreover, a discrete ejector primary flow control system, based on three solenoid valves, was designed and verified in the PEMFC system. Finally, power ramp-rate capabilities of the PEMFC system employing the ejector and the discrete primary flow control system were studied.

A custom-made ejector was designed and manufactured from stainless steel with 3D printing. The ejector was characterized with dry and humid air and humid hydrogen, and its performance was compared to a commercial ejector. The custom-made ejector performed notably better than the commercial one.

Ejector performance maps visualized how close to optimum conditions the ejector operated. Optimum performance is achieved when the ejector operates close to maximum efficiency throughout its operating range. The maximum efficiency occurred close to pressure drops that were half of the maximum pressure differences against which the ejector could operate. This can be used as an initial sizing rule for ejectors.

It was found that an ejector can be sized for optimal operation either at high currents or at low currents, but not both. Sizing an ejector for high currents would inevitably compromise its performance at low currents, and vice versa. A
relatively high recirculation rate is usually required at low currents (compared to high high currents) for stable stack performance.

The custom-made ejector was modelled with CFD in 2D axisymmetric geometry, and three turbulence models were tested. It was found that, while none of the three turbulence models provided accurate results (ca 60-70% error in entrainment ratio), there were clear differences in accuracies. The SST k-ω turbulence model predicted ejector performance better at high primary and secondary gas flow rates, in general. The RNG k-ε and the Realizable k-ε turbulence models, on the other hand, more accurately predicted the position of maximum efficiency.

The custom-made ejector was installed in a 5 kW PEMFC system, and the system was characterized with stack currents ranging from 15% to 81% of maximum. The fuel utilization achieved per pass varied between 40% at lowest stack current and 64% at highest stack current. This high recirculation with a single ejector was possible because of 1) low stack flow resistance, and 2) ejector sizing that favored operation at low currents.

The effect of anode pressure and inert concentration on the recirculation rate achieved with the ejector was studied with the 5 kW PEMFC system. The recirculation rate increased with anode pressure level. A possible explanation for this is the increase in gas density. On the other hand, an increase in inert concentration resulted in an added mass-based recirculation rate but decreased the molar-based recirculation rate. This is explained by the high molar mass of nitrogen (compared to hydrogen), which is the main constituent of impurities that enter the anode. The net effect of added inert concentration on the removal of liquid water from gas channels was, however, unclear because of the added viscosity.

A discrete primary flow control setup was designed for a 5 kW PEMFC system. The control setup was based on three discrete solenoid valves, thereby enabling seven discrete open states (and one closed state). The setup was proven to function in practice.

The main benefits of the discrete ejector control setup are its robustness and the minimum requirement of moving parts. However, because operation is only possible at specified discrete states, some sort of balancing between hydrogen consumption and supply is necessary. For this reason, two methods were tested: 1) varying the load current, and 2) a hydrogen purge triggered by a pressure limit. Both methods were proven to work.

When using the discrete ejector primary flow control, the fuel supply and consumption rates temporarily mismatched during a load change, which resulted in variations in anode pressure. One method to manage the mismatch is to optimize the timing of fuel supply with respect to the load change. This was studied for the 5 kW PEMFC system.
It was found that, in this system (with ~0.3 dm³/kW anode volume), the mismatch between fuel supply and consumption was relatively easy to manage. The anode pressure variation with optimal timing was 20-25 mbar. The optimal timing depends mainly on fuel supply valve opening times and the volume that is required to pressurize upstream of the ejector primary inlet.

When the load ramp-up timing relative to fuel ramp-up deviated 200 milliseconds from the optimal, the pressure variation was little above 100 mbar, which is a modest variation. The pressure variation is inversely proportional to the anode volume and, thus, depending on the anode volume, the pressure variation might be several times that reported here.

### 7.4 Concluding remarks and future work

PEMFCs are regarded as an important part of a future carbon neutral energy supply. PEMFC technology is developing but still remains too expensive for commercialization in many applications. The total cost of a PEMFC system consists of two main parts: the stack and the BoP.

The design of a PEMFC BoP is application specific. PEMFC stacks are well suited for a wide range of applications, but limitations in BoP performance might constrain PEMFC system operation. A BoP design is intended to maximize PEMFC system lifetime and efficiency while minimizing cost and meeting the targets placed for the system.

This thesis contributes to this topic by presenting applied studies on the fuel supply subsystem. The results presented are useful when designing the fuel supply for cost-effective, efficient, and long-lasting PEMFC systems. Even though the focus of this work is on stationary systems, the findings are applicable to other applications as well.

Because of the wide variety of possible applications for PEMFCs, each one with its own specific requirements, the work with BoP design for PEMFC systems is far from finished. For example, the design and operation of a bubble humidifier with 5-10 cm water bed and either an internal or external heat exchanger is an interesting topic for future studies. In addition, questions related to hydrogen supply based on an ejector with discrete primary flow control during fast power transients deserves future study to avoid conditions that compromise stack lifetime.

One interesting topic for future work is the recirculation rate achieved with an ejector during fast power transients. When the stack current is abruptly increased, the anode pressure decreases, as was shown in Section 6. If the impurity content of anode gas is high, the hydrogen inside the cells might be temporarily consumed unless the ejector recirculates the hydrogen-richer anode gas from the anode loop. However, since the ejector operation relies on hydrogen feed, the recirculation rate will not increase until the hydrogen feed is ramped-up. Therefore, fuel starvation might occur during power transients unless the timing of a fuel ramp-up is optimized.

The ejector sizing deserves also further studies. There are numerous studies about ejector modelling with CFD in 3D. However, the ejectors designed for
PEMFC applications are with no exceptions (to the authors knowledge) modelled in 2D. Therefore, there is no information available of the 3D-modelling accuracy under operating conditions relevant to the PEMFC. Finally, there are only few studies regarding ejector dimensioning. How should the ejector dimensions be chosen to achieve the desired performance at specified conditions? How does the choice of dimension affect ejector performance at “off-design” conditions? What is the best approach to size a dual-ejector system (with two ejectors in parallel)? These questions all deserve further work.
References


Appendix A: Purged gas amount and composition

This appendix presents the calculation of the amount and composition of purged gas assuming a perfectly mixed anode volume. All species are assumed to be in their gaseous phase ($y_{i,j} = z_{i,j}$). The schematic of such a system is shown in Figure A 1.

![Figure A 1. Schematic of a PEMFC system with perfectly mixed anode volume and all species in their gaseous phase ($y_{i,j} = z_{i,j}$).](image)

The total material balance and species balance equations for the perfectly mixed anode volume are:

\[
\frac{dn_{an}}{dt} = \dot{n}_f - \dot{n}_p - \dot{n}_s \tag{A1}
\]

\[
\frac{dn_{i,an}}{dt} = \frac{d(n_{an,y_{i,an}})}{dt} = \dot{n}_f \cdot y_{i,ff} - \dot{n}_p \cdot y_{i,an} - \dot{n}_s \cdot y_{i,s} \tag{A2}
\]

where it has been recognized that the purged gas has the same composition as the perfectly mixed anode ($y_{i,an} = y_{i,p}$). Further, the correct way of expressing hydrogen consumption, inert gas permeation through the membrane, and water transport ($\dot{n}_{i,s}$) has been replaced with a more generic representation ($\dot{n}_s \cdot y_{i,s}$). In this representation, the $y_{i,s}$ represents the fraction and direction of, e.g. hydrogen consumption relative to $\dot{n}_s$, not the species mole fraction in a stream (there is no actual stream). This representation proves to be useful later.

The flow rates and, consequently, the amount of anode gas are assumed constant:

\[
\frac{d(\dot{n}_f)}{dt} = \frac{d(\dot{n}_p)}{dt} = \frac{d(\dot{n}_s)}{dt} = 0 \tag{A3}
\]
Then, the species balance equation may be written as follows:

\[
\frac{d y_{i,an}}{dt} = \frac{n_p}{n_{an}} \cdot (y_{i,ff} - y_{i,an}) + \frac{n_s}{n_{an}} \cdot (y_{i,ff} - y_{i,s}) \quad (A5)
\]

Integrating this over an arbitrary time period from the time \( t = 0 \) to \( t = t \) and from the initial composition \( y_{i,an,0} \) to \( y_{i,an} \), yields:

\[
\ln \left( \frac{n_p (y_{i,ff} - y_{i,an,0}) - n_s (y_{i,s} - y_{i,ff})}{n_p (y_{i,ff} - y_{i,an}) - n_s (y_{i,s} - y_{i,ff})} \right) = \frac{n_p}{n_{an}} \cdot t \quad (A6)
\]

This equation can be simplified by recognizing that the composition of the fresh fuel \( y_{i,ff} \) is typically close to \( y_{i,s} \) (i.e. \( y_{H_2,ff} \approx y_{H_2,s} \approx 1 \)). The simplified equation is:

\[
\ln \left( \frac{y_{i,ff} - y_{i,an,0}}{y_{i,ff} - y_{i,an}} \right) = \frac{n_p}{n_{an}} \cdot t \quad (A7)
\]

or

\[
y_{i,an} = \left[ 1 - \exp \left( -\frac{n_p t}{n_{an}} \right) \right] \cdot y_{i,ff} + \exp \left( -\frac{n_p t}{n_{an}} \right) \cdot y_{i,an,0} \quad (A8)
\]

This equation is valid when

\[
\dot{n}_p \cdot (y_{i,ff} - y_{i,an,0}) \gg \dot{n}_s \cdot (y_{i,s} - y_{i,ff}) \quad (A9)
\]

and

\[
\dot{n}_p \cdot (y_{i,ff} - y_{i,an}) \gg \dot{n}_s \cdot (y_{i,s} - y_{i,ff}) \quad (A10)
\]

This is true when the purge is not performed too frequently \( y_{i,ff} \gg y_{i,an,0} \) and when the purge is not too long \( y_{i,ff} \gg y_{i,an} \), or when the flow rate of the purged gas is high compared to the rate of hydrogen consumption \( \dot{n}_p \gg \dot{n}_s \). At least the first two requirements are generally true.

The total amount of gas purged \( n_p \) and species \( i \) purged \( n_{i,p} \) are obtained by integrating over one purge from the time \( t = 0 \) to \( t = t_p \), as follows:

\[
n_p = \int_0^{t_p} \dot{n}_p \, dt = \dot{n}_p \cdot t_p \quad (A11)
\]

\[
n_{i,p} = \frac{1}{n_p} \int_0^{t_p} (\dot{n}_p \cdot y_{i,an}) \, dt
\]

\[= \left( \dot{n}_p \cdot t_p - \left[ 1 - \exp \left( -\frac{n_p t_p}{1/n_{an}} \right) \right] \right) \cdot y_{i,ff} + \left[ 1 - \exp \left( -\frac{n_p t_p}{1/n_{an}} \right) \right] \cdot y_{i,an,0} \]

\[= \left( n_p - \left[ 1 - \exp \left( -\frac{n_p}{1/n_{an}} \right) \right] \right) \cdot y_{i,ff} + \left[ 1 - \exp \left( -\frac{n_p}{1/n_{an}} \right) \right] \cdot y_{i,an,0} \quad (A12)
\]
Appendix A: Purged gas amount and composition

In other words, the purged gas can be thought as being a mixture of 1) fresh fuel and 2) gas present in the anode before the purge is executed (“old anode gas”). The amount of old anode gas purged \( n_{p,0} \) is:

\[
 n_{p,0} = \left[ \frac{1 - \exp\left( -\frac{n_p}{n_{an}} \right)}{1/n_{an}} \right] \tag{A13}
\]

as seen in Eq. A12. Consequently, the amount of fresh fuel purged \( n_{p,ff} \) is the remaining part:

\[
 n_{p,ff} = n_p - \left[ \frac{1 - \exp\left( -\frac{n_p}{n_{an}} \right)}{1/n_{an}} \right] \tag{A14}
\]

During long purges \( n_p \) is large), the amount of old anode gas purged relative to the total amount of gas purged is small, and the composition of the purged gas approaches that of fresh fuel. During short purges, the opposite is true, and the composition of purged gas approaches that of the old anode gas.

The composition of the anode gas at any instance can be calculated from Eq. A8. In the beginning of a purge (at time \( t = 0 \) s), it is \( y_{i,an,0} \) and at the end of a purge (at time \( t = t_p \)):

\[
y_{i,an,1} = \left[ 1 - \exp\left( -\frac{n_p t_p}{n_{an}} \right) \right] \cdot y_{i,ff} + \exp\left( -\frac{n_p t_p}{n_{an}} \right) \cdot y_{i,an,0} \\
= \left[ 1 - \exp\left( -\frac{n_p}{n_{an}} \right) \right] \cdot y_{i,ff} + \exp\left( -\frac{n_p}{n_{an}} \right) \cdot y_{i,an,0} \tag{A15}
\]

The average composition of purged gas \( \overline{y}_{i,p} \) can be calculated using Eq. A12:

\[
 \overline{y}_{i,p} = \frac{n_{p,p}}{n_p} = \left( 1 - \frac{1 - \exp\left( -\frac{n_p}{n_{an}} \right)}{n_p/n_{an}} \right) \cdot y_{i,ff} + \frac{1 - \exp\left( -\frac{n_p}{n_{an}} \right)}{n_p/n_{an}} \cdot y_{i,an,0} \tag{A16}
\]

which, using Eq. A15, can be rewritten in terms of the composition of anode gas before \( y_{i,an,0} \) and after \( y_{i,an,1} \) the purge, as follows:

\[
 \overline{y}_{i,p} = y_{i,ff} - \frac{\left[ 1 - \exp\left( -\frac{n_p}{n_{an}} \right) \right] y_{i,ff} + \exp\left( -\frac{n_p}{n_{an}} \right) y_{i,an,0} - y_{i,an,0}}{n_p/n_{an}} \\
= y_{i,ff} - \frac{y_{i,an,1} - y_{i,an,0}}{n_p/n_{an}} \tag{A17}
\]

The above equations hold, strictly, only in case of a perfectly mixed anode volume when the assumptions made are true. In reality, the anode volume is not perfectly mixed. Neither are the flow rates constant and equal throughout the purge. Nonetheless, the purged gas can be represented with a mixture of fresh fuel and old anode gas as long as the assumptions in Eqs. A9 and A10 hold. In this case, the fractions of these gases are, however, not easily determined because the flow rates vary during a purge. On the other hand, if the assumptions in Eqs. A9 and A10 do not hold, the magnitude of stream “s” (primarily the hydrogen consumption rate) will affect the composition of purged gas.
Appendix B: Errata

This appendix lists the errors found in publications I-VI.

Publication II

Figure 11 in publication II contains erroneous values of calculated Nernst voltage drop. The erroneous values and corrected values are shown Table B 1.

Table B 1. Erroneous \(\varepsilon_{\text{Nernst, err}}\) and correct \(\varepsilon_{\text{Nernst, cor}}\) values of calculated Nernst voltage drop in publication II.

<table>
<thead>
<tr>
<th>(T_{\text{dew,cat, in}} \text{ [°C]})</th>
<th>(t_\text{p} \text{ [ms]})</th>
<th>(\Delta E_{\text{trigger, mV}})</th>
<th>(\Delta E_{\text{Nernst, err, mV}})</th>
<th>(\Delta E_{\text{Nernst, cor, mV}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>52</td>
<td>200</td>
<td>-3</td>
<td>-1.5</td>
<td>-1.5</td>
</tr>
<tr>
<td>52</td>
<td>200</td>
<td>-6</td>
<td>-2.8</td>
<td>-2.8</td>
</tr>
<tr>
<td>52</td>
<td>200</td>
<td>-9</td>
<td>-4.1</td>
<td>-4.1</td>
</tr>
<tr>
<td>52</td>
<td>400</td>
<td>-3</td>
<td>-1.7</td>
<td>-1.5</td>
</tr>
<tr>
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<td>400</td>
<td>-6</td>
<td>-3.1</td>
<td>-3.8</td>
</tr>
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<td>-4.2</td>
<td>-5.2</td>
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<tr>
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<td>-3</td>
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<td>-1.3</td>
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<tr>
<td>58</td>
<td>400</td>
<td>-3</td>
<td>-1.6</td>
<td>-1.6</td>
</tr>
</tbody>
</table>

The error does not change the conclusions drawn since most erroneous values of calculated Nernst voltage drop deviated only little from the correct values. Figure 19 in Section 4.3.3 is plotted with the correct values.

Equation 6 in publication II is erroneous. The correct definition of the stack efficiency \(\eta_s\) reads:

\[
\eta_s = \frac{2 \cdot F \cdot E_{\text{cell, avg}}}{\Delta H^\circ}
\]  

\[\text{(B1)}\]
The correct form of stack efficiency is also shown in Eq. 51 in Section 4.3.4. Stack efficiency in publication II was calculated with the correct equation despite the erroneous equation in the written text.

**Publication III**

Equation 3 in publication III is erroneous. It should show the approximation of time-averaged Sherwood number instead of the approximation of instantaneous Sherwood number. The approximation of time-averaged Sherwood number ($\bar{Sh}$) reads [71]:

$$\bar{Sh} = 4/\sqrt{\pi \cdot Fo} + \frac{63.237/\sqrt{Fo} + 7.892/Fo + \pi^2/16.9 \cdot 16.973 \cdot Fo^{1.5}}{1 + 3.616/\sqrt{Fo} + 45.628/Fo + 16.673/Fo^{1.5}}$$  \hspace{1cm} (B2)

The correct form of time-averaged Sherwood number approximation is also shown in Eq. 62 in Section 5.3. The bubble humidifier in publication III was simulated with the correct equation despite the erroneous equation in the written text.