NEW DESIGN TOOLS AND CHARACTERIZATION METHODS TO STUDY POLYMER ELECTROLYTE MEMBRANE FUEL CELL DEGRADATION

by

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Abstract

An increasing energy demand and the need to reduce greenhouse gas emissions promotes a need for sustainable energy systems. Polymer-electrolyte-membrane fuel cells, comprising a carbon-platinum catalyst layer (CL), have reached (pre-)commercial viability. However, performance, durability, and cost targets are not entirely met yet. In a larger perspective, this thesis aims to contribute to the development of novel catalyst quality monitoring methods, gradual catalyst loading strategies, and the link between water management and catalyst degradation. The objectives of this thesis are to design tools and develop methods of investigation for catalyst degradation, characterize different accelerated stress test (AST) protocols, indicate stressors of the occurring degradation, deconvolute the performance decay, and to analyze the locally occurring degradation. Carbon corrosion and platinum dissolution are the major degradation mechanisms during the operation. Start-up and shutdown (SU/SD) events where air purges through the hydrogen containing anode, accelerates the progression of these mechanisms, and amplified performance decay results.

This study develops an ex-situ tool and a method to link the water content within the CL to the degradation behavior. Higher water content may accelerate CL failure. The comparison of different SU/SD ASTs revealed the degradation behavior and the influence of various mitigation strategies to reduce the occurring voltage decay. The application of an external resistance resulting in the consumption of electrons reduces the degradation. If the voltage is suppressed by applying an external load, the degradation in high current densities is marginal. The deconvolution of the voltage decay at high current densities reveals the ratio of carbon to non-carbon related losses. The non-carbon related losses become significant. The novel multi-channel-characterization-system

revealed larger losses towards the cell's exit during SU/SD and platinum dissolution ASTs. Chemical platinum degradation caused by higher water content towards the exit dominates. Longer residence times of oxygen within the anode promote degradation towards the exit.

In conclusion, this study developed novel diagnostics, assessed the ratio of performance decay related to its mechanisms, estimated a dominance of the non-carbon related losses throughout the initial phase, while localizing the degradation.

Preface

I carried out the primary design, experimental testing and post-processing, analysis and writing of this thesis under the supervision of Dr. Walter Mérida.

Versions and parts of chapters 4 and 5 as well as 7 were published for the dissemination of results in different peer-reviewed journal articles and conference proceedings[1], [2]. Chapter 6 was submitted and is currently under review. My efforts and responsibilities of these publications included, but were not limited to, the following: development of in-situ and ex-situ diagnostic tools, design of the experiments, conducting the experiments, processing and analyzing the data, as well as manuscript writing, editing and submission under the supervision of Dr. Mérida. The contributions of all authors are listed with respect to the corresponding publications.

- Sections of Chapter 1, 2, and 3 were composed of drafts of the Ph.D. research proposal [3] and segments of the publications[1], [2].
- A version of Chapter 4 was published as a peer-reviewed conference proceeding in The Electrochemistry Society's *ECS Transactions* [1]. The post-doctoral fellow Dr. Dhanushkodi and Dr. Mérida supervised this work.
- A version of Chapter 5 has been submitted and remains currently under review. The postdoctoral fellow Dr. Dhanushkodi and Dr. Mérida supervised this work.
- A version of Chapter 6 was published as a peer-reviewed article in The Electrochemistry Society's *Journal of Electrochemical Society* [2]. My role in this publication was to design the novel segmented cell hardware, develop a suitable segmentation technique for the MEA,

commission the power electronics, execute the experiments, analyze and post process the data, as well as assist in editing and writing of the manuscript. A fellow Ph.D. candidate, Devin Todd, offered critique in the apparatus design, assisted in the 3D-CAD design process and the procurement of parts.

A list of all conference presentations and publication is available in Appendix C.

The permission to reprint the published text, figures and tables were acquired from the Electrochemical Society.

References related to the dissertation:

- [1] M. Schwager, S. R. Dhanushkodi, and W. Merida, "Comparison of Startup and Shut down cycles in a non-segmented and segmented polymer-electrolyte-membrane fuel cell hardware," ECS Trans., vol. 66, 2015.
- S. R. Dhanushkodi, M. Schwager, D. Todd, and W. Merida, "PEMFC Durability: Spatially Resolved Pt Dissolution in a Single Cell," J. Electrochem. Soc., vol. 161, no. 14, pp. F1315– F1322, Sep. 2014.
- [3] M. Schwager, "Diagnostic Tools and Experimental Methods to Characterize Water Transport Properties in Polymer electrolyte membrane Fuel Cells - PhD reserach proposal," 2014.

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List of Symbols

А	Fitting parameter
а	Activity
В	Fitting parameter
C _B	Bulk oxygen concentration
Cs	Oxygen concentration at the catalyst surface
D	Diffusion coefficient
Е	Voltage
F	Faraday's constant
G	Gibbs free energy
i	Current density
\mathbf{i}_0	Exchange current density
$\mathbf{i}_{l,i}$	Limiting current density
j	Species j
k'	Apparent dissolution rate constant
L_w	Cathode platinum loading
Μ	Molecular weight
Ν	Particle count
n	Number of electrons
р	Pressure
R	Ideal gas constant
S	Entropy
Т	Temperature
$V_{\rm H}$	Upper potential
V_L	Lower potential
V_m^A	Anode metal potential
$V_m^{\ C}$	Cathode metal potential
v	Stoichiometric coefficient
W_{el}	Electrical energy

α	Transfer coefficient		
$\eta_{\rm i}$	overpotential		
$\eta_{{}_{c,j}}$	Concentration overpotential		
$\eta_{_{mt,j}}$	Mass transport overpotential		
6	Platinum metal density in g cm ⁻³		
σ	Surface tension		
Φ.	Potential		

Subscripts / Superscripts

0	Thermodynamic standard condition		
А	Anode		
В	Bulk		
c	Concentration		
С	Cathode		
el	Electric		
electrolyte	Electrolyte		
Н	High		
i	Numbering element		
j	Species j		
L	Low		
1	Limiting state		
m	Metal		
mt	Mass transport		
Pt	Platinum		
S	Surface		
th	thermoneutral		

List of Abbreviations

AC	Alternate current
AST	Accelerated stress test
BOL	Beginning-of-life
ССМ	Catalyst coated membrane
CERC	Clean Energy Research Centre
CL	Catalyst layer
CV	Cyclic voltammetry
DOE	Department of Energy
e	Electron
ECSA	Electrochemically active surface area
EDX	Energy dispersive X-ray
EIS	Electrochemical Impedance Spectroscopy
EOL	End-of-life
EPSA	Electrochemical platinum surface area
FCC	Four Chamber Cell
FRA	Frequency response analyzer
FUDS	Federal urban driving schedule
GDL	Gas diffusion layer
GHG	Green House Gas
GmbH	Gesellschaft mit beschraenkter Haftung (Limited equivalent in Germany)
HFR	High frequency resistance
HOR	Hydrogen oxidation reaction
ISE	Institute for Solar Energy Systems
LSV	Linear sweep voltammetry
MCCS	Multi-channel characterization system
MEA	Membrane electrode assemblies
METI	Ministry of Economy, Trade, and Industry
MPL	Micro porous layer
NHE	Normal Hydrogen Electrode
OCV	Open circuit voltage
ORR	Oxygen reduction reaction
OX	Oxidant
PEM	Polymer Electrolyte Membrane
PEMFC	Polymer electrolyte membrane fuel cells
PTFE	Poly Tetra Fluor Ethylene
PTL	Porous transport layers
Pt	Platinum
PtO	Platinum Oxide
Pt/C	Platinum-carbon
RH	Relative humidity
red	Reductant
RHE	Reference Hydrogne Electrode

SEM	Scanning Electron Microscopy
SU/SD	Start-up and Shut-down
TEM	Transmission Electron Microscopy
UBC	The University of British Columbia
US	United States

Acknowledgements

"Nicht Kunst und Wissenschaft allein,

Geduld will bei dem Werke sein."

FAUST, DER TRAGÖDIE ERSTER TEIL, HEXENKÜCHE, MEPHISTO, 1808 JOHANN WOLFGANG VON GOETHE (1749-1832), PHILOSOPHER, SCIENTIST, AND STATESMAN

First I would like to express my gratitude to supervisor Dr. Walter Mérida for his constant support, patience, and guidance throughout my doctoral studies at UBC. His passion, vision, and knowledge motivated me every day. Discussions inspired me to think beyond the obvious.

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FELIX QUI POTUIT RERUM COGNOSCERE CAUSAS²

GRATIAS AGO

¹ "Not art and science alone, but patience will be required for the work."

Faust: The First Part of the Tragedy, Witch's kitchen Mephisto, 1808, Johann Wolfgang von Goethe

² Verse 490 of Book 2 of the "Georgica" (29 BC), Publius Vergilius Maro (Vergil), 70 - 19 BC

Dedication

To my parents,

My family, and

My loved ones.

Chapter 1: Introduction

1.1 Motivation

"Oui, mais l'eau décomposee en ses éléments constitutifs,..., et décomposée, sans doute, par l'électricité, qui sera devenue alors une force puissante et maniable, ... je crois que l'eau sera un jour employée comme combustible, que l'hydrogène et l'oxygène, qui la constituent, utilisés isolément ou simultanément, fourniront une source de chaleur et de lumière inépuisables et d'une intensité que la houille ne saurait avoir. ...Je crois donc que lorsque les gisements de houille seront épuisés, on chauffera et on se chauffera avec de l'eau. L'eau est le charbon de l'avenir."

JULES VERNE, L'ÎLE MYSTÉRIEUSE, 1875

Jules Verne once wrote in his novel, <u>The Mysterious Island</u>: "Yes, but water decomposed into its primitive elements... and decomposed doubtless, by electricity, which will then have become a powerful and manageable force, ... I believe that water will one day be employed as fuel, that hydrogen and oxygen which constitute it, used singly or together, will furnish an inexhaustible source of heat and light, of an intensity of which coal is not capable. ... I believe, (... when the deposits of coal are exhausted) we shall heat and warm ourselves with water. Water will be the coal of the future!"³ Decades ago, scientists, engineers, as well as writers and philosophers investigated the possibilities of energy. Today's technical advancements and continuous international efforts brought our society recently closer to the systems, people in the past centuries have only dreamed of being reality. Increasing consumption, diminishing resources, and political changes have challenged society since the early stages of industrialization. In the 21st century developing countries are more and more starting to emerge into their industrial stage; therefore, energy will be the greatest commodity and challenge.

Fuel cells are the most efficient way to convert the chemical energy of hydrogen into electricity. Physicist Christian Schönbein first investigated concepts of the electrochemical energy conversion. One year later, in 1839, Sir Wiliam Grove presented the first functional fuel cell [4]–[6].



Canada Transportation GHG Emission by transportation mode, 2007



Figure 1.1: a) US Green House Gas (GHG) emissions by economic sector for 2013 [7] and b) Canadian transportation Green House Gas emissions by transportation mode for 2007 [8].

³ Jules Verne, The Mysterious Island, 1875

Setting the energy demand aside, pollution caused by the usage of fossil fuels is a second significant challenge of today's age. Figure 1.1 a) shows the Green House Gas (GHG) emissions by economic sector for the United States of America in 2013 [7]. The power generation and transportation sectors are responsible for approximately 60 % of the GHG emissions, whereof circa 85 % are CO_2 emissions [7]–[9]. The Canadian GHG emissions of the transportation sector indicate that approximate 75 % of the emissions are caused by freight and passenger transportation on the road (Figure 1.1 b)) [8]. The emission analysis for the USA show similar ratios (ca. 80 % not shown)[8]. The effect of sustainable energy supply systems in the transportation and power supply sector will have a significant impact towards the reduction of GHG emissions.

The awareness of decreasing fossil fuel resources by increasing energy demand and the environmental impact of GHG emissions led to a rise in research and development of alternative and sustainable energy technology at an academic, as well as, industrial level. Not only economical and ecological targets, yet also a steadily increasing global population, emphasizes the need for a "green" energy technology (r)evolution.

Fuel cell systems, with their high efficiency, are a very promising technology for one green energy solution. Fuel cells are a carbon-free energy conversion solution if supplied by sustainably won hydrogen. Fuel cell technology in its reverse operation mode, electrolyzer, may fulfill this demand. Cost, durability, and performance targets for fuel cell systems are close to being met to fulfill pre-commercial viability [10]. Polymer electrolyte membrane fuel cell systems satisfy the needs of the transportation sector (compact, durable, and agile) well. They are also suited for small and medium stationary power applications. However, lifetime, durability, and cost targets still challenge the industry.

1.2 Aim of the thesis

...is, therefore, to investigate the degradation behavior and to identify major losses occurring during durability studies, in more detail. The conclusions of this thesis should, in greater perspective, assist the development of new design guidelines for the next generation of Polymer Electrolyte Membrane (PEM) fuel cell materials. Further, the outcome may assist in the development of test standards and an improved start/stop accelerated stress test cycle profile.

The objectives of this thesis were:

- I. the characterization of different start-up and shut-down (SU/SD) accelerated stress test protocols in a common in-situ platform to analyze the stressor impacts and proposed mitigation strategies,
- II. the deconvolution of the occurring degradation mechanisms and their critical analysis,
- III. the design and validation of a common in-situ test platform, capable to spatially resolve the PEM fuel cell characterization, and
- IV. the spatially resolved analysis of start and stop accelerated stress test cycles.

1.3 Layout of the thesis

The thesis comprises four parts; the introduction, phase one and two and the conclusion. Figure 1.2 gives an overview of the thesis layout. This Figure also relates the thesis to published works. A publication for chapter 6 was submitted and is indicated in this illustration.

This thesis starts with the introduction, motivation and aim, as well as, governing principles of PEM fuel cells, and possible degradation. A comprehensive literature review of degradation during startup and shut-down processes is presented in Chapter 2:. Chapter 3: summarizes the used experimental methods.

The phase one of this study comprises single cell experiments and method development. Chapter 4: provides the comparative study of different SU/SD protocols. Three known SU/SD protocols are compared to each other in a common test platform. First segmented SU/SD experiments present the spatial degradation differences of one protocol. The deconvolution of performance decay occurring during SU/SD events is represented in Chapter 4:. A selected protocol was utilized to study the different degradation influences on the performance. An empirical model was used to deconvolute the occurring degradation.

In phase two are all segmented cell studies and the development of the segmented cell summarized. Parts of this phase were of collaborative nature. The development of the segmented cell is summarized in Chapter 5:. Chapter 5: contains the spatial platinum dissolution study. While Chapter 6: illustrates a comparative spatially resolved in-situ study; different protocols were compared with each other. The platinum dissolution study was compared to carbon corrosion and a SU/SD accelerated stress test. Chapter 7: concludes this thesis.



Figure 1.2: Thesis layout with related publications.

1.4 Fundamentals

1.4.1 Elemental conditions, the ideal state

PEM fuel cells are electrochemical energy devices. They convert the chemical energy, bound in the fuel, directly into electrical energy. At a given temperature (T), pressure (p), and the particles count (N) the maximum energy of a reaction, which can be converted, is stated by the difference of the Gibbs free energy (ΔG).

$$\Delta G(T, p, N) = \sum G(T, p, N)_{prod} - \sum G(T, p, N)_{react} = W_{el}$$
(1.1)

As electrochemical energy devices, fuel cells utilize the energy in the reactants using separated redox reactions. To reduce a substance, an oxidation will release a definite number of electrons $(ox \rightleftharpoons red + ne^-)$, the redox reaction. The overall exothermic reaction for the PEM fuel cell is stated as:

$$H_{2} + \frac{1}{2}O_{2} \rightleftharpoons H_{2}O, \quad \Delta G^{0} = -237.3 \quad kJ \ mol^{-1}$$

$$(1.2)$$

The overall cell reaction will be separated in the oxidation of hydrogen, hydrogen oxidation reaction (HOR), and the reduction of oxygen, oxygen reduction reaction (ORR). The HOR occurs on the anode, the ORR on the cathode of the cell.

$$H_2 \rightleftharpoons H^+ + 2e^- \quad Anode \tag{1.3}$$

$$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O \quad Cathode \tag{1.4}$$

The membrane ensures the separation of the gases; protons can travel through the proton conducting polymer (ionomer) from the anode to the cathode. The membrane also acts as an electronic insulator, meaning the electrons produced need to travel via the porous media and bipolar plates through an outer circuit to the cathode (Figure 1.3). The electrons can directly be used as electrical energy (W_{el}) In contrast to fuel cells, combustion processes utilize the dissipated heat of the combustion and need an additional conversion step. The Carnot process and respectively the Carnot

efficiency restrict these engines. The Carnot process does not restrict fuel cells, thus conversion efficiencies of circa 50 % are possible.

The electrode potential at standard conditions (T = 298 K, and p = 1 atm) is expressed as the ratio of Gibbs free energy versus the number of electrons (n) involved and the Faraday's constant (F) (96485 C).

$$\Phi_{Cathode} = \frac{-\Delta G^0}{nF} = 1.229 V \tag{1.4}$$

The cathode standard potential uses four electrons; the anode standard potential is, by convention, zero. The standard cell potential is the difference of the cathode and anode potential, and therefore 1.229 V. Using the enthalpy of the reaction will allow calculating the standard thermoneutral cell voltage ($E_{th} = 1.48$ V). With the entropy (S) and the tepmerature (T).

The Gibbs free energy will need to be temperature corrected:

$$\Delta G = \Delta G^{0} - \int \Delta S^{0} dT \tag{1.4}$$

The Nernst equation allows quantifying the reversible cell voltage as a function of activity (a) of the species (j) involved and the temperature.

$$E_{ref}(a) = \frac{-\Delta G^0}{nF} - \frac{RT}{nF} \ln\left(\frac{\prod a_{prod}^{v_j}}{\prod a_{react}^{v_j}}\right)$$
(1.5)

Where R is the ideal gas constant and v the stoichiometric coefficient of the involved species j.

1.4.2 **PEM fuel cell components and related loss mechanism**

In a PEM fuel cell system, the cell voltage is dependent on various different conditions. The major dependencies are categorized into two groups: losses occurring during the open circuit and additional losses when a load is applied to the cell. All losses called overpotentials (η_y) are subtracted from the corrected standard cell potential. The occurring losses may be connected to the different fuel cell components and may occur locally different. Figure 1.3 shows the components of a PEM fuel cell.



Figure 1.3: PEM fuel cell schematics and components.

1.4.2.1 The Membrane and its related crossover losses

The membrane (Figure 1.3) is the core of the PEM fuel cell. It separates the anode and cathode compartment, is impermeable to gases, and electronically insulates while ensuring satisfactory proton conduction and high mechanical and chemical stability.

The membrane consists of a hydrophobic Polytetrafluoroethylene (PTFE) structure as "backbone" with ionically (SO_3^-) attached sulphonic acid (HSO_3) groups as side chains. These side chains ensure the ionic conductivity (ionomer). The SO_3^- groups form hydrophobic clusters; they comprise the ability to absorb high quantities of water. The water / $(SO)^{3-}$ cluster allows the loose attachment of protons and thus the transfer of protons. The proton conductivity is proportional to the amount of water in the membrane. Poor proton conductivity, caused by a relatively dry membrane, may cause higher resistance. Commercial membranes are often reinforced to minimize the thickness (and so maximize the proton conductivity) while still ensuring mechanical stability.

The membrane is also responsible for a drop in the open circuit voltage (OCV). Figure 1.4 demonstrates the occurring loss mechanism and its dominant regions related to the cell potentials and current densities. Hydrogen diffusion, often called crossover, from the anode to the cathode causes mixed potentials and a drop in voltage, often referred as crossover potential. The crossover current can be characterized using linear sweep voltammetry techniques. The crossover may also serve as a membrane degradation indicator.



Figure 1.4: Polarization curve with loss mechanisms.

1.4.2.2 The Catalyst layer and the related activation losses

The catalyst layer (CL) is the electrochemically active layer where the HOR and ORR take place. The layer consists of carbon particles, ionomer, and a catalyst. The most common catalyst for both reactions is platinum. The application of the CL onto either side of the membrane is considered the catalyst coated membrane (CCM).

The major purpose of the layer is the reduction of activation barriers for the HOR and ORR. The layer also assists the reactions by enhanced proton transfer conductivity, improved electronic conductivity, and improved mass transport properties. The electrons, protons, and oxygen molecules need to exist concurrently within the three-phase-domain. The CL design comprises a porous carbon structure, with porosities of ca. 40 to 50 %. Platinum nanoparticles are attached to the carbon structure; ionomer connects the porous structure with the membrane. Some CL additionally comprises a PTFE impregnation to enhance the water removal from the active sites. The CL thickness varies from application to application but rates in between 2 to 30 µm.

To initiate the reaction, a "driving force" needs to be applied to the electrode. The electrode equilibrium potential represents a resting state; the net conversation rate is zero. If this potential is shifted, an anodic or cathodic reaction takes place, resulting in a net current density. The shift of the potential, the electrode overpotential, is this driving force and acts as a loss mechanism. The rate of conversion (i) is dependent on the (activation-) overpotential ($\eta_{(a)}$). The Butler-Volmer equation describes this dependency:

$$i = i_0 \left[e^{\left(\frac{-nF\alpha\eta}{RT}\right)} - e^{\left(\frac{-nF(1-\alpha)\eta}{RT}\right)} \right]$$
(1.6)

with the amount of electrons (n) transferred in the reaction step, Faradays constant (F) the ideal gas constant (R) the temperature (T) a transfer coefficient (α), and the exchange current density (i₀). The exchange current density is a measure of the catalyst activity and defined as the rate of backward or forward reactions at equilibrium. The transfer coefficient states the symmetry of the energy barrier for the forward and backward reactions.

The Tafel equation represents a simplified version of the Butler-Volmer relation:

$$\eta = \frac{RT}{nF\alpha} \ln i_0 - \frac{RT}{nF\alpha} \ln i$$
(1.7)

for the oxidation(forward) reaction, and:

$$\eta = \frac{RT}{nF(1-\alpha)} \ln i_0 - \frac{RT}{nF(1-\alpha)} \ln \left(-i\right)$$
(1.8)

for the reduction (backward) reaction. In PEM fuel cells the current density, i couples both half-cell reactions. The electrode overpotentials adjust accordingly and dependent on i_0 and α . The anode overpotential is much smaller compared to the cathodic overpotential. At low current densities, this anode overpotential may be neglected.

It may further be simplified to:

$$\eta = a + b \ln i \tag{1.9}$$

for the forward reaction, and the backward reaction:

$$\eta = a + b \ln\left(-i\right) \tag{1.10}$$

where b represents the Tafel slope.

1.4.2.3 Gas diffusion layer and microporous layer; and affiliated mass transport and ohmic losses

The gas diffusion layer (GDL) comprises a fibrous carbon material, here considered as the substrate (sometimes named GDL), and a microporous layer (MPL). The substrate consists of carbon fiber paper or felt, and may be impregnated with PTFE. This increases the hydrophobicity, leading

towards an improved water management behavior. Fine carbon particles and PTFE, as a binder, are coated onto the substrate as MPL.

The GDL / MPL links the bipolar plate with the catalyst layer. The bipolar plate acts as the gas distribution structure and the current collecting component; it represents the interface to the macroscopic periphery of the system. The GDL /MPL ensures the diffusion of the reactants to the CL; the product water diffuses in opposing direction from the CL to the bipolar plates. The GDL / MPL facilitates thermal and electrical conduction and supports the catalyst coated membrane mechanically. The MPL improves the contact resistance to the CL. It also enhances the water management behavior of the cell by acting as a liquid water barrier [11]–[15]. The expulsion of water is essential to allow an adequate delivery of reactants in the CL structure; opposing this, the membrane water content must stay as high as possible to ensure sufficient proton conductivity.

The combination of ohmic resistances of all layers and the bipolar plates multiplied by the current density is considered the <u>ohmic loss</u>. The ohmic losses may be quantified by current interrupt or electrochemical impedance techniques. The mass transport overpotentials may also be estimated via an analysis of polarization curve [16].

1.4.3 Lifetime targets for PEM fuel cells during early market

Fuel cells are in the initial stages of commercialization. Fuel cell durability targets, important for the successful market introduction, are not yet internationally established. Dependent on the funding agencies and applications, different regional targets are established. The major contributors are the U.S. Department of Energy (DOE), Japan's Ministry of Economy, Trade, and Industry, and the European Commission. Table 1.1 summarizes international targets.

Targets	American (U.S. Office of Energy Efficiency and Renewable)	European (European Hydrogen and Fuel Cell Technology Platform)	Japanese (Japanese New Energy and Industrial Technology Development)
Transportation	Efficiency: 60% Durability: 5000 hrs Cost: \$30/kW	Efficiency: > 40% Durability: passenger car: 5000hrs / buses: 10000hrs Cost: 100 €/kW	Efficiency: 60% Durability: 5000 hrs Cost: 10000 Yen/kW (108 \$/kW)
Stationary	Efficiency: 40% Durability: 40000 hrs Cost:	Efficiency (residential/industrial): 80 / 90 % Durability: > 12000 / >30000 hrs Cost: 6000 / 1500-5000 €/kW	Efficiency: >40% Durability: 90000 Cost: >0.4 Million Yen/kW (4000 \$/kW)
Consumer Electronics	Efficiency: Durability: 5000 hrs Cost:	80-200 W/kg (Gravimetric density) Durability: 1000-5000 hrs Cost: 3-5 €/W	
APU	Efficiency: 40% Durability: 35000 hrs Cost: \$400/kW	Efficiency: >35% Durability: Passenger car: 5000 hrs / Heavy goods: 40000 hrs Cost: < 500 €/kW	

Table 1.1: International Technology targets for PEM fuel cells 2015.

1.4.4 **Degradation mechanism in PEM fuel cells**

The CL (Figure 1.5) consists of carbon particles as a porous support network, a metal catalyst, and ionomer to ionically connect the three-phase-domain, the electrochemically active surface area (ECSA). The degradation of the ECSA is reflected in performance decay, often considered voltage
decay at a defined current density. The deterioration at the cathode of commercially available CCMs is usually more pronounced compared to the anode CL or other layers [17]. Four platinum catalyst degradation mechanisms in the electrode structure occur in PEM fuel cells: Pt particle detachment, Pt dissolution and re-deposition on larger Pt particles (Ostwald ripening), Pt particle migration of small particles and coalescence to form larger Pt particles on the carbon support, and Pt dissolution with migration into the membrane [18], [19]. The degradation of carbon, carbon corrosion, reduces the mass transport properties of the CL, and the agglomeration of Pt particles.



Figure 1.5: PEM fuel cell degradation mechanism in the catalyst layer: a) Ostwald Ripening, b) coalescence via crystal migration, c) particle detachment, d) carbon corrosion, and e) platinum band formation in the membrane.

1.4.4.1 Electrochemical Ostwald ripening

The Pt dissolution and re-deposition of small particles on larger particles increases the average size and reduces the platinum surface area available for the reaction [20]. This mechanism is caused by the lower stability of small particles dependent on the surface energy of the chemical potential of the phases [18]. Small particles migrate into the electrolyte. They are transported through the electrolyte to the surface of larger particles where they are reduced again, while electrons are reaching the site via the carbon support. Ostwald ripening is potential dependent and happens above potentials of 0.8 V.

1.4.4.2 Pt particle migration and coalescence

Pt particles can migrate, particle coalescence can occur in PEM fuel cells without the need of Pt dissolution and re-deposition. Crystallite migration of Pt on the carbon and coalescence cause a particle size growth and reduces the ECSA [21], [22]. Migration and coalescence occur at operation potentials below 0.8 V; here Pt dissolution does not occur [23]. This mechanism is predicted to be driven by Brownian motion [24]–[28]. While other references contradict this hypothesis, temperatures may not be high enough to cause coalescence. Sintering of catalysts may not be a dominant mechanism in PEM fuel cells [24]–[26]. However, the Pt size distribution can be used as an indicator to differentiate these two mechanisms. Ostwald ripening, and migration/coalescence show different particle size distribution [22], [27]. The increased particle size is assumed to be dominant in the larger Pt size area [29]. Hence, the interpretation of the particle size distribution data is difficult, most likely multiple mechanisms appear simultaneously, and experimental efforts may be difficult [18], [29], [30].

1.4.4.3 Pt dissolution with migration into the membrane

The formation of a Pt band in the membrane is another degradation mechanism occurring in the CL and the membrane. At the cathode and at high potentials Pt dissolves, it diffuses into the membrane caused by a concentration or pressure gradient. Hydrogen (from the anode) and oxygen (from the cathode) constantly permeates and diffuses with small rates through the membrane. The dissolved Pt in the ionomer is chemically reduced by the hydrogen. Repetitively, Pt deposits and re-dissolves within the membrane and moves across the membrane. At a location where the mixed potential is close to 0 V, the Pt forms a stationary band. [27], [31]–[33]. The Pt band is located closer to the anode when the partial pressure of hydrogen is low, e.g. fuel starvation [34], [35]. The band forms in the vicinity of the cathode when cycling with nitrogen and close to the cathode within the membrane after accelerated stress test (AST) cycling with air or oxygen [24], [34]–[38]. The location of the band is a function of the partial pressures of oxygen and hydrogen on cathode and anode respectively, permeability of the reactants through the membrane, and Pt particle size distribution. [31], [33], [39]. It is controversially discussed how the Pt band formation affects the durability. One hypothesis: in the vicinity of the Pt band, close to OCV, hydroxyl radicals are formed. These radicals can attach the main and side chains of the ionomer and cause fluoride and sulfate emissions [40]. Other authors suggest that the Pt particles in the membrane act as a catalyst to chemically convert the hydroxyl radicals and reduce the chemical degradation [41]–[44].

1.4.4.4 Carbon corrosion

Carbon degradation occurs due to the oxidation of the porous carbon support structure and the water-gas reaction. Carbon corrosion causes a collapse of the porous structure; permeability and

porosity decrease while the hydrophilicity of the CL increases. These changes enhance the mass transport losses in the CL [45]–[47]. The carbon loss in the CL causes the collapse of the CL structure; this leads to the agglomeration of Pt particles and reduces the ECSA significantly. An electrode thinning of up to 33% is observed [48]–[50]. The carbon loss can also induce an electronic insulation of the catalyst, this increases the ohmic losses in the CL [17], [51], [52].

During normal operation conditions (cell potentials below 0.9 V) carbon corrosion is not significant. It will become significant if the cell is held for longer periods of time at OCV, or at circumstances where the local potential is elevated, such as start and stop procedures or local fuel starvation. Besides the potential, the carbon corrosion kinetics depends on temperature, potential excursion duration, and catalysts and reactant concentration. The reaction rate remains small at operational ranges of 60 to 90 °C, but elevated temperatures enhance the reaction rates [28], [53], [54]. Thermogravimetric studies have investigated the thermal degradation of Pt-loaded carbon in air atmosphere and concluded that no thermal degradation below 100 °C occurs. Above this temperature, thermal degradation must be considered [55]. At potentials of 0.8 V, Pt catalyzes the subsequent oxidation of surface carbon oxides to CO_2 [18], [51]. The CO_2 evolution in the absence of Pt has only be observed at potentials above 1.1 V [18], [56]. An increase of relative humidity in the air increases the corrosion rate.

1.4.5 Accelerated stress tests in fuel cell durability testing

Real-time degradation studies are relatively rare in the literature. Lifetime expectations of 5000 h for automotive and 40000 h for stationary applications (Table 1.1) will require significant resources. Real-time lifetime tests are economically very challenging [57]. To investigate durability, reliability,

and stability targets accelerated stress testing is necessary. Accelerated stress tests (AST) allow the investigation of PEM fuel cell components, such as the catalyst layer, the membrane, and the gas diffusion layer, within acceptable timescales and economic limits. Studies on platinum dissolution ASTs[34], [58]–[61], carbon corrosion ASTs [62]–[65] and membrane degradation [34], [41], [43] have been extensively reported.

ASTs often focus on the degradation mechanism. Pt degradation, as well as carbon corrosion in PEM fuel cells depend on the potential. Potential cycling or potential holds are most frequently used stressors in AST. The cycling profiles and dwell times vary significantly, triangular, sawtooth, or square wave profiles are very common [51], [57], [66]–[68]. The Pt dissolution depends on the number of cycles, and the accumulated time at upper and lower potentials play only a minor role [69], [70]. The repeated formation of PtO and PtO₂ as a passivation layer and the subsequent rearrangement of the Pt surface area after the reduction accelerate the catalyst degradation. The rapid transient of a square wave cycle profile causes higher degradation compared to triangular or potential hold AST profiles [71], [72]. Elevated temperatures increase the Pt dissolution rate [53], [73], [74]. Water assists in the transport of Pt²⁺ ions. Although, the humidity influence on the Pt degradation is less pronounced [69], [75], [76].

Membrane degradation ASTs often comprises relative humidity cycling to stress the membrane during repeated water uptake and release [51], [77]. Freeze start simulations use a temperature stressor [78]–[80]. While start and stop ASTs simulate a repeated air / hydrogen change in the anode compartment and a subsequent potential transient [81]–[85].

Chapter 2: Start-up and shut-down as accelerated stress test - a review



2.1 Reverse current decay mechanism

Figure 2.1: Potential distribution during the propagation of a hydrogen / air front in a PEM fuel cell [86].

In the normal operational condition, the cathode is fed with air containing oxygen while the anode contains hydrogen. The nature of mobile and automotive fuel cell applications permit that the systems will experience frequent starts and stops. Safety and durability requirements suggest the exchange of hydrogen in the anode compartments [83]. Optimally, the systems are supposed to be purged with an inert gas (such as nitrogen) to avoid any occurrence of degradation. However, mobile and automotive systems do not permit the integration of such additional gas supply units. This units increases the system complexity, weight and costs for system acquisition and usage, which is not desired for this market.

Fuel cell systems at OCV are prone to a multitude of degradation mechanisms. Also, gradual diffusion of oxygen into the anode compartment, due to a longer inactivity of the system, will induce accelerated degradation. This stage would represent a long-residence-time shut-down. A very common start-up and shut-down (SU/SD) strategy is therefore to purge air through the hydrogen containing anode compartment. The air equilibrium on both, anode and cathode, ensures non-detrimental conditions over longer times [83]. To resume to normal operational conditions, hydrogen is purged through the air-containing compartment. At both conditions, start and stop, a hydrogen/air front propagates through the cell.

When both compartments of the cell are filled with air the cell potential $(V_{cell} = V_m^c - V_m^A)$ remains at 0 V. The anode and cathode metal potential, V_m^A , V_m^c are at the equilibrium potential of oxygen $V_{o_2}^{eq} = 1.223 V$ (at 0 CV or 25 C 1 atm) with respect to the electrolyte potential, $\Phi_{electrolyte}$. The electrolyte potential reflects the local potential of the membrane and forms with the metal potentials of the electrodes the surface potential. When hydrogen is brought into the cell, it is oxidized to bring the anode metal potential, V_m^A close to the equilibrium potential of hydrogen $(V_{H_2}^{eq} = 0 V)$. The cell potential, with respect to the electrolyte potential, $\Phi_{electrolyte}$ increases to about 0.85 V. The good inplane conductivity permits the same metal potential along the oxygen containing part of the cell. The 23

remaining oxygen lowers the electrolyte potential, $\Phi_{electrolyte}$ to maintain an anode interfacial potential $(V_m^A - \Phi_{electrolyte})$ close to the equilibrium potential of oxygen. The lowered electrolyte potential in the oxygen containing area and the maintained cathode metal potential, V_m^C causes high voltage differences $(V_m^C - \Phi_{electrolyte})$ in oxygen/oxygen areas of the cell. This voltage difference becomes larger than the equilibrium potential of oxygen. The high cathode interface potential differences cause oxygen evolution and carbon corrosion. Protons, generated in anodic reactions at the cathode, are reduced at the oxygen containing region at the anode. A reverse proton transfer occurs. Reiser et al. proposed this mechanism and referred to it as the *reverse current decay* mechanism [86].

Cell potentials of 1.4 to 1.6 V are feasible and in good agreement with modeling results [83], [86]– [88]. Elevated cell potentials cause carbon corrosion. Accelerated platinum degradation occurs during start and stop procedures as well. Not only elevated potentials, but also the duration of the propagating hydrogen/air front, the cell temperatures and the reactant humidification influence the degradation behavior [81], [83]–[85].

2.2 Start and stop degradation process

2.2.1 Platinum dissolution during start and stop procedures

Electrochemical platinum dissolution occurs during regular fuel cell operation, but is accelerated during start and stop procedures due to the large potential transients occurring at the cathode CL. Aside from operational factors like temperatures or humidity, the platinum dissolution rate is strongly dependent on the electrode potential. At potentials between 0.7 V and 1.2 V platinum oxide formation and dissolution takes place simultaneously and increase with increasing potential. This occurs either, via the reduction of platinum oxide ((2.1) and (2.2)) or from the metallic platinum directly (2.3).

$$PtO + 2H^+ \rightarrow Pt^{2+} + 2H_2O \tag{2.1}$$

$$PtO_2 + 4H^+ + 2e^- \rightarrow Pt^{2+} + 2H_2O$$
 (2.2)

$$Pt \to Pt^{2+} + 2e^{-} \tag{2.3}$$

The repeated oxide formation and dissolution reduces the ECSA, the different mechanisms are explained in 1.4.4. The potential dependent dissolution rate is reaching a maximum at approximately 1.2 V. At higher potentials, extensive PtO and PtO₂ formation passivates the platinum particle surface, leading to a rate decrease again [72], [73], [89]. Frequent potential transients result in a higher platinum dissolution rate compared to constant potentials. The rapid change hinders the formation or limits the thickness of a passive oxide layer; the dissolution is accelerated. Inverting the potential direction instantly reduces the oxide layer. Frequent rearrangements of the Pt surfaces accelerate the degradation as well.

2.2.2 Carbon corrosion during start and stop procedures

SU/SD processes affect significantly the performance of the cell; carbon corrosion is one major cause for this performance decay. Carbon particles, like Vulcan XC-72, Ketjen black, and Pearl 200, form a porous, high surface area network to support the catalyst particles on the electrodes. However, carbon in an electrochemical environment is prone to corrosion at different electrode potentials.

Thermodynamically carbon corrosion occurs above potentials of 0.2 V. Still, the corrosion kinetics remain very slow. The carbon corrosion during regular operation condition of PEM fuel cells is assumed to be negligible [83], [90]. The corrosion rates start to become significant at electrode potentials exceeding 1 V. This section will review the carbon corrosion mechanisms.

The reverse current decay mechanism, proposed in the literature, elevate the electrode potentials on the cathode above 1 to 1.4 V [86]. The mechanism is described in section 2.1.

The carbon corrosion mechanism at elevated potentials is assumed to occur in a two-step process. Oxide species are formed on the carbon surface; these are then further oxidized, which is the ratedetermining step. Equation (2.4) and (2.5) describe this process [83], [91].

$$C + H_2 O \to C - O_{ad} + 2H^+ + 2e^-$$
 (2.4)

$$C - O_{ad} + H_2 O \rightarrow CO_2 + 2H^+ + 2e^-$$
 (2.5)

This mechanism is still not fully understood. A detailed model for carbon corrosion in the PEM fuel cell cathode CL was presented by Gallager and Fuller [92]. Further simplifications were made by Dhanuskodi et al. [18], [65]. Corrosion can also form carbon monoxide; however, the formation rates of CO in fuel cells are relatively low. The positive equilibrium potential of CO₂ formation favors the CO₂ before CO formation. Compared to the CO₂ formation, the formation of CO was found to be one order of magnitudes lower for pure carbon electrodes [93]–[95]. The catalytic behavior of platinum accelerates the CO₂ evolution further. Carbon monoxide formation for common platinum-carbon (Pt/C) electrodes is considered to be negligible [93], [94], [96].

Accompanied by Pt, the rates of reaction for carbon corrosion can be significantly accelerated. Maass et al. [93] proposed a catalyzed reaction pathway. The reaction of the carbon surface oxides with an OH-containing species (Eq. (2.6) and (2.7)) is catalyzed on the Pt particles[83].

$$Pt + H_2 O \rightarrow Pt - OH_{ad} + H^+ + e^-$$
(2.6)

$$C - O_{ad} + Pt - OH_{ad} \rightarrow Pt + CO_2 + H^+ + e^-$$

$$(2.7)$$

Other groups identified occurring carbon corrosion on Pt/C electrodes at potentials below 1 V. CO_2 formation occurred dependent on the potential sweep and the presence of Pt, [56], [93], [94]. CO_2 evolved during cathodic sweeps at potentials of 0.8 to 0.7 V. The occurring corrosion may be associated to effects related to the platinum oxide reduction. OH-like species formation can lead to carbon corrosion once the potential drops below 0.8 V.

The carbon corrosion at potentials of 0.2 V during sweeps occurs at Pt/C and pure carbon electrodes. CO₂ is released at low potentials during the sweep. The carbon may chemically oxidized by hydrogen peroxide. Hydrogen peroxide may be formed in small quantities during the sweep at an equilibrium potential of 0.695 V [83], [93], [97], [98]. This mechanism is not yet fully understood. The carbon corrosion rates for the described processes below 1 V are generally smaller compared to rates above 1 V. The contribution to the overall corrosion is often marginal [83].

These catalytic effects of Pt on the carbon corrosion promote the corrosion in the vicinity the Pt nanoparticles. This may influence the ionic or electronic conduction to the Pt particles or causes the detachment of the catalyst particle [99]. The detached particles migrate to inactive sites or agglomerate on other Pt particles. Some authors assume coalescence is the dominant mechanism

[22], [99]. Other investigations assume electrochemical particle growth as prevailing mechanism [53], [100] or both combined [30], [101]. However, the contributions of detachment and agglomeration as well as dissolution and re-deposition are still under discussion, but all contribute to a decay of ECSA.

Aside from the Pt nanoparticle loss, morphological changes of the porous carbon support cause a significant degeneration of the ECSA and increase the mass transport overpotential. The carbon corrosion induces carbon particle sintering and agglomeration, which leads to a significant porosity decrease and electrode thinning [32], [65], [86], [102]–[105]. The exact mechanism which leads to the morphological changes in the CL is not fully understood.

TEM analysis allows to investigate the morphology changes during SU/SD [105]–[108]. Several mechanism are proposed [106]. Carbon corrosion can result in a uniform removal of material from the primary carbon particles. This may not lead to dramatic porosity changes. Structural weak or very small particles can be completely removed. Also, the carbon corrosion may start in the center and progresses to the surface of the particles. Further, the authors describe the dissolution of the connection between carbon particles as the *neck-breaking* mechanism. However, this neck-breaking mechanism is not observed in all experiments. The interaction between fuel cell conditions and the other test setups (gas cell and electrochemical cell) are not yet fully developed [106]. Depended on the kinetics, the mechanism may occur in sequence or simultaneously [106]. The neck-breaking and the inside out carbon corrosion majorly cause the collapse of the structure resulting in porosity and thickness changes of the cathode CL [106], [109].

2.3 Degradation of other fuel cell components

The harsh start and stop related conditions accelerate the morphology and ECSA degradation of the CL. Additionally, high potentials, pressure transients, elevated local temperatures, and other stressors may influence the lifetime of the cell during SU/SD experiments. Flow field plate, membrane, and GDL degradation may occur.

The bipolar plate often consists of a graphite composite material. During SU/SD and normal operational conditions graphite offers superior electrochemical and chemical stability. Metal bipolar plates are not as resistant in the fuel cell environment. Modern coatings allow using metal plates with great durability aspects. The literature offers extensive reviews regarding bipolar plate durability [51], [67], [110]–[112].

The (perfluorinated sulfonic acid) membrane may be affected during SU/SD, which leads to durability issues concerning the membrane functions. Typical membrane failures are: the formation of pin holes, cracks, and membrane thinning. Two different mechanisms are identified: chemical and mechanical degradation[44], [66], [108], [113], [114].

The chemical degradation describes the decomposition of the polymer caused by radicals from the dissociation of hydrogen peroxide or formation on the catalyst [115], [116]. The chemical decomposition of the ionomer thins the membrane, the gas permeability increases, causing higher crossover overpotentials. The elevated crossover of hydrogen and oxygen accelerates the formation of radicals. This accelerates the membrane thinning until pinholes and cracks form. Chemical degradation increase at elevated temperatures, OCV holds, and low humidity conditions [117]–[119].

The mechanical degradation of the membrane is caused by mechanical stress due to pressure gradients across the membrane or swelling and shrinking caused by humidity changes, pinholes and cracks result. The direct recombination of hydrogen and oxygen at the defect location elevates the local temperature, causing a propagation of the damage. Mechanical degradation occurs most severe during frequent changes in humidification [120], [121].

The GDL and MPL undergo degradation caused by SU/SD as well. Water induced GDL and MPL degradation is one important degradation mode and may causes severe mass transport losses in the fuel cell. Mérida [122] provided an overview on GDL degradation and described failure pathways. PTFE loss of the GDL is identified as one of the major failure modes of the porous transport layers (PTL). Borup et al. and Seidenberger et al. reported that the PTL failure mode is further assisted by liquid water produced during the reactions [66], [118]. Other groups recently investigated influences of the MPL towards the CL degradation [62], [123]. The MPL influences the carbon corrosion of the CL due to flooding [123]. Isolating the contribution of MPL degradation from the overall cell failure is not well understood. Borup et al. described various diagnostic tools, degradation protocols, and the implementation to gauge the magnitude of the water induced fuel cell failure [66]. In summary, it is important to investigate the morphology and the failure of the MPL to gain a better understanding of water management in the MPL. It is evident from previous research found in the scientific literature that no suitable protocol is available to study the MPL degradation that is influenced by the water flux.

2.4 Research efforts in the literature

The degradation occurring during start-up and shut-down processes retains a multitude of mechanisms.

2.4.1 Start-up and shut-down processes, the propagation of the hydrogen/air front

Start-up and shut-down degradation investigation can be very diverse. Table 2.1 summarizes the research efforts. Dependent on the objective of the work, SU/SD research can involve half-cell experiments with carbon and platinum/carbon electrodes. Full fuel cell research can be separated into two major areas. First, the experimental efforts carried out using potential hold and cycling in an inert atmosphere. Here the cell is purged with hydrogen and nitrogen. The cell potential is cycled between 1 V and various upper potential limits (e.g. between 1.3 V and 1.6 V) using triangular or square wave patterns with different dwell times. Some groups investigated degradation effects holding the cell potential cycling targets the investigation of isolated mechanisms since operational parameters are well controlled. Second, the degradation protocols involve a propagating hydrogen/air front as stressor. The gas front propagation induces more realistic SU/SD degradation mechanism, however, with more degrees of freedom. The cell produces its *natural* elevated and locally different potential. These protocols are later referred to as start and stop protocols, while potential cycling is considered carbon corrosion protocol. The following literature overview will focus on SU/SD degradation investigations, while not excluding potential cycling completely.

Based on the aforementioned complexity, SU/SD degradation mechanisms are difficult to investigate. Many groups investigated SU/SD using reference electrodes and mapped the (local) potential [124]–[128]. Voltages of 1.5 V are observed and in general agreement with the model predictions [86]. Potentials at start procedures are in agreement with the stop process, but the duration of these determinable conditions during shut-downs are extended [126]. This is confirmed

by the simultaneous potential and CO_2 evolution measurements using a novel reference electrode array [127].

Kim et al. investigated a proportional correlation between CO_2 evolution and the occurring potential above 1 V by measuring the CO_2 concentration in the exhaust stream of the cathode [125]. They confirmed longer durations of elevated potentials during shut-downs and a temperature correlation. Longer durations of prominent potentials and elevated temperatures accelerate the occurring degradation due to its faster reaction kinetics.

Other groups investigated SU/SD processes using segmented cell approaches to measure local potentials, and current densities, or in-plane currents [81], [84], [85], [124], [129]–[135]. Current densities of approximately 1 A cm⁻² suggest that multiple mechanisms occur during SU/SD. Aside from the carbon corrosion current, this may attributed to double layer charges, and platinum oxide formation. However, internal currents are dependent on the hydrogen-air ratio and decrease towards the cell's exit.

The local degradation was investigated using an oxygen sensitive polymer sheet in a transparent cell [136]. The duration of the gas exchange may be much slower at the CL, which may be attributed to the gas diffusion in the CL. Degradation occurs mainly at inlet and outlet.

The local influence in lateral direction was the objective of a different group [84], [137], [138]. The degradation of the CL is not only dependent on the distance from the gas inlet, it is also dependent on the channel land difference (of the flow field structure). More degradation occurs underneath the land area possibly caused by a slower gas exchange rate.

Various groups investigated the influence of operational parameter such as temperatures, gas flow rates and humidity. Elevated temperatures result in accelerated degradation caused by faster kinetics [49], [83], [125], [131], [139]. Higher relative humidity during SU/SD cause better proton conductivity in the membrane and accelerates the degradation as well [49], [81], [83], [127], [140]. Some integrated SU/SD-membrane AST also show membrane degradation, this may be related to the humidity cycling during the tests [141]. While higher gas flow rates reduce the duration of the hydrogen-air front in the cell and, therefore, the degradation [49], [83], [85], [135].

Different cycling profiles, as part of a possible mitigation strategy to reduce the amount of degradation, were investigated [82], [90], [127], [129], [130], [142]. Most of these studies involve either a special fuel cell application or an individual system. Oyarce et al. compared different cycle profiles with the objective to reduce degradation using reformat gas [142]. Most of the literature, involving different cycle profiles, however are patent application to minimize degradation [143]–[149]. The effectivity, feasibility and physical mechanisms remain unclear. The comparison of different SU/SD profiles in at common condition and in a standardized test cell are lacking in the literature.

Carbon particle types influence significantly the carbon corrosion rates. Low surface area carbon particles are generally more resistant compared to high surface area carbon [150]. Graphitisation leads to reduced CO_2 evolution and increased carbon corrosion onset potential [97], [150], [151]. This is identified as mitigation strategy to reduce degradation occurring during SU/SD [151].

	Method	Investigation	Reference
1	Reference electrode and potential mapping	Local potentials of 1.5 V are observed and confirm reverse current decay mechanism.	[124]–[128]
2	Segmented approaches, internal currents, local performance and EIS	Internal currents during SU/SD large, which may be caused by capacitive effects and Pt oxidation	[81], [84], [85], [124], [129]–[135]
3	Parametric studies, influence of temperature, humidity and flow rates	Elevated temperatures, higher humidification accelerate the degradation, while larger flow rates reduce degradation	[49], [81], [83], [85], [127], [131], [135], [139], [140]
4	Flow field influences	Diffusion may influence the local degradation under the land area	[84], [137], [138]
5	Different cycle profiles	External load applied reduces degradation. Often not fully investigated	[82], [90], [127], [129], [130], [142]–[149]
6	Material dependencies	Low surface area carbon more resistant compared to high surface carbon material.	[97], [150], [151]
		Graphitisation reduces CO ₂ evolution.	

Table 2.1: Start-up and shut-down literature review.

2.4.2 Catalytic effects of platinum on carbon corrosion

Several groups investigated the catalytic effects of platinum on carbon [56], [93], [95], [152]–[155]. The CO_2 evolution rate during potential cycling significantly increases in the presence of Pt. Further, two effects of Pt are observed. The onset potential of carbon corrosion decrease and two additional CO_2 evolution potentials occur below 1 V.

The proposed mechanism from Maass et al. (eq. (2.6) and (2.7)) requires water. The investigations were done in inert atmosphere and potential cycling. The investigations show a linear dependency of CO_2 evolution and humidification [93]. Further details are described in chapter 2.2.2.

Chapter 3: Experimental methods

This section describes the details of electrochemical and morphological techniques used. One important aspect of this work includes the fuel cell and in-situ hardware development and their commissioning. The design and validation of the segmented cell hardware is described in the appendix A.1. The first results were shown at the Canadian Chemistry Conference 2014 [60], [156].

3.1 Electrochemical analysis

The materials used in this study are summarized in Table 3.1. All materials are commercially available and show no significant performance differences. Parameters of the characterization techniques are reported in Table 3.2.

	Thickness	Loading	Air permeability
Commercially available CCM (reinforced membrane)	18 μm	$0.4 \ / \ 0.1 \ mg_{Pt} \ cm^{-2}$	n.a.
SIGRACET [®] GDL 25BC (with MPL)	235 µm	5 % PTFE	$1 \text{ cm}^3 \text{ cm}^{-2} \text{ s}^{-1}$
SIGRACET [®] GDL 25BA (without MPL)	190 µm	5 % PTFE	$210 \text{ cm}^3 \text{ cm}^{-2} \text{ s}^{-1}$

Table 3.1: Materials used in this thesis.

3.1.1 Fuel cell testing / test station

For fuel cell testing an Arbin 1kW FCATS test station was utilized. Test station temperature and humidity calibrations were conducted prior to the experiments. The supply and control was fully

automated. The ASTs and segmented experiments were conducted using the test bench with accurate humidity, temperature and concentration of the reactants. The test station was modified with a second, heated and humidifier equipped gas supply line (Figure 3.1).



Figure 3.1: Gas supply of the start-up and shut-down experiments.

3.1.2 Segmented cell and multi-channel-characterization-system

The segmented membrane electrode assemblies (MEA) was utilized to study the performance changes using a multi-channel characterization system (MCCS). Each segment of the MCCS is electronically isolated from each other and sealed via nitrile rubber gaskets to each other (Figure 3.2b)). The cell comprises 4x4 segments (Figure 3.2) equipped with a multi-meander flow field geometry.

The MEA was characterized using an in-house built segmented hardware (Figure 3.3 a)[156] and a sixteen channel MCCS [60], [156]. Reactant metering and conditioning were achieved with an Arbin[™] fuel cell test station. Air from the in-house compressor and ultra-high purity hydrogen was used. The MCCS platform is equipped with sixteen independent power electronics channels (i.e.

frequency response analyzers and potentiostat or galvanostat at each channel) to perform electrochemical measurements. The multi-serpentine flow field of the segmented cell comprises sixteen electrically isolated segments in a 4x4 matrix (Figure 3.3 -c). To facilitate the reactant transport, anode and cathode flow fields were: a) designed to build up concentration gradient over successive segments (without intra-segment gradients); b) optimized to provide similar pressure profiles and liquid water removal; and c) assembled in co-flow. Unlike prior works, where the current signals were amplified in the segments [157], [158], the current design does not include any current amplification or additional circuitry. Connecting the cell without an amplifier to the electronic load bank provides flexibility to simulate real conditions.



Figure 3.2: Segmented membrane electrode assemblies (MEA) a) CCM in Kapton frame with laser ablated segmentation on both sides, b) segmented membrane electrode assemblies (MEA) with GDL segments and rubber gasket at the cathode.

3.1.2.1 Segmented membrane electrode assemblies (MEA)

MEAs were laser ablated for segmented cell testing. Commercial catalyst coated membranes (CCMs) of 18 µm thickness were used. The cathode and anode catalyst loadings of the CCM were 0.4 & 0.1 mgPt·cm⁻² respectively. The CCM were cut and laser ablated using Nd:YAG-LASER ('Rofin Sinar Laser GmbH') at the Franhofer ISE facilities (Figure 3.2 a)). For laser ablation, wavelength of the laser source were optimized for the respective CCMs and the transmittance of its membrane was estimated before the laser segmentation (Laser wavelength 1064nm with a power of 7.5 W). Using a laser frequency within the transmittance window of Nafion enabled the ablation of the CL while the membrane is not damaged [12], [159]. A Kapton⁴ frame was placed around the segmented CCM. GDLs were cut and aligned in the segmented CCM. The MEA was then hot pressed using a hydraulic press at the Clean Energy Research Centre (CERC) lab, UBC. Each segment of the CCM was sealed with a nitrile rubber gasket and framed with polyimide film. The segmentation procedure prevents crosscurrent and gas crossover. The porous transport layers (PTLs, SGL 25 BC in this study) comprising the MEA were cut using a die cutter.

⁴ Kapton is a trademark by DuPont, its chemical name is 4,4'-oxydiphenylene-pyromellitimide.



Figure 3.3: Schematics of the multi-channel characterization system a) spatial arrangements of the segment and b) flow field of the cathode and anode

3.1.3 Cell temperature and relative humidity

The cell temperature and dew point of the cell using Vaisala dew point analyzer was monitored at the inlet and the outlet of the cell. Relative humidity of the respective segments was calculated from the dew point temperature. The analyses were repeated several times with a baseline MEA to calculate the average temperature and RH of the cell.

3.1.4 Cell conditioning and crosscurrent testing

Leak testing was done with an assembled cell operating in H_2/N_2 mode. Gaskets ensured no internal or external gas leaks from anode side to cathode side. The laser ablated regions of the active area of the CCM were scanned using a microscope. Any CCM debris present between the two-segmented regions was removed from the MEA. High frequency resistance was measured using impedance spectroscopy between each segment to detect leakage current. Once segments passed the cross current test.

All cells were conditioned at 0.6 V cell voltage at 60 °C and 100 % RH. Ultra-high purity hydrogen and air at a flow rate of 0.5 sl min⁻¹ and 1 sl min⁻¹ was fed to the anode and cathode respectively. After 12 hours of cell conditioning, the BOL characterization took place.

3.1.5 **Polarization curve**

The polarization curve maps the steady voltage response to an operational current. Kinetic, ohmic and mass transport losses can be extracted from the polarization curve. Data acquisition during cell polarization was carried out at constant temperatures, gas flow rates and humidification. The current or voltage were swept from the open circuit potential to 2.4 A cm⁻². The polarization loss (normalised to the original state) is an indicator for the obtained degradation. Voltage decay in low current density regions reflects the activation overpotential loss. Voltage drops in the high current density region reflect carbon corrosion related degradation.

Steady-state polarization curves were acquired after a re-conditioning time of 30 min at a constant voltage of 0.6 V at 60 °C cell temperature. Fully humidified hydrogen and air with flow rates of 2 sl min⁻¹ and 6 sl min⁻¹ were supplied to the anode and cathode respectively. The cell's backpressure was

maintained at 270 kPa and 250 kPa for the anode and cathode respectively. The steady-state cell voltage was recorded from 0 A cm⁻² to 2.4 A cm⁻² for the BOL sample. The polarization curve data acquisition for degraded MEAs was terminated when reaching 0.05 V cell potential. The performance losses in this study are presented at low current density (0.1 A cm⁻²) and high current density (1 A cm⁻²) and represents the voltage difference.

3.1.6 Electrochemical impedance spectroscopy (EIS)

To determine the impedance of the cell, an alternate current (AC) signal is pulsed to the cell and its response was recorded. The relevant parameter such as DC bias potential, frequency range and amplitude were optimized. An equivalent circuit model was used to extract the resistance and capacitance information.

Electrochemical impedance spectra (EIS) measurements were acquired at the cell conditions of the polarization curve measurements. A BioLogic frequency response analyzer (FRA) was utilized for the EIS measurements. Polarization resistance and high-frequency resistance were calculated using an equivalent circuit model (resistance in series with a resistance parallel to a capacitance).

To acquire the spatially resolved EIS spectra a sixteen channel BiologicTM FRA were used in H_2/air mode cell operation. EIS measurements were performed at the individual segments with a 5 mV AC signal superimposed over a 0.85 V bias potential, swept over a frequency range of 10 mHz to 10 kHz. To avoid any anomaly in the EIS signals, a recovery step was performed before the EIS analysis. Load banks of the BiologicTM system are capable of producing quality impedance data at the low frequency. The hardware calibration tests showed negligible skin effect during EIS

measurement. EC lab[™] software was used to analyze the EIS spectra obtained during the ASTs. The EIS spectra were fit to an equivalent circuit model to compute the polarization resistances.

3.1.7 Cyclic voltammetry

Cyclic voltammetry (CV) is used to determine the electrochemical active surface area (ECSA) of the MEA. In an inert atmosphere, the cell potential is swept with a defined sweep rate from low to high potential and vice versa. The corresponding current is recorded and analyzed (Figure 3.4). The area under the hydrogen desorption peak was used to calculate of the ECSA. Linear sweep voltammetry utilizes a similar technique, its range and sweep rate differ from CV measurements.



Figure 3.4: Example of a cyclic voltammogram of a Pt/C electrode in H₂/N₂ atmosphere.

The CV measurements were completed in fully humidified H_2 / N_2 mode at 60 °C cell temperature and flow rates of 0.202 sl min⁻¹ and 0.620 sl min⁻¹ on anode and cathode respectively. The cell potential was cycled between 0.05 V and 1.20 V with a scan rate of 20 mV s⁻¹. A BioLogic potentiostat was used for these measurements. The CV data was iR corrected utilizing electrochemical impedance data. The electrochemical active surface area (ECSA) was calculated via the hydrogen desorption peak. Similar cell and reactant conditions and a scan rate of 5 mV s⁻¹ enabled the acquisition of linear sweep voltammetry data. The cell was scanned from 0.05 V to 0.60 V and not repeated

The spatially resolved ECSA mapping was acquired utilizing similar parameters. CV was conducted to compute the ECSA of each segment of the MEA. The analysis was carried out using H_2/N_2 operating mode. To avoid any distortion in the hydrogen evolution reaction region of the CV, a flow rate of 0.203 and 0.623 slpm of hydrogen and nitrogen, respectively was chosen. The potential of the cathode at each segment was swept simultaneously from 0.05 to 1.2 V versus Normal Hydrogen Electrode (NHE). A sensitivity analysis was also carried out to optimize the nitrogen purging time and scan rates. A scan rate of 20 mV·s⁻¹ was used in all segments. Since this method was sensitive to reactant flow rates, control measurements were carried out to verify the CV results at different temperatures during preliminary analysis. Reliable and repeatable CV spectra (5% error) were obtained at 60° C during the baseline testing. The integration of the area under the hydrogen desorption peak obtained from the CV was used to find the ECSA. The ECSA of each segment was determined from the following expression [57], [160]:

$$ECSA = \frac{Q}{210 \times L \times A} \tag{3.1}$$

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Where Q is the integral area calculated from the hydrogen desorption region, L is the catalyst loading $(mg_{Pt} \cdot cm^{-2})$, and A is the superficial active area of the cathode (cm^{2}) . During the performance evaluation, five cyclic voltammogram was obtained from every segment. ECSA was computed from the last spectra of the CV cycle. The EPSA of the MEA can be presented as [161]:

$$EPSA = 10 \times U_{Pt} \times ECSA \times L \tag{3.2}$$

here $U_{\rm Pt}$ is Pt utilization.

Characterization technique	Parameters (anode / Cathode)		
Polarization curve	Cell temperature: $T_{Cell} = 60 \text{ °C}$ Reactant humidification: 100 / 100 % RH Flow rate: 2 / 6 sl min ⁻¹ Gas mode: Hydrogen / Air Reactant pressure: 250 / 280 kPa		
Electrochemical Impedance Spectroscopy	Cell temperature: $T_{Cell} = 60 \text{ °C}$ Reactant humidification: 100 / 100 % RH Flow rate: 2 / 6 sl min ⁻¹ Gas mode: Hydrogen / Air Reactant pressure: 250 / 280 kPa Bias potential: 0.85 V AC potential: 10 mV		
Electrochemical Impedance Spectroscopy N_2 mode	Reactant pressure: 250 / 280 kPa Cell temperature: $T_{Cell} = 60 ^{\circ}C$ Reactant humidification: 100 / 100 % RH Flow rate: 0.202 / 0.620 sl min ⁻¹ Gas mode: Hydrogen / Nitrogen Reactant pressure: atmospheric / atmospheric Bias potential: 0.45 V AC potential: 10 mV		
Cyclic Voltammetry	Cell temperature: $T_{Cell} = 60 \text{ °C}$ Reactant humidification: 100 / 100 % RH Flow rate: 0.202 / 0.620 sl min ⁻¹ Gas mode: Hydrogen / Nitrogen Reactant pressure: atmospheric / atmospheric Potential range: 0.05 V - 1.2 V Sweep rate: 20 mV s ⁻¹		
Linear Sweep Voltammetry	Cell temperature: $T_{Cell} = 60 \text{ °C}$ Reactant humidification: 100 / 100 % RH Flow rate: 0.202 / 0.620 sl min ⁻¹ Gas mode: Hydrogen / Nitrogen Reactant pressure: atmospheric / atmospheric Potential range: 0.05 V - 0.6 V Sweep rate: 5 mV s ⁻¹		
Cell (re-)conditioning	Cell temperature: $T_{Cell} = 60 \text{ °C}$ @ 100 % RH Flow rate: 2 / 6 sl min ⁻¹ Gas mode: Hydrogen / Air Reactant pressure: atmospheric / atmospheric		

Table 3.2: Characterization techniques and parameters.

3.2 Morphological analysis

3.2.1 Scanning electron microscopy (SEM)

A SEM uses a focused beam of electrons and scans the surface of the carbon fiber samples. To create the images the electrons interact with the atoms of the sample, various reflections of signals are emitted and collected by a detector. The detected signals contain information on surface and topology of the samples. PTL samples will be gold coated before scanning the images. Beginning-of-life (BOL) MEA and end-of-life (EOL) MEA samples from the ASTs were tested using SEM analysis. The changes in thickness and surface morphologies were determined from SEM images.

After the completion of experiments, the individual MEAs were removed from the system. Three samples each from a degraded segment and a new MEA were used for the SEM analysis. Samples were dissected, pre-treated and cast in epoxy resin [59]. The samples were polished prior to imaging with a Philips XL30 SEM to study the CL morphological changes in the MEA.

3.2.2 Transmission electron microscopy (TEM)

The TEM uses a focused electron beam as well. The sample thickness however must be very small. The electron beam transmits through the ultra-thin sample and interacts with its morphology. The diffracted electrons are collected and saved as an image. The resolution is higher compared to SEM techniques but requires a laborious sample preparation. TEM images allow the estimation of Pt particle sizes. Beginning-of-life (BOL) to end-of-life (EOL) comparison of Pt particle sizes allows a different observation of occurring degradation.

Chapter 4: Comparison of SU/SD protocols and spatial distribution of SU/SD

Start-up and shut-down (SU/SD) protocols of PEM fuel cells are neither fully understood nor standardized. The literature reveals a lack of comparable results during SU/SD accelerated stress tests. This chapter reviews the most common types of SU/SD ASTs, conducts these ASTs, and compares the results. The comparison reveals large differences in the degradation behavior. This assists to select suitable SU/SD ASTs for the spatially resolved study and the deconvolution of performance losses.

4.1 Introduction

For automotive applications, fuel cell systems require a fast start-up from any weather condition with minimal hydrogen consumption. Reducing the transient times and energy during start-up or shut-down (SU/SD) of fuel cell stacks are needed to avoid thermal stresses in the membrane. Hence, control strategies and suitable testing protocols are required to characterize SU/SD related failures. Accelerated Stress Tests (ASTs) are used to study failures of catalyst layers (CL) and design new catalyst layer materials. Repeated SU/SD AST enable rapid screening of catalyst components to determine their durability characteristics. It is vital to preserve the durability of the CL in order to reduce the costs or increase fuel cell performance [162], [2], [59], [64], [65].

Platinum dissolution [2], [59] and carbon corrosion [64], [65] from the CL represent areas of concern for the commercialization of automotive fuel cells. Fuel cell SU/SD and fuel starvation events are two major contributors to the corrosion effect. Several SU/SD ASTs are available in the

literature to investigate the carbon corrosion and SU/SD [81], [82], [84]. According to these studies, the corrosion rate increases the performance loss in the membrane electrode assemblies (MEA). Air purging, at both cathode and anode, has been used to start or stop fuel cells [86]. When air is purged into the anode, a hydrogen-air front passes through the cell. This causes mixed potentials and reverses currents within the cell. During startups, hydrogen is fed to the oxygen containing anode, which leads to another hydrogen-air front. Raiser et al. reported a reverse current decay mechanism which leads to high cathode potentials and thus to accelerated carbon corrosion [86].

Severe catalyst layer degradation effects have been reported when the cell experiences uncontrolled SU/SD [81], [84], [86]. Uncontrolled SU/SD cycles increase the voltage degradation. Several fundamental aspects need to be addressed to achieve the targeted lifetime with minimum voltage decay. These aspects include: how the carbon corrosion varies spatially; how the corrosion rate affects the performance of each segment, and what is the mechanism of failure within and across the cell. To develop a universal SU/SD ASTs, a common platform that spatially resolves the voltage loss induced by different SU/SD cycles is needed. This work discusses an electrochemical platform as well as methodologies to compare three different SU/SD ASTs to identify the degradation mode and spatially resolve the voltage loss of the MEA. We correlate durability test data to fuel cell performance.

4.2 Experimental



Figure 4.1: Start-up and Shut-down ASTs a) a Dummy Load incorporated SU/SD-AST [81], b) a Load on/off- SU/SD-AST [84], and c) a Load Ramping SU/SD-AST [82].

We have fabricated non-segmented and segmented fuel cell hardware to compare the effect of the SU/SD cycling in a fuel cell MEA. The design details of the hardware are reported elsewhere [2], [60], [61], [156]. To examine the degradation induced by SU/SD cycles, MEAs with an active area of 49 cm² [2], [60], [61], [156] were assembled in a non-segmented cell (Figure 4.2). The test station was modified with an additional bubble humidifier for the reactant gases to run SU/SD ASTs. Solenoid and check valves were installed upstream of the fuel cell to switch the reactant gases. All MEAs were subjected to three different SU/SD ASTs. The details of the SU/SD cycles used in this study are shown in Table 4.1 and Figure 4.1.

	A (dummy load)	B (Load cycle)	C (Load ramping)
Total cycle time	80s	900s	220s
Time to 5% performance loss (@ 0.1 A cm ⁻)	12.2 h	62.5 h	51.9 h
Was load applied during SU/SD?	Yes	Yes	Yes
Strategy employed to minimize degradation			

Table 4.1: Comparison of Start-up and shut-down accelerated stress tests



Figure 4.2: Common non-segmented and segmented PEM fuel cell test platform.

4.2.1 **Test protocols**

All MEAs were conditioned at 60°C cell temperature and 100% relative humidity (RH). The conditioning details are shown in Figure 4.3. All three SU/SD ASTs switch the load and reactant gases off during shut-downs. During startups, the fuel cell ran at open circuit potential or (dummy-) 51
load with humidified air at the cathode side and humidified hydrogen for at least 20 seconds. Controlled baseline experiments on SU/SD were conducted to verify each SU/SD ASTs (shown in Figure 4.3 and Table 4.1). The SU/SD ASTs were repeated to verify the reproducibility of the findings. Electrochemical characterization such as steady state cell polarization and cyclic voltammetry is done periodically between ASTs (Figure 4.3). After each set of SU/SD ASTs, the cell was kept at a constant voltage for 15 minutes before the polarization analysis and cyclic voltammetry (CV) to recondition the MEA. A CV analysis was used to compute the electrochemically active surface area (ECSA) of the Pt in the catalyst layer [2], [61]. The cell was swept between 0.05 and 1.2 V with a scan rate of 20 mV s⁻¹ in H₂/N₂ mode. The spatial potential mapping of the cathode was done for Cycle A using a 49 cm² (4x4) segmented cell. The schematics of the in-house built hardware are shown Figure 4.2. The details of the segmented cell hardware and operation procedures are described elsewhere [2], [60], [61], [156], [163].



Figure 4.3: Characterization protocol.

4.3 Results



Figure 4.4: Polarization curves of non-segmented test cell experiments of the three different SU/SD protocols a) Dummy Load incorporated SU/SD-AST, b) Load on/off- SU/SD-AST and c) Load

Ramping SU/SD-AST.

4.3.1 Cell polarization measurement

The polarization curves are measured for all three SU/SD ASTs at 60 °C and 270/250 bar_g, (Figure 4.4 a, b and c). The cell voltage degrades for all three SU/SD-AST during testing compared to their BOL. However, closer comparison (Figure 4.5) of the EOL curves with the BOL of all three protocols showed a larger mass transport overpotential. Large mass transport overpotential may have contributed to the Pt dissolution and carbon corrosion from the catalyst layer [81], [84], [85]during repeated SU/SD events. The cell voltage decay is measured from the polarization curve at a current density of 0.1 and 1.4 A cm⁻² after n cycles. The difference in voltage loss is computed from equation (4.1).

$$Voltage \ Loss\left(\%\right) = 100 \times \frac{V_{BOL_{at0.1A\,cm^{-2}}} - V_{n \ cycles_{at0.1A\,cm^{-2}}}}{V_{BOL_{at0.1A\,cm^{-2}}}}$$
(4.1)

At 0.1 A cm⁻², the cell performance decay of 5 % is observed after 12.2, 62.5, and 52 hours of total experimental time for all SU/SD-AST, respectively. It is evident that the load on/off SU/SD-AST shows higher voltage degradation than the other two SU/SD ASTs. Higher voltage degradation is observed mainly at the kinetic and mass transport regions at shorter experimental time for the dummy load incorporated SU/SD-AST (Table 4.1). Similar cell polarization losses were reported by Kim et al. for the dummy load incorporated SU/SD-AST [81]. However, the composition of the MEA, cell conditioning procedure and size of the cell may have resulted in variations in the polarization measurement compared to Kim et al. [81].

4.3.2 Electro chemical active surface area measurement

The electro chemical surface area (ECSA) (Figure 4.5) was calculated from the hydrogen desorption peak of the cyclic voltammogram. The ECSA loss is computed using equation 2 after each cycle.

$$ECSA \ Loss\left(\%\right) = \frac{ECSA_{BOL} - ECSA_{n \ cycles}}{ECSA_{BOL}} \times 100 \tag{4.2}$$

A plot of percentage ECSA loss vs. percentage voltage loss is shown in Figure 4.5 for all three cycles. At low current density (Figure 4.5 a), all three SU/SD ASTs show a linear relationship between ECSA and the measured cell voltage loss from its BOL. The ECSA loss increases rapidly all three experimental protocols. The ECSA loss of 80% was observed for the load on/off SU/SD-AST. The final ECSA loss of the dummy load AST is 70% of its initial value and 50 % for the load ramping AST. The corresponding voltage loss from its BOL value for the load cycle AST is eight percent. The Voltage losses of the dummy load and load ramping ASTs are 3 % and 2.7 % respectively. The dummy load and load ramping SU/SD ASTs showed similar ECSA and voltage loss rate response at low current density.

Figure 4.5 b) shows the empirical correlation of ECSA loss to the cell voltage loss at 1.4 A cm⁻². The relationship between ECSA and cell voltage loss are not linear for dummy load added SU/SD-AST and the load on/off SU/SD-AST at higher current densities. These SU/SD ASTs show exponential changes until it reaches the EOL. The decay rate of cell voltage and the degradation rate of the ECSA are different for these two SU/SD ASTs. The percentage voltage decay of the MEAs in their EOL (550 cycles) states after being subjected to SU/SD ASTs are approximately 45, 18 and 3 %. These voltage losses arise due to the frequency of gas switching and load changes. Figure 4.5 a and b

show relatively small losses in cell performance at 0.1 A cm⁻², but considerably more degradation is observed at 1.4 A cm⁻². The degradation rate of the dummy load incorporated AST is higher than load ramping SU/SD AST. The cycle profile results of the SU/SD protocols are similar to a combination of Pt dissolution and carbon corrosion potential cycling profiles. Load ramping SU/SD-AST expresses lower performance loss induced by carbon corrosion and demonstrates a higher resistance to performance losses related to Pt dissolution. Hence, the rate of degradation of the MEA by catalyst failure is less. Local variation in the cell operating parameters, cycling profile, variation in the potential during SU/SD, variation in the cell temperature across the cathode and relative humidity variation could be reasons for differences in cell and ECSA loss during ASTs.



Figure 4.5: ECSA loss during all three SU/SD-ASTs.at a) low current density and b) high current

density.

4.3.3 Spatial distribution of start-up and shut-down protocols

To investigate the spatial variation in the cell voltage and ECSA loss across the MEA, we performed dummy load incorporated SU/SD-AST in a sixteen channel segmented cell. MEAs were laser ablated into sixteen segments. We conducted polarization and CV analysis at each segment simultaneously at regular intervals during the AST. Figure 4.6a) shows the spatial voltage loss computed from the BOL and EOL polarization curves at 0.05 A cm⁻². We observed the variation in the potential between segments during SU/SD. The direction of the gas flow as 4x4 cell (serpentine flow field) and the voltage loss are shown in y, x and z directions respectively. The changes in gas flow rate and pressure across the flow field affect the cell voltage loss. Higher voltage and ECSA losses (Figure 4.6 b) were observed near the exit segments. The amount water accumulated through the exit sections of the MEA, the impact of the gas switching may have induced chemical dissolution of catalyst and resulted in the performance decay.



Figure 4.6: a) Spatial voltage loss for the low current density region and b) ECSA loss after the Dummy Load incorporated SU/SD AST.

4.4 Summary

The importance of identifying suitable start-up/shut-down accelerated stress tests (SU/SD-ASTs) was demonstrated in a common fuel cell test setup. Three different SU/SD- ASTs were investigated. Differences in the gas switching rate and load ramping affected the cell polarization measurement in all three tests. After 550 cycles, each of the SU/SD- AST showed 20, 45 and 3% voltage loss at high current density. Longer gas switching time induced a larger hydrogen/air front at the anode during the load on/off SU/SD- AST. This may have attributed to the higher (45%) voltage loss. The rate of consumption of residual hydrogen in the flow field is fast during the load ramping SU/SD-AST. This led to a smaller area of the hydrogen/air front and 3% (lowest) voltage loss at high current density. On the other hand, a dummy load cycle showed a delay in the hydrogen consumption rate during SU/SD- AST. The residual hydrogen is consumed only when the dummy load is applied. This delay may have extended the hydrogen/air boundary and accelerated the degradation (20% voltage loss) during SU/SD- AST. The faster cycling time and the moderate Pt dissolution and carbon loss observed in a dummy load added SU/SD- AST compared to the two other tests prompted us to spatially resolve the durability components of the catalyst layer. We observed higher losses in cell voltage and catalyst surface area near the exit segments of the fuel cell membrane electrode assembly.

Chapter 5: Deconvolution of the performance losses to study the degradation mechanisms of start and stop events

Two major degradation mechanisms are well known in the literature. One mechanism affects the Pt catalyst, while the other degrades the carbon substrate. The exact amount of performance loss during SU/SD ASTs remains difficult to decipher. Identifying the performance loss participation may allow a deeper understanding of the occurring degradation mechanisms during SU/SD events. In this chapter one of the SU/SD ASTs from the comparative study was further analyzed. The performance losses were deconvoluted.

5.1 Introduction

Carbon supported platinum nanoparticles remains the most frequently used PEM fuel cell catalysts for the oxygen reduction reaction (ORR). The catalyst layer consists of porous carbon support, platinum particles, and ionomer. The major function of the catalyst layer (CL) at the cathode is to overcome the activation barrier of the ORR. Also, the CL needs sufficient supply of oxygen, protons, and electrons; and must expel product water and heat at satisfactory rates. Therefore, a healthy and durable CL is the primary goal to enable PEM fuel cell operation. Operational factors like temperature, humidity, pH, and electrochemical potential influence CL degradation. Two major degradation mechanisms are well known in the literature: one mechanism affects the Pt catalyst, while the second degrades the carbon substrate. Platinum dissolution, sintering, and redeposition reduces the active surface area for the ORR [2], [34], [59], [61] while carbon corrosion changes the morphology of the CL [64]–[66], [105].

Mobile and automotive fuel cell application are prone to frequent system start-up and shut-down (SU/SD) events. Safety and durability requirements recommend purging unused hydrogen from the system. Air is used instead of an inert gas for purging; a nitrogen supply does not meet cost and packaging requirements. The propagation of a hydrogen/air front causes large local mixed potentials [86]. These large overpotentials at the cathode induce accelerated carbon corrosion[91] (eq. (2.4) (2.5) and eq. (2.7)):

The presence of Platinum may affect the carbon corrosion [91]. The exact mechanism(s) of carbon corrosion is not yet fully understood. The catalytic effect of platinum on the CO_2 evolution was proposed by Maass et al. (eq.(2.6) and eq.) [93]. An OH-like species reacts with carbon surface oxides, whereby Pt acts as a catalyst.

Several studies have been undertaken to investigate SU/SD induced degradation[84], [140]. Reference electrode measurements mapped the cathode potential during start and stop scenarios [124]–[128]. The measured potentials are in general agreement with model predictions [86]. The CO_2 concentration in the cathode exhaust behave, above 1 V cell voltage, proportional to the occurring potentials [125]. However, the exact mechanisms remain controversially discussed.

It is important to distinguish the performance losses occurring during SU/SD to understand the degradation mechanisms. Dhanushkodi et al. developed an empirical model to link the carbon loss to the occurring performance loss and applied this model to various potential cycling AST [64].

However, they have not demonstrated their deconvolution technique on different degradation data featuring realistic SU/SD conditions.

In the present study, we report on the source of performance degradation SU/SD ASTs. The objective is to deconvolute the degradation (voltage decay at high current densities) of the cathode CL due to carbon corrosion and non-carbon corrosion related degradation separately. The non-carbon related losses comprise Pt dissolution and CL ionomer degradation. The present study assumes the Pt dissolution to be dominant. A carbon corrosion fingerprint, an empirical model, [64] was applied to separate the voltage decay caused by carbon corrosion.

5.2 Experimental

5.2.1 Membrane electrode assembly preparation

All experiments in this study used commercial catalyst coated membranes (CCM). The sample thickness of the CCM is 18 μ m with a catalyst loading of 0.4 and 0.1 mg cm⁻² for the cathode and anode catalyst layer respectively. The CCM was hot pressed between gas diffusion media equipped with a microporous layer (SGL 25 BC) on either site.

5.2.2 Test platform

The common characterization platform consists of a nine channel serpentine flow field cell with an active area of 49 cm² and a modified Arbin fuel cell test station. The test station achieves the reactant delivery and humidification. The test station was upgraded to deliver a third humidified and heated gas stream to the cell (see 3.1.1). The humidification of the gas path was configured to provide 100% RH, monitored with a Viasalla dew point sensor. A dual gas inlet, equipped with

check valves was integrated into the gas path at the anode inlet. All lines and valves were heated to prevent condensation of the saturated gasses.

5.2.3 Start – stop accelerated stress tests

Three different SU/SD accelerated stress test (AST) protocols were investigated prior to this study [1]. All AST's include air/hydrogen gas changes at the anode and were adapted to common cell and test station conditions. Temperatures, gas humidities and gas delivery rates were kept constant, if not otherwise specified. The CO_2 evaluation was adapted from the literature [91]. The experiments begin with conditioning, beginning-of-life (BOL) characterization, SU/SD AST cycling with periodic characterization until the end-of-life (EOL) is reached.

5.2.4 Carbon corrosion accelerated stress test

The applied carbon corrosion AST comprised voltage cycling (1.0 - 1.4 V) in hydrogen/nitrogen atmosphere. The square wave profile utilized dwell times of 5s / 5s. The cell was supplied with fully humidified nitrogen and hydrogen at 6 sl min⁻¹ and 2 sl min⁻¹ for cathode and anode respectively. This experiment was utilized to confirm the carbon corrosion finger print parameter from the literature with the different cell hardware.

5.2.5 Effective diffusivity

The effective diffusivity of oxygen in the CL was calculated using a limiting current density approach. At the limiting current density, the rate of oxygen consumption equals the rate of oxygen delivery to the CL [164]–[166]. The effective diffusivity of oxygen is calculated using equation (5.1).

$$i = D \ \frac{nF\left(C_{B} - C_{S}\right)}{\delta},\tag{5.1}$$

where i represents the current density, n the amount of electrons used in the reaction, δ the thickness of the CL, and F Faraday's constant. C_B represents the bulk concentration and C_s the concentration at the catalyst sites. At limiting current (i = i_L) condition, no oxygen concentration at the catalyst (C_s = 0) is available.

5.3 Results and discussion

5.3.1 Selection of accelerated stress test cycle profile

The three SU/SD ASTs results from Chapter 4: show well-differentiated MEA degradation patterns. Figure 5.1 a) displays the differences in performance losses between BOL and EOL versus current density for the three different SU/SD AST protocols. All protocols show accelerated degradation at low current densities, but only SU/SD AST protocols A and B demonstrate significant performance decay in medium and high current densities respectively. The voltage loss behavior of the SU/SD AST protocols A and B indicate losses which can be attributed to carbon corrosion. The voltage stepping mitigation strategy of SU/SD AST protocol C reduces the carbon corrosion related performance decay significantly. The voltage loss, compared to SU/SD AST protocol A, at high current density of AST protocol B is approximately 15 % higher. The hydrogen/air front remains the only SU/SD related stressor in this SU/SD AST. The following investigation towards the deconvolution of performance losses at high current density will use SU/SD AST protocol B. SU/SD AST data in the following paragraphs will refer to the SU/SD AST protocol B.

In Figure 5.1 b) shows the polarization curves of SU/SD AST (protocol B) from BOL to EOL. Figure 5.1 c) and d) show the voltage loss at low (0.1 A cm⁻²) and high (1.0 A cm⁻²) current densities versus the number of cycles to analyze the degradation in more detail. The voltage degradation is exponentially increasing for low current densities while high current densities show pronounced exponential voltage decay. At EOL, the performance loss at low current densities is 8 % and approximately 25 % at high current densities.



Figure 5.1: Performance behavior of the start and stop cycles: a) Voltage loss differences (V_{BOL} - V_{EOL}) versus current density of ASTs A, B, and C; b) Polarization curves of AST B from beginning-of-life to end-of-life; c) Voltage loss versus the number of cycles at 0.1 A cm⁻² of AST B; d) Voltage loss at 1 A cm⁻² of AST B.

5.3.2 Carbon corrosion fingerprint

This study implemented a previously reported empirical carbon corrosion model [64]. The carbon corrosion fingerprint equation (5.2) relates the carbon corrosion induced performance loss to the carbon mass loss. The exponential behavior of the model is dependent on the CL material only. The

objective of the carbon corrosion AST (voltage cycling) in this study is to confirm the hardware independence of the fingerprint from the literature.

$$y = A e^{B x}$$
(5.2)

Figure 5.2 shows experimental results of the carbon corrosion AST and the carbon fingerprint adapted from the literature. The parameter of the fingerprint and the carbon corrosion AST of this study are tabularized in Table 5.1. Both cells from this work and from the literature have approximately the same dimensions, operational conditions, and catalyst loadings but different flow field geometries. The results suggest that the fingerprint reported in the literature is independent from the hardware.



Figure 5.2: Carbon corrosion fingerprint reproduced in this work using a 1 V - 1.4 V, 5s/5s square wave carbon corrosion AST compared to the results reported by Dhanushkodi et al.

5.3.3 Start-up and shut-down experiments

Figure 5.3 shows the performance loss at high current density versus the carbon mass loss of the SU/SD AST experiments. The data follows an exponential trend reaching circa 25 % performance loss at 45 % carbon mass loss. The results of the SU/SD AST can be mathematically expressed (equation (5.2)) and the trend remains similar to the carbon fingerprint. Table 5.1 summarizes the parameters of the fingerprint equation from literature, the reproduced fingerprint equation from the carbon corrosion AST and the SU/SD AST.



Figure 5.3: Performance loss versus carbon loss for SU/SD cycle B.

Figure 5.4 presents the voltage loss at high current density versus the carbon mass loss of the SU/SD AST and the carbon fingerprint. The degradation behavior of the SU/SD AST shows more performance loss compared to the carbon fingerprint at similar carbon loss. A second, non-carbon corrosion related performance decay is evident in the data. Further, the SU/SD AST behavior illustrates a different exponential coefficient. By subtracting the carbon related losses from the SU/SD AST data the non-carbon related losses at high current densities can be quantified. The non-carbon related curve increases slightly until reaching a maximum. After the maximum, the percentage of non-carbon related losses decrease. There are multiple reasons for this percentage decrease. First, the carbon loss increases exponentially whereas the non-carbon related losses do not follow such rapid growth. Pt dissolution investigations in the literature show rapid performance and

ECSA decay initially; during the experimental propagation the rate of performance and ECSA loss decreases until reaching a plateau [59], [167]. The ratio of carbon to non-carbon related losses changes with progression. Second, oscillatory effects may originate from subtracting the two empirical exponential expressions. Both the carbon fingerprint and the SU/SD AST data show errors (see R^2 in Table 5.1). This uncertainty can be magnified at high losses because the data density decreases.

Pt catalyst degradation is assumed to be mainly responsible for the non-carbon related performance losses since Pt dissolution, and carbon support corrosion are the major degradation mechanism in the CL [66]. Pt dissolution can occur electrochemically or chemically from the metal phase. Ionomer degradation remains the third possible degradation mechanism; however the temperature and RH conditions during the SU/SD AST suggest only minor ionomer degradation in the CL. It is also assumed that membrane degradation does not occur during this degradation study [59], [64]. The LSV measurements (not shown) confirm negligible hydrogen crossover current increases. Thus, membrane failure as one reason for the higher performance loss can be excluded.

Table 5.1: Parameter of the carbon fingerprint from the literature reproduced fingerprint and the start and stop AST.

	А	В	R^2
Carbon fingerprint [64]	0.025	0.13695	0.98
Carbon corrosion test in this study	0.03616	0.13528	0.94987
Start and stop AST, cycle profile B	1.21057	0.06383	0.71787



Figure 5.4: Performance loss versus carbon loss data of the start and stop AST (cycle profile B) compared to the carbon fingerprint and the deconvoluted non-carbon related performance loss.

We will examine the time dependence in the next section. Figure 5.5 shows the degradation at high current densities of SU/SD AST as a function of time. The carbon fingerprint relates the performance loss induced by carbon corrosion to the occurring carbon loss. This empirical model is independent of the cycle repetition. The total degradation of the SU/SD AST and the carbon-related degradation show exponential growth versus cycle repetitions. The non-carbon related degradation behaves linearly until it reaches a peak (circa 9.8 %). The carbon related loss starts to be dominant loss mechanism at this peak. The deconvolution of SU/SD AST protocol A show similar trends (not shown).



Figure 5.5: Total performance loss, carbon corrosion induced and non-carbon induced performance loss at high current density during start and stop AST cycle B versus the number of cycles.

TEM was used to analyze the morphology of the BOL and EOL samples. Figure 5.6 shows the images of the cathode CL, comparing the BOL to the EOL. The Pt particles in Figure 5.6 a) are dispersed homogeneously. Most of the Pt particles were found to be primary particles. Only a small number of agglomerates can be seen. The porous carbon structure before the SU/SD AST is well defined and the pores are visible. The porous structure at the EOL stage may be compacted, no pores remain visible. A lower number of Pt particles are found in the CL while Pt particles agglomerate to larger, often "L- or T-shaped" clusters. At the membrane-CL interface small spherical Pt particles are observed. This occurrence is not visible for BOL samples. However, distinguishing between coalescence and Ostwald ripening is difficult. Smaller Pt particles in the

membrane appear close to the membrane/CL interface. A strong Pt band formation can be identified in the membrane near the cathode CL. Larger, often "cubic- and star- shaped" particles (Figure 5.6 b)) are observed at the in the Pt band. Severe Pt dissolution occurs during SU/SD AST (Figure 5.7). The image analysis supports that the remaining performance decay potentially originates from the Pt dissolution. Large Pt particle size distribution changes in the vicinity of the membrane are observed.



Figure 5.6: TEM images of a) the BOL cathode catalyst membrane interface, b) of the EOL catalyst membrane interface.

Figure 5.8This study relates the performance losses to CL properties. Figure 5.8 a) shows the noncarbon related performance loss at high current densities versus the number of cycles. The noncarbon related performance loss is well represented by the performance loss at low current density. The polarization resistance data shows significant increases during the SU/SD AST. The resistance increases from approximately 0.25 Ohm cm² to 2 Ohm cm². The resistance increase rate supports the low current density performance loss degradation. The ECSA loss illustrates an exponential trend; initially with a high loss rate and later with an almost stagnant rate reaching approximately 85 % ECSA loss. The increasing performance loss at low current density relates directly to the ECSA loss. The low current density performance loss and ECSA loss behavior is in general agreement with the literature [59], [167].



Figure 5.7: Pt particle size distribution of the cathode CL of the BOL and EOL sample unsing TEM imaging.

Decreased mass transport properties may increase the non-carbon induced losses at high current densities [105]. At circa 300 cycles, the ECSA loss starts to stagnate. The amount of active Pt sites available for protons, electrons, and reactants remain similar while the non-carbon related performance loss increases. The changes of the oxygen diffusivity in the CL and the carbon induced performance loss in Figure 5.8 b) supports this interpretation.



Figure 5.8: High current density performance losses: a) non-carbon induced performance loss versus number of cycles related to ECSA loss, low current density performance loss, and polarization resistance, b) carbon corrosion induced performance loss versus number of cycles related to the effective diffusivity of oxygen in the catalyst layer (not considering a CL thickness change) and the limiting current density. The dotted line represents the BOL and EOL value of the effective

diffusivity accounting a thickness change of the CL.

Figure 5.8 b) presents the carbon corrosion related performance loss at high current densities versus the number of cycles. The carbon corrosion induced performance loss was related to the limiting current density, which decreases as the performance loss increases. The graph correlates this performance loss with the effective diffusivity of oxygen in the CL. The effective diffusivity was calculated using a limiting current density approach (eq. (5.1)). The influence of the GDL / MPL was neglected. Further is assumed, that the active sites are only present at the CL / membrane interface and a limitation of the effective diffusivity correlation. The effective diffusivity approach demonstrates the exponential trend, which corresponds to the carbon corrosion, induced performance loss. Effective diffusivity values of oxygen in the cathode CL at BOL are in general

agreement with the literature[168]. The diffusivity decreases from $4 \ge 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ to 2.5 $\ge 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, a change of approximately 40 %. The dotted line shows the diffusivity values from BOL and EOL with regards to a CL thickness change of 50 %. At EOL, a diffusivity of $1.25 \ge 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ represents a loss of circa 68 %. The CL thickness was evaluated via SEM at BOL and EOL. The invasive nature of thickness estimations limits the measurements to CL thicknesses at BOL and EOL and EOL only. At circa 300 cycles the oxygen diffusivity and carbon corrosion related performance loss start to increase significantly. The morphology of the CL may start to be significantly affected which affects the performance loss.

5.4 Summary

This study linked carbon loss and performance loss to SU/SD ASTs in polymer electrolyte membrane fuel cells. The mechanisms of performance loss were related to the time dependence during the SU/SD AST propagation. The losses occurring during the SU/SD AST were deconvolved into carbon and non-carbon related losses. The deconvolution concludes that Pt dissolution is responsible for the performance loss initially, after further progression of the AST carbon corrosion becomes dominant. The performance loss was related to the structure and properties of the CL. Initially, irrespective of the current density, the non-carbon related performance loss is 5 %. After further progression of the SU/SD AST the non-carbon related performance loss increases to 9.8 % and is attributed to Pt dissolution. Analysis of the ECSA loss and the effective diffusivity loss of oxygen in the CL suggest that a morphological change of the catalyst structure causes the greater non-carbon related performance loss. TEM analysis further supports this conclusion. The porosity of the CL has changed significantly. The oxygen diffusivity in the CL decreases by 68 %.

Chapter 6: Spatially resolved degradation: Platinum dissolution

The developed segmented cell hardware, the MEA segmentation procedure, and the multi-channel power electronics form a unique multi-channel characterization system (MCCS). The MCCS was utilized to spatially resolve a platinum dissolution accelerated stress test. This study has not been reported in the literature before.

6.1 Introduction

Carbon supported Pt nanoparticles represent the most stable electro-catalysts for the polymeric electrolyte membrane fuel cell in automotive applications [59], [64], [65]. The cost of the platinum, durability of the catalyst layer (CL) and degradation of the CL components poses a significant challenge for the commercialization of fuel cell technology [169]. To attain the targets, the fuel cell industry requires improved models and correlations for catalyst layer degradation and the related degradation processes. AST is the primary tool for investigating PEMFC durability in reasonable timescales; yet, designing AST protocols that target specific degradation mechanism remains challenging. One of the objective of the DOE targets is to find and develop a suitable protocol that can reduce the oxygen reduction reaction (ORR) current on the catalyst by a factor of 1000 [170]. Operational gradients such as temperature, humidity and reactant concentrations prevail over an active area; these may yield variation in degradation rates. The way in which such degradation is distributed over the active area or the MEA is not well understood. The impact of the ORR current may not be uniform across the MEA. Mapping cell potential, ORR current, component resistances

and active area across the catalyst layer can be an innovative strategy to study and understand the CL failure.

The potential cycling AST methods can increase the kinetic overpotential of the cell. Effective Pt dissolution ASTs can be developed by varying the dwell time, pulse shape, upper, and lower cycling voltage [59]. To study the durability of the catalyst layer, drive cycles such as the federal urban driving schedule are mimicked to degrade the CL [66]. During the drive cycles, the power density of the fuel cell stack varies from idle to peak load. Due to the fluctuations in the power density by ASTs and start-up / shut-down transients, the potential across the cell varies. This results in severe catalyst dissolution and agglomeration [170]. Pt dissolution is accelerated by the number of potential cycles, temperature, relative humidity, cycle profile and the frequency of the cycles [53], [171]. The cycle profile depends on wave pattern, scan rate, upper and lower limit of the cell. The upper and lower potential for the higher chemical and electrochemical Pt dissolution are identified as 0.6 and 1.0 V, respectively [172]. The impacts of the square wave potential cycling, the electrochemical system parameters, variables and the morphological changes on fuel cell MEA were reported by several authors [66], [172], [173]. Electrochemical diagnostic tools such as CV and polarization curves are used to analyze the Pt dissolution rate and the performance loss [57]. However, to develop and optimize the catalyst layer, the spatially resolved voltage and Electrochemical Platinum Surface Area (EPSA) loss across the cathode of the MEA are required. To our knowledge, no reports on the spatially resolved fuel cell performance indicators are available for the Pt dissolution AST.

In this work, segmented cell techniques were used to address the fundamental aspects of the nanoengineered fuel cell catalysts. The specific objectives were: a) to demonstrate how the heterogeneities in EPSA affect the cell performance and the durability of the cell across the MEA; b) to investigate the Pt dissolution rates and their impact in the individual segment; and c) to present a method to characterize CL component durability for a segmented cell and show the dominant parameters that can influence the fuel cell failure across the MEA. This work provides a new multi-channelcharacterization-system (MCCS) and a diagnostic procedure to spatially characterize the catalyst layer degradation of the MEA. Pt dissolution ASTs were conducted for ten thousand cycles, using an electronically insulated MEA within a segmented cell. This approach makes it possible to assess the cell voltage and the EPSA across the area of the CL.

6.2 Experimental

6.2.1 Pt dissolution accelerated stress test

The rationale behind the choice of operating parameters has been discussed in detail inChapter 2:. The amplitude of the wave, input waveform and the dwell periods at which the cell voltage was held at the upper (V_H) and lower (V_I) potentials determine the Pt dissolution rate. We aimed to develop a protocol for the segmented cell based on the following criteria: a) a protocol to yield a higher electrochemical active surface area (ECSA) and mass activity losses; b) an optimized dwelling time to effect higher surface coverage on the Pt in the CL; and c) a upper and lower potential to higher Pt dissolution with minimum carbon loss. Several studies have reported higher rate of Pt dissolution when MEAs was cycled with a square wave voltage signals than with triangular waves. Hence, the square wave input waveform was applied in the current study in all the segments. A dwell period of 5 s at each of the upper and lower limits was selected based on the literature [59], [65]. The

application of cell voltages from 0.6 - 1.0 V is a well-documented potential cycling window for assessing Pt dissolution for automotive applications. Therefore, each segment of the MEA was cycled between 0.6 V and 1.0 V with a square wave profile to induce degradation in the catalyst layer. This AST was done at 60°C, 100% relative humidity in H₂-N₂ mode. Further, the spatial distribution of the Pt loss induced by the AST was compared and contrasted with Dhanushkodi et al. [59] on Pt dissolution AST in a non-segmented cell. Two runs of the calibration phase experiments were completed using a laser ablated segmented MEA. The reproducibility of the temperature and RH was calibrated during a baseline testing.

6.2.2 Recovery

After completion of cell conditioning and end of cycle (500, 1000, 2000 and 10000), segments were disconnected. Nitrogen was purged at the cathode at a rate of 1 slpm to remove the water accumulated in the sections during AST. The cell was reconditioned for 2 hours prior to running cell diagnoses.

6.3 Results and discussion

6.3.1 Cross Current and Sample heterogeneities

EIS analysis of the crosscurrent testing show large high frequency resistance (HFR), measured at 10 kHz, between segments for the BOL MEA. HFRs above 1000 Ohm suggest absence of leakage current between segments and qualify the segmentation procedure employed in this study. To check leakage current between the segments of the MEA, a multimeter is connected and DC current is measured. The results suggest the absence of the leakage current between each segment to segment.

The objective of the current study is to cycle the potential at the cathode catalyst layer between 0.6 V and 1.0 V for every 5 s. A load is drawn through a load bank from the MEA when it is held at 0.6 V. During the extraction of the load, iR drop occurs. The actual cathode catalyst layer potential will be higher than the voltage measured across the cell due to an iR drop. Hence, it is important to adjust the iR corrected cell voltage to cycle the MEA during testing. The iR corrected value is measured and periodically fed to the program, in order to cycle the cell at the appropriate potential window. The measured ECSA values for the BOL segments show acceptable variation (\pm 5%) from an average ECSA value of $65 \pm 3.0 \text{ m}^2\text{g}^{-1}$ was computed for all the segments from the CV analysis. The CV of beginning-of-life (BOL) of each segment is displayed in Figure 6.1. The difference found in the CV spectrum from each segment may be due to the a) difference in the conditioning period, b) catalyst dispersion, c) sample to sample variability, d) operating parameters, and e) impact of the laser ablation on the individual segments. This suggests that the BOL ECSA values are acceptable to investigate spatial resolution of Pt dissolution in the catalyst layer. EPSA is calculated using Equation (3.2) and then normalized to its BOL value to assess the variation in ECSA during degradation studies. The difference and significance of the ECSA and EPSA values are reported elsewhere [59].



Figure 6.1: Cyclic voltammogram of the each segment at BOL.

6.3.2 EPSA loss during AST

To discuss the variation in the EPSA (Figure 6.2), the MCCS is classified as the inlet (segments 1- 4), middle (segments 5-12), and outlet (13-16) regions (Figure 3.3-c). The rate of EPSA loss is higher during the first 500 cycles at all three sections during the entire AST. Higher magnitudes of EPSA loss are calculated at the segments near the reactant outlet. Inlet sections of the segments show lower degradation. The EPSA loss determined at the inlet sections decrease by 46% after 10000 cycles of AST. For the middle segment sections, the EPSA loss decreases from 223 to 118 cm² Pt/ cm² (an average of 53% loss from its BOL value). EPSA in the middle segments did not level off

uniformly. The loss of EPSA at the exit region is higher compared to the inlet and middle regions. The EPSA drops from 221 to 132.6 cm² Pt/ cm² (60% loss) for BOL to end-of-life (EOL) of the MEA, respectively due to the AST. This suggests that the rate of EPSA loss occurred during the AST is not homogenous across the MEA. The computed EPSA loss values are not uniform for all the segments. A value of 65% EPSA loss is calculated at the last segment (segment sixteen). The difference in the EPSA loss between each segment is unusual especially when a same square wave potential cycling is applied at the isothermal (T = 60° C), saturated (100 % RH) and inert conditions (nitrogen atmosphere). The difference in the EPSA loss of the EOL outlet segment 16 increased to 21% from that of the segment 1. The difference in EPSA loss may be due to the shift in the local conditions in the segments (Figure 3.3-d). Both temperature and relative humidity varies linearly from the inlet to outlet segments of the hardware. These two factors could have attributed to different Pt dissolution rates; in addition, a) pressure drop across the segments; b) water accumulation between the segments (from a slight decrease in gas temperature from inlet to outlet) c) hydrogen crossover from the anode to cathode, d) the design of the flow field, e) the material variability between the CL segments, and f) possible CL material loss during laser ablation of the CCM, could have resulted in the difference in the EPSA loss.



Figure 6.2: Spatial distribution of the effective Pt surface area loss during AST and EPSA is calculated from the hydrogen desorption peak of the CV

6.3.3 Effect of temperature and relative humidity

To investigate the reasons for variation in the EPSA loss, the impact of temperature and relative humidity is studied using a model developed by Bi and Fuller [53]. This model uses a simplified version of the Darling and Meyers [89] model to calculate Pt dissolution rate; the simplified equation is as follows (eq. (6.1)):

$$\frac{dm_{P_t}}{dN} = k e^{\left(\frac{1}{RT} \frac{\sigma M}{\rho} \frac{1}{D}\right)} \times ECSA \times L_w$$
(6.1)

Where, k' is the apparent dissolution rate constant in g cm⁻² Pt min⁻¹; R is the gas constant in J mol⁻¹ K^{-1} ; T is the temperature in K; σ is the surface tension in J mol⁻¹; M is the Pt molar weight in g mol⁻¹; ρ is the Pt metal density in g cm⁻³; D is the Pt particle diameter obtained from the energy dispersive X-ray (EDX) analysis in cm, ECSA is the catalyst surface area measured during AST in cm² g⁻¹ Pt and L_w is the cathode Pt loading in g per MEA. The values used for the Pt molecular weight and the Pt metal density are 0.1951 kg mol⁻¹ and 21,450 kg m⁻³, respectively [89].

The electrochemically active catalyst surface area is calculated from the CV. Pt mass loss rate is evaluated over the number of cycles during AST. The initial diameter of the particle was obtained from BOL SEM-energy dispersive X-ray (EDX) images. Particle sizes were examined using SEM coupled with an energy dispersive X-ray system (EDX). The EDX analysis was carried out at catalyst layer and the Pt present in the regime were measured qualitatively and quantitatively. The weight percentage of each element present in the spectrum was identified. Separate qualification experiments were conducted to collect the CCM samples after every 500, 2000 and 10000 cycles. Using Image J, the average geometrical size of the particle was determined. Particle sizes were calculated for BOL, EOL samples of 500, 2000 and 10000 cycles from the images. The temperature and relative humidity of the cell was monitored during the whole experiments. Pt dissolution rates were calculated based on the average temperatures and RHs of the respective segments. Assumptions similar to Bi et al. [53] were incorporated to estimate the dissolution rate.

The catalyst loading in the cathode remains the same for all three sections (0.4 mg cm⁻¹ of 2.25 cm² MEA). A plot of Pt dissolution rate in grams per cycle for the cathode over the AST is shown in Figure 6.3 for segments 1, 7 and 16. The dissolution rates are in similar magnitude in all the three sections during potential cycling. Similar observations were reported on dissolution of Pt in acid

solutions [174]–[176]. Generally, the measured dissolution rate, during the first 1000 cycles, is high compared to the full AST. As the AST proceeds, flattened dissolution rates are observed in all three regions (results not shown). The literature reports that slight variations in the local humidity or temperature may increase Pt dissolution rates and affect the stability of the Pt particles [75].



Figure 6.3: Pt dissolution rate of the inlet, middle, and outlet segments during ASTs.

6.3.4 Morphological changes

To study the morphological changes, the EOL SEM images of an inlet segment (segment 1), middle segment (segment 7), outlet segment (segment 16) and a BOL sample are presented in Figure 6.4 ad. The thickness of the cathode catalyst layer (4 µm) measured from the SEM images of the BOL is similar to vendor specifications. EOL samples show the presence of Pt band near the CL membrane interface and thinning of cathode CL. Dissolved Pt ions from the CL diffuse into the 85 electrolyte membrane. Pt bands are formed when the Pt ions are reduced by hydrogen coming from the anode [171]. The ion diffusion process is assisted by the partial pressure of reactant gases, hydrogen cross over, the ionic radius of the Pt atoms and the repeated reduction and oxidation of Pt ions [17], [171]. The location of the Pt band formed at the interface is calculated based on the procedure reported elsewhere [17], [37], [39], [59]. Pt band was formed at a distance of 4 ± 0.5 µm from the cathode CL-membrane interface for the EOL samples. A relatively thicker Pt band is observed for segment 16 and may be attributed to variations in localized conditions. Higher Pt dissolution rate (Figure 6.4 b-d) and Pt ionic concentration gradient may have resulted in a thicker Pt band at the segment 16 of the EOL MEA [177]. Higher EPSA loss observed in Figure 6.2 at EOL of the segment 16 supports this observation.



Figure 6.4: SEM images a) BOL state and EOL states b) close to the inlet (segment 1) c) the middle (segment 7) and d) the outlet (segment 16).

6.3.5 Changes in the cell resistance

All the EIS spectra were fitted with an equivalent circuit model presented in the literature [59]. The values of polarization resistance are extracted from the nonlinear least square fitting. To demonstrate the variation in polarization resistance during degradation studies, a plot of polarization resistance values against the number of cycles is shown in Figure 6.5. The R_p values reported are area normalized. Similar to the discussion reported in the EPSA section, the average R_p extracted from the EIS fitting are classified into three regions. The average R_p of the inlet segments increased from 3 to 15 Ω -cm². BOL and EOL averaged polarization resistance from the fitted spectra of the middle region are between 4 and 24 Ω -cm². Higher R_p values are observed at the outlet section of the segments where $R_{\rm p}$ increased from 4.2 to 32 $\Omega\text{-cm}^2$. A linear increasing $R_{\rm p}$ trend is observed from segments 1 to 16 during the AST. This increase was likely caused by the Pt dissolution at the cathode catalyst layer from BOL to EOL. A higher R_p and lower R_s for segment 16 show increased Pt dissolution and/or ionomer corrosion due to water activity [65]. The polarization resistance of the EOL segment increased to 14%, from that of the segment 1. Higher water activity may accelerate the Pt dissolution rate and form a Pt band [178]. Higher loss of EPSA (Figures 1-d and 3) and thicker Pt band (Figure 6.5) substantiate the significant differences observed in the R_p. Although carbon corrosion is not expected during Pt dissolution AST, a small magnitude of carbon oxidation is possible especially when the cathode potential raises above 1 V vs. Reference Hydrogen Electrode (RHE) during the AST. MCCS systems can have a flow transient and pressure drop inside the cell due to segmentation of the flow field and laser ablation of the CCM. Due to the flow transient, potential at the cathode can reach above 1 V vs. RHE for a short duration. During the gases switching and cell start-up/shut-down, potential transient conditions have been reported [65]. Also,
Dhanushkodi et al reported the presence of very low carbon corrosion when the cell was held at 0.6 and 1.0 V for Pt dissolution AST [65]. Other factors such as mechanical erosion of the catalyst and support particle and Pt particle wash out with the water can cause higher polarization resistance in the MEA.



Figure 6.5: Spatial distribution of the polarization resistance with the number of cycles during ASTs.

6.3.6 Spatially resolved performance loss

To compute the increase in kinetic loss during the AST, polarization curves were obtained periodically during the testing. The kinetic loss is calculated from iR corrected curves, which are free

of anode and diffusion losses. An empirical curve fitting approach similar to Young et al. [179] was used to calculate the kinetic loss from the polarization curve at 1 A cm⁻² (eq. (6.2)):

$$\eta_{ORR} = E_{rev} - b \log\left(j + j_L\right) \tag{6.2}$$

where, η_{ORR} is kinetic loss (mV), *j* is the current density (A cm⁻²), *j*_L is the leakage or hydrogen cross over current density (A cm⁻²), *b* is the Tafel slope, and E_{rev} is the reversible cell potential (mV). A plot of kinetic loss against each segment is displayed in Figure 6.6. The assessment of the EOL kinetic loss with the BOL data demonstrates that higher losses in the outlet segments can be caused by Pt dissolution. Evaluation of the kinetic losses shows a low rate of 3.5 μ V cycle⁻¹ at the inlet segments compared to the outlet segments (4 μ V cycle⁻¹). This indicates that variation in temperature and humidity and hydrogen crossover in the outlet region may have occurred during the AST. The average increase in kinetic loss calculated from the equation (6.2) for the inlet, middle and outlet segments are 34, 35 and 37 mV, respectively after 10000 cycles of the AST. The increase in the polarization loss (Figure 6.6) in the kinetic region varied from segment to segment. Higher increase in kinetic loss was observed in segment 16. Higher charge polarization resistance contributed by AST could be the reason for the increased kinetic loss. The kinetic loss, of the EOL outlet segment increased to 4%, from that of the inlet value calculated.



Figure 6.6: Spatial distribution of the increase in the kinetic loss measured during AST. Kinetic loss is obtained from polarization curves at 1.0 A cm^{-2} .

6.3.7 Deconvolution of spatially resolved cell performance due to EPSA Loss

The kinetic loss computed at 1 A cm⁻² from all the polarization curves for all the segments is plotted against the percentage EPSA loss in Figure 6.7. The results reported by Dhanushkodi et al. for the non-segmented cell is also included in the Figure 6.7[59]. Similar exponential trends prevail between kinetic loss and percentage EPSA loss for both the segmented and non-segmented cells. However, the non-segmented cell shows lower kinetic loss for the given EPSA loss. The continuous cycling of the individual segments and shifts in the segment conditions may have accelerated Pt dissolution in the segmented cell.

6.3.8 Oxide layer changes during ASTs

During the Pt dissolution process, the degradation of Pt in the CL can occur by either chemical or electrochemical dissolution (eq. (6.3) - (6.5)).

$$Pt \to Pt^{2+} + 2e^{-} \qquad E_0 = 1.19 + 0.029 \log [Pt]$$
(6.3)

$$Pt + H_2 O \rightarrow PtO + 2H^+ + 2e^- \qquad E_0 = 0.98 - 0.59 \, pH$$
(6.4)

$$PtO + 2H^{+} + 2e^{-} \rightarrow Pt^{2+} + H_{2}O \qquad \log[Pt] = -7.06 - 2pH$$
 (6.5)

During the AST, the cell voltage degrades in the upper-sweep (0.6-10 V) and the next down-sweep (1.0-0.6 V) while no change is observed when the cell potential was held at 1 V or 0.6 V. Uchimura et al reported a similar behavior, where the repeated PtOx formation and reduction resulted in chemical dissolution of the Pt [172]. A dwelling time of 5 s maintained between upper and lower potential in the current study is reported to be a favorable voltage cycling window to accelerate the Pt chemical dissolution [172]. To investigate the mechanism further, CV spectra of segments 1 and 16 (Figure 6.8) was analyzed. The fractional coverage of platinum oxides (Θ) was calculated from the ratio of the hydrogen adsorption peak area (Q_{11}) and Pt oxide reduction peak area (Q_0). Q_{11} is the charge associated with the cathodic peak area and corresponds to proton reduction and hydrogen adsorption regions; it is witnessed from 0.05 to 0.4 V in the CV. Q_0 is the charge associated with the reduction of platinum oxides. This method yields approximate estimation on the Pt coverage for the fuel cell MEA. Repeated analysis was conducted to calculate Pt fractional coverage for each of CV spectra. The fractional coverage of platinum oxides in the BOL of segments 1 and 16 are 0.41 and 0.42, respectively. For both segments 1 and 16 of BOL, a P-value of approximately 0.02 is obtained

between the three replicates of CV spectra used for calculating the fractional platinum oxides coverage. This shows that the difference from the mean in the replicates of CV spectra is not statistically significant (P-value < 0.05). The Pt oxides fractional coverage of the EOL samples of segment 16 increase by 20 % from its BOL value. The rate of platinum oxidation depends on local fluctuation in the segments of the MEA such as temperature, RH and pressure. A 10 % increase in Pt oxides fractional coverage is found in segment 1. The increase in PtOx coverage could be due to a) chemical dissolution of Pt by the AST, b) abrupt shift in the local partial pressure of the individual segment, c) inhomogeneity in the hydrogen evolution regions of the CV (Figure 6.1, d) variation caused due to MEA preparation and conditioning and e) reduction in the temperature and increase in the RH towards the outlet segment (Figure 3.3 d). However, further investigations are required to prove the exact phenomena, which are responsible for the degradation of Pt electro-catalysts (e.g. agglomeration, coalescence and Ostwald ripening); the focus of our current efforts aimed at elucidating the relevant the mechanisms.



Figure 6.7: Comparison between non segmented and segmented cell EPSA - increase in kinetic loss.

6.3.9 Hardware dependency in Pt dissolution ASTs

Maintaining the relative humidity in the segmented flow field is one of the difficult tasks while running the ASTs. The saturation pressure of the reactant gas (p_{sat}) is dependent on temperature (Figure 3.3-d). A temperature difference of 0.5 and 3°C, respectively, during the ASTs and hydrogen – air polarization curve measurements across the segmented cell was observed. A small difference in temperature between the reactant gases and the segmented cell can have a large effect on the cell potential during the AST. The kinetic loss of the BOL MEA varied by ±3 % between each segment at 1 A cm⁻² (Figure 6.6). This may be associated with the deviation in the partial pressure of air across the cell and the design of the flow field. The flow fields of the MCCS systems are designed to inject the flow of reactants in a serpentine path. During the AST, the reactant gases are forced to make several passes before it reaches the reactive area in each of the segments. The extra length and the bends increase the pressure difference and reactant utility between the segments. During this transport, the reactant loses its saturation pressure; hence, a higher humidity is observed near the outlet segments (Figure 3.3-d) contributing towards higher Pt dissolution rates. With the particular cell hardware used in the present study, the total Pt dissolution rate during the ASTs appear to depend on both electrochemical and structural components of the segmented cell; ideally, a uniform Pt dissolution rate is expected in each segment. A detailed study on the interaction of the MEA components and the segmented flow field plates is important to yield better understanding on the Pt dissolution rate and performance loss.



Figure 6.8: a) CV analysis at the Segment 1 b) Segment 16 during ASTs

6.4 Summary

This study reports PEMFC catalyst durability measured using newly developed methodologies and a novel cell hardware. A sixteen-segmented cell and a new laser ablated procedure are developed to spatially resolve the catalyst coated membrane. The heterogeneity of the commercial CCM is 94

identified and substantiated using CV and ECSA of the individual segments of the cell. The dissolution of Pt from the catalyst layer is shown to be non-homogenous during the AST via spatially resolved polarization resistance, kinetic polarization loss and the distance of the Pt band; Pt dissolution rate increased by 50 % at the outlet compared to the inlet segment reducing the durability of the cell. The efficacy of the Pt dissolution AST protocol is proved from the location of the Pt band formed at the same distance from the cathode-membrane interface for all sixteen segments. A comparison of kinetic and EPSA loss show the degradation in the non-segmented cell to be lower than the segmented cells. In the segmented cell, the outlet regions show a kinetic loss of 37 mV for a corresponding EPSA loss of 65 %. The rate of Pt dissolution could have accelerated due to a decrease in the partial pressure of the gas from the inlet to the outlet, increase in the relative humidity and the temperature of the cell that were measured during the AST. An increase in the fractional coverage of Pt oxide by 10 % at the outlet compared to the inlet segments indicates chemical dissolution of Pt at the outlet segment.

Chapter 7: Case studies - spatial Pt dissolution & carbon corrosion vs. SU/SD

This chapter analyses the spatially resolved electrochemical characterization of start-up and shutdown accelerated stress tests. This study complements the previous study of the spatially resolved platinum dissolution. Carbon corrosion and SU/SD accelerated stress test were compared with the results of the platinum dissolution tests.

7.1 Introduction

Unlike batteries, PEM fuel cells deliver, utilizing the gas distribution structure, the reactants constantly to the active sites in the CL and expel the product water. Pressure, temperature, humidity, pH, and reactant concentration gradients prevail over the MEAs active area. Many studies describe performance inhomogenities across the cell [180]–[187]. Local performance differences and the gradients may cause variations in MEA degradation. However, the origins of these degradation variations are not yet well understood. Mapping the local voltage decay, spatial ECSA, and kinetic polarization resistances is one possible pathway to gain a better understanding of these local degradation differences.

Previously, we reported on the spatial variations of platinum dissolution accelerated stress tests (AST) [2], [61]. The work presented higher Pt dissolution near the outlet area of the cell. Pt oxide analysis concluded chemical degradation near the cell's exit. More liquid water towards the outlet due to hardware dependencies during cycling may have introduced this inhomogeneity. The study reported a potential cycling AST. Start-up and shut-down (SU/SD) ASTs add a new dimension of

complexity and the comparison of SU/SD ASTs to their potential cycling equivalent was not yet reported.

In this study, the spatially resolved SU/SD AST is analyzed and compared to the spatial behavior of Pt dissolution and carbon corrosion ASTs. The objectives were to present to demonstrate the occurring heterogeneities in the ECSA and performance during SU/SD AST across the MEA and to compare the results to potential cycling ASTs.

7.2 Experimental

7.2.1 Segmented cell platform with multi-channel-characterization-system - MCCS

The MEA was characterized using an in-house developed segmented hardware (3.1.2) [156] and a MCCS [60], [156]. A Arbin fuel cell test station allowed the reactant conditioning and delivery. Chapter 3: and section 3.1.2 describe the multi-serpentine flow field.

7.2.2 Accelerated stress testing

The spatial degradation of one of the SU/SD ASTs from section 4.2.1 was used to compare the SU/SD condition to Pt dissolution and carbon corrosion ASTs. The dummy load cycle (cycle A) from section 4.3 shows accelerated degradation throughout the full spectrum of current densities. However, the degradation rates of this protocol are slower when comparing to the load (B) SU/SD AST. The medium degradation rate allows to spatially resolve the occurring degradation without possible membrane damage at the laser ablated segment boundaries.

	SU/SD AST	Pt dissolution AST	Carbon corrosion AST
Stressor	Propagating H_2/Air front	Potential range	Potential range
Potential limits	Evolves from H ₂ /Air front	1 V to 0.6 V	1 V to 1.4 V
Dwell time	Evolves from H_2/Air front	5 s/5 s	5 s/5 s
Cycle profile	Evolves from H ₂ /Air front	Square wave	Square wave
Cycle maximum	1200	10000	1500

Table 7.1: Spatially resolved degradation ASTs.

The Pt dissolution and carbon corrosion AST oscillates the potential between its potential boundaries in the inert gas atmosphere. Figure 7.1 shows the three different cycles. All gas streams were fully humidified at 60°C cell temperature and flow rates of 2 sl min⁻¹ and 6 sl min⁻¹ respectively. The Pt dissolution AST uses the potential boundaries of 0.6 V and 1 V while the carbon corrosion AST cycles the potential between 1 V and 1.4 V. The dwell times of 5 s/5 s and a square wave profile are similar for both ASTs. Periodically, characterization steps were done until the end-of-life (EOL) was reached. Table 7.1 summarizes the used parameters for all spatially resolved ASTs.



Figure 7.1: Accelerated stress test protocols: a) start-up and shut-down cycle, b) platinum dissolution cycle, and c) carbon corrosion cycle.

7.1 Results and discussion

Preliminary results of the SU/SD AST were presented in section 4.3.3. In this chapter, a detailed discussion of the electrochemical data of the SU/SD AST is provided. The ECSA and voltage loss over the progression of the AST is analyzed in detail and compared to full cell experiments.



Figure 7.2: Spatially resolved ECSA loss during the SU/SD AST.

Figure 7.2 presents the ECSA loss of all 16 segments of the cell at the characterization steps of 400, 800, 1000 and 1200 cycles. At segment one the gases enter the cell; the hydrogen/air front propagates through the flow field and exits at segment sixteen. An EOL ECSA loss close to the inlet of the cell of approximately 45 % compared to 85 % to 90 % at the outlet section can be observed. The ECSA loss of full cell experiments is in general agreement with the segmented cell measurements. The EOL ECSA loss of the full cell is approximately 75 % versus the averaged loss of 63 %. At 400 cycles, the ECSA loss remains evenly distributed. The inlet section undergoes an ECSA loss of circa 20 % versus 25 % losses at the outlet area. With propagating hydrogen/air front the corrosion accelerates towards the cells exit. Similar behavior was observed in other segmented cell approaches [84], [85]. The propagation of the hydrogen/air boundary passes the inlet of the cell, while the middle and exit area of the cell still remain in reverse current mode [86].

One MEA for each segmented AST was assessed; this restricts applicability of statistical analyses to the data. Material availability and extensive sample preparation limited the extent of study; test time and sufficient material were only sufficient for one run per AST. Sixteen segments are evaluated for a given MEA. They are effectively individual cells, each with a different local environmental and operating condition. As a preliminary estimate, the data are grouped into inlet, central and exit segments. These data are averaged and plotted in Figure 7.2 with error bars representing one standard deviation. A trend of increasing ECSA loss towards the exit might be hypothesized; but limited data prevents application of any statistical test (e.g. p-value). Additional grouped segment statistics are not pursued further in this chapter as they do not provide any significant insight beyond visual inspection of plots. A propagation of error analysis to establish the instrument accuracy is provided in appendix (B.1). The ECSA determination comprises an error of one percent for BOL samples.

Aside from the influence of temperature, relative humidity and pressure inhomogenities on the degradation rates [2], [61], [180], higher potentials resulting in hydrogen evolution and carbon corrosion promote accelerated degradation of the cathode CL in this area [84], [85]. The accumulation of product water promotes the degradation. Larger amounts of water promote carbon corrosion. The catalytic effect of platinum on carbon may accelerates the degradation [93].

The EOL ECSA loss of the SU/SD AST compared to the Pt dissolution and carbon corrosion AST is shown in Figure 7.3. The ECSA loss of the carbon corrosion AST at 1500 cycles remains constant across the cell. The ECSA loss of the carbon corrosion AST can be quantified with approximately 50 %. The ECSA loss during the Pt dissolution AST increases slightly from the inlet to the exit. The ECSA loss at 10 000 cycles of the Pt dissolution AST shows a variation of 10 % from inlet to outlet.

In contrast, the SU/SD AST at 1200 cycles reveals a difference of approximately 40 % across the cell.

In previous studies, the influence of occurring gradients on the Pt dissolution were discussed [2], [61]. The rate of Pt dissolution may have increased the dissolution rate due to a decrease in the partial pressure of the gas, increase in the relative humidity, and the temperature from the inlet to the outlet of the cell. An increase in the fractional coverage of Pt oxide by 10% at the outlet compared to the inlet segments indicates the chemical dissolution of Pt at the outlet segment. Inhomogenities of pressure and temperature and resulting higher relative humidities may promote a higher dissolution rate towards the cell's exit. More residual water results in a change of the Pt dissolution degradation rate. This may influence the electrochemical and chemical degradation, PtOx formation, and the performance decay [2]. However, the differences in the degradation rates are not as enhanced during the Pt dissolution AST compared to SU/SD ASTs. The corroded carbon is more distinct near the outlet due to longer residence times and more residual water, which may influence the ECSA loss more dominantly.



Figure 7.3: Spatially resolved ECSA loss of SU/SD AST compared with the Pt dissolution and carbon corrosion AST.

Figure 7.4 presents the voltage losses at low current densities for the SU/SD AST of all 16 segments. The voltage loss of the characterization steps at 400, 800, 1000 and 1200 cycles increases towards the cell's exit. This behavior supports the ECSA loss distribution. The loss increases with accelerated degradation. At EOL, an average loss of approximately 6.5 % can be observed. The inlet undergoes a voltage decay of 3 % while the exit segments show almost 8 %. The segments 8 and 9 as well as 12 and 13 show accelerated degradation during the SU/SD AST. The multi-serpentine flow field undergoes a change in direction in these areas. Gas change directions may cause a longer duration of oxygen in these areas. Additionally, water may accumulate in the curve of the flow field. This may promote the accelerated degradation. Local water blockages may also cause fuel starvation in some areas. Differences in the flow field design effecting the performance are well investigated

[188]–[190]; degradation studies correlating the flow field geometry with occurring degradation are rare. However, the cause of this observation is pure speculation. Further detailed investigations regarding flow field geometries and the influence on degradation will allow better understanding. This is beyond the scope of this work.



Figure 7.4: Voltage loss at 0.1 A cm^{-2} for the SU/SD AST.

Figure 7.5 shows the voltage loss at low current densities at EOL. The voltage loss of the SU/SD AST is compared to the Pt dissolution and carbon corrosion ASTs. The potential cycling ASTs show homogen degradation with a loss of 5 to 6 %. The trends of the voltage decay of the SU/SD studies support the ECSA loss behavior. Potential cycling induces a homogen stressor across the flow field and the propagating hydrogen/air gas front induces large local differences.



Figure 7.5: Voltage loss comparison at 0.1 A cm⁻² of the SU/SD AST with the Pt dissolution and carbon corrosion ASTs.

7.1 Summary

This study analyzes the spatial differences of start-up and shut-down (SU/SD) accelerated stress tests (AST). The SU/SD AST shows strong gradients across the cell. The electrochemical active surface area (ECSA) and voltage losses increase significantly towards the cell's exit. ECSA loss differences of approximately 40 % from the inlet to the outlet are observed. The residence time of oxygen near the outlet is longer, compared to the hydrogen filled inlet segments. Reverse currents occur longer closer to the anode exit. Further, influences of the flow field may be observed. A larger voltage decay of segments compriseing a gas-path-change compared to segmetns with straight channel geometry is observed. The voltage decay of segments with a gas path change accelerated

compared to the surrounding segments. Additional investigations are necessary, inorder to understand this behavior which is currently out of the scope of this work.

The spatial degradation of the SU/SD AST is compared to the local behavior of Pt dissolution and carbon corrosion induced deterioration. Both, the Pt dissolution and the carbon corrosion AST comprise potential cycling. The potential cycling ASTs show slightly increasing performance and ECSA losses towards the outlet. In addition, the SU/SD AST shows strong gradients towards the exit on the cell.

Chapter 8: Conclusions

8.1 Conclusions of the studies

Fuel cells are in the early stages of commercialization and current performance requirements are met. However, durability improvements, standardization and large scale manufacturing procedures are still challenging. This study presents approaches to investigate degradation, particularly start and stop (SU/SD) induced degeneration. A comprehensive review summarized the scientific gaps. This thesis targeted these gaps, developed novel tools and methods, and analyzed PEM fuel cell degradation under a variety of conditions. To date, no adequate comparison and no standard for SU/SD accelerated stress tests (ASTs) have been identified. The deconvolution of performance losses occurring during SU/SD ASTs allowed the detailed understanding of important degradation mechanisms. Efforts to deconvolve the performance decay during SU/SD degradation have been sparse. A novel apparatus and methods to identify local performance decay during different degradation modes were developed. The spatially resolved degradation during start and stop events was compared to platinum (Pt) dissolution and carbon corrosion ASTs, and the relevant differences were analyzed systematically.

The contributions of this thesis include:

- The characterization of different SU/SD ASTs in a common in/situ platform to analyze stressors, which affect the degradation and mitigation strategies.

- The deconvolution of performance losses and their related mechanism, whereby Pt dissolution prevails in early stages of the AST, later carbon corrosion dominates the high current density performance loss.
- The design and validation of a novel in-situ test platform to spatially resolve PEM fuel cell performance.
- The spatially resolved performance degradation during different ASTs whereby the accumulated water towards the cells exit accelerates the Pt dissolution, chemical dissolution is favored and the longer residence time of the hydrogen/air front near the exit increases the degradation during SU/SD ASTs.

Three different SU/SD- ASTs in a common PEM fuel cell platform were compared. The importance of this comparison was demonstrated and filled a gap in the literature. Mitigation strategies to reduce SU/SD related degradation were investigated. The consumption rate of protons during the propagating hydrogen/air front is strongly dependent on the application of a resistor (dummy load) or the voltage suppression by the external load bank (voltage ramping). However, suppressing high cell voltages, utilizing an external load bank may not be feasible in commercial systems. It may require significant improvements in the control and power electronic unit of a stack system. An optimized resistor application seems technically and economically more feasible. The exact timing of the application and dimensions of the resistor requires further analysis, but no investigated mitigation strategies are viable technically or economically.

The deconvolution of performance losses caused by SU/SD degradation was feasible by applying an empirical carbon corrosion degradation model from the literature. This study concludes a hardware independent relationship between the performance versus the carbon loss of the model. The 108

deconvolved performance losses comprise a carbon induced performance loss and a non-carbon induced performance loss. The chronological dominance of the different performance losses change throughout the progression of the test. In the initial stages of the SU/SD AST, the non-carbon induced performance loss at high current densities remains comparable to the low current density performance loss and is the dominant over the carbon related losses. After accelerated degradation, the non-carbon induced performance loss increases to approximately 10 % performance loss; however, the carbon related performance loss starts to be dominant. It is suggested that decreasing mass transport properties are responsible for the higher non-carbon related performance decay in high current densities. Pt dissolution as one participating loss mechanism was identified prevailing utilizing image analysis and was supported by the electrochemical active surface area (ECSA) loss. The decreasing oxygen diffusivity in the CL suggests a structural change which influences the properties of the layer and so the performance. Ionomer and membrane degradation may also participate on the non-carbon induced performance loss but was assumed negligible.

A novel diagnostic tool and methodologies were developed to resolve spatially the degradation of the MEA. The analysis of spatial Pt dissolution AST concludes that chemical degradation near the cell's outlet is favored over electrochemical degradation. Accumulated water towards the cell's exit influences the mechanisms. Large gradients within the cell were observed when comparing SU/SD AST with the behavior of potential cycling ASTs. The ECSA and voltage losses increase significantly towards the cell's exit. Larger residence times of air in the anode compartment, resulting in longer reverse current mode in this area, were responsible for this behavior. Influences of the flow field on degradation were suggested; however, a more detailed analysis is necessary to prove this hypothesis. Residing water within the turns of the gas path may accelerate degradation. Nonetheless, these influences are, at present, completely speculative nature. The spatial analysis suggests design changes of the CL dependent on the flow field geometry. Structures and properties (e.g. graphitization, Pt content, and porosity) may be optimized with regards to the flow field.

The thesis contributes to degradation investigation and in larger perspective to cost reduction strategies for the next generation of PEM fuel cell material. Future design criteria for the CL may be customized dependent on the stack design and the prevailing degradation. SU/SD mitigation strategies will need to be improved to accommodate future cost and lifetime targets of stack systems. The analysis of different SU/SD ASTs suggest to standardize these ASTs to compare scientific studies in detail.

8.2 Outlook

One possible technical improvement remains the development of a mitigation strategy to suppress SU/SD degradation. The analyzed strategies seem technically or economically not viable for portable applications and the automotive mass market. Material, parameter, and strategy approaches seem more feasible, economically. Further development may be undertaken to develop this issue.

A standardized SU/SD AST in a common test cell platform will allow more rigorous linkage of literature results. To date, no standard has been identified. Most of the reviewed approaches use special test cells and small active areas. The presented spatial degradation results suggest a minimum active area size to analyze SU/SD degradation in detail.

Degradation may causes significant changes of the GDL and MPL morphology. The exact quantification of this degradation was not yet possible. A reliable technique to separate the MPL from the CL is not developed yet. Attempts to separate both, MPL and CL, point the related 110 difficulties out. The CL may remain on the MPL, the MPL may peel off from the substrate, and damages on the substrate are unavoidable, as of now. Successful methods will allow the layer depended deconvolution of in-situ and ex-situ performance losses. Investigations of the GDL and MPL degradation mechanism will be possible and are lacking in the literature. Ex-situ analysis of artificially aged GLD/MPL may give insight of structure property performance influences. In-situ testing and a rigorous voltage loss breakdown may reveal detailed voltage loss influence. This knowledge allows the recommendation of design criteria suited to the degradation behavior for the next generation transport layer.

The performance deconvolution was investigated at 1 A cm⁻², next generation CCM material may be able to reach higher current densities. The degradation behavior at higher current densities will be of large interest. Modern CCM materials suggest current densities of 2.5 to 3 A cm⁻² as feasible. Compared to the current scenario, the amount of water produced is three times larger and will influence the carbon corrosion significantly. Further, the mass transport overpotential will be more significantly interacting with the platinum induced performance loss.

The stepwise morphological investigation of SU/SD may allow monitoring the temporal resolution of the related degradation. The changing rates of degradation, observed in the spatially resolved measurements suggest a change in the mechanism. TEM images and related particle size distribution at different progress stages (e.g. 200, 400 cycles) of the AST may allow the deconvolution of platinum related degradation. It may be possible that initially particle detachment dominates; in further stages Ostwald ripening, and dissolution may be more pronounced. The results may be compared to potential cycling ASTs to further deconvolve catalyst degradation.

By using a reference electrode approach, the anode independent degradation of the cathode can be analyzed. It is assumed that the PEM fuel cell anode plays only a minor role in performance and degradation losses. However, the exact determination of occurring voltages is only possible with the aid of an independent reference electrode potential.

The electrochemical analysis of the spatially resolved SU/SD ASTs shows large performance gradients within the cell. A detailed morphological study to analyze these gradients will give more detailed insight to the occurring degradation FIB-SEM results that will allow monitoring porosity changes of the CL in relation to local performance and ECSA losses. A detailed TEM image analysis will give insight to the platinum behavior in different areas of the cell. This can be used to deconvolve the participating degradation mechanism qualitatively.

Some results in this study suggest that reversible degradation effects occur. Conditioning phases prior to the characterization steps mitigated these reversible occurrences. A detailed analysis of causes, mechanism, and dependencies may contribute to the understanding of SU/SD degradation and may assist possible recuperation of aged CL as a technical mitigation strategy.

Segmented cell measurements show accelerated degradation in gas path changing areas of the flow field. More focus on the degradation investigation of these areas may reduce the deterioration of the overall MEA significantly. Sharp gas path changes may result in large local damage. Therefore, gas path changes should be avoided or defused.

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Appendices

Appendix A

A.1 Flow field evaluation

First objective of this work was the development of a suitable segmented cell. First results were presented at the Canadian Chemistry Conference [156]. The single serpentine flow field plate design induces multiple gradients in the cell, spatially resolved data interpretation is difficult. A predictable gradient across the flow field was needed.



Figure A.1: Existing flow field plate design a) with major gradients, new developed flow field plate design b) with progressing gradient along the gas path.

The existing flow field geometry induces major and minor gradients: a minor gradient along the channel, a major gradient in the general direction. The major gradient is indicated with the arrows in Figure A.1 a). Every segment in the cell of the existing flow field accumulates water from the

following segments and in the next serpentine this water induces a gradient to the previous channel of the same segment. Figure A.2 shows the water accumulation of a unit channel element for the existing and the new design. All channels in a segment of the new design show homogen water accumulation, assuming a constant current density of 1 A cm⁻². This makes future data interpretation more predictable.



Figure A.2: Calculated water accumulation (at 1 A cm⁻²) within a unit channel element of the existing flow field design (1) and the new design (2). The new design shows a uniform water amount per segment while large differences of water are observed for the existing design.



Figure A.3: Polarization curves a) and pressure drop of the cathode b) of the existing and the new designed flow filed plate.

Figure A.3 a) shows polarization curve data of the existing and the new flow field plate design. Both are in general agreement to each other. The pressure drop of the cathode, assuming a steuchiometric coefficient of 3.5, is shown in Figure A.3 b). The new flow field was designed with a smaller but still existing pressure drop. A pressure drop ensures liquid water removal. However, large pressure drops induce large gradients within segments, across the membrane and across the flow field.

Appendix B

B.1 Error analysis

Acquired data varies due to systematic and random measurement errors. In part, the systematic errors occur due to variations in the measurement devices capabilities. These devices interact with the measurement setup and comprise systematic errors due to offsets, aging, and environmental influences. Most of the instrument errors are quantifiable and usually stated in the documentation of the measurement tool. Sampling errors are quantifiable by repeated measurements within consistent conditions. The average of (n) repeated measurements

$$\overline{x} = \frac{1}{n} \sum_{i=1}^{n} x_i \tag{11.1}$$

is presented in equation (11.1).

With the standard deviation (σ)

$$\sigma_{x} = \sqrt{\frac{\sum_{i=1}^{n} (x_{i} - \overline{x})^{2}}{n-1}}$$
(11.2)

for a sample of the population (n) as seen in equation (11.2).

A propagation of error calculation is desirable when multiple independent quantities are measured and their random error impact the output of a function. A linear regression eq. (11.3)

$$\Delta x = \sum_{i=1}^{n} \left| \frac{\partial x}{\partial x_i} \right| \Delta x_i$$
(11.3)

can be applied for small errors (Δx_i) versus the quantified value. The Taylor series expression neglects higher order terms of minimal consequence.

The specification of the implemented BioLogic apparatus (model VMP3) are presented in Table B.1. The desired outcome is to choose the suitable full-scale range for the measurement. The VMP3 instrument automatically selects the suitable range.

	Current measurement	Voltage measurement
Ranges	automatic on every range	±2.5 V, ±5 V, ±10 V, ±10 V
	$\pm 10 \ \mu A$ to $\pm 1 \ A$ (7 ranges)	adjustable
Maximum resolution	0.004% of the range,	0.0015% full scale range, down
	760 pA on the 10 μ A range	to 75 μ V
	< 10 mA on 5 A range	
Acquisition speed	200,000 samples/second	200,000 samples/second
Accuracy	< 0.1% full scale range	< 0.1% full scale range

Table B.1: BioLogic VMP3 specification

The corresponding error in the measurement for the ECSA can be calculated using equation 3.1. The charge (Q) is the only measured quantity to determine the ECSA and comprises a voltage and current measurement.

The total error (ΔQ) can be calculated using equation (11.3) and the accuracy of the measuring device. The full-scale range for ECSA measurements are 2.5 V and 1A.

$$\Delta Q = \left| \frac{\partial Q}{\partial I} \right| \Delta I + \left| \frac{\partial Q}{\partial V} \right| \Delta V$$

$$\Delta Q = \left| \frac{0.15V}{0.02Vs^{-1}} \right| 0.1\% 1A + \left| \frac{0.1A}{0.02Vs^{-1}} \right| 0.1\% 2.5V = 0.023C$$
(11.4)

The determined error is approximately 0.8% of the BOL value. EOL measurements may comprise maximal errors of approximately 6.0%.

Appendix C

The author's publication and conference history follows.

Journal publications

M. Schwager, S.R. Dhanushkodi, W. Mérida, *Start-up/Shut-down Cycles in a Non-Segmented and Segmented Polymer Electrolyte Membrane Fuel Cell*, ECS Transactions 66(25) (2015)

M. Schwager, S.R. Dhanushkodi, W. Mérida, *A Novel Diagnostic Approach to Measure the Water Breakthrough in Porous Carbon Materials*, ECS Electrochemistry Letters 4(4) F32-F34 (2015)

D. Todd, **M. Schwager**, W. Mérida, *Three-dimensional anisotropic electrical resistivity of PEM fuel cell transport layers as functions of compressive strain*, Journal of Electrochemical Society 162(3) F265-F272 (2015)

S.R. Dhanushkodi, M. Schwager, D. Todd, W. Mérida, *PEM fuel cell durability: spatially resolved Pt dissolution in a single cell*, Journal of Electrochemical Society 161(14) F1315-F1322 (2014)

S.R. Dhanushkodi, **M. Schwager**, W. Mérida, *PEM fuel cell characterization and diagnostics*, ECS Transactions 64(3) 547-557 (2014)

D. Todd, **M. Schwager**, W. Mérida, *Thermodynamics of high-temperature, high-pressure Water Electrolysis*, Journal of Power Sources 269 424-429 (2014)

S. Flick, **M. Schwager**, E. McCarthy, W. Mérida, *Designed experiments to characterize PEMFC material properties and performance*, Journal of Applied Energy 129 135-146 (2014)

R. Alink, J. Hausmann, H. Markötter, **M. Schwager**, I. Manke, D. Gerteisen, *The Influence of Porous Transport Layer Modifications on the Water Management in PEM Fuel Cells*, Journal of Power Sources 233 358-368 (2013)

D. Gerteisen, W. Mérida, T. Kurz, P. Lupotto, M. Schwager, C. Hebling, *Spatially resolved Voltage, Current and Electrochemical Impedance Spectroscopy Measurements*, Fuel Cells 11 339-349 (2011)

Manuscripts in Preparation

M. Schwager, S.R. Dhanushkodi, W. Mérida, *Deconvolution of degradation mechanism caused by start-up and shut-down cycles in Polymer Electrolyte Membrane Fuel Cells,* (submitted)

S.R. Dhanushkodi, **M. Schwager**, W. Mérida, *PEM fuel cell durability: Spatially resolved carbon corrosion mechanism in PEM fuel cells*, (in progress)

S.R. Dhanushkodi, **M. Schwager**, W. Mérida, *PEM Fuel Cell Catalyst Layer characterization, A Review,* Electrocatalysis (in progress)

Reports

R. Alink, D. Gerteisen, U. Groos, S. Keller, T. Kurz, W. Mérida, **M. Schwager**, C. Hebling, *50-Kanal-Impedanz-Spektroskopie für Brennstoffzellen und Stapel*, Annual Report Fraunhofer- Institut for Solar Energy Systems ISE 2010, page 106

Conferences

M. Schwager, S.R. Dhanushkodi, W. Mérida, *A proposal for a standardized start-up and shut-down protocol for polymer electrolyte membrane fuel cells*, Vancouver, BC, Canada, 18. August 2015

M. Schwager, S.R. Dhanushkodi, W. Mérida, *Start-up/Shut-down Cycles in a Segmented Polymer Electrolyte Membrane Fuel Cell*, 227th ECS meeting, Chicago, USA, 27. May 2015

D. Todd, **M. Schwager**, S.R. Dhanushkodi, W. Mérida, *Recent development for the PEM fuel cell at UBC*, UBC Sustainability symposium, UBC, Vancouver, BC, Canada, 4. March 2015

L. Damron, **M. Schwager**, S. Flick, D. Todd, S.R. Dhanushkodi, W. Mérida, *Recent development of diagnostic tools for the PEM fuel cell catalyst layer at UBC*, International Symposium on Electrocatalysis 2014, Whistler, BC, Canada, 27. October 2014

S.R. Dhanushkodi, **M. Schwager**, W. Mérida, *Polymer electrolyte membrane fuel cells: characterization and diagnostics*, 226th ECS and SMEQ joint international meeting, Cancun, 7. October 2014

S.R. Dhanushkodi, **M. Schwager**, D. Todd, W. Mérida, Use of segmented cells in Durability Testing: Experimental studies to measure the spatial distribution of Pt surface area and performance loss in PEM fuel cells, 97th Canadian Chemistry Conference and Exhibition, Vancouver, BC, 4. June 2014

M. Schwager, D. Todd, S.R. Dhanushkodi, W. Mérida, *Spatially resolved fuel cell diagnostics via segmented cell featuring independent power electronics applied to water and catalyst management*, 97th Canadian Chemistry Conference and Exhibition, Vancouver, BC, 4. June 2014

D. Gerteisen, A. Spadinger, M. Schwager, W. Mérida, C. Hebling, *Spatially resolved analysis of water transport mechanisms*, European Fuel Cell Forum 2011, Lucerne, 1. July 2011

D. Gerteisen, W. Mérida, T. Kurz, **M. Schwager**, A. Spadinger, R. Alink, C. Hebling. *Voltage, current and electrochemical impedance spectroscopy measurements on a 7 x 7 segmented fuel cell*. Canadian Hydrogen & Fuel Cells Conference, Vancouver, BC, 15 May 2011

R. Alink, **M. Schwager**, W. Mérida, *Water sorption of commercial Membrane Electrode Assemblies*, 219th ECS biannual meeting 2011, Montréal, 3. May 2011

D. Gerteisen, W. Mérida, T. Kurz, R. Alink, A. Spadinger, M. Schwager, C. Hebling, *Spatially resolved Voltage, Current and Electrochemical Impedance Spectroscopy Measurements*, MODVAL Meeting 2011, Bonn, 09. March 2011