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UNIVERSITAT POLITÈCNICA DE CATALUNYA

Doctoral Program:

Automatic Control, Robotics and Computer Vision (ARV)

Doctoral Thesis:

**Experimental and Model-based Analysis
for Performance and Durability Improvement
of PEM Fuel Cells**

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Directors:

Dr. Jordi Riera i Colomer and Dr. Attila Husar

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Abstract

Increasing global energy demand, growing carbon emissions and the depletion of fossil fuel sources are some of the most important driving forces for the development of sustainable energy solutions. Proton Exchange Membrane (PEM) fuel cells have been demonstrated to be a potential candidate for clean energy conversion in a wide range of applications reaching from highly dynamic transportation systems to stationary systems. Despite their benefits, such as high efficiency and wide operating range, PEM fuel cells must still meet or exceed the technological advantages, such as durability and cost, of conventional power systems in order to be truly competitive. Thus, current research is focused on improving these aspects.

This doctoral thesis combines experimental and model-based studies in order to improve performance and durability of PEM fuel cells, that work without external humidification, as demanded by recent government-supported research programs. Improved performance and durability can be obtained by proper system control. The key factor for the development of successful control strategies is adequate thermal and water management considering their interconnections. Therefore, this work investigates the important links between performance, efficiency and lifetime with respect to fuel cell temperature and humidification.

The experimental evaluation of temperature-related and purge-related effects shows the great potential of improving the system performance by proper thermal management. *In-situ* and *ex-situ* experiments, such as electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), gas chromatography (GC), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and scanning electron microscopy (SEM) were utilized in order to explore short-term and long-term effects of operation modes on performance and durability.

To provide a better understanding of the experimentally observed phenomena and their different dynamics with respect to the development of efficient controllers, mathematical models have been derived. The dynamic models allow for relating electrode structure to the cell voltage transient behavior during changes in fuel cell

temperature and humidification, including important phase change and ionomer sorption dynamics of water. The experimentally validated, model-based analysis provides recommendations of proper operating conditions and catalyst structure, such as optimal fuel cell temperature and adequate pore-size-distribution, in order to improve the PEM fuel cell performance.

The modular character and inherent adaptability of the models has been successfully demonstrated in the study of water transport in a high temperature PEM fuel cell stack. It is shown how mathematical modeling can improve the interpretation of experimental results and provide insight into experimentally non-observable interactions.

In conclusion, the presented laboratory and model-based work, including the developed experimental and mathematical tools, contribute to current international research targets for advancing sustainable energy solutions.

Resumen

La creciente demanda mundial de energía, el crecimiento de las emisiones de dióxido de carbono y el agotamiento de las fuentes de combustible fósiles son algunos de los factores más importantes para el desarrollo de soluciones basadas en energías sostenibles. Las pilas de combustible de tipo Proton Exchange Membrane (PEM) han demostrado ser un candidato potencial para la conversión limpia de la energía en una extensa gama de aplicaciones, desde los sistemas de transporte altamente dinámicos hasta sistemas estacionarios. No obstante sus beneficios, tales como una alta eficiencia y un amplio rango de operación, las pilas de combustible PEM todavía deben cumplir o superar las ventajas tecnológicas de los sistemas de energía convencionales, como son su durabilidad y coste, con el fin de ser verdaderamente competitivas. Por lo tanto, la investigación actual se centra en la mejora de estos aspectos.

Esta tesis doctoral combina estudios experimentales y estudios basados en modelos físicos con el fin de mejorar el rendimiento y la durabilidad de las pilas de combustible PEM que trabajan sin humidificación externa, tal y como exigen recientes programas de investigación apoyados por los gobiernos. La mejora del rendimiento y de la durabilidad se puede obtener por control apropiado del sistema. El factor clave para el desarrollo de estrategias de control exitosas es la gestión adecuada de la temperatura y del agua y sus interconexiones. Por lo tanto, este trabajo investiga los vínculos importantes entre el rendimiento, la eficiencia y la vida útil con respecto a la temperatura de la pila de combustible y su humidificación.

La evaluación experimental de los efectos relacionados con la temperatura y las purgas de hidrógeno muestra el gran potencial para mejorar el rendimiento del sistema pila mediante una gestión térmica adecuada. En esta tesis se emplean experimentos *in-situ* y *ex-situ*, tales como la espectroscopía electroquímica de impedancia (EIS), la voltametría cíclica (CV), la cromatografía de gases (CG), la espectroscopia de fotoelectrones emitidos por rayos X (XPS), la difracción de rayos X (XRD) y la microscopía electrónica de barrido (SEM) con el fin de explorar los efectos a corto plazo y a largo plazo de los modos de operación sobre el rendimiento y la durabilidad

de una pila PEM.

Para proporcionar una mejor comprensión de los fenómenos observados experimentalmente y sus diferentes dinámicas para el correcto desarrollo de controladores eficientes, se derivan modelos matemáticos dinámicos. Los modelos permiten relacionar la estructura de los electrodos con el comportamiento transitorio del voltaje durante los cambios de temperatura y de humidificación de la pila de combustible, incluyendo las dinámicas importantes del cambio de fase y de adsorción y desorción del agua. El análisis basado en modelos validados experimentalmente proporciona recomendaciones de las condiciones de funcionamiento y de la estructura del catalizador, tales como la temperatura óptima y la distribución de tamaño de poros apropiada, con el fin de mejorar el rendimiento de la pila de combustible PEM.

El carácter modular y la adaptabilidad inherente de los modelos propuestos se demuestra con éxito en el estudio de transporte de agua en un stack de pilas de combustible PEM de alta temperatura. Se muestra como el modelado matemático puede mejorar la interpretación de los resultados experimentales y proporcionar información sobre las interacciones que experimentalmente no son observables.

En conclusión, el trabajo de laboratorio y el basado en modelos que se presenta en esta tesis doctoral, incluyendo las herramientas experimentales y matemáticas desarrolladas, contribuyen a la consecución de los actuales objetivos internacionales de investigación que deben permitir aportar mejoras en las soluciones basadas en energías sostenibles.

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List of Abbreviations

BPP	Bipolar plate
CFD	Computational fluid dynamics
CL	Catalyst layer
CV	Cyclic voltammetry
DEA	Dead-ended anode
ECSA	Electrochemically active surface area
EERE	U.S. Office of Energy Efficiency and Renewable Energy
EUREC	Association of European Renewable Energy Research Centers
EIS	Electrochemical impedance spectroscopy
FCH JU	Fuel Cells and Hydrogen Joint Undertaking
FP7	Seventh Framework Program for Research
FT	Flow-through
EOD	Electroosmotic drag
GDL	Gas diffusion layer
MEA	Membrane electrode assembly
MPL	Micro-porous layer
PEM	Proton exchange membrane, also called polymer electrolyte membrane
PFSA	Perfluorocarbon-sulfonic acid
PSD	Pore-size distribution
SEM	Scanning electron microscope
SOFC	Solid oxide fuel cell
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

1 Introduction

Growing concerns on energy supply and environmental issues emphasize the development of alternative energy sources due to the fact that modern industrialized society is heavily dependent on energy which is mostly obtained from fossil fuels. The demand for energy, especially petroleum, and the accompanying carbon emissions have been increasing almost steadily over the past century [EIA 2014]. In order to maintain future economic standards and minimize the environmental impact caused by energy production, the investigation in sustainable energy systems is mandatory.

1.1 Hydrogen and Fuel Cells

Several studies, such as [de Vries *et al.* 2007] or reports conducted by the association of European Renewable Energy Research Centers (EUREC) for the Seventh Framework Programme for Research and Development, have shown that renewable energy sources have the potential to satisfy today's energy demands [EUREC 2009]. However, there are some serious problems, constraints and uncertainties that are involved in a shift towards renewable energies, such as high equipment cost, temporal and spatial mismatch between availability and demand, as well as aspects of the food versus energy trade-off. The equipment cost problem may be weakened by an increase in manufacturing volumes and the simultaneous increase of fossil fuel prices, which will make fuels from renewable energy sources competitive. The availability problem may be solved by converting excess energy that cannot be utilized immediately, which occurs for example frequently in wind turbine systems, to energy carriers that can be stored, transported and converted to useful forms of energy.

An energy carrier that complies with these requirements is hydrogen, which can be produced by all forms of renewable energy. Furthermore, it has significant advantages compared to other energy storage mediums, such various kinds of batteries, compressed air, or pumped hydro. These are for instance the possibility of long-term energy storage, long distance transport via pipelines with minimal flow resistance, light weight and

high energy density. However, topics such as hydrogen storage, infrastructure and low cost production are still challenges that have to be overcome.

Hydrogen can be used in many ways to produce thermal, mechanical or electrical energy by burning it directly, for example in a gas turbine, using it in a combustion engine or efficiently transforming it into electricity through a fuel cell in a non-polluting way, since the only products are water, heat and electricity.

For highly dynamic applications, such as automotive systems the feasibility and advantages of the usage of Proton Exchange Membrane (PEM) fuel cells have been demonstrated over the last decade [Today 2012]. Figure 1.1 shows a schematic of a single PEM fuel cell with its main components and the involved electrochemical reactions, namely hydrogen oxidation at the anode and oxygen reduction at the cathode. The proton conducting membrane is situated between the porous catalyst layers (CL), gas diffusion layers (GDL) and bipolar plates (BPP) on each side.

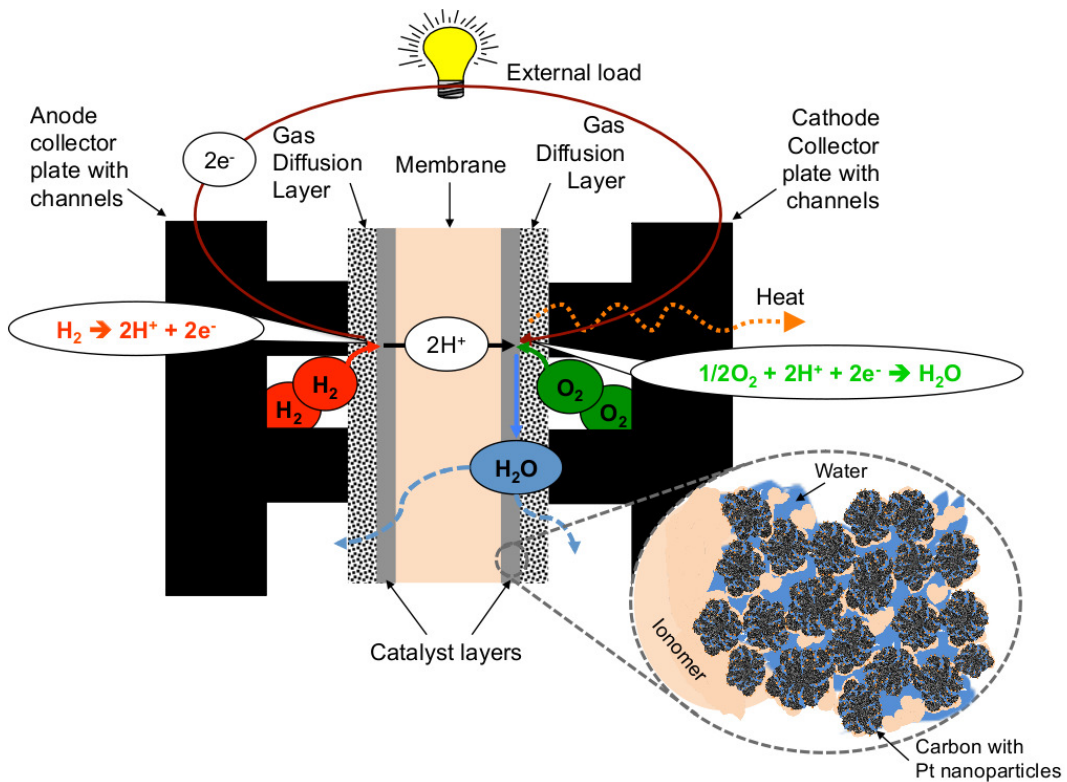


Figure 1.1: Basic operation principle of a PEM fuel cell

The function of the membrane in a PEM fuel cell is to transport protons from the anode to the cathode catalyst layer, and at the same time to block electrons from

passing the membrane, forcing them to travel through the external circuit. Moreover, the membrane has to be a barrier for reactant gases in order to prevent them from mixing directly. To ensure high fuel cell efficiency the membrane must present good proton conductivity. Typically, PEM materials are based on perfluorocarbon-sulfonic acid (PFSA) ionomers, e.g. Nafion[®], which is the most common membrane material [Barbir 2005]. This material's SO_3^- subgroup allows the transport of protons through the membrane. State-of-the-art PFSA membranes for high power density are typically not thicker than $25\ \mu\text{m}$.

The CLs of anode and cathode are located between the membrane and the GDLs with a thickness of around $10\ \mu\text{m}$ each. Common CLs currently used in PEM fuel cells are composed of platinum nano-particles supported by carbon black in close contact with the ionomer, as shown in Figure 1.1. The carbon black support allows a high dispersion for the platinum nano-particles and provides the demanded porous and highly electronically conductive structure. On the surface of the platinum nano-particles the electrochemical reactions take place.

The GDL connects the CL with the flow channels and the BPPs. The GDL material has to provide high electrical and thermal conductivity, and is responsible for proper reactant gas distribution at the catalyst surface while allowing for the evacuation of produced water, at the same time. At the moment these requirements are fulfilled by carbon cloth and carbon fiber papers. The latter (e.g. Toray TPG-H) is preferred by fuel cell manufacturers due to its low cost and ease of applying a micro-porous layer (MPL). Typical GDL thicknesses are between 100 and $400\ \mu\text{m}$, depending on fuel cell design, operating conditions and application [Mench *et al.* 2011].

The compressed multilayer assembly of the membrane sandwiched between the CLs and the GDLs is called membrane electrode assembly (MEA). A magnified image of a cut MEA, recorded by a Scanning Electron Microscope (SEM), is shown in Figure 1.2.

In a fuel cell stack of several cells, bipolar plates are needed to electrically connect the anode of one cell to the cathode of the next cell and thereby isolate the reactant gases. The gas flow channels are typically included in the bipolar plates. The collector plates in figure 1.1 can be regarded as two halves of a bipolar plate.

Reactant gases, namely hydrogen in the anode flow channel and oxygen from air in the cathode flow channel, diffuse through the GDL to the catalyst where the electrochemical reactions take place. The bulk ionomer in the membrane as well as the ionomer in the CL requires the presence of water to guarantee high proton conductivity and finally to allow the protons to reach the so-called three-phase-contacts in the CL,

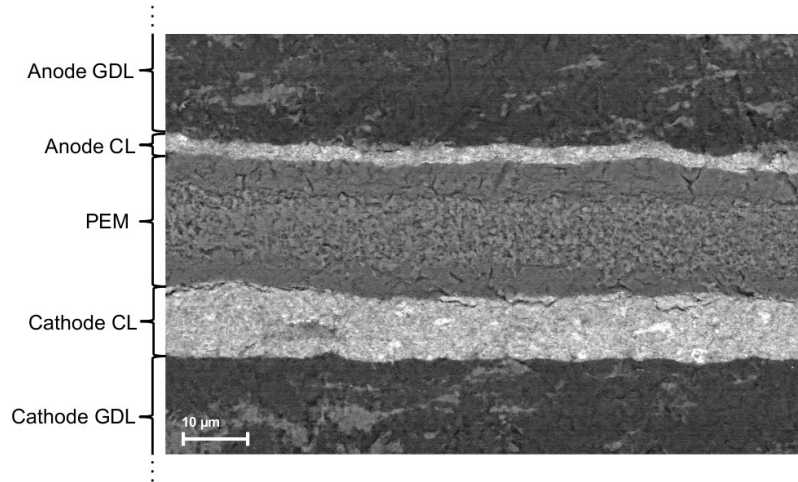


Figure 1.2: SEM image of a cut MEA sample

between reactant gas, electrons and protons, as shown in Figure 1.1. The produced water can leave the fuel cell either via the cathode flow channels, or via the anode flow channels by back-diffusion through the membrane. The overall reaction equation of a PEM fuel cell (Eq. 1.1) describes the oxidation of hydrogen, which is an exothermic reaction and thus energy is released in this process.



PEM fuel cells operate at relatively low temperatures compared to other fuel cell types, such as solid oxide fuel cells (SOFC), which reduces material costs. The major advantages besides their low operating temperature are the short start-up time, fast transient response, high efficiency and compactness that make them a serious candidate for automotive and portable applications. In terms of commercial success among different fuel cell technologies the PEM fuel cell technology is the market leader by comparing unit shipments [Today 2012]. The disadvantages of PEM fuel cells are their relatively low durability as well as high costs for the platinum catalysts. The low durability is a result of the membrane, catalyst and carbon support structure degradation under the highly corrosive fuel cell operating conditions. The reasons are, among others, membrane thinning, pinhole formation, carbon support corrosion, platinum dissolution, oxidation and agglomeration, involving a loss in electrochemically active surface area (ECSA), which reduces fuel cell performance. The degradation

mechanisms are promoted by long operation at high potentials, power and subsequent thermal cycling or by operation incidents such as reactants starvation or inadequate water management [Mench *et al.* 2011][Wu *et al.* 2008]. Thus, investigation has to focus on the factors that impact durability and the links to the fuel cell performance.

Several government programs have been established in order to overcome the difficulties of market introduction for fuel cell systems. For example, the targets for durability announced by the U.S. Office of Energy Efficiency and Renewable Energy (EERE) are 5000 h for transportation by 2017 and 60,000 h for stationary application by 2020 with less than 10 % voltage decay over the system's lifetime [EERE 2013]. However, in most fuel cell systems this decay is already reached after around a thousand hours of operation at present [Wang *et al.* 2011], which makes the durability of cells and components one of the greatest technological challenges at the moment.

In order to achieve these ambitious goals the EERE sets special targets for the individual cell components, such as membrane durability at voltage cycling, ECSA loss, BPP corrosion, etc. [Mench *et al.* 2011]. In transport applications for example, the membrane must be capable of maintaining its performance with less than 5 % loss from beginning to end of life without external humidification [EERE 2013]. By removing humidifiers from the system, the size, weight and parasitic load can be decreased, which is essential for automotive applications. Thus, self-humidified systems that do not require external humidification, such as open-cathode systems, present an attractive option. However, the effects of operating conditions on performance and durability of these systems have not been sufficiently investigated. The optimization of operating conditions allows for reaching better system efficiencies and thus permits decreasing the platinum loading, which decreases cost and avoids severe depletion of platinum resources.

Even though great advancement in terms of materials, component design, production and system power density has been achieved over the past 20 years, there is still a lot to be done in the field of fuel cell controls in order to improve efficiency and durability by manipulation of operating conditions, such as temperature, humidity and reactant flow rates. Moreover, performance, efficiency and durability of PEM fuel cells are strongly interconnected which demands for an in-depth understanding of the competing effects when it comes to the design of proper control strategies.

In order to provide this deep understanding, experimental work is needed as well as a mathematical model that describes the involved physical phenomena. Mathematical modeling is an important tool in the development of fuel cells and control strategies,

that helps to lower costs by reducing the number of experiments, accelerate the pace of building prototypes and improve efficiency by development of proper fuel cell controllers. It is paramount to understand the interplay of the involved phenomena and their dependence on the system's operating conditions, which is not always observable experimentally. Thus, this doctoral thesis combines experimental analysis, theoretical studies and mathematical modeling for performance and durability improvement of PEM fuel cells, which promotes the design of efficient control strategies.

1.2 State of the Art

Designing appropriate controllers for PEM fuel cells operating at low relative humidities necessarily undergoes the study of the interacting dynamics between water transport and thermal aspects. Water management in PEM fuel cells is a crucial issue. On the one hand, water is needed to maintain good proton conductivity and therefore has to be kept in the membrane and the ionomer of the CL. On the other hand, too much water, especially in the liquid state, present in the pores of the CL and the GDL hinders the reactant gases to diffuse to the catalyst surface, which reduces the fuel cell performance. The goal is to maintain a balance between the two conflicting water content requirements. To control water transport and spatial distribution within a fuel cell and thereby optimize the MEA hydration at any operating point, adequate dynamic water management strategies have to be developed, as discussed in the work of [Hussaini & Wang 2010].

Today most PEM fuel cell systems work either with a Dead-Ended Anode (DEA) fed by dry hydrogen at a regulated inlet pressure or in a flow-through (FT) configuration. A DEA system provides savings in costs, volume and weight compared to a FT system, as it does not require a hydrogen recirculation loop with the specific auxiliary components, such as a pump, water separator and humidifier. Water accumulation in the anode during DEA operation, by diffusion from the cathode through the membrane, leads to a certain degree of self-humidification. Thus, the anode may be fed by dry hydrogen, which is in accordance with the EERE targets, as explained in section 1.1. However, there are some major problems involved in DEA operation, such as performance reduction due to excess water and nitrogen accumulation in the anode, as investigated by [Siegel *et al.* 2010]. The primary factors and their quantitative contribution for the significant performance decay during DEA operation are still under debate, as recently demonstrated by [Jiang *et al.* 2014], who discovered

a paradox phenomenon under DEA operation. Their experiments show an increasing high frequency resistance while the cell is suffering from hydrogen starvation due to accumulation of liquid water and nitrogen. However, one would expect the high frequency resistance to decrease due to the increased liquid water content in the anode and the involved increase of water content in the ionomer. Their study highlights the need for further research for understanding the water transport properties in the CL. A similar high frequency resistance transient behavior during DEA operation was observed by [Meyer *et al.* 2014]. Moreover, the experimental work of [Meyer *et al.* 2014] includes exhaust gas analysis and Electrochemical Impedance Spectroscopy (EIS) measurements during flow-through and DEA operation. However, a clear explanation for the observed changes in the impedance spectra could not be derived directly from the experimental data due to the difficulty and the lack of specific local measurements within the fuel cell, such as current density and temperature distributions.

Some limited experimental and modeling results of current density and cathode flow rate effects on the transient performance of a PEM fuel cell stack under DEA operations are presented by [Gomez *et al.* 2014]. However, the effect of the operating temperature is not analyzed and optimization of the purge strategy by manipulation of the operating conditions is not discussed.

Most importantly, improper control of the purge can lead to hydrogen starvation along the channel, which in turn decreases the lifetime by promoting carbon support corrosion [Chen *et al.* 2011]. The phenomenon of increased carbon corrosion rates in the hydrogen starved regions along the gas flow channel has been explained first by [Reiser *et al.* 2005], who showed experimentally and mathematically a local increase of the cathode electrode potential above 1 V. [Meyers & Darling 2006] proposed a mathematical model for the involved electrochemical reactions and gas transport equations in a single cell for the study of non-uniform hydrogen distribution effects along the channel on carbon corrosion rates. Corrosion causes the carbon support structure of the CL to fall apart and the platinum particles to agglomerate which decreases the electrochemically active surface area. Carbon corrosion and water electrolysis on the cathode side due to hydrogen starvation on the anode side has been modeled in a steady-state, two-dimensional Computational Fluid Dynamics (CFD) approach by [Ohs *et al.* 2011]. They modeled dilution of hydrogen via gas permeation through the membrane which leads to potential gradients greater than 1.2 V between electrode and membrane on the cathode side, resulting in significant carbon corrosion and electrolysis reaction rates. However, there are only few articles

available in the literature on how to decide on an appropriate purge control strategy under dynamic system perturbations and changes in operating conditions, such as load current, temperature, humidity and reactant flow rates, and the resulting effects on performance and lifetime.

Optimal water management in PEM fuel cells always has to consider thermal management, as the fuel cell temperature has a strong effect on the water content in the ionomer of the membrane and the CLs: Water diffusion through the membrane as well as the water uptake dynamics of the ionomer are strong functions of temperature as shown by the experiments of [Strahl *et al.* 2011] and [Majsztrik *et al.* 2007], respectively. The temperature effects on water transport in the CLs are based on absorption and desorption of water into and from the ionomer, as well as evaporation and condensation in the pores of the CL. Water content in the catalyst layer has a direct effect on the electrochemical active surface area as analyzed by steady-state modeling of electrode structure effects on performance of [Wang *et al.* 2004] and [Eikerling 2006]. If water is evacuated from the pores of the CL, the protons may not reach the active sites for the electrochemical reaction with the reactant gases and the electrons, which is the key factor of PEM fuel cell performance. This effect has also been shown experimentally by [Song *et al.* 2007], explaining that the higher water evaporation flux at elevated temperature causes a reduction in active platinum sites. Even though many steady-state agglomerate models have shown up in the literature, a complete dynamic analysis of temperature-dependent water transport, including pore-filling dynamics, in relation with the electrode structure and its effects on performance is still not available.

In order to maintain optimal CL humidification and thus guarantee maximum performance, proper fuel cell temperature control is essential. A higher temperature may improve the stack performance but at the same time intensify the degradation of the membrane and the catalyst [Mench *et al.* 2011][Rodatz *et al.* 2004]. A lower temperature decreases the reaction kinetics and may also cause flooding due to lower water saturation pressures at lower temperatures, which is also a major concern from the water management perspective [Zhang & Kandlikar 2012].

Optimal thermal management related to humidification is a crucial issue in every PEM fuel cell-based system. In this context, the use of external reactant gas humidification is intended to be avoided because the required humidifiers consume space and power, which decreases the overall system efficiency. [Zhang *et al.* 2007] experimentally demonstrated the strong effects of low humidity operation on fuel cell performance. However, there is still a lack of information on how to control the temperature of a fuel

cell system that works without reactant humidification with respect to performance optimization. The important links between temperature management and fundamental understanding of the catalyst layer humidification and activity have not sufficiently been explored.

The presented motivation for research in the field of sustainable energy systems and the analysis of the state of the art of PEM fuel cells led to definition of the hypothesis and the derivation of a strategy on how to prove this hypothesis in this doctoral thesis, as explained in the following section.

1.3 Thesis Hypothesis, Objectives and Methodology

The hypothesis of this doctoral thesis is that the performance and durability of PEM fuel cells operating without external humidification can be improved by manipulating the operating conditions, such as temperature, reactant flow rates and purge intervals. This will consequently promote the design of effective control strategies.

In order to achieve the global objective of confirming the above-stated hypothesis, this doctoral thesis combines experimental and model-based analysis. Thus, an intermediary objective is to develop dynamic models that can capture and explain the experimentally observable interplay between temperature-related and water-related performance effects.

The thesis is based on the following methodology:

- Experimental study of hydrogen purge effects on performance and efficiency under different operating conditions
- Experimental characterization of temperature effects on fuel cell performance
- Experimental identification and quantification of major degradation mechanisms in a PEM fuel cell stack
- Development of dynamic models for thermal management, water transport and electrochemistry
- Validation of the developed models against the experimental findings
- Model-based evaluation of water and thermal management effects on fuel cell performance

1 Introduction

This methodology resulted in research activities, that have been described and discussed in international journal articles. In the following the unified body of work is provided and the important results are discussed. Finally, the main conclusions of this doctoral thesis are presented and future work is suggested.

2 Body of Work

The thesis is based on the research activity that led to the publication of five international journal articles.

- **[Strahl *et al.* 2014a]** S. Strahl, A. Husar, A. Franco. *Electrode structure effects on the performance of open-cathode proton exchange membrane fuel cells: a multiscale modeling approach*. International Journal of Hydrogen Energy, vol. 39, pages 9752 - 9767, 2014.
- **[Strahl *et al.* 2014b]** S. Strahl, N. Gasamans, J. Llorca, A. Husar. *Experimental analysis of a degraded open-cathode PEM fuel cell stack*. International Journal of Hydrogen Energy, vol. 39, pages 5378 - 5387, 2014.
- **[Strahl *et al.* 2014c]** S. Strahl, A. Husar, P. Puleston, J. Riera. *Performance improvement by temperature control of an open-cathode PEM fuel cell system*. Fuel Cells, vol. 14, pages 466 - 478, 2014.
- **[Strahl *et al.* 2014d]** S. Strahl, A.P. Husar and J. Riera. *Experimental study of hydrogen purge effects on performance and efficiency of an open-cathode PEM fuel cell system*. Journal of Power Sources, vol. 248, pages 474 - 482, 2014.
- **[Bezmalinovic *et al.* 2014]** D. Bezmalinovic, S. Strahl, V. Roda, A. Husar. *Water transport study in a high temperature proton exchange membrane fuel cell stack*. International Journal of Hydrogen Energy, vol. 39, pages 10627 - 10640, 2014.

The involved research can be grouped into two sub-topics, namely experimental and model-based analysis of PEM fuel cell performance and durability. In order to provide a deeper understanding of the experimental findings and the involved phenomena, mathematical models have been developed that allow for the computational analysis and separation of the physical interactions and system dynamics. The combination of experimental and model-based analysis enables the identification and characterization

of the important system variables and their dynamics in order to improve performance and durability via adequate system control.

2.1 Experimental analysis

Due to additional cost, weight and power consumption of external humidification system components, open-cathode systems, that do not require external reactant humidification, are of great interest. Thus, the principle system under observation in this doctoral thesis is the commercially available 100 W, 20-cell PEM fuel cell stack *H-100* from *Horizon Fuel Cells Technologies*, schematically shown in Figure 2.1. This compact open-cathode system with an active area of 22.5 cm^2 per cell, includes a cooling fan directly attached to the fuel cell housing, which removes heat from the stack by forced convection and at the same time provides oxygen to the cathode. The pressure-regulated anode inlet is supplied with dry hydrogen and the outlet features a normally-closed electromagnetic valve for dead-ended operation and purging.

All *in-situ* experiments were carried out in the fuel cell laboratory of the *Institut de Robòtica i Informàtica Industrial* (IRI) using an in-house built and customized test station that features an environmental chamber for manipulating the ambient conditions, depicted in Figure 2.1.

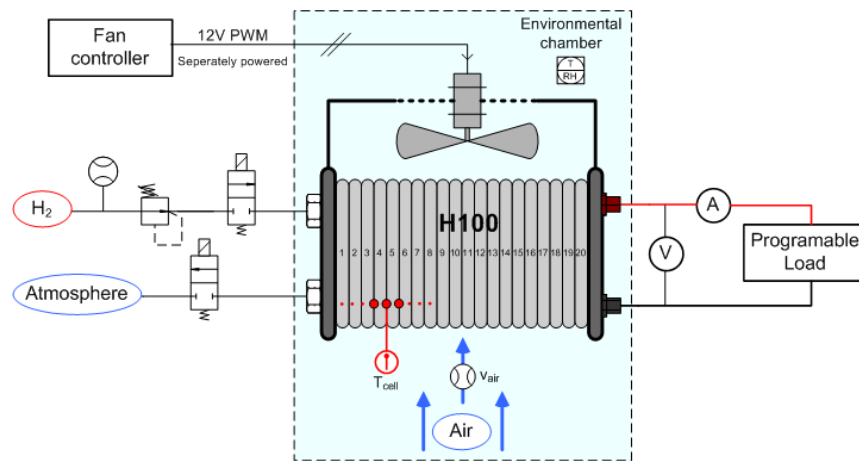


Figure 2.1: Schematic of the H100 fuel cell system installed in the laboratory test station

In [Strahl *et al.* 2014d] the performance and efficiency of the open-cathode PEM fuel cell system in DEA configuration and under hydrogen purges is analyzed. Excess

water and crossed-over nitrogen in the anode decrease the hydrogen concentration at the catalyst surface, which in turn causes performance losses. Purging the anode with hydrogen removes water and nitrogen and thus recovers the performance. However, this means wasting hydrogen and decreasing overall system efficiency. The duration of the purge interval directly affects the performance loss during DEA operation, which strongly depends on the current density, as shown in figure 2.2. At high current densities the purged system loses power due to the big voltage drop, because the stack suffers from the accumulation of excess water in the anode. However, at moderate current densities at which the stack creates less water, the voltage swing diminishes. For a successful application of DEA fuel cell systems the voltage drop during DEA operation has to be minimized to an acceptable limit. Thus, the trade-off between performance and efficiency has to be evaluated and optimized application-dependent.

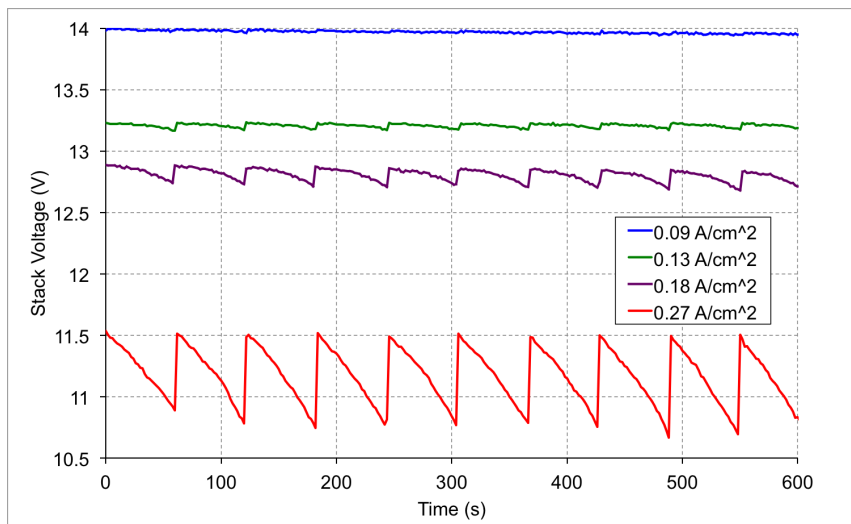


Figure 2.2: Comparison of stack voltages at different current densities during DEA operation and 100 ms purges every 60 s

EIS experiments showed that the low frequency resistance increases significantly under DEA operation due to accumulation of water and nitrogen whereas the high frequency resistance remains constant. This means that the membrane is well humidified but the excess water and permeated nitrogen in the anode increase the mass transport resistance.

Experimental observations of single cell and stack voltage responses to changes in stack current, temperature and cathode inlet flow rate revealed that the need for a hydrogen purge strongly depends on the operating conditions, especially the

stack temperature, and the state of humidification of the cathode CL. The dynamic experiments demonstrate that flooding on the anode and drying of the cathode catalyst layer may occur simultaneously during purged operation. Therefore, purge decisions must be evaluated online, depending on the operating conditions.

In order to compare the purged system to a recirculation system in terms of efficiency, experiments were carried out in flow-through mode with humidified hydrogen, since the recirculation of the exhaust hydrogen leads to certain degree of anode humidification. Thus, both system designs achieve performance improvement via anode humidification, although in a different way. The comparison of the total system efficiency shows that a purge strategy with a purge interval of 60 s and a purge duration of 100 ms is comparable to the use of a hydrogen recirculation pump with an additional power consumption of 3 W.

Moreover, it has been demonstrated in [Strahl *et al.* 2014d] that monitoring the drop in anode inlet pressure during a purge gives information of the accumulation of liquid water. Thus, it may be used as an indicator for the online adjustment of the applied purge strategy.

Finally, gas chromatography was used to detect and quantify the accumulated nitrogen in the anode during DEA operation. Moreover, oxygen was detected in the anode exhaust gas due to permeation through the membrane and hydrogen starvation in the anode during long purge intervals. This is an indicator for corrosion of the cathode carbon support structure, as demonstrated by [Reiser *et al.* 2005], [Tang *et al.* 2006] and [Chen *et al.* 2011].

Not only a non-optimal purge strategy leads to significant performance degradation due carbon corrosion, but also uncontrolled start-ups and shut-downs. Thus, experimental data that relate the performance loss to morphological changes in the catalyst layer are very important in order to improve the lifetime of PEM fuel cells by proper control strategies. The work presented in [Strahl *et al.* 2014b] focuses on degradation mechanisms that are present in open-cathode PEM fuel cell systems and their links to the decaying fuel cell performance. Therefore a degraded stack was analyzed by means of *in-situ* and *ex-situ* techniques. Voltage transients during external perturbations, such as changing temperature, humidity and stoichiometry show that towards the end of life of the stack, degradation affects individual cells quite differently, depending on their location within the stack. Cells located close to the endplates of the stack show the biggest performance decay. EIS data present non-reversible catalyst layer degradation but negligible membrane degradation of several cells.

Post-mortem, ex-situ experiments, such as cyclic voltammetry (CV), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) show a significant active area loss of the first cells within the stack due to platinum dissolution, oxidation and agglomeration.

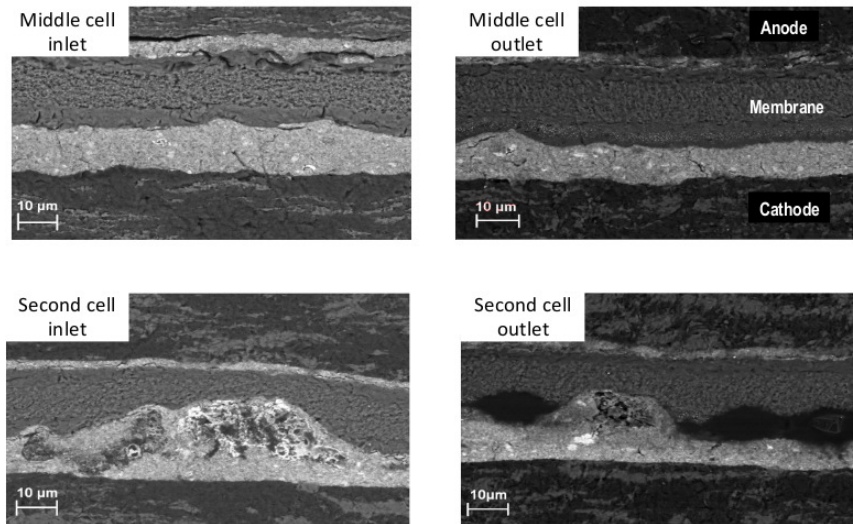


Figure 2.3: SEM images of cut MEA samples close to the anode inlet and outlet of the second cell and the middle cell of a 20-cell stack

Scanning electron microscope (SEM) images of the degraded cells in comparison with the normally working cells in the stack show severe carbon corrosion of the cathode catalyst layers. Cells located next to anode outlet of the stack degrade much faster than others due to hydrogen starvation during DEA operation and uncontrolled start-ups and shut-downs. For the same reasons carbon corrosion within individual cells increases from the anode inlet towards the outlet, as shown by transversal SEM images in Figure 2.3.

As demonstrated by the *in-situ* experiments of [Strahl *et al.* 2014d] the cathode CL performance as well as its degradation due to hydrogen starvation strongly depends on the liquid water content in the CL and thus on the fuel cell temperature. Therefore, the effect of fuel cell temperature on performance and the potential performance improvement by temperature control was investigated in [Strahl *et al.* 2014c]. This work combines experimental analysis and theoretical studies of temperature effects on the performance of open-cathode PEM fuel cell systems for the design of optimal control strategies. The experimental analysis shows the great potential of improving the system performance by proper thermal management over the entire operation

range, as depicted in Figure 2.4. Especially at the higher current densities a significant system performance gain can be obtained due to improved reaction kinetics at higher temperatures.

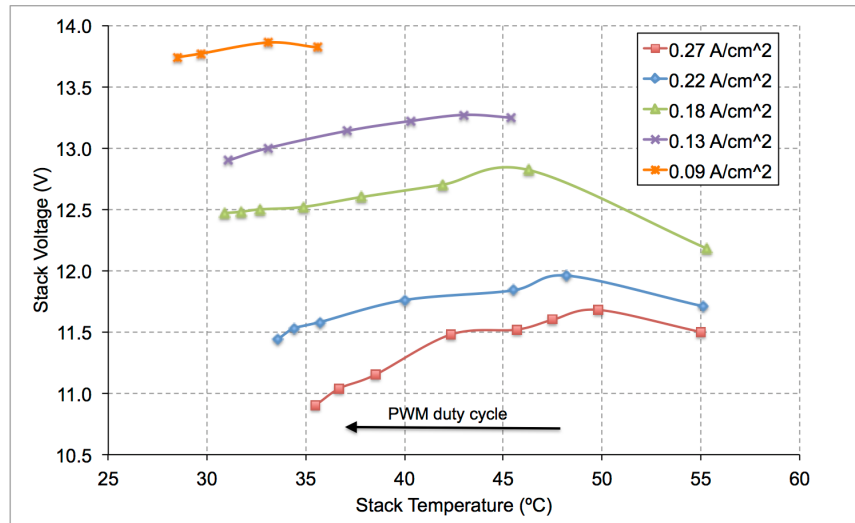


Figure 2.4: Steady-state stack temperature mapping against stack voltage

To provide a better understanding of the involved phenomena and their different dynamics, mathematical models for the observed temperature and voltage evolutions have been developed.

2.2 Model-based analysis

Mathematical modeling is an important tool in the development of fuel cells and the necessary control strategies. It helps to understand the interplay of all involved physics and their dependence on the system's operating conditions, which is not always observable experimentally.

In the second part of [Strahl *et al.* 2014c] dynamic, control-oriented models for fuel cell temperature, liquid water transport and the related electrochemistry have been developed and validated against the experiment. A theoretical evaluation of temperature effects on the performance of the PEM fuel cell shows that the improved reaction kinetics, which results in a higher exchange current density, is responsible for the majority of the observed voltage gain obtained by increasing the temperature. On the one hand the exchange current density is influenced positively by a temperature increase as this lowers the activation barrier. On the other hand a higher temperature

causes a reduction of the electrochemical active sites in the cathode catalyst layer due to lower liquid water content in the ionomer and primary pores. The combination of these two competing effects leads to the presence of a maximum in the Voltage-Temperature map in Figure 2.4, with a sharp drop in performance after passing the optimal temperature. Hence, performance improvement by temperature control means optimizing the tradeoff between increasing reaction kinetics and decreasing liquid water content in the catalyst layer.

The experimental model validation has shown that the stack voltage can be predicted with less than 0.5% error at different operating points. The validated model can be used to develop appropriate control strategies for the performance optimization problem by temperature control. As a first approach, a cascaded Extremum Seeking control algorithm with a local Proportional-Integral controller is proposed to regulate the temperature to a fuel cell voltage maximum. However, the slow dynamics of the temperature related catalyst-drying effect on performance complicates the optimal thermal management with model-free control strategies.

In order to analyze the dynamics of temperature and water content related CL performance the dynamic model of [Strahl *et al.* 2014c] was upgraded by including spacial distribution effects of the state variables across the MEA and by linking temperature-driven water transport to CL morphology. As a result, the model presented in [Strahl *et al.* 2014a] describes two-phase water transport, electrochemistry and thermal management of a PEM fuel cell cathode within a multiscale modeling framework that combines a CFD approach with a micro-structurally-resolved model of the cathode CL, as depicted in Figure 2.5. The developed analytical catalyst structure models are based on spherical pores using either a single pore size or a pore size distribution (PSD). As shown in Figure 2.5, the spherical pores in the carbon support structure contain water and a number of platinum particles, dependent on the platinum loading of the CL, in the case of the smaller primary pores. In the bigger secondary pores, that are depicted in Figure 2.5, the platinum particles are covered by a thin-film of ionomer, which guarantees proton conduction from the membrane to the platinum reaction site, if it is well humidified.

In this framework, the CL model predicts the water filling dynamics of the electrode pores and the impact of these dynamics on the evolution of the ECSA (red lines on the platinum particle surface in Figure 2.5). The multiscale model allows relating for the first time the cathode electrode structure to the cell voltage transient behavior during experimental changes in fuel cell temperature.

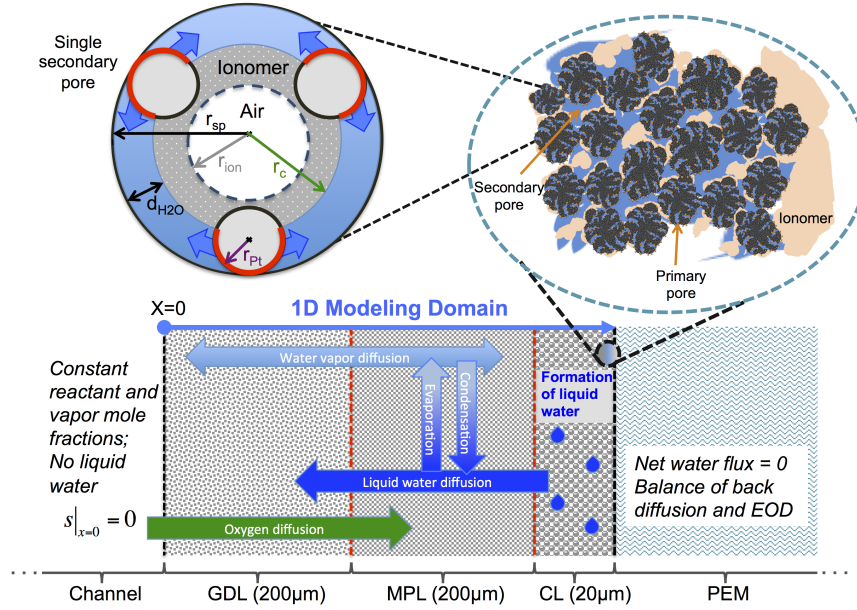


Figure 2.5: Multiscale modeling domain of the fuel cell cathode

The effect of evaporation rates, desorption rates and temperature changes on the performance of four different electrode PSDs are explored using steady-state and transient numerical simulations. The results are discussed with respect to water management and temperature control.

Finally, in [Bezmalinovic *et al.* 2014] the gained experience in experimental and model-based analysis of water transport within low temperature PEM fuel cells was applied to study water transport phenomena in a high temperature PEM fuel cell ($> 140^\circ\text{C}$). Tests with different stoichiometries on the dry cathode and different humidity levels at the anode showed that water transport across the phosphoric-acid-doped polybenzimidazole (PBI) membrane is noteworthy and that the water vapor partial pressure on the anode outlet is almost always higher than on the cathode outlet, even when using dry hydrogen. The water transport is a strong function of current density, stoichiometry and relative humidity. The water transport coefficient was determined experimentally by means of a similar methodology as proposed in an earlier publication [Strahl *et al.* 2011].

In order to relate the experimentally determined water transport curves to the internal water distribution in a single cell within the stack, a 2D steady-state CFD model was developed and validated against the experimental findings. The two-dimensional water transport analysis in this work is based on the water transport model for low

temperature PEM fuel cells, as presented in an earlier publication [Strahl *et al.* 2011]. Since the catalyst layers are treated as infinitely thin layers, analytical boundary conditions are applied, based on the electrochemical model presented in [Strahl *et al.* 2014c]. Internal water transport profiles across the membrane and along the gas flow channels are presented and discussed. The model is also used to investigate limiting operation cases due to hydrogen starvation during operation with humidified hydrogen and reformed hydrogen, which may lead to similar along-the-channel effects as under DEA operation, described in [Strahl *et al.* 2014d]. Figure 2.6 shows the profiles of hydrogen mole fraction along the flow channel for a dry and wet anode inlet at different cell potentials.

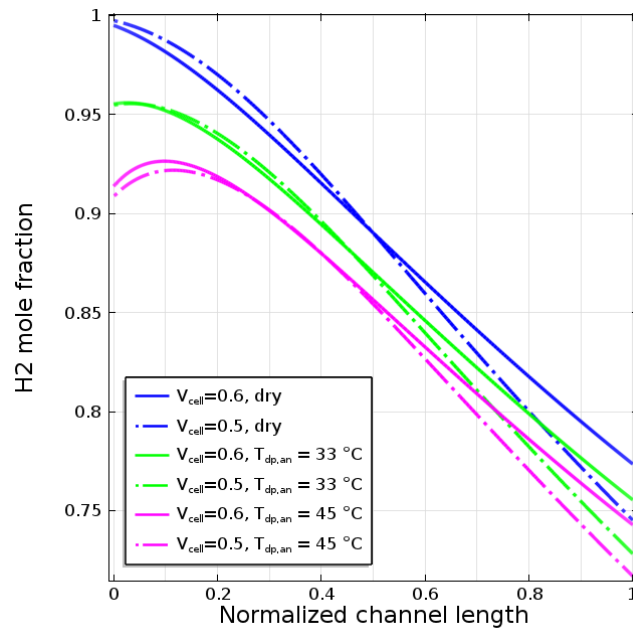


Figure 2.6: Comparison of simulated hydrogen mole fraction at the anode catalyst layer along the flow channel at different cell voltages and anode humidification

3 Discussion of Results

The presented experimental work on PEM fuel cell systems with hydrogen purges shows that this kind of system still has a great potential for optimization based on water and thermal management. The electrical and chemical experiments under DEA operation, presented in [Strahl *et al.* 2014d], such as EIS and gas chromatography highlight the water-related performance challenges. On the one hand, water is building up in the anode during DEA operation, which causes the blockage of active sites and thus a voltage drop due to local hydrogen starvation. On the other hand, even during anode flooding, the cathode catalyst layer is very sensitive to elevated fuel cell temperatures and tends to dry, which in turn leads to a continuously dropping voltage.

The experimental findings during DEA operation, presented in [Strahl *et al.* 2014d], have been evaluated with respect to overall system efficiency compared to a recirculation system. The comparison shows that the system-topology-dependent efficiency gain depends on the stack size and the system's power output. Thus, a purged system will always be more cost-efficient for low power applications, such as the studied one, while large systems may be more cost-effective and also more efficient in the recirculation mode. Nevertheless, it has been demonstrated that optimization of the purge strategy can significantly improve the DEA system performance and its cost-efficiency.

The negative aspect of the trade-off between increasing efficiency by increasing the purge intervals and the system's durability has been proven experimentally: Carbon support degradation accelerates during DEA operation, since oxygen in the anode was detected at the longer purge intervals. However, carbon corrosion rates can thus be estimated and incorporated in a purge control strategy to account for system durability. Referring to the comparison of a DEA system to a recirculation system, the latter may suffer from the same effect: The recirculation system has to be purged regularly as well (however less frequently) in order to avoid nitrogen accumulation in the anode, which leads to hydrogen dilution and starvation. Optimizing the durability of both systems is directly related to avoiding hydrogen starvation in the anode by either water or nitrogen accumulation, and thus improving the system's durability.

In conclusion, a trade-off between maximum power, system efficiency and durability is necessary when the question for the need of a purge has to be evaluated.

Since only few experimental data on the degradation PEM fuel cell stacks without external humidification are available in the literature, especially if the effects are different from cell to cell, the experimental *in-situ* and *ex-situ* results presented in [Strahl *et al.* 2014b] contribute to the understanding and improvement of the system durability. The results show that the cells at the beginning and at the end of the stack suffered from higher degradation rates than cells in the middle of the stack. Especially the first cells show the largest ECSA loss, which is the result of severe carbon corrosion due to their location close to the anode gas inlet and outlet of the stack. The corrosion of the carbon support led to platinum dissolution, agglomeration and migration into the membrane, which was detected by XPS, XRD and SEM analysis.

The transversal SEM analysis of the first cells compared to a reference cell supports the hypothesis, that cells located close the anode gas inlet and outlet suffer first from carbon corrosion, in accordance with the post-mortem analysis results presented by [Tang *et al.* 2006]. Therefore the performance decay, observed by *in-situ* experiments, was first detected in cell 1 and advanced towards cell 3, until reaching almost complete loss of ECSA of the first two cells, while the rest of the stack was still operating reasonably well. Moreover, transversal SEM imaging within individual cells demonstrated the increased carbon support degradation towards the anode outlet of the cell. This leads to the conclusion, that the uncontrolled start-ups and shutdowns, as well as non-optimal purge strategies had the strongest effect on the stack's durability. This work shows the severe operation-dependent effects on durability of an, apart from that, simple and robust open-cathode PEM fuel cell system. The advantage of system simplicity results in this case in a disadvantage for the durability. Hence, the lifetime of the system can be improved significantly by controlled start-up/shutdown procedures, avoidance of operation at high cell voltages and proper purge control.

The effects of the fuel cell temperature on performance have been analyzed thoroughly in [Strahl *et al.* 2014c]. As shown in the experiments, the capability of improving performance by increasing temperature is given, but limited due to drying of the cathode CL at elevated temperatures and the related loss of active sites. The experimental and model-based analysis demonstrates that the dynamics of the temperature-related drying effect on fuel cell voltage is much slower than the dynamics of the activity gain, which follows the temperature response of the fuel cell.

The simulation results with the presented thermal and electrochemical models under

operation with the designed Extremum seeking controller show promising results in terms of optimal temperature control. However, the experimental validation resulted in insufficient capability of the controller to stabilize the voltage at the detected maximum. This is a result of the slow system dynamics, especially the gradual voltage decay due to the temperature related drying of the catalyst layer. A possible solution for this problem is the use of a model-based controller in conjunction with the control-oriented model of the fuel cell system that accounts for the observed drying effect. However, the robust performance improvement only by temperature control is still a challenging task. Incorporation of a second control action that has direct influence on the liquid water saturation in the CL will improve the controllability of the system.

In order to obtain a deeper understanding of the performance related liquid water and thermal aspects of the CL structure, the mesoscopic effects, such as temperature dependent hydration and dehydration dynamics in the pores of the CL, have been investigated in [Strahl *et al.* 2014a]. The presented dynamic, multiscale modeling approach helps to interpret the experimentally observed thermal and electrochemical system dynamics, explained in [Strahl *et al.* 2014c].

The transient simulation results show that the dynamics of the voltage response with respect to an increase in cell temperature are dominated by water desorption dynamics of the ionomer thin-film in secondary pores. The CFD model in combination with a PSD-based CL structure model gives a good representation of temperature-related water saturation and voltage transients. Moreover, the parametric numerical analysis of temperature-related transients gives information about the CL structure and its links to fuel cell performance. Hence, the model serves as an important simulation tool for the development of proper temperature controllers including the latest research advances in electrode material properties and structure. For instance, the performance gain by optimal temperature control can be linked directly to a reduction in platinum loading for improving the fuel cell efficiency.

The modular character of the developed models allows for the easy adaption of modeling techniques and sub-models to high temperature PEM fuel cell systems, as presented in [Bezmalinovic *et al.* 2014]. The simulated local water transport profiles along the flow channel for a dry anode inlet at the three tested cathode stoichiometries confirm the experimental findings that the water vapor transport along the channel changes its direction from initially cathode to anode to the opposite direction towards the end of the channel. The higher water production rate at higher current densities results in a sharper gradient of water transport, which leads to a faster water vapor

accumulation in the anode gas stream. This information is important for the design of high temperature PEM fuel cells and their control. For instance, at low stoichiometry or DEA configuration water transport from cathode to anode leads to an elevated water concentration close to the anode outlet, which in turn lowers the concentration of hydrogen. This may be even more critical when operating with reformed gases where the hydrogen concentration is already low.

As shown in this work by experimental and model-based analysis, the water and hydrogen concentration in the anode under FT operation can be controlled by the cathode flow rate. Proper cathode stoichiometry control may be used to manipulate the magnitude, direction and distribution along the channel of water transport, which can prevent local hydrogen starvation and the involved degradation effects that are explained in the experimental work on low temperature fuel cells [Strahl *et al.* 2014d][Strahl *et al.* 2014b]. Prevention of degradation-promoting scenarios in high temperature fuel cells is even more crucial since degradation mechanisms, such as carbon corrosion are strong functions of temperature.

4 Conclusions and Contributions

The experimental and model-based analysis of PEM fuel cells presented in this doctoral thesis demonstrates the great potential and importance of effective thermal and water management for performance and durability improvement. Proper thermal and water management implies the design and application of the appropriate control strategies. For this design process a good understanding of the involved system dynamics is essential. As explained in this work via experimental observations and computational simulations, the decision on an adequate strategy may be difficult due to counteracting effects of control actions, such as changes in temperature, reactant flow rates and purge intervals. Therefore, the control strategy has to be a trade-off between system performance, efficiency and durability, adapted to the respective application or operating mode.

Based on the presented experimental results, adequate dynamic models for water and thermal management have been developed. The experimentally validated multiscale models have the capability of relating for the first time the cathode electrode structure and liquid water content to the cell voltage transient behavior promoted by changes in fuel cell temperature. It has been shown that the limiting dynamic for the performance improvement via temperature control is related to water sorption and desorption, since the time constant for water desorption from the ionomer is about two orders of magnitude lower than the thermal time constant of the system.

Moreover, the different models provide the necessary link between the important system level dynamics and material properties with respect to thermal management, water transport and electrochemistry in order to study and improve novel fuel cell electrode materials. Thus, the models may speed-up both material and controller development and decrease investigation costs via the reduction of time-intensive experiments.

More specifically, the models developed in this doctoral thesis will help to design controllers for applying the optimal purge and temperature management strategy, for different performance, efficiency and lifetime objectives. For instance, a total system

performance improvement of 4% was obtained just by optimizing the temperature set point.

The experimental identification of the different degradation mechanisms contributes to important scientific knowledge on the durability of low temperature PEM fuel cell systems without external humidification, which promotes the design of proper system controllers that take into account fuel cell durability. The effects of insufficient control have led to an almost 99% loss of ECSA in two cells of a 20-cell stack, only after about 300 hours of normal operation, as identified experimentally.

The obtained simulation and experimental results on performance and durability improvement strategies will facilitate the technology transfer to system and stack manufacturers. Recommendations of proper operating conditions and CL materials, such as optimal fuel cell temperature and CL PSD, in order to improve the PEM fuel cell performance can either be directly derived from the published articles represented in this thesis, or by simulation with the respective models.

Finally, the involved publications of this doctoral thesis contribute significantly to the European Seventh Framework Program for Research (FP7) project of the Fuel Cells and Hydrogen Joint Undertaking (FCH JU): *Physical Bottom-up Multiscale Modelling for Automotive PEM Fuel Cell Innovative Performance and Durability Optimization* (PUMA-MIND FP7 303419) and to the Spanish national project MESPEN: *Desarrollo de sistemas de control para la mejora de la eficiencia y la vida útil en sistemas basados en pilas de combustible PEM* (MICINN DPI2011-25649).

Significant scientific outreach was obtained with this doctoral thesis by regular presentation of intermediate and final results at international conferences and seminars in Spain, Portugal, Switzerland, France, Germany and Argentina.

5 Ongoing and Future Work

The results of this doctoral thesis and their publication in international journals lead to further research in the field of optimal temperature and purge control, and have as well initiated new multiscale investigations of degradation mechanisms:

The control-oriented fuel cell model developed in [Strahl *et al.* 2014c] is currently being used for the design of optimal temperature control strategies for performance and efficiency optimization. Therefore, a study of the equilibrium points of the 2-state-model (temperature and liquid water saturation) is carried out with the subsequent evaluation of model linearization. Finally, linear controllers will be designed by means of H_∞ and μ -synthesis, for instance. The linear controller is responsible for taking the states close to the efficiency/performance optimum. Optimization in the vicinity of the optimum could be conducted via Extremum Seeking. This project will be carried out in collaboration with the *Advanced Control of Energy Systems Group* (ACES) in Barcelona, Spain.

The multiscale performance model developed in [Strahl *et al.* 2014a] will be extended by including the operating-conditions-dependent electrochemical reactions for platinum dissolution in order to study temperature and water management-related effects on durability. The experimental results published in [Strahl *et al.* 2014b] serve for the model validation, for example by comparing the simulated change in platinum particle size distribution over the lifetime to the experimental XRD results of the degraded cells. The model will be developed in collaboration with the *Laboratoire de Réactivité et Chimie des Solides* (LRCS) of the *Université de Picardie Jules Verne* in Amiens, France.

Finally, the one-dimensional multiscale modeling approach for the fuel cell cathode developed in [Strahl *et al.* 2014a] will be extended to a 2D model of a complete single cell in order to study hydrogen purge and temperature control strategies and their effects on fuel cell performance. By including the electrochemical reactions for carbon corrosion and taking into account reactant permeation through the membrane, effects of the purge strategy on durability can be studied. Model validation will be carried

out with the experimental results published in [Strahl *et al.* 2014d]. All these future works are in accordance with the project plan of the FP7 project PUMA-MIND that will continue until December 2015.

Additionally, this doctoral thesis can initiate new relevant future works such as the derivation of adequate reduced order models or lumped parameter models, including the experimental and model-based characterization results. These reduced models may be directly used for the design of real-time diagnostics, controllers and dynamic observers, necessary for optimal fuel cell system operation, especially for highly dynamic applications.

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