NEW METHODOLOGIES TO CHARACTERIZE PEMFC PERFORMANCE LOSSES

by

Sarah Flick

Diplom-Ingenieur (TU), Hamburg University of Technology, 2010

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

in

THE FACULTY OF GRADUATE AND POSTDOCTORAL STUDIES

(Mechanical Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA

(Vancouver)

November 2014

© Sarah Flick, 2014
Abstract

As fuel cells reach the early stages of commercialization, the need for effective research methods and efficient characterization tools is increasing. Industrial demands allowing for serial production require methods for standardized testing and efficient quality control while developing new materials and production methods. This thesis work presents two methodologies: Design of Experiments (DoE) applied to Polymer Electrolyte Membrane Fuel Cells (PEMFCs) to analyze for sparsity of effects and performance mapping; and a systematical Voltage Loss Breakdown (VLB) method based on experimental polarization featuring anodic contributions. Both concepts were validates and the effects of commercial porous transport layer (PTL) material on the fuel cell’s voltage under galvanostatic conditions were investigated.

The results of this work demonstrate the use of DoE to assess the differences and parameter dependencies of different materials in the PTL of PEMFC. Split-plot and general blocked design models were used to analyze the voltage and pressure drop of PEMFC at different current densities of 1.0 A cm\(^{-2}\), 1.4 A cm\(^{-2}\) and 1.6 A cm\(^{-2}\). The empirical models show good fit and prove that these methodologies based on experimental designs can be useful to predict and analyze fuel cell performance within this design space. The use of designed experiments allows a scientifically objective analysis of the data compared to one-factor-at-a-time (OFAT) testing while reducing the overall required test runs. Our results show, that this analysis can capture and model the effects of PTL materials and operating conditions as statistically and physically significant.
The VLB method developed in this work systematically analyzes the different dominant loss contributions and shows the relevance of the anode under varying operating conditions. A reference electrode system was designed and validated in order to measure the anodic and cathodic contributions to the cell’s polarization separately. A mathematical approach was developed to break down the polarization curve into the individual contributing losses, distinguishing between anode and cathode and the individual kinetic, ohmic and mass-transport overpotentials. Based on this study it can be concluded, that a micro-porous layer (MPL) leads to reduced mass-transport losses inside the cathode electrode and decreases the ohmic losses.
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.

The majority of Chapters 3, 4 and 5 were published for dissemination of the results in different peer-reviewed journal papers and conference proceedings as follows. I was responsible for all efforts related to these publications including, but not limited to, developing and proving experimental and numerical concepts and designs, carrying out experiments, data post-processing and analysis, numerical analysis, as well as manuscript writing, editing and submission under the supervision of Dr. Mérida. The contributions of the co-authors are listed with respect to the corresponding publications.

Chapter 3 is partly published in Flick and Merida (2013) and Flick et al. (2014). The experimental set-up of the reference electrode described in Chapter 3 is submitted as Flick et al. (2014b).

The methodology and the majority of the results presented in Chapter 4 as well as parts of Chapter 6 are published in Flick et al. (2014). The co-authors M. Schwager and E. McCarthy provided helpful consultation with the data analysis and experimental set-up, as well as the editing of the final manuscript. Some results presented in Chapter 4 were also presented in Flick and Merida (2013).
A section of Chapter 4 was published in McCarthy et al. (2013). My role in this publication was to create and evaluate the designed experiment, conduct the analysis of variance and writing and editing of the manuscript.

Chapter 5 and parts of Chapter 6 are based on a manuscript in submission, Flick et al. (2014c)\(^3\) and one manuscript in preparation Flick et al. (2014c)\(^5\). The co-authors assisted me with the experimentation and discussion of the data as well as the final editing of the manuscript. I developed the improved design and experimental concept for the reference electrode and the co-author J. Schoenweiss was responsible for manufacturing, implementation and validation of the reference electrode system.


Text excerpts and figures were also reproduced with permission from ECS Transactions, 58 (1), 843-850 (2013). Copyright 2014, The Electrochemical Society.


Text excerpts, figures and tables were reprinted with permission from Applied Energy, 129, Flick et al., Designed Experiments to characterize PEMFC material properties and performance, 135-146, Copyright 2014, with permission from Elsevier.


Text excerpts were reprinted with permission from the Journal of Power Sources, 239, McCarthy, Flick and Mérida, Response surface methods for membrane humidifier performance, 399-408, Copyright 2014, with permission from Elsevier.

Table of Contents

Abstract .......................................................................................................................... ii
Preface............................................................................................................................ iv
Table of Contents .......................................................................................................... vii
List of Tables ................................................................................................................. xi
List of Figures ............................................................................................................... xii
List of Symbols ........................................................................................................... xvii
List of Abbreviations ................................................................................................... xx
Acknowledgements ..................................................................................................... xxii
Dedication ..................................................................................................................... xxiv
Chapter 1: Introduction ................................................................................................. 1
Chapter 2: Voltage Loss Characterization ..................................................................... 15
  2.1 Reference Electrodes in PEMFC ............................................................................. 15
  2.2 Voltage Loss Breakdown ...................................................................................... 19
    2.2.1 Cross-Over Overpotential .............................................................................. 24
    2.2.2 Activation Overpotential .............................................................................. 25
      2.2.2.1 Anodic Activation Overpotential ......................................................... 25
      2.2.2.2 Cathodic Activation Overpotential ..................................................... 25
    2.2.3 Ohmic Overpotential ................................................................................. 27
    2.2.4 Mass-Transport Overpotential ................................................................. 28
  2.3 Water Management in PEMFCs ........................................................................... 30
    2.3.1 Influence of the PTL on Voltage Losses ................................................... 31
A.3  Diagnostic Tools ........................................................................................................ 154

Appendix B .................................................................................................................. 157
  B.1  Response Selection ............................................................................................... 157
  B.2  Split-plot Designs ............................................................................................... 159
  B.3  General Blocked Factorial .................................................................................. 177

Appendix C .................................................................................................................. 188
  C.1  Exemplary Voltammetry Results ....................................................................... 188
  C.2  Voltage Loss Breakdown .................................................................................... 190
List of Tables

Table 2.1: Summary of selected recent efforts employing internal RE systems in PEMFC research ................................................................. 18
Table 2.2: Summary of the literature review on VLB ................................................................. 23
Table 2.3: Comparison of Tafel slopes (b), exchange current densities $i_{0(T)}$, and iR-free current densities at 0.9 V, $i_{0.9V(T)}$, normalized to 101.3 kPa O$_2$. Data taken from Gasteiger et al.\textsuperscript{26} ....... 26
Table 3.1: Flow-field specification ................................................................................................................ 35
Table 3.2: Properties of SIGRACET\textsuperscript{®} GDL 25 according to the SGL Carbon Group .......... 38
Table 4.1: Selection of factor values ............................................................................................................. 56
Table 4.2: Model equations in coded values with terms ordered in descending order of their impact on the cell voltage. (A: Anode Stoichiometry, B: Cathode Stoichiometry, C: Temperature, D: Anode RH, E: Cathode RH, F: Pressure, G: Type of GDL) ............................................. 67
Table 4.3: Specific humidity in the randomized block design ................................................................. 85
Table 4.4: Summary of the ANOVA for the general design ................................................................. 86
Table 5.1: Kinetic parameters from polarization analysis ................................................................. 101
Table 5.2: Summary of the individual loss contributions .............................................................................. 102
Table A.1: Properties of GDL material used for the ex-situ pressure drop experiments ........... 153
List of Figures

Figure 1.1: Simplified functional scheme of a PEMFC ................................................................. 4
Figure 1.2: Thermodynamics of a PEMFC .................................................................................. 6
Figure 1.3: Exemplary polarization curve with governing loss regions as function of current density .................................................................................................................. 11
Figure 2.1: Exemplary schematic of PEMFC polarization measurements with reference electrodes (RE) ................................................................................................................. 16
Figure 3.1: Schematic of test apparatus .......................................................................................... 35
Figure 3.2: Cathode (left) and Anode (right) flow fields ................................................................ 36
Figure 3.3: Low gradient research cell with an active area of 49 cm$^2$ ...................................... 37
Figure 3.4: SEM picture of a) SGL 25 BC substrate and b) SGL 25 BC MPL .............................. 39
Figure 3.5: Assembled 49 cm$^2$ MEA .......................................................................................... 40
Figure 3.6: Schematic of the measured circuits between RE, cathode and anode (not to scale).. 41
Figure 3.7: Flow diagram of test set-up including the reference electrode system ..................... 42
Figure 3.8: Optical microscopy image of the laser ablated CCM .................................................. 43
Figure 3.9: MEA with reference section ready to be tested .......................................................... 44
Figure 3.10: Schematic of the new design of the reference system (not to scale) ....................... 45
Figure 4.1: Schematic of the test methodology, adapted from$^{[22]}$ ................................................. 53
Figure 4.2: Schematic of test apparatus .......................................................................................... 59
Figure 4.3: Force distribution on cathode (left) and anode (right) side using pressure sensitive paper at 75 and 120 psi clamping pressure ............................................................................. 60
Figure 4.4: Cathode flow versus pressure drop at 70 °C, 80% RH and gas inlet pressures of 200 kPa ................................................................................................................................. 61
Figure 4.5: Anode flow versus pressure drop at 70 °C, 80% RH and gas inlet pressures of 200 kPa.............................................................................................................................................................................................................. 62

Figure 4.6: Optical microscopy images of 24 BC PTL material before (BoL) and after (EoL) clamping pressure cycling of the substrate side (top) and MPL side (bottom) ............................................. 63

Figure 4.7: Pareto charts for the split-plot designs. (A: Anode Stoichiometry, B: Cathode Stoichiometry, C: Temperature, D: Anode RH, E: Cathode RH, F: Pressure, G: Type of GDL) 70

Figure 4.8: Normal plot of residuals and predicted versus actual cell voltage for the split-plot design employing cell voltage as the response ........................................................................................................... 72

Figure 4.9: Pressure drop and cell voltage at all current densities for the cell with MPL, 25 BC, at 100 kPa. All other factors were kept at a normalized value of 0 (see Section 4.3.1). ................. 76

Figure 4.10: Pressure drop and cell voltage at all current densities for the cell with MPL, 25 BC, at 300 kPa. All other factors were kept at a normalized value of 0 (see Section 4.3.1). .............. 80

Figure 4.11: Pressure drop and cell voltage at all current densities for the cell without MPL, 25 BA, at 100 kPa. All other factors were kept at a normalized value of 0 (see Section 4.3.1). ......... 81

Figure 4.12: Pressure drop and cell voltage at all current densities for the cell without MPL, 25 BA, at 300 kPa. All other factors were kept at a normalized value of 0 (see Section 4.3.1). ....... 82

Figure 4.13: Pareto chart for the general design at 1.0 A cm\(^{-2}\). (A: Anode Stoichiometry, B: Cathode Stoichiometry, C: Temperature, E: Cathode RH, F: Pressure)...................................................... 86

Figure 5.1: Polarization results ............................................................................................................................................................................................................. 98

Figure 5.2: iR-free polarization results averaged for all three samples ......................................................................................................................... 99

Figure 5.3: Tafel plot featuring the full cell (b) and the RHE versus cathode (b*) ...................... 100

Figure 5.4: Structure of the tool to separate the individual overpotentials ................................................. 106
Figure 5.5: Measured baseline polarization curve for GDL material 25 BC, including standard deviations of the signals ................................................................. 108

Figure 5.6: Resistance corrected baseline polarization, 25 BC ......................................... 109

Figure 5.7: Breakdown into the individual overpotentials .................................................. 110

Figure 5.8: Comparison of measured baseline polarization data for 25 BC and 25 BA including standard deviations ................................................................. 112

Figure 5.9: Comparison of iR-corrected potentials under baseline conditions for 25 BC and 25 BA .................................................................................. 113

Figure 5.10: Comparison of the voltage loss breakdown for 25 BC and 25 BA (note that the y-axis is discontinuous) ................................................................. 114

Figure 5.11: Measured polarization results at 100 kPa, 75 °C and 100% RH for 25 BC and 25 BA .................................................................................. 116

Figure 5.12: VLB at 100 kPa, 75 °C and 100% RH for both 25 BA and 25 BC ..................... 117

Figure 5.13: Measured polarization results at 100 kPa, 40 °C and 100% RH for 25 BC and 25 BA .................................................................................. 119

Figure 5.14: VLB at 100 kPa, 40 °C and 100% RH for 25 BC and 25 BA .............................. 119

Figure 5.15: Measured polarization results at 300 kPa, 40 °C and 100% RH for 25 BC and 25 BA .................................................................................. 121

Figure 5.16: VLB at 300 kPa, 40 °C and 100% RH for 25 BC and 25 BA .............................. 122

Figure 5.17: Measured polarization results at 300 kPa, 75 °C and 100% RH for 25 BC and 25 BA .................................................................................. 123

Figure 5.18: VLB at 300 kPa, 75 °C and 100% RH for 25 BC and 25 BA .............................. 124
Figure A.1: Humidity and temperature sensor mount with heating capability ......................... 149
Figure A.2: Drawing for humidity and temperature sensor mount ...................................... 150
Figure A.3: Sensirion SHT75 datasheet, Source: www.sensirion.com ................................. 151
Figure A.4: Vaisala HMT 337 datasheet, source: vaisala.com ............................................. 152
Figure A.5: Test set-up ........................................................................................................ 153
Figure A.6: Drift of the measured potentials over time at 75 °C and 100 % RH at OCV .......... 154
Figure A.7: Signal of the measured potentials over time at 75 °C and 100 % RH at 60 A ....... 155
Figure A.8: Potentials stability of the RHE versus cathode over time at constant load of 20 A for varying reference section flow rates. Standard deviations are shown in error bars .............. 156
Figure B.1: Profilometry traces and photographs of 24 EA, (a) and BA, (b), GDL materials. Particularly for 24 EA, the imprint of the flow field is clearly visible after the test. .............. 157
Figure B.2: Hysteresis after the clamping pressure was cycled from 75 psi to 120 psi and back twice on the cathode side ........................................................................................................ 158
Figure B.3: Hysteresis after the clamping pressure was cycled from 75 psi to 120 psi and back twice on the anode side ........................................................................................................ 159
Figure B.4: Pareto Chart for 25 BC at 1.4 A cm$^{-2}$ ............................................................... 177
Figure B.5: Pareto Chart for 25 BA at 1.4 A cm$^{-2}$ ............................................................... 177
Figure B.6: Pareto Chart for 25 BC at 1.6 A cm$^{-2}$ ............................................................... 178
Figure B.7: Pareto Chart for 25 BA at 1.6 A cm$^{-2}$ ............................................................... 178
Figure C.1: Exemplary CV results for 25 BA sample ......................................................... 188
Figure C.2: Exemplary LSV result for 25 BA sample ......................................................... 189
Figure C.3: Baseline polarization data for GDL material 25 BA, including the standard deviation of the signal in error bars ................................................................. 190
Figure C.4: iR-corrected polarization results at baseline conditions for 25 BA .......................... 190
Figure C.5: VLB at baseline conditions for 25 BA .............................................................. 191
Figure C.6: VLB at 100 kPa, 75 °C and 100% RH for 25 BC ............................................. 191
Figure C.7: VLB at 100 kPa, 75 °C and 100% RH for 25 BA ............................................. 192
Figure C.8: VLB at 100 kPa, 40 °C and 100% RH for 25 BC ............................................. 192
Figure C.9: VLB at 100 kPa, 40 °C and 100% RH for 25 BA ............................................. 193
Figure C.10: VLB at 300 kPa, 40 °C and 100% RH for 25 BC ............................................ 193
Figure C.11: VLB at 300 kPa, 40 °C and 100% RH for 25 BA ............................................ 194
Figure C.12: VLB at 300 kPa, 75 °C and 100% RH for 25 BC ............................................ 194
Figure C.13: VLB at 300 kPa, 75 °C and 100% RH for 25 BA ............................................ 195
List of Symbols

A  Area, m²
b  Tafel slope, V decade⁻¹
D₇  Hydraulic diameter, m²
E  Voltage, V
F  Faraday’s constant, 96485 C
f  Friction factor
G  Gibbs free energy, J
H  Enthalpy, J
f  Friction factor
i  Current density, A cm⁻²
i₀  Exchange current density, A cm⁻²
L  Channel Length, m; Pt loading, mgₚt cm⁻²
M  Molar mass, kg mol⁻¹
m  Mass, kg
n  Number of transferred electrons
p  Pressure, kPa
Q  Heat, J; Charge, C
R  Universal gas constant, 8.314 J (mol K)⁻¹; resistance, Ω
Re  Reynolds number
S  Entropy, J
T  Temperature, °C / K

u  Utilization factor, %

V̇  Velocity, m s⁻¹

x  Specific humidity, g/kg

Greek symbols

α  Activity; transfer coefficient

γ  Reaction order

δ  Electrode thickness, cm

ε  Volume fraction

η  Overpotential, V

λ  Water content, mol_{H₂O}/mol_{SO₂H}

μ  Fluid viscosity, kg m s⁻¹

ρ  Fluid density, kg m⁻³

σ  Conductivity, S m⁻¹

Subscripts/Superscripts

Ca  Cathode

c_t  Charge transfer

eff  Effective
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>elec</td>
<td>Electric</td>
</tr>
<tr>
<td>j</td>
<td>Species j</td>
</tr>
<tr>
<td>l</td>
<td>Limiting</td>
</tr>
<tr>
<td>Pt</td>
<td>Platinum</td>
</tr>
<tr>
<td>pp</td>
<td>Peak power</td>
</tr>
<tr>
<td>rev</td>
<td>Reversible</td>
</tr>
<tr>
<td>sat</td>
<td>Saturated</td>
</tr>
<tr>
<td>tot</td>
<td>Total</td>
</tr>
<tr>
<td>tx</td>
<td>Mass-transport</td>
</tr>
<tr>
<td>w</td>
<td>Water</td>
</tr>
<tr>
<td>x</td>
<td>Cross-over</td>
</tr>
<tr>
<td>0</td>
<td>Thermodynamic standard conditions</td>
</tr>
<tr>
<td>Ω</td>
<td>Ohmic</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>ANOVA</td>
<td>Analysis of Variance</td>
</tr>
<tr>
<td>BoL</td>
<td>Beginning of life</td>
</tr>
<tr>
<td>CCM</td>
<td>Catalyst coated membrane</td>
</tr>
<tr>
<td>CE</td>
<td>Counter electrode</td>
</tr>
<tr>
<td>CL</td>
<td>Catalyst layer</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>DHE</td>
<td>Direct hydrogen electrode</td>
</tr>
<tr>
<td>DMFC</td>
<td>Direct methanol fuel cell</td>
</tr>
<tr>
<td>DoE</td>
<td>Design of Experiments</td>
</tr>
<tr>
<td>EoL</td>
<td>End of life</td>
</tr>
<tr>
<td>ESCA</td>
<td>Electrochemical surface area</td>
</tr>
<tr>
<td>GDL</td>
<td>Gas diffusion layer</td>
</tr>
<tr>
<td>HER</td>
<td>Hydrogen evolution reaction</td>
</tr>
<tr>
<td>HFR</td>
<td>High frequency resistance</td>
</tr>
<tr>
<td>HOR</td>
<td>Hydrogen oxidation reaction</td>
</tr>
<tr>
<td>LSV</td>
<td>Linear sweep voltammetry</td>
</tr>
<tr>
<td>MEA</td>
<td>Membrane electrode assembly</td>
</tr>
<tr>
<td>MPL</td>
<td>Micro-porous layer</td>
</tr>
<tr>
<td>OFAT</td>
<td>One-factor-at-a-time</td>
</tr>
<tr>
<td>ORR</td>
<td>Oxygen reduction reaction</td>
</tr>
<tr>
<td>OCV</td>
<td>Open circuit voltage</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>---------------------------------</td>
</tr>
<tr>
<td>PEMFC</td>
<td>Polymer Electrolyte Membrane Fuel Cell</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>PTL</td>
<td>Porous transport layer</td>
</tr>
<tr>
<td>RE</td>
<td>Reference electrode</td>
</tr>
<tr>
<td>RH</td>
<td>Relative humidity</td>
</tr>
<tr>
<td>RHE</td>
<td>Reversible hydrogen electrode</td>
</tr>
<tr>
<td>VIF</td>
<td>Variance Inflation Factor</td>
</tr>
<tr>
<td>VLB</td>
<td>Voltage loss breakdown</td>
</tr>
<tr>
<td>WE</td>
<td>Working electrode</td>
</tr>
</tbody>
</table>
Acknowledgements

There are many people without whom I could not have produced this work. First, I would like to thank my supervisor Dr. Walter Mérida for his guidance and support throughout the last four years. His knowledge and passion for research truly inspired me.

I would like to express my gratitude to my supervisory committee: Dr. Dana Grecov, Dr. Nima Atabaki, and Dr. Elod Gyenge for your helpful feedback and guidance throughout the years.

I offer my gratitude to the agencies that funded and supported this project: Dr. Haijiang Wang from the National Research Council, the Catalysis Research for Polymer Electrolyte Fuel Cells Network and MITACS.

I would also like to thank the former and current members of Dr. Mérida’s research group and the CERC fuel cell laboratory for the support, friendship and many interesting and helpful discussions. Thank you to Ed McCarthy, Max Schwager, Jochen Schoenweiss, Peter Kalisvaart and Shankar Dhanushkodi for their valuable contributions and insight to this work and the many inspiring and open dialogues on research. I would also like to thank my colleagues Devin Todd and Mauricio Escalante for their support over the years. Thank you to Chris Clarke for taking the time to proof read this work.

Special thanks are owed to my parents and my brother Moritz, who have supported me all the way and in every aspect of my life. You have taught me that anything is possible and your trust has given me strength and confidence throughout my years of education.
I am infinitely grateful for having amazing friends to have supported me through the ups and downs of higher education: Ida Karimfazli, Rob Kehoe, Christina Starke and Sapphire Vanderlip. Thanks for the many hours spent discussing and laughing; and many much needed coffee breaks.

Finally, the biggest THANK YOU to my husband and partner in all adventures. Without you, it would not have been possible.
To my beloved parents
Chapter 1: Introduction

This chapter presents an introduction to polymer electrolyte membrane fuel cell (PEMFC) fundamentals, the motivation for this thesis work and an overview of the structure of this thesis work.

1.1 Motivation

Energy and mobility are part of the most pressing and complex challenges of this century. The principle of a fuel cell, to utilize the electrochemical reaction of oxygen and hydrogen to release electrical energy, has been known for many years. The first noted record of a fuel cell experiment was in 1838 by the physicist Christian Friedrich Schoenbein. One year later Sir William R. Grove presented a functional fuel cell in London. Even though the technology has been known for almost 200 years, fuel cells were only used for special applications in aeronautical or military engineering until the 1960s. Over the last decade, the public awareness of environmental and energy related topics has been steadily increasing, demanding the development for alternative and sustainable energy technologies. Ecological and economical developments combined with a growing and more globalized population require new approaches and solutions for affordable and sustainable energy. This led to a significant increase in research and development in fuel cell technology. As a result of the oil embargo and enhanced environmental awareness during the seventies and eighties of the 20th century, several commercial companies started to develop an interest in fuel cell technology. Decreasing oil resources and increasing emission restrictions nurture a growing demand for “clean”, zero carbon emission, energy sources. Current research efforts around the world, both academic and
industrial, are developing commercially viable and competitive fuel cell technology for both stationary and mobile applications.

1.2 Thesis Layout

This thesis is organized into six chapters. The motivation, background and objective are presented in Chapter 1. This chapter also introduces the governing principles of PEMFC. Chapter 2 provides a comprehensive literature review on previous research efforts related to this thesis. Chapter 3 describes the experimental hardware and materials as well as new diagnostic tool developments that were part of this thesis work. The use of Design of Experiment (DoE) methodologies to evaluate the porous transport layer (PTL) in PEMFC and corresponding results are presented in Chapter 4. Chapter 5 presents a novel method and mathematical tool to conduct voltage loss breakdown (VLB) in operational PEMFC. The results from Chapter 4 were incorporated to study the effect of a micro-porous layer (MPL) on the PEMFC voltage losses. Chapter 6 concludes the findings of this thesis work, presents current efforts resulting from the efforts described and recommends future avenues of research.

1.3 Objectives

This thesis work presents two objectives. The first is based on an applied contribution to improve the efficacy and scientific accuracy of in-situ fuel cell testing by presenting and analyzing novel methodologies both in the design of experiments and the development of diagnostic tools.

The second objective lies in the fundamental understanding of in-situ fuel cell losses with a focus on the mass-transport losses in both anode and cathode electrode and PTL. A
mathematical tool to de-convolute and analyze polarization data is presented and the results from the designed experiment study are applied to investigate the role of the MPL on the voltage loss breakdown under varying operating conditions. Two cell configurations employing different PTL materials are to be analyzed in order to study the influence of the MPL on the mass-transport losses in cathode PTL and catalyst layer separately and the mass-transport losses in the anode PTL and catalyst layer combined.

1.4 PEM Fuel Cell Fundamentals

Fuel cells are electrochemical devices that convert the chemical energy of their reactants directly to electrical energy via the means of spatially separated redox reactions. A redox reaction is a reaction where electrons are being transferred. For a half cell it can be written as

\[ \text{Red} \leftrightarrow \text{Ox} + ne^- \]  (1.1)

where Red is the reductive, Ox is the oxidant and \( n \) the number of transferred electrons. For PEMFCs, operating with hydrogen as fuel, the simultaneous electrochemical half reactions proceed in the following way: At the anode the hydrogen oxidation reaction (HOR) occurs. Hydrogen is separated into \( \text{H}^+ \) ions and electrons \( e^- \).

\[ \text{Anode: } \text{H}_2 \rightleftharpoons 2\text{H}^+ + 2e^- \]  (1.2)

The \( \text{H}^+ \) ions migrate through a proton conducting polymer membrane to the cathode electrode. The membrane is an electrical insulator. Therefore the electrons are forced through an external circuit, where a load can be applied. At the cathode, the oxygen reduction reaction (ORR) takes place. Electron and hydrogen ions react with an oxidant and form product water.

\[ \text{Cathode: } \frac{1}{2}\text{O}_2 + 2\text{H}_2 + 2e^- \rightleftharpoons \text{H}_2\text{O} \]  (1.3)
Figure 1.1 shows a simplified functional diagram of a PEMFC.

The overall reaction for a hydrogen fuel cell is an exothermic, meaning heat producing, process given according to:

$$2H_2 + O_2 \rightarrow 2H_2O + \text{Heat}$$

(1.4)

The heat or enthalpy, $H$, of a chemical reaction is the difference between the heats of formation of products and reactants. At standard conditions of 298 K, 1 atm and activities of 1 for all reactants and products this leads to a standard thermoneutral potential of 1.48 V. But the second law of thermodynamics dictates that not all of the change of enthalpy can be converted to work,
part of it is released as heat associated with a change in entropy, $\Delta S$ [J]. The maximum usable energy of a reaction at constant pressure and temperature is given by the change in Gibbs free energy, $\Delta G_{(T,p)}$:

$$\Delta G_{(T,p)} = G_{\text{products}(T,p)} - G_{\text{reactants}(T,p)}$$  \hspace{1cm} (1.5)

The Nernst equation describes the reversible voltage of a fuel cell as a function of the temperature and activity, $\alpha$, of the species involved.

$$E_{\text{rev.}(\alpha)} = \frac{-\Delta G^0}{nF} - \frac{RT}{nF} \ln \left[ \frac{\prod \alpha_{\text{products}}^s}{\prod \alpha_{\text{reactants}}^s} \right]$$  \hspace{1cm} (1.6)

In the above equation $n$ is the number of transferred electrons, which is equal to two for the hydrogen fuel cell as each molecule of hydrogen passes two electrons. $T$ is the temperature in Kelvin, $R$ is the universal gas constant (8.314 J (mol K)$^{-1}$), $F$ is Faraday’s constant (96485 C), $\alpha$ the respective activities and $s$ is the stoichiometric coefficient for the electrochemical reaction of the species $j$. At standard conditions this leads to a reversible fuel cell potential of

$$E_{\text{rev}}^0 = \frac{-\Delta G^0}{nF} = \frac{237160 \text{ J mol}^{-1}}{2 \cdot 96458 \text{ C mol}^{-1}} = 1.229 \text{ V}$$  \hspace{1cm} (1.7)

As stated above, the Gibb’s free energy is temperature dependent.

$$\Delta G = \Delta G^0 - \int \Delta SdT$$  \hspace{1cm} (1.8)

Assuming a constant change in entropy, and gas phase reactants and an activity of one for the product, Bernardi and Verbrugge$^1$ proposed the following formula to calculate the reversible or equilibrium potential of a PEMFC operating with hydrogen as fuel.

$$E_{\text{rev}(p_{H_2},p_{O_2},T)} = 1.23 - 0.9 \cdot 10^{-3} (T - 298) + \frac{2.303RT}{4F} \log \left[ \left( \frac{p_{H_2}^0}{p_{H_2}} \right)^2 \left( \frac{p_{O_2}^0}{p_{O_2}} \right) \right]$$  \hspace{1cm} (1.9)
Figure 1.2 summarizes the derivation of the reversible cell potential.

\[ Q_{\text{rev}} = T \Delta G_{\text{reaction}}^0 = \Delta H_{\text{reaction}}^0 - \Delta G_{\text{reaction}}^0 = \Delta H_{\text{reaction}}^0 + nF \Delta E_{\text{reaction}}^0 \]

**Figure 1.2: Thermodynamics of a PEMFC**

### 1.4.1 Components and Materials

As shown in Figure 1.1, a PEMFC, also called proton exchange membrane fuel cell, is based on a proton conducting membrane that is placed between two electrodes. The assembly of membrane and a catalyst layer (CL) is called a catalyst coated membrane (CCM) because the electrodes require a catalyst, usually platinum or platinum compositions, to facilitate the reactions. Adjacent to the electrodes are the PTLs. The combination of a CCM and a PTL on each side are called a membrane electrode assembly (MEA). Gases are supplied via flow-channels and the electrical contact is achieved through the landings of these channels. These channels are usually integrated into a bipolar plate that is used as the current collector. A fuel cell stack is comprised of multiple (up to hundreds) MEAs stacked in series to achieve required voltages.
1.4.1.1 The Bipolar Plate

The bipolar plate, or flow-field plate, is a multi-functional component. Its purposes are the reactant and product transport through the flow channels as well as providing electrical connections between the individual cells. Therefore, it must provide excellent electrical conductivity and its thermal properties must allow for heat removal. Bipolar plates have to provide mechanical stability to allow for compression of the cell or stack in order to generate homogeneous contact between the channel landings and the MEA. They need to be chemically stable and withstand the required operating temperatures. Especially in mobile applications, they need to be compact and light weight. Bipolar plates are commonly made from graphite composite or metallic materials. Different flow-field configurations are possible (e.g. serpentine, parallel or interdigitated flow channels). The material has to be impermeable to gases and allow for the integration of sealing between individual cells.

1.4.1.2 The Porous Transport Layer

The PTL in PEMFC is usually made of a dual layer structure comprising of a macro-porous gas diffusion layer (GDL), also called substrate, and a micro-porous layer (MPL). The GDL and MPL serve a plurality of important functions in operating PEMFC:

- Provide a homogeneous reactant distribution from the flow field to the reaction sites. This requires high gas permeability for GDL > 1 x 10^{-13} \text{ m}^2 and MPL > 1 x 10^{-14} \text{ m}^2.
- Minimize the pressure drop to reduce efficiency losses.
- Facilitate heat removal from the CL to the bipolar plate. This requires high thermal conductivity which varies with PTFE content but through-plane measurements have given values between 0.2 – 1.8 W m\(^{-1}\) K\(^{-1}\).\(^5\)

- Remove liquid product water from the CL in order to prevent catalyst flooding, which requires a high porosity of the GDL, typically between 0.7 – 0.8.\(^5\)

- Provide good electrical contact and good interfacial contact between CL and PTL in order to facilitate the electron transfer and minimize ohmic losses. This requires low electrical resistivity which is influenced by the compression of the material. Experiments have measured the through – plane resistivity < 0.1 \(\Omega\) cm and the in - plane resistivity between 0.055 and 0.009 \(\Omega\) cm.\(^3,5\)

- Provide mechanical support to the CCM.

- Be thermally and chemically resistant and provide durability.

These functions sometimes lead to some contradicting requirements. For example air and water permeability increase with higher porosity, contrary to mechanical strength and electrical as well as thermal conductivity. A compromise to fulfill all aspects partially is needed to get the best possible performance under varying operating conditions. Therefore, the design and composition of the GDL and MPL have to be considered carefully. The GDL and MPL characteristics are defined by their thickness, hydrophobicity and alignment of the carbon fibers. GDL substrates are usually made of carbon cloth and carbon paper. Carbon fiber shows good thermal and electrical conductivity. It can have high porosities up to 70% or higher and provides good mechanical strength at a low weight per unit. In order to improve liquid water transport, this substrate is infused with a hydrophobic agent, e.g. polytetrafluoroethylene (PTFE). The applied
percentage of PTFE varies between 5 to 30 wt%. Increasing PTFE content leads to a decrease in electrical conductivity and gas permeability.

The macro-porous substrate is the macro-porous features typical pore diameters from 10 \( \mu \text{m} \) to 30 \( \mu \text{m} \).\(^6\) The MPL is a thin layer consisting of carbon black and hydrophobic agent and is usually coated on the macro-porous substrate.

1.4.1.3 The Catalyst Layer

The catalyst layer is where the electrochemical reactions occur. The CL is a complex structure that serves several important functions: It must provide a large, three-phase boundary, active area to minimize activation overpotentials.\(^7\) It needs to be porous so that reactants can be transported to the active sites and product water can be removed. It also needs to incorporate a catalyst in order to improve reaction kinetics. These requirements are met by employing a porous structure of dispersed carbon supported catalyst, usually platinum based. Ionomer is added to the carbon structure to act as a binder and facilitate ionic transport. Common CL thicknesses vary between 10 – 30 \( \mu \text{m} \). Recent efforts have investigated ultra-thin, ionomer free CL with thicknesses between 20 nm – 1 \( \mu \text{m} \).\(^8,9\)

1.4.1.4 The Membrane

The membrane of a PEMFC has to be impermeable to gases in order to separate anode and cathode and facilitate the proton transport. It needs to provide:

- excellent proton conductivity > 10 S m\(^{-1}\) at the working temperature,\(^10\)
- thermal and chemical stability,
- strength and flexibility,
• impermeability to gases,
• low water drag,
• as well as low production cost and good availability, as a commercial supply chain may not be fully established in the early stages of commercialization.

Commonly polymers with sulfonic groups that facilitate the proton transport are used. Currently the most popular polymer material is Nafion® (DuPont). Nafion® is a perfluorinated polymer and has a PTFE backbone structure including sulfonic acid (SO$_3$H$^-$) groups and called an ionomer. Most polymer materials used in PEMFC rely on water-based ionic transport mechanisms. This means that the membrane has to be humidified to provide sufficient ion conductivity. Springer et al. give the following empirical relationship between ionic conductivity in (Ω cm)$^{-1}$ and water content $\lambda$ for $\lambda > 1$ for Nafion 117:

$$\sigma_{\text{ion}}(T_{\text{cell}}) = \exp \left[ 1268 \left( \frac{1}{303} - \frac{1}{T_{\text{cell}} + 273.15} \right) \right] (0.005139 \cdot \lambda - 0.00326).$$  \hspace{1cm} (1.10)$$

The water content $\lambda$ is defined as

$$\lambda = \frac{n_{H_2O}}{n_{SO_3H}},$$  \hspace{1cm} (1.11)$$

the ratio between water molecules per sulfonic acid site.

**1.4.2 PEMFC Loss Mechanism**

Depending on the operating conditions and achieved current density, a fuel cell is subject to irreversible losses. There are three major types of losses. If operated at low current densities activation losses due to limitations of the reaction kinetics are the governing form of losses. At medium current densities activation losses and ohmic losses from ionic and electronic
conduction resistances dominate. At high current densities there are activation losses, ohmic losses and concentration losses due to mass transport limitations. These losses are called overpotentials, as they represent the deviating between the applied electrode potential and the reversible potential. Figure 1.3 illustrates the dependence of the controlling losses on current density.

 Activation Overpotential

The **Butler-Volmer** equation describes the current-potential relationship.

\[
i = i_0 \left[ \exp \left( {\alpha n F \eta \over RT} \right) - \exp \left( {\left( 1-\alpha \right) n F \eta \over RT} \right) \right]
\]  (1.12)
In the above equation $i$ is the current density, $i_0$ is the exchange current density, $\alpha$ is the transfer coefficient and $\eta$ is the overpotential. The derivation of the Butler-Volmer equation can be found elsewhere.\textsuperscript{12} In the case of a PEMFC, the cathode current density is defined as positive and the anode current density is defined as negative. The activation kinetics of fuel cells can be simplified using two approximations: one approximation for large overpotentials $|\eta| < 50–100$ mV at room temperature or $i > i_0$ and one approximation for small overpotentials $|\eta| < 15$ mV or $i \ll i_0$. Therefore, the Butler-Volmer equation for the forward reaction, at large negative overpotentials, can be written as:

$$i = i_0 \exp \left( \frac{-\alpha n F \eta}{RT} \right) \text{ for } \eta \gg \frac{RT}{nF}$$  \hfill (1.13)

and the backward reaction, for large positive overpotentials can be written as:

$$i = i_0 \exp \left( \frac{(1-\alpha) n F \eta}{RT} \right) \text{ for } \eta \gg \frac{RT}{nF}.$$  \hfill (1.14)

This is often written in the form of the \textbf{Tafel equation}. For the forward reaction:

$$\eta = \frac{RT}{\alpha n F} \ln i_0 - \frac{RT}{\alpha n F} \ln i$$  \hfill (1.15)

and for the backward reaction:

$$\eta = \frac{RT}{(1-\alpha) n F} \ln i_0 - \frac{RT}{(1-\alpha) n F} \ln (-i).$$  \hfill (1.16)

These equations can be simplified to

$$\eta = a + b \log i$$  \hfill (1.17)

and

$$\eta = a + b \log(-i).$$  \hfill (1.18)
In the above equations $b$ is the Tafel slope. For large overpotentials the forward reaction direction dominates and the second exponential term in the Butler-Volmer equation becomes negligible.

**Mass-Transport Overpotential**

If the reaction is controlled by kinetics the exchange current density in Equation (1.12) is assumed to be constant. In the mass transport dominated region of the polarization curve, the reactant concentration becomes the limiting factor. The reactant concentration decreases with increasing current density. Mass-transport limitations of the reactants lead to a drop in reactant concentration at the active sites as the reactants are consumed in the reaction. This overpotential is hence called mass-transport or concentration overpotential. The concept of a limiting current, $i_l$, combined with the Nernst Equation (1.6) yields:

$$
\eta_{\alpha,j} = \frac{RT}{nF} \ln \left( \frac{i_{l,j}}{i_{l,j} - i} \right).
$$

(1.19)

In the above equation $\eta_{\alpha,j}$ is the mass-transport overpotential cause by a species $j$ with a limiting current density $i_l$.

**Ohmic Overpotential**

Ohmic losses are caused by ohmic polarization due to electronic transfer resistances and protonic transfer resistances in the fuel cell. Ohmic losses are dictated by Ohm’s law,

$$
\eta_\Omega = iR_\Omega
$$

(1.20)
where $\eta_\Omega$ is the ohmic overpotential and $R_\Omega$ is the internal ohmic resistance.

A more detailed account of voltage loss breakdown methods and the individual loss mechanism are given in Chapter 2 and Chapter 5.
Chapter 2: Voltage Loss Characterization

As stated in the Introduction, a PEMFC is subject to several voltage losses during operation. The electric power of the fuel cell, which can be utilized, is the product of the extracted current and the measured potential difference between anode and cathode electrode. In order to improve the fuel cells efficiency and reduce voltage losses intensive research efforts have been concerned with the characterization of PEMFC voltage losses. Water transport inside the PEMFC is a complex process and has a significant influence on the cell’s power generation. The role of the MPL within the PEMFC is still not fully explained. There have been many efforts investigating the effect of an MPL on the voltage output of an operational PEMFC. This chapter presents the current state of the art of VLB methods in PEMFCs diagnostics to measure the individual losses.

2.1 Reference Electrodes in PEMFC

The working potential between anode and cathode of an operating PEMFC is always smaller than the reversible cell potential at standard thermodynamic conditions, \( E^{0}_{th} \). This is smaller than the standard thermoneutral potential, \( E^{0}_{rev} \), as described in the previous Chapter 1. Losses occur at both anode and cathode electrodes, though the magnitude of the individual losses varies depending on material properties and operating conditions (e.g. temperature, gas flow-rates, gas humidification and reactant partial pressures). During conventional operation, the fuel cell voltage is measured as the potential difference between anode and cathode electrode and it is not possible to distinguish between the loss contributions of each individual electrode. Understanding the behaviour of the individual electrodes during operation is fundamental to
developing operating strategies and validation of half-cell models. Three electrode measurements, traditionally known from aqueous electrochemical systems, allow to quantitatively measure the anode’s and cathode’s potential. In an operating PEMFC hydrogen reference electrode (RE) systems have been used. An ideal RE is a reversible electrode that does not polarize, has good signal stability during measurements, exhibits no signal drift over time, and has fast transient response times.

Figure 2.1 shows a schematic relation between the measured potentials for the full cell, anode versus RE and cathode versus RE.

![Figure 2.1: Exemplary schematic of PEMFC polarization measurements with reference electrodes (RE)](image-url)
Internal reference electrodes are in direct contact with the polymer electrolyte membrane of the working fuel cell and can be incorporated either inside the active area\textsuperscript{24} or in separately sealed chambers.\textsuperscript{18} They do not require a liquid electrolyte bridge (e.g. salt bridge). There are two types of internal reference electrodes that are applied in in-situ PEMFC characterization: a direct hydrogen electrode (DHE) and a reversible hydrogen electrode (RHE). DHEs are usually constructed of platinum or palladium wires or meshes that are in contact with the membrane. An external current is applied at the DHE to generate hydrogen during experimentation. This leads to a constant hydrogen concentration at the DHE and generates a stable signal that is not subjected to external contamination or fluctuating conditions at the RE. Construction of a DHE can be challenging due to high contact resistances and geometric restrictions\textsuperscript{16,25} and a parasitic overpotential of 5 mV has been reported due to the internal current.\textsuperscript{22}

A RHE is a RE that requires an external hydrogen feed either from the anode directly or from a separate system. Commonly, platinum or gold wires are used to create electrical contact either directly onto the membrane or onto an electrically separated CL.\textsuperscript{13,18} While this type of RE has more challenging requirements to the system design due to the sealing requirements and need for constant and homogeneous hydrogen supply, it can be fed with hydrogen at variable temperature and humidification and is not subject to parasitic, internal currents.\textsuperscript{18}

Previous efforts have assumed that the cross over and non-ohmic anode losses are small, negligible, or constant over the range of practical current densities.\textsuperscript{26–29} However, recent work demonstrates that this assumption is not valid under out-of-specification conditions (e.g., dry anodes, fuel starvation, etc.).\textsuperscript{19,30} Herrera et al. have researched the anode and cathode overpotentials separately employing reference electrodes and multi-component gas analysis.\textsuperscript{19} Their work looked at three different operating conditions: a) baseline, b) flooding and c) drying.
They found that anodic losses (including ohmic contributions) play a significant role regarding the total losses in a fuel cell accounting for 5 – 18.5% of the total potential losses during baseline operation. Under flooding and drying conditions the anodic contribution increased in percentage. Baumgartner et al. observed similar characteristics in hydrogen starvation measurements and cathode dead-end operation. This thesis work combines a novel RHE design with a systematic voltage loss breakdown method.

Table 2.1 summarizes selected recent efforts in PEMFC research employing RE techniques.

<table>
<thead>
<tr>
<th>RE System</th>
<th>Analysis</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>DHE</td>
<td>Dependence on geometric effects, CO poisoning,</td>
<td>Li and Pickup\textsuperscript{15,16}</td>
</tr>
<tr>
<td></td>
<td>PEMFC and DMFC</td>
<td></td>
</tr>
<tr>
<td>Pseudo RE (carbon filament)</td>
<td>EIS measurements to determine kinetic parameters</td>
<td>Kuhn et al.\textsuperscript{31}</td>
</tr>
<tr>
<td>Detachable RE</td>
<td>Edge effects and RE alignment with respect to potential distribution, RE as diagnostic tool</td>
<td>He and Van Nguyen\textsuperscript{14}</td>
</tr>
<tr>
<td>DHE</td>
<td>Catalyst corrosion processes</td>
<td>Lauritzen et al.\textsuperscript{17}</td>
</tr>
<tr>
<td>RE System</td>
<td>Analysis</td>
<td>References</td>
</tr>
<tr>
<td>-----------------------------------</td>
<td>-------------------------------------------------------</td>
<td>------------------</td>
</tr>
<tr>
<td>DHE</td>
<td>Anode and cathode degradation</td>
<td>Zhang et al.²²</td>
</tr>
<tr>
<td>DHE</td>
<td>DHE overpotential evaluation</td>
<td>Siroma et al.²²,²³</td>
</tr>
<tr>
<td>Through-plate Nafion RE with salt bridge</td>
<td>Start-up behavior and catalyst support corrosion measurements</td>
<td>Hinds and Brightman²⁴,²⁵</td>
</tr>
<tr>
<td>RHE inside active area</td>
<td>RE by laser ablation, PEFC and DMFC operation</td>
<td>Gerteisen¹³,²⁴</td>
</tr>
<tr>
<td>RHE and sensing electrodes</td>
<td>Sensing electrodes for failure diagnostic and spatially segmented RE approach</td>
<td>Herrera et al.¹⁸,¹⁹,³⁶</td>
</tr>
<tr>
<td>RHE in separate chambers</td>
<td>Voltage loss breakdown with different GDL material under varying operating conditions</td>
<td>Flick et al.</td>
</tr>
</tbody>
</table>

### 2.2 Voltage Loss Breakdown

The voltage of an operating PEMFC, $V_{cell}$, is described as the difference between the equilibrium potential $E_{rev} (p_{H_2}, p_{O_2}, T)$ and the total overpotential $\eta_{total}$.
\[ V_{\text{cell}} = E_{\text{rev}}(p_{H_2}, p_{O_2}, T) - \eta_{\text{total}} \]  

(2.1)

The total overpotential can be expressed as the sum of all individual polarization sources:

\[ \eta_{\text{total}} = \eta_{\text{ORR}} + \eta_{\text{HOR}} + \sum \eta_\Omega + \eta_{\text{tx,elec}} + \eta_{\text{tx,PTL}} + \eta_{\text{elec,PTL}} + \eta_x \]  

(2.2)

In the above equation \( \eta_{\text{ORR}} \) is the activation overpotential for the ORR, \( \eta_{\text{HOR}} \) is the activation overpotential for the HOR, \( \eta_{\text{tx,elec}} \) are the respective mass-transport losses in the respective catalyst layers, \( \eta_{\text{tx,PTL}} \) represent the mass-transport losses inside the PTL (GDL substrate and, if applicable, MPL) for both anode and cathode side and \( \eta_x \) is the overpotential due to reactant cross-over. The collective ohmic overpotential \( \sum \eta_\Omega \) includes sources from membrane and both electrodes. This can be written as

\[ \sum \eta_\Omega = \sum \eta_\Omega,\text{Anode} + \sum \eta_\Omega,\text{Cathode} + \eta_{\text{HFR}} \]  

(2.3)

where \( \sum \eta_\Omega,i \) are the respective overpotentials within the anode and cathode electrode layers. \( \eta_{\text{HFR}} \) is the overpotential from the high frequency resistance (HFR) including the total ohmic overpotential from all sources except for the electrode layers.

The breakdown of the measured cell voltage into the individual loss components is called VLB. Understanding of the individual loss components is fundamental for the improvement of the cell’s performance and durability. Several researchers have used empirical models, mathematical models and mathematical fitting tools to evaluate the individual
polarization sources in PEMFC but there have been only a number of efforts on separating the individual cathode PTL and cathode CL mass-transport overpotentials.\textsuperscript{29}

Gasteiger et al. developed a comprehensive approach to characterize the beginning-of-life (BoL) MEA performance and the individual efficiency loss contributions. The major loss contribution in his analysis was the activation ORR overpotential. Using this approach they compared the 50 cm\(^2\) single research cell results to a 500 cm\(^2\) short stack and found the results from the 50 cm\(^2\) cell relevant for understanding and prediction of the performance of the 500 cm\(^2\) cell. Williams et al. developed a step-by-step technique to evaluate six individual polarization sources, with a focus on the cathode.\textsuperscript{28} Their model was based on the assumptions of a first order cathode reaction, Butler-Volmer equation kinetics and oxygen transport by Fickian diffusion in the gas phase. Their model accounted for the PTL and electrode mass-transport resistance by employing a modified Tafel slope as a function of limiting current density under H\(_2\)/air operation. Their calculation required a complex iterative process to extract the mass-transport overpotentials and was focused on high temperatures and low oxygen partial pressures.

Wood and Borup developed a method to estimate the mass-transport overpotentials in the cathode electrode and cathode PTL over a long term experiment.\textsuperscript{29} Their approach distinguished between cathode PTL and cathode electrode mass-transport losses in combination with an ohmic and kinetic analysis. They combined the analysis of polarization data and cyclic voltammetry as a function of time to account for changes in the electrochemically active surface area (ECSA).

Beuscher used polarization data to extrapolate the limiting current in order to determine an average mass-transport resistance.\textsuperscript{27} He developed a resistor in series model to extract the individual cathode mass-transport resistances while the anode was assumed to act as a reference electrode with an ideal potential of zero.
All of these reported approaches were developed based on the following assumption: the non-ohmic anodic contributions to the overpotential are negligible. Herrera et al. conducted an analysis that distinguished between anode and cathode losses using a reference electrode system.\textsuperscript{19} Their work featured an analysis of the mass-transport overpotential based on limiting current measurements and calculations but their distinction between anodic and cathodic limiting current and the approach to determine these is not fully explained. This thesis work developed a systematic method to separate the individual overpotentials including the anodic contributions via reference electrode measurements and a mathematical tool based on an indirect mathematical approach without using limiting current measurements or calculations. Unlike the works of Herrera et al. this work can distinguish between the mass-transport losses in the cathode catalyst layer and cathode porous transport layer. Table 2.2 summarizes a selection of recent VLB efforts.
<table>
<thead>
<tr>
<th>Techniques</th>
<th>Losses Analyzed</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$/O$_2$ and H$_2$/air polarization fitting based on Tafel kinetics</td>
<td>BoL $\eta_{ORR}$, $\eta_\Omega$</td>
<td>Gasteiger et al.$^{20}$ Neyerlin et al.$^{42,43}$</td>
</tr>
<tr>
<td>Hydrogen pump cell, fitting based on Butler-Volmer kinetics</td>
<td>$\eta_{HOR}$, $\eta_\Omega$, HOR kinetics</td>
<td>Neyerlin et al.$^{44}$</td>
</tr>
<tr>
<td>Polarization measurements, fitting based on Butler-Volmer kinetics, Fick’s law and limiting current condition</td>
<td>$\eta_{\Omega,elec}$, $\eta_{\Omega,non-elec}$, $\eta_{tx,O_2,elec}$, $\eta_{tx,O_2,GDL}$, $\eta_{ORR,Tafel}$, $\eta_{ORR,activity}$</td>
<td>Williams et al.$^{28}$</td>
</tr>
<tr>
<td>Limiting current interpolation based on polarization measurements, resistors in series approach</td>
<td>$\eta_{tx}$ in: cathode CL, cathode gas diffusion media, cathode flow-channel, cathode ionomer and water film</td>
<td>U. Beuscher$^{27}$</td>
</tr>
<tr>
<td>Polarization analysis, durability tests, hybridized method to account for ECSA, cross-over and exchange current density over time, mathematical fitting tool</td>
<td>BoL and EoL analysis of: $\eta_\Omega$, $\eta_{ORR}$, $\eta_{tx,O_2,elec}$, $\eta_{tx,O_2,GDL}$</td>
<td>Wood and Borup$^{29}$</td>
</tr>
<tr>
<td>Polarization analysis using reference electrodes and multi-component gas analysis, mass-transport analysis using limiting current interpolation</td>
<td>BOL analysis of $\eta_\Omega$, $\eta_{activation}$, $\eta_{tx}$ for anode and cathode</td>
<td>Herrera et al.$^{19}$</td>
</tr>
<tr>
<td>Polarization measurements, reference electrode measurements, HFR measurements, electrochemical analysis, Tafel kinetics, systematic fitting tool</td>
<td>BoL: $\eta_{ORR}$, $\eta_{tx,O_2,elec}$, $\eta_{tx,O_2,GDL}$, $\eta_{tx,H_2}$, $\sum \eta_\Omega$</td>
<td>Flick et al.$^{45,46}$</td>
</tr>
</tbody>
</table>
2.2.1 Cross-Over Overpotential

The open circuit voltage of a PEMFC is typically around 0.95 – 1.05 V and a function of operating temperature. The difference between the reversible potential and the maximum cell voltage can be more than 200 mV. These losses arise primarily from internal shorts and hydrogen cross-over from the anode to the cathode through the membrane. Vilekar and Datta conducted a detailed analysis of PEMFC losses at OCV based on a numerical model and experimental data. They found for a pin-hole free membrane the electrical short-circuit current is an order of magnitude smaller than the H$_2$ permeation current. They suggest that hydrogen crossover entirely accounts for the observed loss of 200 mV under open-circuit conditions. Membrane properties such as thickness and composition as well as gas pressure, temperature and humidification, have a direct effect on the observed cross-over rate. Thinner membranes are prone to higher cross-over rates. Fuel cross-over rates increase with increasing fuel partial pressure and temperature. Recent work by Baik et al. investigated the effect of the gas diffusion layer structure on the OCV and hydrogen cross-over of a PEMFC. They used three different GDL materials under different clamping pressures and analyzed the cathode exit stream for levels of hydrogen using a mass spectrometer. They found an increased rate of hydrogen crossover for all GDL samples with the increase of clamping torque. Fuel cross-over through the membrane can be measured in-situ employing linear sweep voltammetry (LSV). BoL cross-over current densities for commercial PEMFC membranes with a thickness of 50 µm are reported between 1.0 – 3.3 mA cm$^{-2}$. 


2.2.2 Activation Overpotential

Activation losses are caused by slow reaction kinetics at the electrodes. They are the dominating source of overpotentials at low current densities. Activation losses are functions of the operating conditions of the fuel cell, such as humidity, pressure, temperature, reactant concentration and purity of the reactants.

2.2.2.1 Anodic Activation Overpotential

Several studies have concluded that the hydrogen oxidation reaction contributes little to the overall cells’ polarization. Neyerlin et al. have conducted studies on the contribution of the HOR to the performance losses employing several diagnostic techniques. They used a hydrogen pump cell, AC impedance and cyclic voltammetry (CV). They found the exchange current density for the HOR in the order of 200 – 600 mA cm\(^{-2}\)Pt. Their results show that the reaction occurs dominantly at the anode electrode to membrane interface, which leads to a negligible protonic resistance. High limiting current density, exchange current density and transfer coefficient values indicate that the contributions of the HOR overpotential to the overall voltage loss are negligible and that the fast kinetics of the HOR reaction allow for further reduction of catalyst loading without imposing measureable voltage loss.

2.2.2.2 Cathodic Activation Overpotential

The reaction kinetics of the ORR, the ECSA and catalyst utilization at the cathode are strongly influenced by the catalyst layer morphology and material composition. The incorporation of an ionomer, e.g. Nafion®, leads to an integration of porous catalyzed carbon into the electrolyte. This leads to an extended three-dimensional reaction zone and an
improvement in the ORR efficiency. The amount of ionomer strongly influences the proton conductivity and water retention properties of the CL and hence has an impact on ohmic and mass-transport losses as well. Several studies have been carried out to determine the optimal Nafion content for PEMFC under different operating conditions. Neyerlin et al. found strong dependences of the ORR kinetics on water and proton activity at relative humidity (RH) values below 50 – 60%. At 30% RH they observed significant losses in the ORR kinetics of approximately 20 mV, leading to a reduction in ORR exchange current density of 50%. This is consistent with a reduced H\(^+\) activity at low RH. Gasteiger et al. and Neyerlin et al. systematically analyzed the ORR kinetic parameters at different temperatures and oxygen partial pressures. Established techniques are available to characterize the ORR at the PEMFC cathode electrode. Kinetic parameters like transfer coefficient, exchange current density, reaction order with respect to oxygen partial pressure and activation energy can be derived using a combination of experimental techniques. A combination of steady state polarization, CV and LSV has been employed in the literature. Gasteiger et al. published a comprehensive summary of ORR kinetic parameters in PEMFC. Table 2.3 list a summary of the reported results for material with a loading between 0.3 – 0.4 mg\text{Pt}\ cm\(^{-2}\) at temperatures between 60 – 95 °C and oxygen partial pressures between 53 – 453 kPa.

Table 2.3: Comparison of Tafel slopes (b), exchange current densities \(i_{0(T)}\), and iR-free current densities at 0.9 V, \(i_{0.9V(T)}\), normalized to 101.3 kPa O\(_2\). Data taken from Gasteiger et al.

<table>
<thead>
<tr>
<th>b / mV decade(^{-1})</th>
<th>(i_{0(T)}) / A\ cm(^{-2})</th>
<th>(i_{0.9V(T)}) / mA\ cm(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>59 – 66</td>
<td>(1.5 \times 10^{-9} – 8.5 \times 10^{-9})</td>
<td>0.06 – 0.48</td>
</tr>
</tbody>
</table>
2.2.3 Ohmic Overpotential

Ohmic losses occur due to electronic and ionic resistances in the MEA. The electronic resistances inhibit the electron flow across the cell components, and they include interfacial (contact) resistances across the bipolar plates and MEA layers. A uniform pressure distribution minimizes the electrical contact resistances within the cell. The ohmic resistance of the cell can be directly measured under in-situ conditions but the in-situ differentiation between the individual ohmic loss contributions is challenging. The reported methods include:

i. AC impedance spectroscopy

ii. High Frequency Resistance measurements

iii. Current interrupt method

iv. H₂/O₂ polarization at high stoichiometries

v. MRED method.

Cooper and Smith compared different measurement techniques listed under i. – iii. They found the measured ohmic resistances within a range of 10 – 30% of each other for the different methods. Wood and Borup report resistance values of the purely resistive component of the cell’s electrochemical impedance or HFR of 50 – 75 mΩ cm² for conventional membranes with a thickness ≤ 50 μm under fully humidified operating conditions. Under sub-saturated conditions this value increases to 75 – 300 mΩ cm². They also investigated the cathode protonic resistance under different operating conditions and electrode compositions and found an average value of 21 mΩ cm². Saab et al. conducted a systematic study of the ionic and electronic conductivities of electrode catalyst layers with different ink compositions by employing AC impedance and DC polarization measurements. They found the catalyst layer electronic
resistance to be \(< 1 \, \Omega \, \text{cm}\) which corresponds to an areal resistivity \(< 0.5 - 2.5 \, \text{m\Omega} \, \text{cm}^2\) for conventional CL thicknesses between 5 – 25 \(\mu\text{m}\). Saab et al. found the ionic resistivity of a Los Alamos National Laboratory MEA between 104 – 242 \(\Omega \, \text{cm}\). This corresponds to an areal resistivity between 30 – 50 \(\text{m\Omega} \, \text{cm}^2\) for electrode thicknesses between 3 – 5 \(\mu\text{m}\). Recent studies by Stumper and Stone have used Pt. micro wires to determine the ohmic losses of GDL, flow field, membrane and the cathode and anode plate. They ascribed 70% of the losses to be non-membrane ohmic losses. Cimenti et al. have performed AC impedance measurements to analyze the CL proton conductivity and CL ohmic resistance. They found impedance employing \(\text{H}_2/\text{N}_2\) to be advantageous over the \(\text{H}_2/\text{O}_2\) method described as it allows shorter testing times, simpler data analysis and resistance measurements at equilibrium. Stumper et al. developed an in-situ method to measure the MEA resistance and electrode diffusion coefficient for a fuel cell named the MRED method. They presented a way to determine the true ohmic cell resistance without the influence of mass-transport effects. The cathode was subjected to a galvanostatic discharge with interrupted reactant supply while the anode was continuously supplied with \(\text{H}_2\). They measured an averaged ohmic fuel cell resistance of 120 \(\text{m\Omega} \, \text{cm}^2\), independent of the reactants. The use of an MPL was found to have a positive impact on the contact resistance between the electrode and the GDL.

2.2.4 Mass-Transport Overpotential

A fuel cell’s performance is determined by the reactant and product concentration within the catalyst layer. Hence a sufficient mass transport of reactants to the active sites and a simultaneous removal of reaction products are required. The transport of reactants and products is governed by multi-phase gas transport and depends on operating conditions, structure,
constitution and wetting properties of the PTL. Mass transport losses increase when liquid phase water agglomeration in the CL and/or PTL. This phenomenon commonly referred to as flooding of the PTL, leads to blocked reaction sites due to liquid water and a limited reactant gas supply to the reaction sites. This phenomenon intensifies at higher current densities where more product water is generated and under lower gas flow rates. As water is generated at the cathode, it is often the performance limiting side due to flooding of the CL and PTL. In-situ determination of mass-transport overpotentials is a non-trivial task. Most measurements are based on limiting current measurements.\textsuperscript{27,28,29} Studies of mass-transport under reduced RH have shown decreasing limiting current density with increasing RH. This is attributed to limiting oxygen transport within the catalyst layer at low RH.\textsuperscript{80} Kim et al. found that drying of the cathode at low RH combined with low current densities leads to an increase in ionic resistance of the CL as well as an increase in charge- and mass-transfer resistances.\textsuperscript{81} Wood and Borup developed a hybridized method to extract and separate the mass-transport overpotential in the cathode CL and cathode GDL.\textsuperscript{29} After long term operation (1000 h) they observed a significant decrease in the mass-transport overpotential in the CL (< 25 mV after 1000 h) and an increase in the mass-transport overpotential in the GDL (> 220 mV at 1.5 A cm\textsuperscript{-2} after 1000 h).

This summary shows that there have been significant efforts in characterizing the individual losses at each electrode in operating PEMFC but there are still gaps in the detailed understanding of mass-transport losses, especially associated with water management. A systematic breakdown of the anodic overpotentials has not yet been reported in literature. This thesis work is aiming to close this gap by analyzing in-situ mass-transport overpotentials at both cathode and anode electrode.
2.3 Water Management in PEMFCs

One remaining technical challenge in PEMFC development is the management of water inside the fuel cell stack. The proton conductivity of the membrane is a function of the water saturation in the membrane. Operating a PEMFC at temperatures above 60 °C requires external humidification in order to provide sufficient hydration for the membrane.\textsuperscript{7} A dry membrane can not only become limiting for the overall fuel cell performance; it can also damage the membrane electrode assembly itself. For example, membrane swelling that takes place upon hydration can increase the membrane’s dry volume by 10 – 20%.\textsuperscript{82,83} Repetitive volume changes can introduce mechanical stresses which may cause permanent damage or failures, such as membrane rupture.\textsuperscript{84,85} Excess liquid water in either CL, GDL or flow channels can decrease the available active electrode area for the reaction and block the reactant transport to the active sites, inducing mass-transport losses. For optimal performance, it is therefore necessary to maintain the operating conditions, particularly relative humidity, in the fuel cell stack within a narrow range of operating conditions which causes neither dehydration nor flooding.\textsuperscript{86,87} Transport processes of liquid water within the PTL is still debated among different research groups. The Nam and Kaviany proposed a tree like transport mechanism, where micro-droplets agglomerate to form macro-droplets. The water then flows preferentially towards larger pores, creating converging capillary pathways through the porous structure.\textsuperscript{88} Pasaogullari and Wang support this hypothesis. They also expect tree-like liquid water percolation in the GDL after condensation begins.\textsuperscript{4} These views are opposed by the work of Lister et al. who proposed the water transport to be dominated by fingering and channeling of the water, followed by dynamic eruptive water outbreaks at the surface.\textsuperscript{89} A detailed review of water management in PEMFC with a focus on liquid water flooding and diagnostic is given by Li et al.\textsuperscript{90}
2.3.1 Influence of the PTL on Voltage Losses

There have been several efforts, both experimental and using modeling techniques, to study the effect of PTL properties on the overall fuel cell performance.\textsuperscript{2,4,8,89,91–108} The water transport within a multi-layered porous medium is still not fully understood.\textsuperscript{104,109} The role of the MPL is still debated within the research community. Especially at higher current densities, experimental studies have shown that the MPL improves the fuel cell performance even though it adds a diffusive resistance to the mass-transfer.\textsuperscript{104,110} This has led to the assumption, that the MPL alters the liquid water distribution in the PTL and CL to allow improved mass-transfer.\textsuperscript{4,88} The MPL also reduces the contact resistance between PTL and CL due to its flat and smooth surface properties.\textsuperscript{3} Weber and Newman proposed that the MPL acts as a water barrier, preventing product water to enter the GDL.\textsuperscript{92,110,111} This leads to an increased water permeation from cathode to anode via the membrane and results in an improved ohmic resistance and an improved mass-transport resistance inside the cathode PTL as the amount of liquid water inside the PTL is reduced.\textsuperscript{104,105,112–115} Other experiments by Ge and Wang and Atiyeh et al. found contradicting results as they did not observe an increased amount of water at the anode when employing a cathode MPL.\textsuperscript{6,116} Ex-situ experiments by Gostick et al. showed that the PTL liquid water saturation at water breakthrough is significantly reduced when an MPL was present which leads to a reduction of dead end water clusters that may impede the gas transport within the GDL.\textsuperscript{104}

Based on the description in current literature, it can be concluded that the experimental investigation of the MPL in operating PEMFC is a challenging and complex process. Current
gaps in the literature include a comprehensive understanding of the transport phenomena inside the PTL and CL. Especially the influence of liquid water on the material properties of the CL and PTL is not fully understood. The measurement and experimental de-convolution of the mass-transport losses into the contributions from CL, GDL and MPL remains a major challenge. This thesis work is presenting two novel, systematic approaches to study of the role of the MPL. One is based on Design of Experiment methodology, the second combines the analysis of the effect of an MPL with a systematic characterization of the voltage loss breakdown in an operating PEMFC with a focus on mass-transport losses on both anode and cathode side.
Chapter 3: Experimental

This chapter comprises the experimental methods, protocols and diagnostic tools employed for this thesis work. A re-designed and improved reference electrode system was developed as part of this thesis work. Parts of this chapter have been published elsewhere and text excerpts, figures and tables were reprinted with permission from Applied Energy, 129, Flick et al., Designed Experiments to Characterize PEMFC material Properties and Performance, 135–146, Copyright 2014, with permission from Elsevier. Text excerpts, figures and tables were also reprinted with permission from ECS Transactions, 58 (1), 843-850 (2013). Copyright 2014, The Electrochemical Society.117–119

3.1 Test Apparatus

All in-situ experiments were carried out employing a Greenlight FCATS-S 800 fuel cell test system. The fuel cell test systems components, including load bank, all thermocouples, mass flow controllers, pressure transmitters and humidity sensors were calibrated by the manufacturer in house or were send out for calibration at the start of the experimentation. The software of the test station was adjusted accordingly. The gas flow rates for the reactants were controlled by Watlow mass flow controllers. For the anode the flow range was 0.15 – 2 SLPM with ±1% full scale accuracy. The cathode flow range was 0.35 – 16 SLPM at ±1% full scale accuracy. The gas inlet pressures were back pressure regulated and measured with WIKA S-10 pressure transmitters with a range of 0 – 60 PSI and an accuracy of ≤ 0.25% full scale. The gases used for this thesis work were laboratory grade hydrogen with a purity of 99.95% and nitrogen with a
purity of 99% on the anode side, as well as oxygen (purity of 99.0%), air and nitrogen on the cathode side. A differential pressure measurement was carried out over both anode and cathode flow-fields. The differential pressure transducers on both anode and cathode side were made by Honeywell Sensotec with a range of 0 – 30 PSI and ±0.25% full scale accuracy. Heating/cooling of the cell was provided through an external water bath. All gas inlets and outlet temperatures were measured. All thermocouples were type K thermocouples with an accuracy of ±1 °C or 0.4% of the reading value. The inlet RH at the cell was measured using Sensirion SHT75 relative humidity sensors with an accuracy of ±1.8% RH in the range of 10 – 90 % RH and an integrated temperature sensor (a detailed data-sheet can be found in Appendix A) as well as Vaisala HMT 337 humidity and temperature sensors with an accuracy of ±1.5% RH (data-sheet is given in Appendix A). In order to allow for an accurate measurement of the RH and dew-point temperature of the gases entering the cell, a heated and sealed sensor integration apparatus was designed to integrate the humidity sensors in the system. Technical details and specifications for the humidity sensors and the heated sensor mounts are given in A.1. Figure 3.1 shows a flow diagram illustrating the test apparatus used to carry out the experimental measurements.
The test hardware was a research cell with an active area of 49 cm$^2$. The configurations of the carbon flow-fields were single serpentine channels on both anode and cathode in cross-flow configuration. Specifications for the flow-field are given in Table 3.1.

Table 3.1: Flow-field specification

<table>
<thead>
<tr>
<th>Channel</th>
<th>Landing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Width / mm</td>
</tr>
<tr>
<td>Anode</td>
<td>1.27</td>
</tr>
<tr>
<td>Cathode</td>
<td>1.58</td>
</tr>
</tbody>
</table>

Figure 3.2 shows the flow fields for both anode and cathode side.
Figure 3.2: Cathode (left) and Anode (right) flow fields.
A photographic image of the research cell can be seen in Figure 3.3.

![Figure 3.3: Low gradient research cell with an active area of 49 cm²](image_url)

More photos of the test apparatus and research cell can be found in Appendix A.

### 3.2 Test Materials

#### 3.2.1 Catalyst Coated Membrane

All experiments were conducted using commercial CCM. The experiments carried out without RE measurements employed a membrane with platinum loadings of 0.4/0.1 mgₚt cm⁻² for cathode/anode. All CCM of this type came from the same batch. The CCM used for all experiments featuring reference electrode diagnostics was commercial material from the same batch. Both electrodes featured a symmetric loading of 0.4 mgₚt cm⁻² and the electrode thickness was stated as 25 µm according to supplier specifications.
3.2.2 Porous Transport Layer Material

Commercially available Sigracet® PTL materials (SGL Carbon) were used for all experiments for both the active area and the reference electrode. Unless otherwise stated, all GDL materials used were 25 BC with an MPL and 25 BA without an MPL. The materials are made from identical substrate with 5% polytetrafluoroethylene (PTFE) content. The difference between the materials is the presence or absence of a standard Sigracet® MPL featured only on the 25 BC material. The SGL Carbon Group reports the material properties according to Table 3.2.

Table 3.2: Properties of SIGRACET® GDL 25 according to the SGL Carbon Group

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>25 BA</th>
<th>25 BC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness</td>
<td>µm</td>
<td>190</td>
<td>235</td>
</tr>
<tr>
<td>Areal Weight</td>
<td>g m⁻²</td>
<td>40</td>
<td>86</td>
</tr>
<tr>
<td>Air Permeability</td>
<td>cm³ cm⁻² s⁻¹</td>
<td>210</td>
<td>1.0</td>
</tr>
<tr>
<td>Electrical Resistance</td>
<td>mΩ cm²</td>
<td>&lt; 10</td>
<td>&lt; 12</td>
</tr>
</tbody>
</table>

Burheim et al. conducted extensive research both ex-situ and in-situ to determine the thermal properties of the PTL in PEMFC.¹²⁰⁻¹²² A recent study by Burheim et al. compared the thermal properties of differently composed PTL and CL under varying humidification levels.¹²³ They report through-plane thermal conductivities for dry Sigracet® PTL material between 0.3 – 0.4 W K⁻¹ m⁻¹. The presence of liquid water inside the PTL was found to increase the thermal conductivity by a factor of 2 – 3 at room temperature. Elevated temperatures were found to
further increase the through-plane thermal conductivities (20 – 40% at 70 °C) due to the heat pipe effect.\textsuperscript{120,123}

The ex-situ study of the pressure drop reported in Section 4.3.2.2 was conducted employing commercially available Sigracet\textsuperscript{®} 24 series material with varying PTFE content from 0 – 30 wt.%. Datasheets for these materials can be found in Appendix A.2. A Scanning electron microscopy picture of the 25 BC PTL material is shown in Figure 3.4.

---

![SEM picture of a) SGL 25 BC substrate and b) SGL 25 BC MPL](image)

**Figure 3.4:** SEM picture of a) SGL 25 BC substrate and b) SGL 25 BC MPL

---

### 3.3 Test Protocol

The CCM materials were assembled into a Kapton\textsuperscript{®} frame and a PTL was added via pressure or hot-pressing. A hollow punch was used to create the apertures for the reactant feed and reactant removal. Figure 3.5 shows an MEA ready to be assembled into the cell.
Figure 3.5: Assembled 49 cm$^2$ MEA

All materials were conditioned adapting protocols described previously,$^{36,124}$ for at least 8 hours under galvanostatic conditions at 1 A cm$^{-2}$ at 75 °C and 100% RH for both inlet gases and 200 kPa gas back pressure. Steady state conditions were defined to correspond to a standard deviation in voltage of < 0.005 V over a time period of 360s with measurements taken at a 1 Hz sample rate. When this condition was established, a measurement was taken as an average over a period of at least 180s. All presented results were tested with a minimum of two independent samples tested with at least two repetitions each.

3.4 Diagnostic Methods

3.4.1 Reference Electrode Measurements

In order to measure the individual polarization contribution of anode and cathode in-situ, a reference electrode was employed. The reference electrode is connected to the working anode
and counter electrode (cathode) via the electrolyte but there is no current extraction, see Figure 3.6.

Figure 3.6: Schematic of the measured circuits between RE, cathode and anode (not to scale)

There are several types of reference electrodes, as discussed in the previous Chapter 2, Section 2.1. For this work a reversible hydrogen electrode was chosen to be used because there is no parasitic DC potential required to generate hydrogen. Previous works from this group have proven the RHEs suitability in PEMFC research to extract individual overpotentials and as sensing electrodes.\textsuperscript{18,19} A separate system was added to the test apparatus in order to supply
heated and humidified hydrogen at a constant flow rate to the reference section. The gas feed to the SE section was controlled by Watlow mass flow controller with a range of 0.15 – 2 SLPM and ±1% full scale accuracy. A process diagram of the modified experimental set-up and gas flows can be seen in Figure 3.7.

Figure 3.7: Flow diagram of test set-up including the reference electrode system

This reference electrode system was in order to match the experimental needs and requirements of this thesis. Two major objectives were to ensure a repeatable and stable measurement signal by improving the contact between the CL/GDL of the reference electrode and the wire to extract the signal. The second objective was to develop a system that had good thermal and mechanical stability.

3.4.2 Preparation of the RE Section

The reference section was generated by laser ablation using a QuikLaze 50ST which has a frequency-doubled Nd:YAG laser with a wavelength of 532 nm. This allowed creating an electrically insulated section of CCM without damaging the membrane.13 Scanning electron
microscopy and optical microscopy was used to analyze the CCM after the ablation process. An optical microscopy picture of the laser ablated area can be seen in Figure 3.8.

![Figure 3.8: Optical microscopy image of the laser ablated CCM](image)

The distance between WE and RE is determined by the thickness of the ablated section as shown in Figure 3.8. The chosen distance in this work was 600 µm in order to enable sufficient membrane humidification within the RE section but far enough to avoid edge effects due to the potential distribution through the membrane between working electrode and counter electrode. The area of the RHE was 1 cm² leading to an area ratio of 1/49 between the reference and counter electrode. Laser ablation techniques allow removing catalyst coating for
electrical insulation of the reference electrode. Using laser ablation also ensured a perfect alignment of the RHE. After laser ablation, the CCM was framed and GDL material was hot-pressed onto both active area and reference section as our experiments showed that this improved the stability of the signal. Figure 3.9 shows an assembled MEA that features a reference section.

An electrically insulated spring was used to create a constant and repeatable mechanical contact between a thin platinum wire (d < 1mm) used to measure the RE potential and the PTL material of the RE. Figure 3.10 shows the schematic design of the RE system that is then stacked and compressed for testing.
In order to prove the concept of the design of the RE system the signal stability was measured and experimental results were compared to published data.\textsuperscript{13,18,24,36} The signal drift over time and signal variation as function of varying hydrogen flow rates were measured. The system was found to produce repeatable and reliable measurements and was not fluctuating with flow rate. Drift measurements over time showed a small standard deviation $< 0.001V$. Results of these measurements are shown in Appendix A3. Based on these measurements the process parameters were optimized for the measurements of this work.

### 3.4.3 Cell Polarization

Polarization measurements for this work were obtained using hydrogen at varying stoichiometric flow-rates as reactant at the anode. Experiments featuring RHE measurements used fully humidified hydrogen at constant flow conditions of 20 ml min$^{-1}$ for the reference
section. The cathode electrode was supplied with oxygen or air. Air was fed under varying stoichiometric conditions. Hydrogen - oxygen polarization curves were obtained at the same flow rates and temperature to ensure constant conditions. Humidity, temperature and gas inlet pressures of the reactants were varied according to the need of the individual experiment. The inlet gas to the RHE section was always under atmospheric conditions and averaged over 180 s to determine the standard deviation of the signal. Each polarization measurement was taken under steady state conditions. The HFR between working electrode and counter electrode was measured at 1 kHz for each point on the polarization curve employing a Gwinstek LCR meter. The HFR between RHE versus cathode was measured at selected points using a Solartron SI 1260 Impedance/Gain-Phase analyzer at a constant frequency of 1 kHz. The HFR values were interpolated over the full polarization curve based on these measurements.

3.4.4 Cyclic Voltammetry

The electrochemical surface area (ECSA) was determined using cyclic voltammetry with a Solartron SI 1260 Impedance/Gain-Phase Analyzer supplying fully humidified hydrogen on the anode side and fully humidified nitrogen on the cathode. These experiments were carried out at 75 °C between 0.05 V – 1.2 V with a scan rate of 10 mV s\(^{-1}\). The ECSA was determined by integration of the area under the desorption peaks from 0.1 V ~ 0.45 V\(^{29,126-128}\) to calculate the charge. This was then corrected to the specific Pt surface area, \(A_{Pt,cat}\) in m\(^2\)g\(^{-1}\), according to

\[
A_{Pt,cat} = \frac{Q}{K \cdot L_{cat} \cdot A_g} \times 10^5
\]  

(3.1)
where $Q$ is the total quantity of charge in C, $K$ is a specific capacity of 210 µC cm$^{-2}$, $L_{Ca}$ is the cathode loading of the MEA in mg Pt cm$^{-2}$ and $A_g$ is the geometric active area in cm$^2$. The accessible Pt surface area, $A_{pt,el}$ was determined based on the Pt utilization factor $\eta_{pt} = 88\%$.\textsuperscript{26}

### 3.4.5 Linear Sweep Voltammetry

The hydrogen cross-over current was determined using linear sweep voltammetry (LSV) between 0.4 – 0.6 V at 75 °C at a scan rate of 5 mV s$^{-1}$ employing a Solartron SI 1260 Impedance/Gain-Phase Analyzer. Fully saturated hydrogen/nitrogen at a constant flow was supplied to the anode/cathode respectively.

All experiments for this thesis work are based on the here presented test-protocols, diagnostic tools and methods.
Chapter 4: Design of Experiments for PEMFC

This chapter introduces Design of Experiments methodology for PEMFC. It features a comprehensive literature review of the subject followed by the presentation of the novel methodologies employing DoE to PEMFC research developed as part of this thesis work.

Two novel methods to analyze in-situ experimental fuel cell research based on designed experiments are being presented: a split-plot design and a blocked 2-level factorial design. The results of this chapter have been published elsewhere. Text excerpts, figures and tables were reprinted with permission from Applied Energy, 129, Flick et al., Designed Experiments to Characterize PEMFC material Properties and Performance, 135-146, Copyright 2014, with permission from Elsevier. Text excerpts and figures were also reproduced with permission from ECS Transactions, 58 (1), 843-850 (2013). Copyright 2014, The Electrochemical Society.

4.1 Introduction and Literature Review

Operating PEMFC systems are subject to a multitude of variables. Operating conditions, e.g. temperatures, pressures, flow-rates, reactants, etc., design parameters, such as geometry, size, flow-field configuration, cooling system, etc., and material properties, like catalyst composition and loading, membrane type and geometry, catalyst support, gas diffusion layer material properties, etc. Hence developing experimental protocols and standardized test-conditions is challenging. A reliable approach for developing statistically meaningful experimental results and an objective data analysis is provided by the Design of Experiments (DoE) methods. Designed experiments have the ability to cover a full range of operating conditions and assess the effects of interactions between chosen factors. These methods are of particular use in complex systems affected by numerous factors, and are commonly used in the
The practice of chemical engineering. Recently, the literature shows a growing body of work using DoE methods for the study of PEM fuel cells, which are themselves complex systems. A broad range of DoE techniques have been used in PEMFC research. Modeling PEMFCs is a non-trivial task due to the complexity of the fuel cell system and the physical interactions between cell components and process conditions. Performance determining phenomena are non-linear and dependent on a high number of input variables, including material properties and operating conditions. One-factor-at-a-time testing of fuel cells is time-consuming and expensive; it also fails to account for potential factor interactions. A designed experiment using statistical methods enables an efficient and economical experimental approach, accounting for factor interaction. The MEA preparation, cell assembly, hardware setup, and membrane conditioning are time-consuming steps in conventional PEMFC testing. The application of DoE for material characterization has the potential to reduce the required testing time while, given an appropriate selection of design and factors, offering insight into dependencies between material properties and performance characteristics. Several groups have recently investigated the influence of various operating conditions on fuel cells by employing DoE methods. The main factors considered in these studies include:

- **Temperature**
- **Reactant pressure**
- **Reactant stoichiometry/reactant flow rate**
- **Reactant gas dew point temperature/humidity**
- **Flow orientation**
- **Response: Cell Voltage**
- **Response: Power density/Power**
Many of these studies focused on operational factors only. There have been efforts by various groups to use different DoE methods for material and design characterization purposes. Akyalçın and Kaytakoğlu employed the Taguchi method to study the optimal structural combination for an MEA resulting in maximum power density for a PEMFC. The factors investigated in their study were type of Nafion membrane, platinum loading, ionomer content and PTL material type (cloth or paper). Cheng et al. used a three-level factorial design based on a computational fluid dynamic model of a single cell fuel cell to evaluate the design of the flow channels. An experimental study of the flow plate design for a PEMFC with respect to different operating conditions was conducted by Carton and Olabi. Wahdame et al. used a designed experiment approach to study the durability of a three-cell PEMFC in a 1000h stationary test under constant temperature, atmospheric pressure, constant stoichiometry and constant current conditions while observing the change in voltage over time. They used a Response Surface Model as well as a Dual Response Surface Model to analyze their data and optimize operating parameters over time. They found the cathode stoichiometry to be a dominant parameter as aging time and load current were increased. Wahdame et al. also conducted a durability study under low humidity conditions with the aid of DoE techniques and a Response Surface Model in order to illustrate degradation phenomena, but their research was limited in its ability to explain the underlying phenomena governing the observed behavior. The designed experiments presented in this thesis work, feature both operational factors as well as material parameters in order to investigate masking phenomena based on domineering factors and factor interactions.
4.2 Statistical Terminology

DoE and statistical methods have seen limited application in the field of fuel cell research despite the advantages of statistical methods increasing experimental efficiency and facilitating scientific objectivity when analyzing data. For this reason a short description of the statistical terms and methods used in this study is included here. Further references on terminology can be obtained in literature.\textsuperscript{152–154} Statistical terms used in this paper include:

**Adequate Precision:** Measure of the signal to noise ratio. Values > 4 are desired to be able to navigate the design space and predict responses.

**Internally studentized residuals:** A scaled residual used to check the model adequacy. Studentized residuals care corrected for the inequality of variance. Plotted in a normal plot of residuals, it can be seen whether the error terms follow a normal distribution.

**p-value:** Probability value quantifying the risk of falsely rejecting the null hypothesis. The smaller the p-value, the stronger is the evidence against the null hypothesis.

**F-value:** The model F-value shows the relative contribution of the model variance to the residual variance. Small model F-values indicate the variance may be due to noise and not explained by the model.

**t-value and t-value limit:** The t-value and t-value limit are calculated during hypothesis testing to determine the value of each regressor variable in the model. The t-value limit is based on a specified level of significance (here level of significance = $\alpha = 0.05$).

**Pareto Chart:** Graphic used to illustrate and quantify statistically significant effects based on their t-values.

**Bonferroni Limit:** Familywise corrected t-value limit. Effects with a t-value above this limit are very likely to be significant and should be included in the model.
4.3 Experimental Design

A critical step in developing a designed experiment is to select and quantify the relevant factors from a pool of operating parameters, hardware specifications and material characteristics. Figure 4.1 illustrates the schematic of the applied methodology for this work. One extensive set of experiments was analyzed employing nine separate experimental designs.
All designs presented in this thesis work are based on the same 192 experimental test points consisting of response measurements, for each voltage and pressure drop, under three
different current densities at 64 separate operating points. Each experiment was conducted at steady state conditions in a random run order generated by the design software. The number of test runs is determined by the number of factors and the resolution of the design. The designs have a high resolution of V, therefore the main effects and two-factor interactions are not aliased with each other. Due to the complexity of the fuel cell system, an experimental design featuring a large number of factors was chosen, despite the initial large number of 192 test runs. Based on these results a screening method was developed to identify those factors that have significant effects in order to reduce future testing efforts. This method can also be used to develop standards for testing protocols, as it identifies the relevant and significant factors and factor interactions that affect a chosen response. The dual response structure (featuring two responses: pressure drop and voltage) increases efficacy by maximizing the gained output from the design without increasing the testing efforts. The advantage of this experimental design over conventional one-factor-at-a-time (OFAT) testing lies in the increased efficacy of the testing, as OFAT testing for seven individual effects would require at least 512 test runs per response at two levels. This design can also account for factor interactions and the use of statistical methods to analyze the data enables scientific objectivity. A detailed account on the factor and response selection is given in the previous sections. All models are based on a fully randomized run order of the experiments blocked based on the PTL material. Experimental matrices and post-experimental analysis were conducted with the aid of a software package (Design Expert 8 by Stat-Ease, Inc.).
4.3.1 Factor Selection

All designs feature the same factors based on operating conditions (factors A-F) and the presence of an MPL (factor G).

A. Anode stoichiometry
B. Cathode stoichiometry
C. Temperature
D. Anode gas inlet relative humidity
E. Cathode gas inlet relative humidity
F. Back pressure of reactant gases
G. Type of GDL (here synonymously for PTL = substrate and MPL if applicable).

These factors were selected with the intent of mapping the parameter dependencies of the fuel cell voltage and cathode pressure drop in a relevant range of parameters.

Table 4.1 summarizes the assigned symbol, name, values, scaled value and type used for each of these factors in the experimental design. There are six numeric and one categorical factor with two levels each, leading to a total of 192 test runs with two responses (voltage and cathode pressure drop) measured at three current densities each under 64 different operating conditions. Each response point was taken at three different current densities, leading to 192 test points in total.

By convention, factors in a DoE are assigned symbols “A” through “X” after having been scaled to a coded and normalized value, in this case -1 to 1. The final output of the model can be reported either in terms of the standard unit and value, or in terms of the scaled factors, with different coefficients but the same end result. However, the coefficients in the scaled version are significantly more meaningful because the magnitude and sign of the coefficient correlate.
directly to the size and direction of the effect or interaction. That is not true of the equation involving the real factors.

Table 4.1: Selection of factor values

<table>
<thead>
<tr>
<th>Factor Symbol</th>
<th>Factor Name</th>
<th>Actual values</th>
<th>Factor type</th>
<th>Factor Subtype</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Anode inlet stoichiometry</td>
<td>1.5 / 3</td>
<td>Numeric</td>
<td>Continuous</td>
</tr>
<tr>
<td>B</td>
<td>Cathode inlet stoichiometry</td>
<td>1.5 / 3</td>
<td>Numeric</td>
<td>Continuous</td>
</tr>
<tr>
<td>C</td>
<td>Temperature</td>
<td>40 / 75 °C</td>
<td>Numeric</td>
<td>Continuous</td>
</tr>
<tr>
<td>D</td>
<td>Anode inlet relative humidity</td>
<td>40 / 80 %</td>
<td>Numeric</td>
<td>Continuous</td>
</tr>
<tr>
<td>E</td>
<td>Cathode inlet relative humidity</td>
<td>40 / 80 %</td>
<td>Numeric</td>
<td>Continuous</td>
</tr>
<tr>
<td>F</td>
<td>Pressure</td>
<td>100 kPa / 300 kPa</td>
<td>Numeric</td>
<td>Continuous</td>
</tr>
<tr>
<td>G</td>
<td>Type of GDL</td>
<td>MPL / no MPL</td>
<td>Categorical</td>
<td>Nominal</td>
</tr>
</tbody>
</table>

Extreme conditions, e.g. high temperatures and relative humidity below 40%, were not included for two reasons. First, there would be a significant risk of damaging the MEA under such conditions so that one sample could not perform all 192 experimental test points. Secondly, the underlying physical phenomena change during extreme conditions and regression methods will lose relevance.
4.3.2 Response Selection

4.3.2.1 Voltage Response

In order to choose relevant response points, several polarization curves at different conditions were measured and analyzed. As stated in Chapter 1, Section 1.4.2 a polarization curve can be divided into three main regions dominated by distinct loss mechanisms as current density increases: activation, ohmic, and mass-transport. Most of the activation losses occur at current densities that are too low for automotive applications. The mass transport losses become dominant at current densities that are larger than that corresponding to peak power density occurring at a current density $i_{PP}$. This operating point marks the highest efficiency in terms of power generation for the fuel cell. Moreover, and although the cell potential is used as the main performance metric in scientific studies, practical applications consider economic (e.g., $ of Pt per kW) or volumetric (e.g., kW cm$^{-3}$) design constraints. In typical PEMFC designs, catalyst cost and volumetric power density decrease and increase, respectively, with current density up to $i_{PP}$. Hence, the selected voltage response points were at current densities 1.0 A cm$^{-2}$, 1.4 A cm$^{-2}$ and 1.6 A cm$^{-2}$ which are compatible with practical power density ranges. One of the main objectives of this thesis work is the study of the influence of the material properties of the PTL. As the same CCM is used for all experiments, the most noticeable differences in the voltage response are to be expected in the mass-transport region. Hence, the focus of this experiment is in that region.

4.3.2.2 Pressure Drop Response

The pressure drop was selected as a response for two reasons: to investigate its’ use a diagnostic tool to detect flooding and to identify the behavior of the two different PTL materials
used. In a fuel cell, a certain minimum clamping pressure has to be applied upon assembly to seal the cell and prevent hydrogen leakage and air intrusion into the anode and to ensure electrical contact between the cell components. The applied clamping pressure should also be sufficient to prevent the passage of gas under the land areas between the flow channels. The effects of increasing the clamping pressure further are conflicting. Increasing the pressure reduces the contact resistance between the PTL and the catalyst layers, but also reduces the porosity which increases mass transport limitations. The decrease in contact resistance will improve the cell voltage where ohmic losses are dominant\textsuperscript{155} but the cell voltage at high current densities will deteriorate with increasing clamping pressure as the porosity is decreased\textsuperscript{156}. Increasing clamping pressure will also increase the intrusion depth of the GDL into the flow channels and increase the pressure drop between the inlet and outlet of the flow field. Whereas a higher pressure drop will aid in the removal of water droplets, it will also increase the power needed for circulating the fuel and oxidant gas streams\textsuperscript{157}. In fact, (an increase in) pressure drop has been suggested as a useful diagnostic tool during fuel cell operation to detect flooding\textsuperscript{158}. However, the membrane will expand when its humidification is increased both in-plane and out-of-plane\textsuperscript{159}. This will lead to buckling of the membrane, causing additional intrusion of the GDL into the flow channels and increasing pressure drop which would precede a genuine flooding event. Furthermore, permanent deformation of the PTL after a humidity cycle would leave the pressure drop increased under identical conditions within the cell, complicating the use of pressure drop as a diagnostic tool. This work investigates the pressure drop as a diagnostic tool in two steps:

First, we conduct an ex-situ study on the dependence of the pressure drop on the clamping pressure and hysteresis effects as a function of gas flow rate.
Secondly, we employ the pressure drop as response during in-situ characterization to conclude on the validity of the pressure drop as diagnostic tool to detect flooding.

During the ex-situ experiment the clamping pressure, controlled by a nitrogen bladder, was cycled between 75 and 120 psi and back to 75 to investigate hysteresis effects of the pressure drop versus flow rate. The cell employed is not an electrochemical system as the membrane is replaced by a Kapton\textsuperscript{®} frame. Four different Sigracet PTLs, material properties are listed in Appendix B, were analyzed.

Figure 4.2 shows the schematic of this experiment. Because no hot-pressing steps during cell assembly were involved, full post-mortem analysis of the substrate and MPL was possible. The amount of deformation persisting after cycling the clamping pressure both in terms of ‘imprinting’ by the flow field channels and thickness reduction were investigated in relation to the changes in the pressure drop versus flow rate.

The cell hardware and flow fields for this ex-situ study are based on the same hardware and flow-fields as described in Chapter 3.

![Figure 4.2: Schematic of test apparatus](image-url)
The distribution of the pressure over the flow-fields can be seen in Figure 4.3. The pressure distribution across the cell is homogeneous and there are no notable differences between the two clamping pressures.

Figure 4.3: Force distribution on cathode (left) and anode (right) side using pressure sensitive paper at 75 and 120 psi clamping pressure

Figure 4.4 and Figure 4.5 show the results of the pressure drop study for different substrates with and without MPL. It can be concluded that there is a hysteresis effect when cycling the clamping pressure and that the pressure drop is a function of the respective PTL material. For the materials with an MPL, we observe an overall higher pressure drop which is consistent with our expectation as the dual layer PTL structure is overall thicker and will therefore protrude more into the channel. While the relative hysteresis behavior is consistent for all materials, the pressure drop over the flow field is higher for the material with 5% PTFE and MPL (24 BC) than for the material with 30% PTFE and MPL (24 EC). For the material without MPL, single layer structure, the substrate with 30% PTFE content (24 EA) facilitates a higher pressure drop than
the substrate with 5% PTFE (24 BA). This can be attributed to the increased amount of binder in the substrate, making the material more flexible, and therefore supporting the protrusion into the channels. In the dual layer structure the MPL adds mechanical stability and material is not as elastic.

Figure 4.4: Cathode flow versus pressure drop at 70 °C, 80% RH and gas inlet pressures of 200 kPa
While results from the cathode show a consistent curvature for all measurements, the results at the anode show a jump and change in curvature for the measurements at 120 psi around 1000 – 1100 ml min\(^{-1}\). This observed for three out of the four different materials but not for the material without MPL and high PTFE content. Due to the high clamping pressure the effective channel diameter is reduced as PTL material protrudes into the channel. An explanation for the sudden jump in pressure drop could be the formation of liquid droplets on the channel walls due to condensation inside the cell. The anode channels have a smaller length and width than the cathode which could explain why this is not observed at the cathode. An additional reason for this observation may be due to the limited sensitivity of the pressure sensor at these low pressure drops.

Before and after each test, the PTL material thickness was measured using profilometry and microscopic images shown in Figure 4.6. They were used to quantify the impact of the compression on the PTL and the permanent deformation of the material. Even though the
pressure drop hysteresis is a clear indicator of a structural change in the PTL due to compression, the optical analysis shows no noticeable differences in the appearance of the BoL and EoL materials. Profilometry results and results based on cycling experiments are listed in Appendix B.

Based on these results, the pressure drop was chosen as a second response for the designed experiments, as it is specific to the respective GDL material. In order to avoid the impact of a varying clamping pressure, all cells were kept compressed at a constant clamping pressure of 100 PSI for the duration of the entire in-situ experiment.
4.4 $2^7$-Level Experimental Full Factorial with Split-Plot Design

The first experimental design is a split-plot, 2-level full factorial design with seven factors and the cell’s voltage and cathode pressure drop as a dual response. The purpose of this design was to evaluate the significance, in statistical terms, of the operating parameters and PTL material on the fuel cell performance and to investigate the dominant factor interactions. A split plot design is used because full randomization of the experiments would be inefficient, as varied materials are being tested. It is advantageous to test the materials consecutively because each material needs to be assembled and conditioned prior to testing. It is prohibitively time-consuming, and therefore expensive, to rebuild and recondition the cell for each test. Consequently, the testing was carried out in two consecutive, fully randomized blocks for each GDL material. Based on these randomization restrictions, differences in variance between the two test blocks can be expected. A split plot design enables the estimation of two different error variances, one for comparison within the blocks and one for comparison between the blocks called whole plot and subplot analysis. The analysis of variance (ANOVA) reports for the three whole plots and all three subplots as well as the resulting split-plot design for the response “voltage” are listed in Appendix B. The major difference to the randomized block design, as described in the next section is that factor G, type of GDL, is included in this model, allowing for a direct comparison between the two materials. The split plot design presented here is based on factors A-G in Table 4.1. Two types of commercially available SIGRACET® 25 BC and 25 BA GDL materials were used in this study (factor G). The materials are made from identical substrate with the same PTFE content of 5%. The 25 BC PTL is a dual layer construction featuring an MPL. The SGL Carbon Group reports the material properties according to Chapter 3, Table 3.2. All experiments were conducted using commercial CCM with platinum loadings of
0.4/0.1 mg cm$^{-2}$ for cathode/anode. All CCM came from the same batch. The mathematical models based on the experimental designs were employed as screening tools to evaluate the dominant factors and factor interactions, including interactions up to the fourth order, for each response. While these empirical models are not intended to describe the underlying physics, they are used to screen and assess relevant factors and parameter dependencies. Based on the experimental results, an empirical model can be created to describe the response as a function of the significant factors and factor interactions using non-linear regression. After the initial fit a careful statistical analysis of the empirical model has to be conducted to determine the validity and usefulness of the model. Once the regression parameters have been determined it is necessary to assess the significance of the regression using either hypothesis testing or ANOVA testing, which was employed in this work. Confidence intervals for regression coefficients and mean responses can also be useful to further analyze the model fit.

Once the model is fitted adequacy checking via a residual analysis and lack of fit testing is required to assure a relevant approximation of the empirical model to the physical underlying system. It is important that none of the least squares regression assumptions should have been violated.$^{153}$

### 4.4.1 Split-Plot Design Results

Based on the split-plot designs, non-linear relations for the cell voltage in terms of the statistically relevant factors were derived for all three responses. These are shown in Table 4.2 including the model terms ranked in order of their individual impact. These equations are presented in coded values so that the results can be interpreted in volts and each change in value of a parameter reflects the direct difference in voltage. These model equations do not include
second or third order main effect terms as these terms were not statistically significant in the chosen design space, which is limited to the mostly linear region of the polarization curve between 1.0 – 1.6 A cm$^{-2}$. High Adequate Precision values $>>4$ prove that these equations are valid within their respective design space. The responses between the three current densities can be interpolated due to the mainly linear behavior in the ohmic region of the polarization curve.
Table 4.2: Model equations in coded values with terms ordered in descending order of their impact on the cell voltage. (A: Anode Stoichiometry, B: Cathode Stoichiometry, C: Temperature, D: Anode RH, E: Cathode RH, F: Pressure, G: Type of GDL)

<table>
<thead>
<tr>
<th>Voltage at 1.0 A cm(^{-2}) =</th>
<th>Voltage at 1.4 A cm(^{-2}) =</th>
<th>Voltage at 1.6 A cm(^{-2}) =</th>
</tr>
</thead>
<tbody>
<tr>
<td>- 0.060·G</td>
<td>+ 0.076·C·G</td>
<td>+ 0.076·C·G</td>
</tr>
<tr>
<td>+ 0.051·C·G</td>
<td>+ 0.061·C</td>
<td>+ 0.071·F</td>
</tr>
<tr>
<td>+ 0.051·C</td>
<td>- 0.056·G</td>
<td>+ 0.061·B</td>
</tr>
<tr>
<td>+ 0.039·B</td>
<td>+ 0.055·B</td>
<td>+ 0.057·C·F</td>
</tr>
<tr>
<td>+ 0.037·F</td>
<td>+ 0.048·F</td>
<td>- 0.043·G</td>
</tr>
<tr>
<td>- 0.025·B·C</td>
<td>- 0.038·F·G</td>
<td>- 0.041·F·G</td>
</tr>
<tr>
<td>+ 0.018·E</td>
<td>+ 0.037·C·F</td>
<td>+ 0.038·C</td>
</tr>
<tr>
<td>+ 0.018·C·F</td>
<td>- 0.033·B·C</td>
<td>- 0.032·B·C·G</td>
</tr>
<tr>
<td>+ 0.49</td>
<td>- 0.029·B·C·G</td>
<td>- 0.026·B·C</td>
</tr>
<tr>
<td></td>
<td>+ 0.027·B·G</td>
<td>+ 0.011·B·G</td>
</tr>
<tr>
<td></td>
<td>+ 0.35</td>
<td>+ 0.28</td>
</tr>
</tbody>
</table>

4.4.1.1 Statistical Significance and Impact of Individual Model Terms

For the response at 1.0 A cm\(^{-2}\), the model terms included, in order of their statistical significance, as listed in Table 4.2:

- Type of GDL (G)
- Interaction between GDL and temperature (CG)
- Temperature (C),
- Cathode stoichiometry (B)
- Inlet gas pressure (F)
• Interaction of cathode stoichiometry and temperature (BC)
• Cathode RH (E)
• Interaction between temperature and inlet gas pressure (CF).

All significant model terms were defined based on a confidence level of 95%. The majority of these terms have very high statistical significance indicated by p-values < 0.0001 for analysis of the whole plot, subplot, and the combined analysis of the full model. The second equation listed in Table 4.2, for the response at 1.4 A cm\(^{-2}\), also ranks the individual model terms according to their statistical significance. This model includes more significant terms (p-values ≤ 0.0001) than the first equation. Evidently, at higher current densities, different phenomena govern the cell’s voltage than at lower current densities and this is reflected in the statistical model. The ordered model equation at 1.6 A cm\(^{-2}\) is listed in Table 4.2. This equation features the same relevant model terms as the equation at 1.4 A cm\(^{-2}\). In this case, the interaction BG is included despite a large p-value > 0.05 in order to support hierarchy with the inclusion of the BCG interaction. Maintaining hierarchy within the model is necessary if the coded model is to be transformed to an actual model with several different units of measure.

Figure 4.7 shows the Pareto chart for the models at all three responses. The Pareto chart graphically highlights the statistical significance of the factors and factor interaction and ranks them based on their effect on the response. The Bonferroni limit is based on the Bonferroni correction which is the most conservative method to adjust a test for significance when there are multiple and independent estimates made from the same data. Values above the Bonferroni limit can be considered statistically significant with very high certainty. Figure 4.7 illustrates that the fuel cell system researched is subject to the sparsity of effects principle and is dominated by
main effects and low order factor interactions. The rank of the dominating factors and interactions varies with current density. The Pareto chart at 1.0 A cm\(^{-2}\) in Figure 4.7a shows the most significant factors on the response at 1.0 A cm\(^{-2}\) as listed above. The plot shows that the main effect of factor E, Cathode inlet RH, and the factor interaction CF, temperature and pressure, are included in the model even though their t-values are below the Bonferroni Limit. When conducting the separate analysis of the dual error structure they were above both limits, hence they must be included in the full model. The Pareto Chart in Figure 4.7b shows some significant changes to the most dominant main factor effects and factor interactions compared to the response at 1.0 A cm\(^{-2}\). In this case the factor interaction between temperature and GDL material, CG, becomes the most statistically significant influence on the cell’s voltage. While the significant main effects stay the same as for the model at 1.0 A cm\(^{-2}\), there are additional factor interactions that now need to be included in the model equation and analysis. The three-factor interaction between cathode stoichiometry, temperature and GDL material (BCG) is a dominant effect for this response and can be related to the higher absolute gas flow rates and water production at this current density.
Figure 4.7: Pareto charts for the split-plot designs. (A: Anode Stoichiometry, B: Cathode Stoichiometry, C: Temperature, D: Anode RH, E: Cathode RH, F: Pressure, G: Type of GDL)
The Pareto chart in Figure 4.7c shows that the second ranked term at 1.6 A cm$^{-2}$ is the main effect from the factor F, pressure. This is a notable difference compared to the two other models where pressure was ranked 5$^{th}$. The factor interaction between pressure and temperature, CF, increases in rank with increasing current density. At 1.0 A cm$^{-2}$, this interaction is still below the Bonferroni Limit on rank 8, at 1.4 A cm$^{-2}$, CF ranks at position 7 with distinct significance and at 1.6 A cm$^{-2}$ it is on rank 4. The main effects of factors C and G, which are within the top three ranked terms for the two previous responses, are now in 5$^{th}$ and 7$^{th}$ spot. Notably, for all current densities that were considered, the anode parameters, factor A and factor D, have no significant effect on the response. Factor E, cathode relative humidity, is included in the split plot model equation at 1.0 A cm$^{-2}$ but is not significant for the equations at higher current densities. This is reasonable because there is an increase in product water generation at the higher currents which affects the water management. The positive effect of the factor interaction between temperature and type of GDL is one of the most statistically significant effects at all current densities.

4.4.1.2 Model Fit

Figure 4.8 displays the normal plots of residuals, or normal probability plots, for the split-plot design as well as the predicted versus the measured voltage results. These graphs are graphical representations of the goodness of the fit of the models. The normal plot of residuals shows the fit of the internally studentized residuals to the normal distribution. For the results at 1.0 A cm$^{-2}$, shown in Figure 4.8a, this plot follows a straight line, indicating that the residuals follow a normal distribution. This demonstrates that the assumption of normality holds true indicating that statistical methods can be used to analyze the response. Two outliers can be observed at low voltage points.
The inspection of the model results versus the measured results show a good fit between the model results of the split-plot design and the experimental results. Figure 4.8b shows the difference between the experimentally obtained cell voltage and the cell voltage predicted by the
response model equation at each point. The data closely follows the 45° line, indicating a good fit of the model. Two outliers can be seen at low voltages of 0.117 V. These values show one of the weaknesses of statistical modeling. Once the cell’s behavior becomes unstable, as it did at these two points due to unfavorable operating conditions, the behavior of the response becomes more complex and harder to predict using regression methods. In this specific case, both outlier points can be attributed to the material with no MPL performing poorly at low temperatures and low cathode stoichiometry. The F-value, indicator for the fit of the models, specifies if the model can account for the observed response. The model’s F-values at 1.0 A cm$^{-2}$ indicate significance. Figure 4.8, the normal plot at 1.4 A cm$^{-2}$, shows a close fit to a normal distribution for the studentized residuals. An S-curve is becoming more evident at this response than at the other two responses but the overall fit is sufficient. Figure 4.8d plots the model predicted results versus the measured results at 1.4 A cm$^{-2}$. This plot indicates a good fit for the model over the complete range of observed response values. The model predicts negative voltages under certain conditions which were avoided during this set of practical experiments as safety triggers were set to prevent damage from cell reversal. All model F-values at this current density indicate significance. Figure 4.8e shows a normal distribution for the studentized residuals at 1.6 A cm$^{-2}$, which is a measure of the goodness of the models fit. The model predicted cell voltages compared to the measured cell voltages, shown in Figure 4.8f, show generally a good fit for the model equation but there are again discrepancies for cell voltages of 0 V. Again, the model’s F-values were sufficiently high. All points that displayed unstable performance or cell voltages below 0.1 V were recorded as 0 V and not measured over the full averaging period in order to preserve the membrane. This creates an additional error at very low voltages and unstable conditions that cannot be accounted for in this model. Despite this constraint, the overall fit of
the model equations are satisfying and the errors are distributed normally. Further analysis of the data on the basis of these models is therefore valid and promises to provide insight on the dominant factors and interactions and their effects on the responses.

The same methodology was used to analyze the experimental results of the steady state pressure drop over the cathode flow-field. This was chosen as an additional response, as the pressure drop is not only important to determine the system's auxiliary compressor requirements but also is strongly coupled to the gas density and mean gas velocity in the channel, which directly affects gas transport and convection. Liquid water in the form of droplets can be removed by the momentum of the gas without changing the pressure drop. Liquid water can also accumulate as a film on the channel walls, reducing the effective channel area and therefore increasing the pressure drop \(160\). Analysis of the pressure drop was done using a separate split-plot design, featuring the same factors but the pressure drop over the cathode flow field at the respective current density as response. As expected, the statistically dominant effects are, in rank, cathode stoichiometry (B) and gas inlet pressure (F). Changing the stoichiometry directly changes the gas flow rate through channel area, which, according to the Darcy-Weisbach equation, directly changes the pressure drop \(\Delta p\)

\[
\Delta p = \frac{f L \rho \bar{V}^2}{2 D_H}.
\]  

(4.1)

In this equation \(f\) is the friction factor, \(L\) is the channel length, \(\rho\) is the fluid density, \(\bar{V}\) is the flow velocity and \(D_H\) is the hydraulic diameter. This equation does not account for multiple turns in a single serpentine flow channel which also contribute to the pressure drop, but as the flow field is kept constant, the specific design is not relevant to the parameter dependencies of the studied factors. The inlet gas pressure is back pressure regulated, resulting in a direct influence
on the pressure drop. The pressure drop is reduced with increasing back pressure. At higher
current densities, the factor interaction between cathode stoichiometry and gas inlet pressure
(BF) becomes significant as well. At 1.6 A cm\(^{-2}\), temperature (C) is also a significant factor
included in the model which shows the impact of the increased heat generation on the gas
viscosity and density. At this current density we expect to see an increased influence of liquid
water blocking the flow channels or decreasing the effective channel area, increasing the
pressure drop. Therefore factors identified by the model as having statistically the most impact
on the pressure drop, cathode stoichiometry, inlet pressure and temperature, are in accordance
with the terms that are directly included in the numerical description of the physical phenomena
in Equation (4.1). More details are discussed in combination with the cell performance in the
following section.

### 4.4.1.3 Performance Analysis

In order to interpret the full range of the experimental results, the two split-plot models
were used to generate voltage and pressure drop maps to graphically analyze the parameter
dependencies and differences between the two PTL materials. From the large pool of factors and
factor interactions analyzed, we present here those with the most statistical significance and
impact on the response as identified in Figure 4.7. The parameters discussed are the relations
between type of GDL (G), temperature (C), cathode stoichiometry (B) and inlet gas pressure (F)
as well as their interactions. Figure 4.9 plots the cell’s voltage and pressure drop at each current
density as a function of temperature and cathode stoichiometry for the cell with MPL at 100 kPa.
Figure 4.9: Pressure drop and cell voltage at all current densities for the cell with MPL, 25 BC, at 100 kPa.

All other factors were kept at a normalized value of 0 (see Section 4.3.1).
Figure 4.9 shows that the cell with MPL has small voltage variation as operating temperature and cathode stoichiometry are changed over this range of conditions. Especially in Figure 4.9a and in Figure 4.9c, it can be seen that the maximum voltage change over the range of cathode stoichiometry and the maximum voltage change over the range of temperature are 0.1V. At low flow rate and high temperatures the cell voltage decreases. This cannot directly be attributed to mass-transport losses, as the diffusion of oxygen in air increases with increasing temperature, but this effect is observed more clearly at higher current densities. Under fully saturated conditions, as we expect at these current densities, the absolute amount of oxygen in air decreases with increasing temperatures, as the partial pressure of water increases. This leads to mass-transport or concentration losses, as the reactant supply of air becomes a limiting process.

Due to the very small pressure drop at high temperatures and low stoichiometry at 1.0A cm\(^{-2}\), as shown in Figure 4.9b, the mean gas velocity is decreased and convective transport is not as effective. Increasing the flow rate improves this significantly, as demonstrated in Figure 4.9a, Figure 4.9c and Figure 4.9e. However, this is a simplified assumption and does not include considerations of the effects of liquid water and two-phase flow. Figure 4.9b, Figure 4.9d and Figure 4.9f show the results for the pressure drop. The behavior is in accordance with Equation (4.1). An increase in stoichiometry or current density represents an increase in flow rate and therefore gas velocity. The gas viscosity and density are also affected by temperature: the viscosity increases while density decreases, both impacting the friction factor. Assuming a laminar flow in the single channel, the friction factor \( f \) can be described as a function of the Reynolds number \( \text{Re} \)

\[
f = \frac{64}{\text{Re}} \quad (4.2)
\]
and the Reynolds number can be calculated according to

$$\text{Re} = \frac{\rho V D \mu}{\mu}.$$  \hfill (4.3)

Here $\mu$ is the gas viscosity. When substituting Equation (4.2) and (4.3) into Equation (4.1) the velocity term becomes linear and the effect of the gas density on the pressure drop cancels out. This can be observed in the constant spacing between the contour lines. As viscosity increases with increasing temperature, the pressure drop increases which is reflected by our model. This explanation is neglecting the turbulent terms of the flow which is a common assumption when studying the pressure drop of serpentine PEMFC flow fields.$^{161–163}$ Recent studies have suggested that the flow in serpentine flow-channels becomes turbulent around the bend at $\text{RE} = 660$ and that sectional secondary flows contribute significantly to an enhanced mass-transfer.$^{164}$

Figure 4.10 displays the performance map for the cell with MPL at 300 kPa. At this pressure, the performance does not decline at higher temperatures, which confirms that the decrease in voltage over temperature at lower pressure is due to concentration losses. The overall power density, compared to the 100 kPa, is increased due to the positive effect of the pressure discussed previously. In Figure 4.10e it can be seen that at $1.6 \text{ A cm}^{-2}$ the change in voltage caused by temperature and cathode stoichiometry is smaller than in Figure 4.9e. Drying phenomena can be observed from the change in voltage over the change in temperature at high flow rates in Figure 4.10a. The overall delta p is decreased due to the back-pressure regulation of the station. At $1.0 \text{ A cm}^{-2}$ we observe almost isothermal lines for the pressure drop, which is in contrast to the other profiles which indicate a clear dependency on temperature and may be due to limited sensitivity of our pressure sensor.
Figure 4.11 plots the voltage and pressure drop over temperature and cathode stoichiometry for the cell without MPL at 100 kPa. At all current densities, this cell’s voltage is lower and the change caused by temperature and stoichiometry are higher (>0.25V), compared to the cell with MPL at the same pressure. The dependency on the cell temperature is much stronger for this material as shown by the larger voltage differentiation over the temperature range. Especially at lower temperatures and flow rates significant declines in voltage were observed. This phenomenon is amplified at higher current densities as shown in Figure 4.11c and Figure 4.11e. This can be attributed to flooding of the cell, due to the overall lower areal weight and higher porosity of the GDL material. Liquid water saturates the GDL and impedes the gas transport to the active sites. The pressure drop profile is not conclusive regarding the existence of a liquid water film inside the channel. The changes in pressure drop are regular with the increasing stoichiometry for each current density, but strong differences can be seen when comparing the results at the different current densities with a strong increase at 1.6 A cm$^{-2}$. This may be attributed to both the higher gas velocities and a decreased effective channel area due to liquid water build up in droplets or film form caused by increased water production.
Figure 4.10: Pressure drop and cell voltage at all current densities for the cell with MPL, 25 BC, at 300 kPa. All other factors were kept at a normalized value of 0 (see Section 4.3.1).
Figure 4.11: Pressure drop and cell voltage at all current densities for the cell without MPL, 25 BA, at 100 kPa. All other factors were kept at a normalized value of 0 (see Section 4.3.1).
Figure 4.12: Pressure drop and cell voltage at all current densities for the cell without MPL, 25 BA, at 300 kPa. All other factors were kept at a normalized value of 0 (see Section 4.3.1).
Figure 4.12 shows the results for the cell without MPL at 300 kPa inlet gas pressure. At this pressure, larger changes in voltage > 0.4 V with changes in temperature within the design space of 40°C - 75°C and cathode stoichiometry from 1.5 - 3 can be observed, especially for the two higher current densities. Overall, higher voltages are achieved compared to the voltages at 100 kPa gas inlet pressure shown in Figure 4.11. The flooding of the cell at low temperatures and flow-rates is even more evident. This is ascribed to the higher amount of liquid water due to condensation at 300 kPa, as the mass of water vapor in fully saturated air decreases with increasing pressure. Increasing temperatures compensate for this effect and water can evaporate or will not condensate to begin with. The overall lower pressure drop as seen in Figure 4.12b, Figure 4.12d and Figure 4.12f may contribute to the flooding, especially at low stoichiometries, as the removal of liquid water in the outgoing gas flows becomes insufficient. Again, the steady state pressure drop measurements do not show any signs of liquid droplet formation indicated by increasing pressures. Figure 4.12b does show isothermal behavior, similar to the behavior observed for the cell with MPL at the same pressure and current density.

4.5 General Blocked Design

The general, blocked design was created for two purposes:

1. Can we discover contrasting effects in the significant performance dominating parameters for the two different materials?

2. Are there changes to the results analysis if the interdependencies of the original factors are eliminated?
Since the RH is a function of the vapor pressure of the water $p_w$ and the saturation pressure of water $p_{w}^{sat}$

$$RH = \frac{p_w}{p_{w}^{sat}(T)} \cdot 100\%.$$ (4.4)

RH does not translate directly to the specific amount of water vapor in a gas as this is dependent on temperature and total pressure. In order to eliminate the relationship between factor C, D and E, RH was transformed to the specific humidity $x$ or mixing ratio $r$ equal to the ratio of the mass of water vapor $m_w$ over the mass of the dry gas $m_{gas,dry}$:

$$r = \frac{m_w}{m_{gas,dry}} = \frac{\alpha \cdot p_w}{(p_{tot} - p_w)}.$$ (4.5)

In this case $\alpha$ is a constant factor depending on the gas calculated using the dry molar mass $M$ of the respective component calculated according to:

$$\alpha = \frac{M(H_2O)}{M(gas)}.$$ (4.6)

This allows decoupling the amount of water in the inlet gases from the other operating parameter in the analysis. Based on Equations (4.4), (4.5) and (4.6), 8 points of specific humidity have been calculated for anode and cathode. These points are presented in Table 4.3. The change in factor levels from 2 to 8 for both factors D and E requires a transformation of the design to a general factorial design.
Table 4.3: Specific humidity in the randomized block design

<table>
<thead>
<tr>
<th>RH [%]</th>
<th>Pressure [kPa]</th>
<th>Temperature [°C]</th>
<th>$x_{\text{Anode}}$ [g/kg]</th>
<th>$x_{\text{Cathode}}$ [g/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>300</td>
<td>75</td>
<td>1027.17</td>
<td>71.77</td>
</tr>
<tr>
<td>80</td>
<td>300</td>
<td>40</td>
<td>179.89</td>
<td>12.59</td>
</tr>
<tr>
<td>80</td>
<td>100</td>
<td>75</td>
<td>3994.01</td>
<td>278.32</td>
</tr>
<tr>
<td>80</td>
<td>100</td>
<td>40</td>
<td>561.48</td>
<td>39.15</td>
</tr>
<tr>
<td>40</td>
<td>300</td>
<td>75</td>
<td>485.66</td>
<td>33.93</td>
</tr>
<tr>
<td>40</td>
<td>300</td>
<td>40</td>
<td>89.04</td>
<td>6.23</td>
</tr>
<tr>
<td>40</td>
<td>100</td>
<td>75</td>
<td>1632.24</td>
<td>113.72</td>
</tr>
<tr>
<td>40</td>
<td>100</td>
<td>40</td>
<td>272.19</td>
<td>1405.63</td>
</tr>
</tbody>
</table>

This type of analysis uses a design that is not orthogonal and is not in a standard order, as when RH is transformed, there are 8 levels for the specific humidity. This means that variable effects cannot be estimated independently. The Variance Inflation Factor (VIF) can be used to measure the increase in the variance of the model coefficients due to their lack of orthogonality. VIF values greater than ten indicate problems in the design due to multicollinearity. The ANOVA testing is conducted for six separate cases: for each material at each response. The report for each of these ANOVA can be found in Appendix B. Table 4.4 summarizes parts of the ANOVA analysis. The VIF number is determined for each model term and only the largest number, which is most likely to indicate multicollinearity, for each case is listed. The term “Adequate Precision” describes the signal to noise ratio with ratios > 4 being desirable. The p-value in Table 4.4 shows the largest p-value for a model term in the design apart from model terms that were included for reasons of hierarchy only.
Table 4.4: Summary of the ANOVA for the general design

<table>
<thead>
<tr>
<th>R1 @ 1.0 A cm(^{-2})</th>
<th>R2 @ 1.4 A cm(^{-2})</th>
<th>R3 @ 1.6 A cm(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>MPL</strong></td>
<td>No MPL</td>
<td><strong>MPL</strong></td>
</tr>
<tr>
<td>Model F-value</td>
<td>76.75</td>
<td>11.99</td>
</tr>
<tr>
<td>p-value</td>
<td>&lt; 0.0001</td>
<td>0.0149</td>
</tr>
<tr>
<td>VIF</td>
<td>1.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>

The ANOVA for the general design confirms adequate fit for all models. The design for the material with MPL shows a better model fit at all current densities. The major differences in the two models become evident when the significant factors are analyzed. Figure 4.13 compares the Pareto charts for the design of the material with MPL and the design for the cell without MPL at the first response at 1.0 A cm\(^{-2}\).

The design for the cell employing an MPL only features one significant factor, the positive main effect of the operating pressure, factor F. The model for the cell without MPL...
depends strongly on the negative main effect of the temperature, factor C, and its factor interactions. The specific humidity has no significant effect on the response and remains an inert factor for this design space. Analysis of the Pareto charts at the higher current densities of 1.4 A cm\(^{-2}\) and 1.6 A cm\(^{-2}\) confirm this behavior; the Pareto analyses are presented in Appendix 0 For the cell with MPL the positive main effect of factor F, pressure, continues to be the only significant factor in this design space. The model for the cell without MPL is also based on the same terms as shown in Figure 4.13b but the ranking changes. At 1.0 A cm\(^{-2}\) only two terms are above the Bonferroni limit, the negative main effect of temperature and the positive interaction between cathode stoichiometry and temperature. The interaction between cathode stoichiometry and pressure is included in the model. With increasing current densities the number of Bonferroni significant terms increases but the interaction BF is no longer significant. At 1.6 A/cm\(^{2}\) the order of the ranking changes and the effect of the interaction between temperature and pressure, CF, becomes more significant than the interaction BC. This finding illustrates that there are different underlying physics not only at different current densities but also for the two materials. Because of the different structures for the models for both materials a direct comparison between the two cells using this general design is not possible.

The results of this work demonstrate the use of DoE to assess the differences and parameter dependencies of different materials in the PTL of PEMFC. Based on these experimental designs the relevant and dominant factors that influence the cell performance and pressure drop are determined. For all current densities the type of PTL material, temperature, and the interactions between these two factors had the most significant impact on the voltage, while the anode stoichiometry and anode RH were not relevant. This information and methodology can
now be used to plan efficient experiments where the effects of certain factors, e. g. when testing novel materials, are to be studied and masking of effects due to the influence of other factors is to be avoided. Based on the information extracted during the performance mapping, there are significant differences for the voltage losses for the two investigated materials. In order to analyze the physical phenomena causing these differences, a second methodology, based on VLB techniques described in the following Chapter 5 was applied.
Chapter 5: Voltage Loss Breakdown

This chapter presents a new method to separate the voltage loss contributions of an operating fuel cell by analyzing polarization data from the full cell and the cathode versus a reference electrode (RE). A comprehensive method to separate the individual overpotentials of a PEMFC was developed and the assumptions for the voltage loss breakdown were systematically verified. The individual loss contributions were studied for different PTL materials under different operating conditions such as temperature and inlet gas pressure. The methods and results presented in this chapter have been submitted for publication elsewhere.  

The designed experiments presented in the previous Chapter 4 have shown significant differences in the voltage losses for the two investigated PTL material. The performance mapping based on the DoE models strongly indicates distinct contrasts for the mass-transport overpotentials of the different PTL materials. In order to further the understanding of the underlying phenomena, a systematic break down of the individual contributing loss components is required. This work presents a new method to investigate the individual loss components of polarization measurements by combining the use of a RE and a systematic analytical analysis.

5.1 Approach

A RE was developed to measure the individual voltage loss contributions from both electrodes. An electrically isolated CCM - Pt reference electrode is used in the MEA to measure both anode versus cathode as well as cathode versus RHE polarization. An ideal RHE, supplied with fully humidified hydrogen, has a reference potential of zero. The stability of the reference
The electrode potential is tested by varying the hydrogen flow-rate under multiple constant load conditions. The results can be seen in Appendix C. Based on these stability measurements, the hydrogen flow-rate for the reference section was optimized. The drift of the signal of the reference electrode was measured over time at different relative inlet gas humidities and temperatures were measured, see Appendix C. To prove the concept of the improved design, it’s results were validated based on previously in literature reported designs.\textsuperscript{18,24} Further details on the design of this diagnostic tool and the experimental set-up were presented in Chapter 3.

The mathematical approaches of Gasteiger et al.\textsuperscript{26}, Williams et al.\textsuperscript{28} and Wood and Borup\textsuperscript{29} were consolidated with the added objective to account for anode overpotentials in order to break down the individual loss components of a PEMFC polarization measurement. The second objective was to study the individual loss components employing a sensing electrode system and relate the dependencies between the mass-transport losses and material properties of the PTL as described in the previous chapters.

### 5.2 Kinetic Analysis

In order to elucidate the effects of the individual loss components a detailed analysis of the kinetics of ORR and HOR is required. Unlike ohmic losses, kinetic losses cannot be measured in-situ in an operating PEMFC. A mathematical method originally proposed by Gasteiger et al.\textsuperscript{26} and Neyerlin et al.\textsuperscript{43}, based on Tafel kinetics, was used to extract the kinetic overpotential of the ORR. Their study assumes negligible anode overpotential under the standard operating conditions. Studies by Wagner et al. and Kim et al. have shown that the $\text{H}_2/\text{O}_2$ impedance of a PEMFC at OCV is dominated by the ORR.\textsuperscript{165,166} Wagner et al. measured the
charge transfer resistances of anode and cathode individually employing electrochemical impedance spectroscopy (EIS) at OCV with \( \text{H}_2/\text{H}_2 \) and \( \text{O}_2/\text{O}_2 \) gas feed.\(^{167} \) For small overpotentials, \( \left| \frac{nF\eta}{RT} \right| \ll 1 \), and the Butler-Volmer equation can be simplified to directly correlate the charge transfer resistance \( R_{ct} \) to the exchange current density \( i_0 \):

\[
R_{ct} = \frac{-\eta}{i} = \frac{RT}{nFi_0}
\]  

(Wagner et al. calculated apparent exchange current densities of each electrode and found \( i_{0,\text{anode}} \gg i_{0,\text{cathode}} \). Their work was confirmed by Neyerlin et al. used a hydrogen pump cell and to study the HOR and the hydrogen evolution reaction (HER) for high and ultralow PT loadings.\(^{44} \) Neyerlin et al. determined exchange current densities of 200-600 mA cm\(^{-2}\) Pt. Employing the Butler-Volmer equation they determined anode loss contributions to be < 3 mV, even for low platinum loading of 0.05 mg/cm\(^{-2}\) as targeted by the automotive industry. Recent work has further developed the method of voltage loss breakdown originally proposed by Gasteiger et al. and added contributions by determining detailed individual loss components, both mathematically and experimentally.\(^{27–29,39,41} \)

In this work, the method described by Gasteiger et al. was employed for both cell (WE - CE) and the cathode independently of the working anode (RHE versus cathode) through the means of a RE system in order to develop two sets of kinetic parameters including Tafel slope, exchange current density and ORR reaction order. This approach studies the ORR kinetics in-situ and independently of the anode, while simultaneously determining the anodic contribution to the
voltage losses. This allows demonstrating whether the above stated assumption to neglect the influence of the anode kinetics on the overall overpotential is valid via in-situ experiments.

The voltage of an operating PEMFC, $V_{cell}$, is described as the difference between the equilibrium potential $E_{rev(p_{H_2},p_{O_2},T)}$ and the total overpotential $\eta_{total}$:

$$ V_{cell} = E_{rev(p_{H_2},p_{O_2},T)} - \eta_{total} \quad (5.2) $$

The total overpotential can be expressed as the sum of all individual polarization sources, following the definitions of Wood and Borup$^{29}$

$$ \eta_{total} = \eta_{ORR} + \eta_{HOR} + \sum \eta_i + \eta_{tx,H_2,elec} + \eta_{tx,O_2,elec} + \eta_{tx,H_2,PTL} + \eta_{tx,O_2,PTL} + \eta_x \quad (5.3) $$

In the above equation $\eta_{ORR}$ is the activation overpotential for the ORR, $\eta_{HOR}$ is the activation overpotential for the HOR, $\eta_{tx,i,elec}$ are the respective mass-transport losses in the respective catalyst layers, $\eta_{tx,i,GDL}$ represents the mass-transport losses inside the PTL for both anode and cathode sides and $\eta_x$ is the overpotential due to reactant cross-over.

$E_{rev(p_{H_2},p_{O_2},T)}$ is the equilibrium potential for the $\text{H}_2/\text{O}_2$ reaction, dependant on the partial pressures of the reactants as well as the temperature calculated according to Bernardi and Verbrugge.$^1$

$$ E_{rev(p_{H_2},p_{O_2},T)} = 1.23 - 0.9 \cdot 10^{-3} (T - 298) + \frac{2.303RT}{4F} \cdot \log \left[ \left( \frac{p_{H_2}}{p_{H_2}^*} \right)^2 \left( \frac{p_{O_2}}{p_{O_2}^*} \right) \right] \quad (5.4) $$

92
The collective ohmic overpotential $\sum \eta_{\Omega}$ includes sources from membrane and both electrodes. This can be written as

$$\sum \eta_{\Omega} = \sum \eta_{\Omega, \text{Anode}} + \sum \eta_{\Omega, \text{Cathode}} + \eta_{\text{HFR}}$$  \hspace{1cm} (5.5)$$

where $\sum \eta_{\Omega,i}$ are the respective overpotentials within the anode and cathode electrode layers. $\eta_{\text{HFR}}$ is the overpotential from the high frequency resistance (HFR) including the total ohmic overpotential from all sources except for the electrode layers. According to Wood and Borup $\sum \eta_{\Omega,i}$ can be expanded to show the individual electronic and ionic components of the respective electrode:\textsuperscript{29}

$$\sum \eta_{\Omega, \text{Anode}} + \sum \eta_{\Omega, \text{Cathode}} = \eta_{H^+, \text{Anode}} + \eta_{e^+, \text{Anode}} + \eta_{H^+, \text{Cathode}} + \eta_{e^+, \text{Cathode}}$$  \hspace{1cm} (5.6)$$

These individual ohmic contributions were studied in depth by Saab et al. employing EIS for different ink formulations.\textsuperscript{76,77} Their results show that the areal resistivity for conventional catalyst layers with a thickness between 5 – 25 µm is < 0.5 – 2.5 mΩ cm$^{-2}$, hence these terms can be neglected in the analysis. Neyerlin et al. found the anode protonic resistivity to be < 2 mΩ cm$^{-4}$. Based on their finding, one may infer that the electronic resistances in both electrodes and the protonic resistance in the anode can be neglected and the collective ohmic overpotential may be simplified to

$$\sum \eta_{\Omega} = \eta_{H^+, \text{Cathode}} + \eta_{\text{HFR}}$$  \hspace{1cm} (5.7)$$

Assuming $\eta_{\text{HOR}}$ to be negligible, as stated above, the iR-corrected cell voltage can be mathematically described as:
\[ V_{iR-free} = V_{cell} + \eta_H^* + \eta_{HFR} \]
\[ = E_{rev(pH_2,PO_2,T)} - \eta_{ORR} - \eta_{H_2,elec} - \eta_{O_2,elec} - \eta_{x,elec} - \eta_{x,GDL} - \eta_{x,O_2,GDL} - \eta_x \]  

and

\[ V_{iR-free} = V_{cell} + iR_H^* + iR_{HFR} \]

In Equation (5.9) \( R_H^* \) is the areal resistivity of the protonic transport through the cathode catalyst layer. The ohmic resistance (HFR) is the purely resistive component of the cell electrochemical impedance measured at 1 kHz for this work. This measurement includes contact and bulk electronic resistances of the cell set-up. Literature reports \( R_{HFR} \) values between 50 – 75 mΩ cm\(^2\) under fully saturated conditions. \(^{29}\) \( R_H^* \) can be determined experimentally using impedance/EIS or employing calculations based on material properties of the electrode. The mathematical method employed in this work

\[ R_H^* = \frac{\delta_{elec}}{2\sigma_H \varepsilon_{ionomer}} \]

is based on the thickness of the electrode in cm , \( \delta_{elec} \), the conductivity of the PFSA (poly fluoro-sulphonic acid) ionomer (in S cm\(^{-1}\)) , \( \sigma_H \), and the volume fraction of PFSA in the catalyst layer, \( \varepsilon_{ionomer} \). The cross-over overpotential \( \eta_x \) is determined by measuring the cross-over current density \( i_x \) and correcting the measured current density for this value.

The kinetic parameter analysis in this study was done based on fully saturated H\(_2\)/O\(_2\) polarization measurements. When operating with fully saturated O\(_2\)/H\(_2\) at low current densities
and high stoichiometric flow-rates in order to obtain kinetic parameters, the mass-transport overpotentials are assumed to be zero. In this case, Equation (5.8) simplifies to:

\[ V^*_{iR-free} = E_{rev(p_{H_2}, p_{O_2}, T)} - \eta_{ORR} \]  

(5.11)

Based on this equation the kinetic parameters of the ORR are determined using the Tafel approximation:

\[ \eta_{ORR} = b \log \left[ \frac{i_{eff}}{10(L_{ca} A_{pt,elec} i_0(T, p_{O_2}))} \right] \]  

(5.12)

where \( b \) is the Tafel slope in mV/dec, \( L_{ca} \) is the Pt cathode loading in mg_{Pt} cm\(^{-2}\), \( A_{pt,elec} \) is the electrochemically available Pt surface area in m\(^2\) g_{Pt}\(^{-1}\), \( i_0 \) is the pressure and temperature dependent exchange current density for the ORR and \( i_{eff} \) is the H\(_2\)-cross-over-corrected current density in A cm\(^{-2}\). The cross-over corrected current density, \( i_{eff} \), is calculated based on the measured current density and the cross-over current density \( i_x \)

\[ i_{eff} = i + i_x \]  

(5.13)

where \( i_x \) is the cross-over current density due to hydrogen is cross-over and \( i \) is the measured current density. Gasteiger et al. reported cross-over current densities of 3.3 mA cm\(^{-2}\) for a 50 cm\(^2\) active area cell. \(^{26}\) Combining Equations (5.11), (5.12) and (5.13) yields:

\[ V^*_{iR-free} = E_{rev(p_{H_2}, p_{O_2}, T)} + b \log \left[ 10 \cdot A_{pt,elec} \cdot i_0(T, p_{O_2}) \right] - b \log \left[ \frac{i_{eff}}{L_{ca}} \right] \]  

(5.14)
Based on this equation the Tafel slope, $b$, can be determined

$$\frac{\partial \nu^*_{ir-free}}{\partial \log \left[ \frac{i_{eff}}{L_{Ca}} \right]}_{p_{O_2}, p_{H_2}, T, A_{Pt, elec}} = -b$$

(5.15)

Literature reports typical Tafel slopes for Pt/C catalysts and PFSA membranes at low overpotentials between 59 – 64 mV/decade. Based on the Tafel slope in Equation (5.15) the exchange current density can be determined by extrapolation to the theoretical value of the reversible cell potential.

$$i_{0,(T,p_{O_2})} = \frac{i_{eff}}{L_{Ca}} \left[ \nu^*_{ir-free} = E_{r einzel, p_{O_2}, T} \right]$$

$$10 \cdot A_{Pt, elec}$$

(5.16)

Newman’s approach is used to normalize this exchange current density to the standard O$_2$ partial pressure of 101.3 kPa in order to allow comparison to values reported in literature.

$$i_{0(T)} = i_{0,(T,p_{O_2})} \left( \frac{p_{O_2}}{p_{O_2, ref}} \right)^{-\gamma}$$

(5.17)

In the above equation $\gamma$ is the kinetic ORR order according to

$$\gamma = 1 - \left( \frac{2.303RT}{4Fb} \right)$$

(5.18)
Based on this approach the present study distinguishes between the kinetic parameters obtained from the measurements of the full cell, which are subject to anodic loss contributions from potential kinetic, proton transport and mass-transport terms and kinetic parameters from the RHE - cathode which do not include any anodic contributions.

5.2.1 Results: Kinetic Overpotentials

Three different samples comprised of the same materials, Gore Primea CCM and SGL 25 BC GDL (see Chapter 3, Table 3.2), were tested to evaluate the kinetic parameters of both anode and cathode. The accessible ECSA based on CV measurements was in the range of $54 \pm 5 \text{ m}^2$ $g_p^{-1}$ for all three samples. Our computed value is in good agreement with reported literature values for the same Pt loading.\textsuperscript{26,55} The cross-over current determined by LSV for the beginning-of life conditioned MEA was $< 3 \text{ mA cm}^{-2}$. Details on these results are presented in Appendix C1.

Polarization results of the H$_2$/O$_2$ measurements for all three samples are plotted in Figure 5.1.
Between the three samples there is slight deviation in the voltage measured between cathode and RHE at very low current densities (< 0.1 A cm\(^{-2}\)). At increasing current densities sample one showed a higher voltage between RHE and cathode but a lower cell voltage, indicating increased anode losses. Sample to sample variability and localized changes in the humidity may have attributed to the voltage difference during this experiment. For all three samples the voltage measured between the RHE versus cathode is consistently higher than the voltage of the full cell but the difference is small.

The averaged and resistance corrected polarization results between the three independent measurements are shown in Figure 5.2.
The iR-correction for both measurements was done independently based on separate HFR measurements as stated in Chapter 3. After applying iR-correction the difference between the two measurements becomes almost negligible, especially at very low current densities $\leq 0.1 \text{ A cm}^{-2}$.

Based on these polarization results the approach presented in the previous section was employed in order to extract the kinetic parameters. The Tafel slope and exchange current density, as well as the specific current density at 0.9 V$_{\text{iR-free}}$ for both the full cell and the cathode versus RHE were calculated independently. Figure 5.3 displays the Tafel plots of the iR-corrected cell voltage over the cross-over-corrected current density for both the full cell (anode –
cathode) and RHE versus cathode. The Tafel slopes of the full cell and RHE versus cathode are 65.4 mV decade\(^{-1}\) and 64.8 mV decade\(^{-1}\) respectively.

Table 5.1 summarized the results of the kinetic parameters from the H\(_2\)/O\(_2\) polarization analysis. The temperature dependent exchange current density was normalized to a reference pressure of 101.3 kPa using Equation (5.17). The average and standard deviations for values based on the three different samples are listed. The mass specific current density at 0.9 V\(_{\text{iR-free}}\), \(i^*_{0.9V(T)}\), was normalized according to\(^{26}\)

\[
i^*_{0.9V(T)} = i_{0.9V(T)} \left( \frac{P_{O_2}}{P_{O_2,\text{ref}}} \right)^m
\]

in order to allow comparison with literature values that were not interpolated. In accordance with Gasteiger et al., who proposed this pressure correction, \(m\) is set to one.
Table 5.1: Kinetic parameters from polarization analysis

<table>
<thead>
<tr>
<th></th>
<th>( b ) / mV decade(^{-1})</th>
<th>( i_{0(T)} ) / A cm(^{-2})</th>
<th>( i_{0.9V(T)} ) / mA cm(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Full cell</td>
<td>65.4 ± 1.3</td>
<td>4.69 × 10(^{-9}) - 6.13 × 10(^{-9})</td>
<td>0.121</td>
</tr>
<tr>
<td>RHE - cathode</td>
<td>64.8 ± 1.4</td>
<td>5.5 × 10(^{-9}) - 8.87 × 10(^{-9})</td>
<td>0.144</td>
</tr>
</tbody>
</table>

The average exchange current density from the polarization curve of the full cell is 5.65 A cm\(^{-2}\). These results show good agreement with values for similar CCM reported in the literature.\(^{26,170,171}\) The average exchange current density calculated for RHE versus cathode is 7.19 A cm\(^{-2}\). This value also corresponds with results reported previously for the three electrode measurement but is slightly higher than the result for the full cell.\(^1\) A higher exchange current density correlates to a higher activity on the surface of the electrode.\(^{172}\) This implies that the reaction kinetics of the cathode measured independently of the anode are slightly faster but as Table 5.1 shows the differences become negligible comparing the upper and lower values extracted from the different samples of this study. Therefore, there are anodic contributions but they become negligible when comparing multiple data sets. The normalized mass specific current density at 0.9 V\(_{\text{IR-free}}\) showed no deviation between the measurements within the accuracy of this experiment. The here reported values are in accordance with previous literature.\(^{26,170}\)
After employing the resistance correction based on HFR measurement values, the anode overpotential can be determined according to

\[ \eta_{\text{anode}} = V_{\text{RHE - Cathode}}^{\text{ir-free}} - V_{\text{Full Cell}}^{\text{ir-free}} \]

Table 5.2 summarizes the polarization results, describing the cathode overpotential calculated according to Equation (5.12) and the anode losses at the respective current densities. \( \eta_{\text{ORR}} \) is based on the voltage between RHE – cathode, accounting for the anodic loss contribution and \( \eta_{\text{ORR}} \) is based on the assumption of negligible anodic contribution.

<table>
<thead>
<tr>
<th>( i_{\text{eff}} ) / A cm(^{-2})</th>
<th>( \eta_{\text{ORR}} ) (including anodic contributions) / V</th>
<th>( \eta_{\text{ORR}} ) (neglecting anodic contributions) / V</th>
<th>( \eta_{\text{anode}} ) / mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.268</td>
<td>0.274</td>
<td>6.93</td>
</tr>
<tr>
<td>0.02</td>
<td>0.276</td>
<td>0.281</td>
<td>10.38</td>
</tr>
<tr>
<td>0.05</td>
<td>0.299</td>
<td>0.306</td>
<td>6.46</td>
</tr>
<tr>
<td>0.1</td>
<td>0.324</td>
<td>0.318</td>
<td>11.55</td>
</tr>
<tr>
<td>0.3</td>
<td>0.355</td>
<td>0.349</td>
<td>5.45</td>
</tr>
<tr>
<td>0.4</td>
<td>0.362</td>
<td>0.356</td>
<td>5.79</td>
</tr>
<tr>
<td>0.5</td>
<td>0.369</td>
<td>0.362</td>
<td>6.75</td>
</tr>
<tr>
<td>0.6</td>
<td>0.374</td>
<td>0.367</td>
<td>9.24</td>
</tr>
</tbody>
</table>

The overpotential for the ORR for both measurements is in compliance with values reported in literature for similar materials under comparable operating conditions.\(^{170}\) These results confirm that there is no significant anodic contribution to the overall overpotential under the stated operating conditions.
5.3 Voltage-Loss-Breakdown for Anode and Cathode

Based on the kinetic analysis, it is valid to neglect the anodic contribution to the kinetic overpotential. But anodic mass-transport loss contributions cannot be neglected when operating with H₂/air under certain operating conditions. In order to comply with current standards in literature the term GDL is used as a subscript for the mass-transport overpotential in the porous transport layer. It includes both losses in MPL and GDL where applicable.

Based on the assumption developed in the previous section, Equation (5.8) can be expressed as the following for H₂/air operation

\[ V^\text{Full Cell}_{iR-free} = E_{rev(p_{H_2},p_{O_2},T)} - \eta_{ORR} - \eta_{x,H_2,elec} - \eta_{x,O_2,elec} - \eta_{x,H_2,PTL} - \eta_{x,O_2,PTL}. \]  

Mass-transport losses in the flow fields due to transport resistances in the flow channels are not considered in this study. Beuscher concluded in his resistors in series approach that the gas-phase diffusion resistance was small relative to the other transport resistances. The individual iR-correction based on separate measurements as introduced in Chapter 3 allows combining Equation (5.21) and Equation (5.20) into the following two equations.

Cathode:

\[ V^\text{RHE-Cathode}_{iR-free} = E_{rev(p_{H_2},p_{O_2},T)} - \eta_{ORR} - \eta_{x,O_2,elec} - \eta_{x,O_2,PTL}. \]  

Anode:

\[ \eta_{anode} = V^\text{RHE-Cathode}_{iR-free} - V^\text{Full Cell}_{iR-free} = \eta_{x,H_2,elec} + \eta_{x,H_2,PTL} = \eta_{anode,xx}. \]  

In Equation (5.22) \( V^\text{RHE-Cathode}_{iR-free} \) is measured via reference electrode and HFR measurement, \( E_{rev(p_{H_2},p_{O_2},T)} \) calculated according to Equation (5.4) depending on the operating conditions and
\( \eta_{\text{ORR}} \) is calculated based on \( \text{H}_2/\text{O}_2 \) polarization measurements at the same operating conditions as the corresponding \( \text{H}_2/\text{air} \) measurement as described in Section 5.2. Accurate determination of \( \eta_{\text{tx, O}_2, \text{elec}} \) is non-trivial due to the direct dependence of the proton transport and oxygen transport within the reaction zone. Hence an indirect approach must be used. Wood and Borup\(^{29}\) derived a method to extract \( \eta_{\text{tx, O}_2, \text{elec}} \) based on analysis of the different oxidants by extracting two sets of kinetic parameters: One based on \( \text{H}_2/\text{O}_2 \) polarization analysis as stated above; a second set is derived using \( \text{H}_2/\text{air} \) polarization data at high stoichiometric ratios. They arrive at the following description to distinct the mass-transport overpotential within the cathode electrode:

\[
\dot{\eta}_{\text{ORR}} = \eta_{\text{ORR}} + \eta_{\text{tx, O}_2, \text{elec}}
\]  

(5.24)

where \( \dot{\eta}_{\text{ORR}} \) is an effective ORR overpotential that includes the effects of the mass-transport resistance in the electrode as it is calculated based on kinetic parameters extracted from measurements employing air. With this Equation (5.22) and Equation (5.24) can be combined to extract the mass-transport overpotential inside the cathode PTL based on the measurement between RHE and cathode:

\[
\eta_{\text{tx, O}_2, \text{PTL, RHE - Cathode}} = E_{\text{rev}(p_{\text{H}_2}, p_{\text{O}_2}, T)} - V_{\text{RHE - Cathode, IR-free}} - \dot{\eta}_{\text{ORR}} - \eta_{\text{tx, O}_2, \text{elec}}
\]  

(5.25)

### 5.4 Model for Data Analysis

Based on the equations derived in this chapter, a model was created in Matlab\(^{\circledast}\) (version R2012b) to separate the polarization measurements into the respective loss components. Fitting and optimization of the kinetic parameters were done based on regression methods. An object oriented program structure was used to allow for a modular format of the tool. This improves the
flexibility of the code and to allow efficient calculation. Figure 5.4 illustrates the structure of this tool to analyze polarization data. All functions of this tool were written and programmed by the author.
Figure 5.4: Structure of the tool to separate the individual overpotentials
The input data from the experimental results was formatted into an input structure. A master function was generated to control the sub-functions in order to allow the execution of individual functions. This allowed for validation of the individual calculation steps and sub-functions based on data published in literature.\textsuperscript{26,28,29,170} The individual calculation steps are shown in Figure 5.4. Based on the available experimental data, all sub-functions can be toggle switched in order to access only certain parts of the data analysis. The object oriented structure allows simple and fast adaptation to different materials and geometries and complete data sets can be automatically analyzed.

5.5 Results: Mass-Transport Overpotentials

Based on the results presented in Chapter 4, this part of the thesis work was designed to feature the most statistically relevant and significant factors on the cell’s voltage. Therefore, the breakdown of the individual loss contributors was done for the two PTL materials (25 BA and 25 BC) at the varying temperature as described in Chapter 4 (40 °C and 75 °C) and at the two pressure levels (100 kPa and 300 kPa).

Figure 5.5 shows the measured baseline polarization curve for the 25 BC, including the standard deviation of the measurements in error bars. The baseline was selected to allow comparison to previous works\textsuperscript{36,124} and the conditions were set as follows: cell and gas inlet temperatures equal 75 °C, gas inlet pressures are 200 kPa, stoichiometric rates for anode and cathode are 1.5 and 2.5 respectively and inlet gas RH for both anode and cathode are 100%.
The standard deviations shown in the error bars of Figure 5.5 are very small ($\leq 0.002$ V). This proves that our measurement is stable for all three measured electrodes (WE – CE, RHE – cathode and RHE – anode). It also shows that these measurements correspond to steady state conditions. The anodic overpotential measured between RHE and anode seems large, especially above 0.5 A cm$^{-2}$ but a significant part of this overpotential can be attributed to the ohmic resistance. Corrections for the ohmic losses are based on separate HFR measurements between RHE – cathode and the full cell, measuring the areal resistivity for each set-up in $\Omega$ cm$^2$. The ohmic overpotential is calculated according to Equation (5.9) employing the HFR measurement.

Figure 5.5: Measured baseline polarization curve for GDL material 25 BC, including standard deviations of the signals.
between RHE - cathode. The ohmic overpotential for the anode, based on the assumption that the anode protonic resistivity is negligible as stated above, can thus be calculated according to

\[ \eta_{\Omega, \text{Anode}} = \eta_{\text{HFR}}^{\text{Full Cell}} - \eta_{\text{HFR}}^{\text{RHE - Cathode}}. \] (5.26)

The measured HFR for the full cell was between 65 – 100 mΩ cm\(^2\) under fully humidified operating conditions. These values are in good agreement with published literature.\(^{29}\) The measured HFR between RHE – cathode was between 40 – 50% of the value of the full cell. A reason for the deviation from 50 %, as proposed by Gerteisen\(^ {24}\), is the different type of wire used for the RHE compared to the full cell. The iR-corrected voltages as a function of the cross-over corrected current density are plotted Figure 5.6 for this baseline.

![Figure 5.6: Resistance corrected baseline polarization, 25 BC](image)

Figure 5.6: Resistance corrected baseline polarization, 25 BC
As shown in the previous section, when corrected for the ohmic resistance, the anodic overpotential (RHE – Anode) becomes negligible. Based on this iR-corrected data, the individual loss components were calculated according to the methods derived in Section 5.2 and 5.3 using the Matlab model described in Section 5.4. The pressure and temperature dependent kinetic parameters were measured and corrected to the respective operating conditions. The calculated ORR order \( \gamma \), see Equation (5.18), was 0.73 for the baseline of this material and between 0.7 – 0.8 for all other measurements. This is in accordance with data from ten independent studies summarized by Gasteiger et al.\textsuperscript{26} Figure 5.7 shows the breakdown of the polarization curve into the individual loss contributions as a function of current density.

![Figure 5.7](image)

**Figure 5.7: Breakdown into the individual overpotentials**

It can be clearly seen that \( \eta_{\text{ORR}} \) is the main contributor to the fuel cell’s voltage loss, but the slope of this overpotential decreases significantly above 1 A cm\(^{-2}\) due to the logarithmic nature of the function, see Equation (5.12). At high current densities, as expected, the mass-
transport overpotential from the cathode PTL becomes a dominant factor, with a very steep slope of this curve. It is below 0.05 V until 0.5 A cm\(^{-2}\) but then shows a steep increase to 0.1 V at 1.0 A cm\(^{-2}\) and close to 0.3 V at 2.0 A cm\(^{-2}\). The combined anode mass-transport overpotential is the smallest contributor but at high current densities its value increases to 0.08 V. The ohmic loss contributions are linear as expected and almost equally distributed between anode and cathode. The mass-transport overpotential due to transport resistance in the cathode electrode is another major contributor to the cell’s voltage loss accounting for up to 0.15 V, but this loss starts to become a constant after 1.5 A cm\(^{-2}\). This is in accordance with the results presented by Wood and Borup.\(^{29}\)

5.5.1 Mass-Transport Overpotentials for Different PTL Material

The results from Chapter 4 showed that temperature, type of PTL material and gas inlet pressure and their interactions had the most effect cell’s voltage. Therefore the voltage loss breakdown analysis will be carried out comparing the two PTL materials, 25 BC and 25 BA, based on polarization data at different temperatures and gas inlet pressures.

In order to elucidate the effect of the MPL on the fuel cell’s voltage the voltage loss breakdown method was conducted with and without MPL. Figure 5.8 shows the measured baseline between CE – WE, RHE – cathode and RHE – anode for both materials. To improve the readability of the graphic, the indication of RHE – electrode was dropped from the legend.
It can be seen that both materials show comparable performances of the full cell (anode versus cathode) which are almost identical up to 1.0 A cm\(^{-2}\). At higher current densities, the material without MPL outperforms the material with MPL. Notably, the cathode of the material with MPL shows a higher potential. The losses are more distinct at the anode of the material with MPL.

The iR-corrected baselines are shown in Figure 5.9.
The material without MPL has negligible anodic loss contributions under these conditions when analyzing the iR-corrected potentials. This important finding is in agreement with previously published materials that assume the anodic loss contributions negligible or very small. The cathode performance with respect to the full cell’s performance is improved by the MPL as shown in Figure 5.9. The iR-free baseline exclusively for the 25 BA material is shown in Appendix C.

The breakdown into the individual loss components is shown in Figure 5.10. The voltage loss breakdown for the 25 BA material is shown in Appendix C.
As expected, $\eta_{\text{ORR}}$ does not vary significantly for the two cells, as they are both featuring the same CCM from the same batch, as described in Chapter 3, and the measurements were taken at the same operating conditions. The ohmic losses vary slightly, as the thickness of the PTL is different and one has a dual layer structure but the values are in good agreement with literature as stated in the previous section.\cite{26,28,29} The MPL seems to improve the ohmic losses for both anode and cathode which can be attributed to an improved contact resistance between the PTL and the CL.\cite{3,88,104} The mass-transport loss in the cathode PTL was the overpotential that displayed the greatest disparity between the two materials. The difference was most distinct between 1 – 1.5 A cm$^{-2}$. At high current densities $\geq$ 2.0 A cm$^{-2}$ the mass-transport overpotential of the cell without MPL was converging towards the overall lower mass-transport overpotential of the cell with MPL. The values at 1.0 A cm$^{-2}$ were 100 mV/144 mV with/without MPL. At 2 A

Figure 5.10: Comparison of the voltage loss breakdown for 25 BC and 25 BA (note that the y-axis is discontinuous)
cm$^{-2}$ they were 280/290 mV with/without MPL. The mass-transport losses in the cathode electrode were similar for both materials.

The anodic mass-transport losses were not significant for either material under these baseline conditions. All of these baseline values were compared to data at similar conditions in literature and found to be in good agreement.$^{26,28,29}$

The findings presented in Chapter 4 identify the factor interaction between type of PTL material and temperature as one of the voltage determining parameters.$^{118,119}$ It was shown that the gas inlet pressure was the only significant factor when analyzing the material with MPL. There were indications of flooding at low temperatures for the material without MPL. The measured polarization results for these operating conditions are plotted in Figure 5.11. The measurements for the anode show no significant difference between the two materials but a decreased cell voltage for the full cell and RHE versus cathode can be observed for current densities $> 1.0$ A cm$^{-2}$ for the material without MPL.
In order to prove and further analyze this finding, VLB was conducted using the same factors and factor levels as presented in Chapter 4, Section 4.3.1. The first case shown here is at low gas inlet pressures of 100 kPa and high temperatures of 75 °C. Chapter 4 demonstrates significant differences between the performances of the two materials. Figure 5.12 shows the VLB for both materials under these conditions.
The individual VLBs for each material under these conditions are shown in Appendix C. The most notable difference to the baseline was a closer agreement of the cathode PTL mass-transport between the two materials. At 1.0 A cm\(^{-2}\), both materials have mass-transport losses in the cathode PTL of 135 mV. At 2.0 A cm\(^{-2}\) this loss increased to 300 mV for the material with MPL. The cell without MPL did not reach a stable voltage at 2.0 A cm\(^{-2}\) under these conditions. At the last stable point of 1.9 A cm\(^{-2}\), the mass-transport overpotential for the cell without MPL was already at 360 mV. Both materials are subject to increased mass-transport losses in the cathode PTL compared to the baseline. This effect is enhanced at higher current densities with increased product water production. These results confirm that increased back pressures improve the mass-transport due to the increased partial pressure of oxygen and improved water management as stated in Chapter 4. The material without MPL also shows an increase in mass-transport losses in the cathode catalyst layer, indicating that the MPL plays a significant role in improving the mass transport inside the cathode CL.\(^{88,92,102}\) Notably, also the ohmic resistance...
increases for the material without MPL at current densities > 1.0 A cm\(^{-2}\). This is a surprising result as the increase in product water should counterbalance a drying of a membrane. A potential explanation could be less optimal thermal management compared to the cell with MPL. Increases in temperature in the catalyst layer due to the exothermic reaction could lead to drying inside the catalyst layer and membrane that would increase the ohmic resistance. Yau et al. found that the MPL promotes back diffusion through the membrane which supports this finding.\(^{105}\) Both materials show no notable anodic loss contributions under these conditions.

The next case was conducted at the same pressure, 100 kPa, but at low temperatures of 40 °C in order to further investigate influences of flooding and thermal effect on the cell’s polarization. The measured polarization curves are presented in Figure 5.13. Again, the cell with an MPL shows a higher voltage, this time even at lower current densities. The cell without MPL shows a distinct “knee” in the polarization curve that is commonly attributed to mass-transport losses. The anode overpotential is linear with current density for both cells.
Figure 5.13: Measured polarization results at 100 kPa, 40 °C and 100% RH for 25 BC and 25 BA

Figure 5.14 shows the results of the VLB for both materials.

Figure 5.14: VLB at 100 kPa, 40 °C and 100% RH for 25 BC and 25 BA
These results show an increased ORR overpotential for both cells, which is expected as the temperature was decreased and the kinetic parameters are temperature dependent. The mass-transport overpotential in the cathode electrode yields the most notable difference to baseline and high temperature experiment. Both materials show a significant increase of mass-transport losses in the cathode electrode compared to the 75 °C measurements but for the material without MPL this loss becomes the overall largest and most dominating loss at higher current densities. This loss can be ascribed due to flooding of the cathode catalyst layer as product water is not removed efficiently from the reaction sites and the GDL reaches a high level of liquid saturation within its structure. The increasingly steep gradient of the mass-transport losses in the cathode PTL with higher current densities confirm this. Higher current leads to an increase of product water and the PTL becomes saturated with liquid water that blocks the gas transport. This reveals a significant difference to the results from the cell with MPL. For the cell with MPL the mass-transport loss in the cathode PTL becomes larger than the loss in the electrode at 1.4 A cm$^{-2}$. This illustrates that the MPL plays a very different role on the anode side versus the cathode side.\textsuperscript{173} The ohmic losses show no significant variation between the two materials. This confirms the positive effect of an MPL at the higher temperature as shown in Figure 5.12. At lower temperatures, the absence of an MPL is not as significant for the heat removal. Under these conditions the cell was also not operated at very high current densities, where the heat production increases, because the cells’ voltage was deteriorating due to dominant mass-transport losses.

The next case investigated was at the high pressure level of 300 kPa and the low temperature level of 40 °C. Figure 5.15 shows the polarization results.
The polarization results illustrate the compelling differences in polarization behaviors as already discussed in Chapter 4, Section 4.4.1.3. While there is again no difference for the anodic overpotential, the cell without MPL is showing the lowest voltages of all 8 investigated cases under these conditions. Again, rapidly deteriorating cell voltage with increasing current density, indicative of flooding due to liquid water, is observed and the cell did not reach stable voltages at current densities > 1.0 Acm$^{-2}$. The cell with MPL is showing a higher voltage as the reactant pressure is the dominating positive factor for this material as discussed in Chapter 4. The VLB is shown in Figure 5.16. The reversible cell potential at this temperature and pressure is closed to the reversible cell potential at standard conditions. This explains the increase in OCV that can be observed for both materials, shown in Figure 5.15.
Figure 5.16: VLB at 300 kPa, 40 °C and 100% RH for 25 BC and 25 BA

The mass-transport inside the cathode electrode is significantly improved for the material with MPL at higher pressures. The mass-transport losses inside the cathode PTL are comparable to the results at 100 kPa at 40 °C. The same is true for the ohmic losses for both materials. The material without MPL exhibits mass-transport losses inside the cathode electrode $> 300$ mV between 0.8 and 1.0 A cm$^{-2}$. The losses inside the cathode PTL increase from 150 mV to 250 mV between 0.8 and 1.0 A cm$^{-2}$. The increasing gradients again suggest liquid water accumulation that is blocking the reactant transport and active sites as the reason for this behavior.

These findings support the results from the general blocked factorial design, presented in Chapter 4, Section 4.5. The gas inlet pressure is the dominant positive factor on the cell’s voltage for the cell with MPL but not for the cell without MPL where temperature and its factor interactions have the most significant impact. The final case investigates the high pressure level of 300 kPa in combination with the high temperature level of 75 °C. The measured polarization curves under these conditions are plotted in Figure 5.17 and confirm the results of Chapter 4.
Section 4.4.1.3, as the performance of the cell without MPL is significantly improved under these conditions. Both cells reach the highest current densities and power densities compared to the other cases.

Figure 5.17: Measured polarization results at 300 kPa, 75 °C and 100% RH for 25 BC and 25 BA

The VLB plot under these conditions is shown in Figure 5.18.
It can be seen that the ORR overpotential is decreased due to the faster kinetics at higher temperatures. The mass-transport losses inside the cathode electrode are significantly decreased compared to the low temperature cases in Figure 5.14 and Figure 5.16. The combination of high pressure and temperature leads to the lowest mass-transport overpotentials inside the cathode electrode for both materials. This further confirms that the high mass-transport overpotential at low temperatures for the material without MPL can be attributed to liquid water blocking the CL. The mass-transport losses in the PTL of the material without MPL are significantly larger than for the material with MPL. The mass-transport overpotentials inside the GDL are 110/180 mV with/without MPL at 1.0 A cm\(^{-2}\) and 255/322 mV with/without MPL at 2.0 A cm\(^{-2}\). The higher temperature does yield improved mass-transport but the mass-transport losses inside the PTL become the largest contributing loss, exceeding the value of the ORR overpotential, at 1.8 A cm\(^{-2}\) with a value of 318 mV. For the cell with MPL this occurs after 2.35 A cm\(^{-2}\) and the value is 320 mV. The ohmic losses are lower for the cell with MPL which shows that the MPL improves the
contact resistance and thermal management as this effect may be enhanced via improved proton transport inside the catalyst layers. The anodic contributions become noticeable for the cell with MPL but they remain below 50 mV over the range of tested current. This confirms theories of the MPL acting as a barrier which leads to water permeation from cathode to anode as there are no anodic mass-transport losses observed for the cell without MPL.\textsuperscript{104,105,110,112–115} This theory is confirmed by the decrease in mass-transport losses in PTL and CL for the material with MPL, especially at higher current densities. The material with MPL’s mass-transport was improved by an increase in gas inlet pressure. The pressure did not have a positive effect on the mass-transport in the GDL of the material without MPL, as it was already concluded in Chapter 4.

Based on this study it can be concluded, that the MPL significantly improves the water management of the cell, especially inside the electrode, and therefore the mass transport within the cathode CL. This study supports the theory that the MPL on the cathode leads to an increase in water permeation from cathode to anode due to its function as a barrier that decreases the liquid water saturation inside the PTL. This is reflected in increased anodic mass-transport overpotential, decreased ohmic losses and decreased cathode mass-transport losses, especially in the cathode electrode. The improved ohmic resistance can also be attributed to an improved contact resistance between transport layer and CL. A summary and highlights of this study are stated in the concluding Chapter 6.
Chapter 6: Conclusions

After a comprehensive literature review the need for systematic methodologies to experimentally study the voltage loss of a PEMFC was identified. Two approaches to analyze and evaluate fuel cell performance and losses are presented in this thesis. This chapter summarizes the conclusions and highlights of this work. It also gives an overview about the ongoing and future efforts that were derived from this thesis work.

As fuel cells reach the early stages of commercialization, the need for effective research methods and efficient characterization tools is increasing. Industrial demands allowing for serial production require methods for standardized testing and efficient quality control while developing new materials and production methods. This thesis work presents two methodologies: Design of Experiments applied to PEMFC to analyze for sparsity of effects and performance mapping; and a systematical Voltage Loss Breakdown method based on experimental polarization featuring anodic contributions. Both concepts were validated and the effects of commercial PTL materials on the fuel cell’s galvanostatic polarization curve were investigated. The here developed methodology and tools are now presented to be applied to novel materials and to minimize testing efforts.

6.1 Designed Experiment

The results of this work demonstrate the use of DoE to assess the differences and parameter dependencies of different materials in the PTL of PEMFC. Split-plot and general blocked design models were used to analyze the voltage and pressure drop of PEMFC at different current densities between 1.0 A cm\(^2\) – 1.6 A cm\(^2\). The empirical models show good fit
and prove that these methodologies based on experimental designs can be useful to predict and analyze fuel cell performance within this design space. The use of designed experiments allows a scientifically objective analysis of the data compared to OFAT testing while reducing the overall required test runs. The empirical models based on the ANOVA analysis provides an adequate fit to the measured results at all tested operating points. Applying these methods to PEMFC testing avoids the masking of effects and falsifying results due to systematic errors. Using designed experiments also allows reducing the number of required test runs. In this case seven carefully selected factors, six responses and all interactions up to the 4\textsuperscript{th} order were tested with 192 experiments. A one-factor-at-a-time (OFAT) experiment aiming to capture the main effects of seven factors, OFAT experiment cannot capture factor interactions, would require 512 test runs in comparison.

### 6.1.1 Split-Plot Designs

This method was used to screen the cell voltage’s governing factors and factor interactions. Employing ANOVA and statistical techniques it was shown that the sparsity effects principle holds true and statistically dominating main effects and factor interactions were identified at each current density. Factors and responses were chosen to represent the fuel cell’s performance in a desirable range for efficient power production. The selected voltage response points were at current densities 1.0 A cm\textsuperscript{-2}, 1.4 A cm\textsuperscript{-2} and 1.6 A cm\textsuperscript{-2} which are compatible with practical power density ranges. As the same CCM is used for all experiments, the most noticeable differences in the voltage response are to be expected in the mass-transport region. Hence, the focus of this experiment is in that region. For all current densities the type of PTL
material, temperature, and the interactions between these two factors had the most significant impact on the voltage, while the anode stoichiometry and anode RH were not relevant. The models based on these designed experiments were used to map the parameter dependencies of the statistically most significant factors and interactions as a function of both pressure drop and cell voltage for both materials tested. None of the anode operating parameters were found to have a relevant influence on the cell’s voltage when changed within the proposed ranges. The cathode inlet RH was found statistically significant but did not account for significant factor interactions.

Performance maps for both cell’s voltages and pressure drops as functions of all significant factors and factor interactions were analyzed. These performance maps were generated from empirical models based on the ANOVA of the split-plot designs. The equations showed good fit and due to the more linear nature of the polarization curve between 1.0 – 1.6 A cm\(^{-2}\) under the chosen operating conditions, interpolation of the results between these current densities is possible. The cell with an MPL showed voltage changing only 0.1V with temperature and cathode stoichiometry variation within the design space. The cell without MPL’s voltage had a strong dependence on temperature indicated by large voltage differences of 0.4 V over the range of temperatures between 40°C - 75°C. The cell without MPL’s decrease in voltage at low temperatures and cathode stoichiometries can be attributed to flooding.

This approach allows the use of one model for materials that are governed by different underlying physical phenomena depending on the operating conditions developing framework that can be used to identify differences and trend for underlying physical phenomena. Our results show, that this analysis can capture and model the effects of PTL materials and operating
conditions as statistically and physically significant. Expanding these equations into the ohmic region of the polarization curve is possible using interpolation from an added response point at 0.6 V. In order to map the kinetic region, the empirical equations need to be revisited as there are different governing factors at low current densities and the design space is increased. The VLB measurements show little difference between the two different PTL materials studied in this thesis for low current densities < 0.6 A cm\(^{-2}\) as the same CCM material from one batch is used. If DoE methods were to be applied to map the performance in the kinetic region of the polarization curve a separate empirical model should be developed based on experimental results in order to guarantee adequate fit of the model equations within the design space.

### 6.1.2 General Blocked Design

The general blocked design was created to decouple the factor interdependencies and analyze the effect of this for each GDL material (25 BA and 25 BC) separately. The relative gas inlet humidity is a direct function of temperature and indirectly dependent on total temperature. To avoid this interaction, the inlet RH was replaced with the specific humidity in the gas inlet stream for each condition. This resulted in eight levels of specific humidity and therefore required a transformation of the 2-level design to a general design to accommodate the extra six levels. A Pareto analysis was conducted for both materials individually, to determine what factors had dominant effects on the cell’s voltage at three different galvanostatically controlled current densities. At 1.0 A cm\(^{-2}\) the only statistically significant and voltage determining factor for the cell with MPL (25 BC) was the gas inlet pressure as a positive effect on the voltage. This factor had a t-Value of its effect greater than 8.76 and the t-value limit was 2.04. At 1.4 A cm\(^{-2}\)
the inlet pressure remains the only significant factor but the t-value decreases slightly to 6.26. At 1.6 A cm\(^{-2}\) this behavior is confirmed. The inlet pressure remains the only relevant factor and its t-value is 5.87. The cell without MPL (25 BA) shows different voltage governing factors. At 1.0 A cm\(^{-2}\) the temperature is the most significant factor having a positive effect on the cell’s voltage. The factor interaction between temperature and cathode stoichiometry has a significant negative effect and the interaction between temperature and pressure has a significant positive effect on the cell voltage. At 1.4 and 1.6 A cm\(^{-2}\) these factors and factor interaction remain significant with the addition of the cathode stoichiometry as a main positive effect. The specific humidity has no effect on the cell’s voltage within the design space of this experiment.

This analysis shows that there are different underlying factors that dominate the cells voltage for each material.

### 6.2 Voltage Loss Breakdown

The VLB method developed in this work systematically analyzes the different dominant loss contributions and shows the relevance of the anode under varying operating conditions. A reference electrode system was designed and validated in order to measure the anodic and cathodic contributions to the cell’s polarization separately. A mathematical approach was developed to break down the polarization curve into the individual contributing losses, distinguishing between anode and cathode and the individual kinetic, ohmic and mass-transport overpotentials. The tool to extract the individual loss components was programmed in Matlab®, version R2012b and based on object oriented programming. The modular structure of the program allowed individual validation of each sub-function. This tool can be easily adapted and
modified and is not specific to a data input from a fixed experimental set-up. Further
development of this tool can be incorporated without changes to the structure of having to
redefine all input data. A kinetic analysis was conducted to confirm the assumption of negligible
anodic contribution in the kinetic region. A systematic study of the mass-transport overpotential
was conducted for two commercial PTL materials (25 BC and 25 BA) in order to evaluate the
influence of the MPL on the individual loss components.

6.2.1 ORR Kinetic Analysis

This work presents a new methodology to study the ORR kinetics of a PEMFC
independently of the anode. A newly designed and developed RE system was used to study the
kinetic parameters of a PEMFC with commercial materials and symmetrical loading. A
mathematical approach to extract the kinetic parameters from measured polarization data for
both a full cell and RHE versus cathode based on Tafel kinetics was used. The fitting and
optimization of the polarization data was done based on regression methods. All results were
based on multiple measurements with three independent samples. All kinetic parameters for the
full cell were in compliance with data previously published for similar materials. The parameters
for the RHE versus cathode were similar but showed small anodic contributions. The calculated
Tafel slope for the full cell was 65.4 mV decade\(^{-1}\) and for RHE versus cathode 64.8 mV decade\(^{-1}\).
The exchange current densities for full cell / RHE versus cathode were 5.65 A cm\(^{-2}\) and 7.19 A
cm\(^{-2}\) respectively. The pressure normalized mass specific current density at 0.9 V\(_{\text{irr-free}}\) were
0.121 mA cm\(^{-2}\) (full cell) and 0.144 mA cm\(^{-2}\) (RHE – cathode).
In order to investigate the above stated parameters we employed independent ohmic corrections for both measurements. We present cathode kinetic parameters based on in-situ measurements independently of anodic contributions. Comparisons to the values from the full cell show anode losses in the range of 5 - 12 mV for the described operating conditions. This confirms that the assumption to neglect anode contributions to the overpotential is valid when studying the kinetics of the fuel cell under fully humidified conditions using H₂/O₂ polarization analysis. Further, ongoing efforts complimenting this work include AC impedance measurements to independently investigate the charge transfer resistances of the anode and cathode electrode in-situ.

6.2.2 Mass-Transport Losses

A step-by-step, mathematical method to extract the mass-transport losses in the cathode PTL, the mass-transport losses in the cathode and the combined mass-transport losses in the anode was developed. This method is based on measured iR-corrected polarization data and reference electrode measurements. A reference electrode system featuring a RHE was designed and its’ concept was validated. The results from the designed experiments were used to create an experiment with two PTL materials, one featuring an MPL (25 BC) and one without MPL (25 BA), in order to study the effect of the MPL on the mass-transport overpotential under varying temperature and gas inlet pressures. All results are based on steady state polarization results. The mass-transport loss calculations were generated employing H₂/air as reactants. A baseline polarization curve at 200 kPa gas inlet pressure, 75 °C and stoichiometric flow rates of 1.5 at the anode and 2.5 at the cathode was analyzed and the voltage breakdown was calculated. The
absolute biggest overpotential was the ORR kinetic overpotential. It was the same for both PTL material as the commercial CCM used was the same and from the same batch. At 1.0 A cm$^{-2}$ the ORR overpotential was equal to 290 mV, increasing to 320 mV at 2.0 A cm$^{-2}$. The ohmic losses for both materials were separated into anodic and cathodic contributions based on separate HFR measurements. All ohmic losses were linear with current density and the ratio between anodic and cathodic ohmic loss was $\approx 50\%$. The cell without MPL exhibited higher ohmic losses, at 2.0 A cm$^{-2}$ the combined (anode and cathode) ohmic loss for the cell without MPL was 370 mV and for the cell with MPL the combined loss was 316 mV. The mass-transport loss in the cathode PTL was the overpotential that displayed the greatest disparity between the two materials. The difference was most distinct between 1 – 1.5 A cm$^{-2}$. At high current densities $\geq$ 2.0 A cm$^{-2}$ the mass-transport overpotential of the cell without MPL was converging towards the overall lower mass-transport overpotential of the cell with MPL. The values at 1.0 A cm$^{-2}$ were 100 mV/144 mV with/without MPL and at 2 A cm$^{-2}$ they were 280/290 mV with/without MPL. The mass-transport losses in the cathode electrode were approximate for both materials with values of 123 mV at 1.0 A cm$^{-2}$ and 127 mV at 2.0 A cm$^{-2}$. The anodic mass-transport losses were not significant for either material under these baseline conditions. All of these baseline values were compared to data at similar conditions in literature and found to be in good agreement.\textsuperscript{26,28,29}

Further voltage loss breakdown analysis was conducted under the same conditions that were employed for the designed experiments. Only the factors that were found to have the most effect on the cell’s voltage, this being temperature and inlet gas pressures, were varied. At low inlet gas pressures, 100 kPa, and high temperatures, 75 °C, the most notable difference to the baseline was a closer agreement of the cathode GDL mass-transport between the two materials.
At 1.0 A cm\(^{-2}\), both materials have mass-transport losses in the cathode PTL of 135 mV. At 2.0 A cm\(^{-2}\) this loss increased to 300 mV for the material with MPL. The cell without MPL did not reach a stable voltage at 2.0 A cm\(^{-2}\) under these conditions. At the last stable point of 1.9 A cm\(^{-2}\), the mass-transport overpotential for the cell without MPL was already at 360 mV. These results confirm that increased back pressures improve the mass-transport in the PTL. The ohmic resistance increases for the material without MPL at current densities > 1.0 A cm\(^{-2}\). This indicates a less favorable thermal management compared to the cell with MPL that influences the liquid water saturation of the membrane and protonic resistance in the catalyst layer of both electrodes. At the low pressure, 100 kPa, and low temperature, 40 °C, the cell without MPL shows a distinct “knee” in the polarization curve that is attributed to mass-transport losses. At these conditions a rapid increase of mass-transport losses inside the cathode electrode can be observed for the material without MPL. This can be attributed to flooding as active sites in the catalyst layer get blocked by liquid water. The increasingly steep gradient of the mass-transport losses in the cathode PTL with higher current densities confirm this. Higher current leads to an increase in product water and the GDL becomes saturated with liquid water that blocks the gas transport. The case of high pressure level, 300 kPa, and low temperature level, 40 °C, showed very similar behavior to the low pressure and low temperature case for the cell without MPL. Again, steep gradients in cathode mass-transport overpotentials were observed and the cell did not reach stable voltages at current densities > 1.0 Acm\(^{-2}\). For the material with MPL the mass-transport inside the cathode electrode is significantly improved at the higher pressure level. This finding is supporting the results from the general blocked factorial design, presented in Section 4.5. The gas inlet pressure is the dominant positive factor on the cell’s voltage for the cell with MPL but not for the cell without MPL where temperature and its factor interactions have the
most significant impact. This is confirmed by the last case at high pressure level, 300 kPa, and high temperature level, 75 °C. The mass-transport overpotential in the cathode electrode is significantly decreased compared to the low temperature level cases for the material without MPL, reaching a maximum of 140 mV at 2.25 A cm$^{-2}$. This further confirms that the high mass-transport overpotential at low temperatures for the material without MPL can be attributed to liquid water blocking the CL as high temperatures alleviate this problem due to increasing the evaporation of product water. The mass-transport overpotentials inside the PTL are 110/180 mV with/without MPL at 1.0 A cm$^{-2}$ and 255/322 mV with/without MPL at 2.0 A cm$^{-2}$. The anodic contributions become noticeable for the cell with MPL but they remain below 50 mV over the range of tested current.

Based on this study it can be concluded, that the MPL significantly improves the water management of the cell, especially inside the electrode, and therefore the mass transport within the cathode CL. This can be attributed to a decreased liquid water saturation of the PTL. This study supports the theory that the MPL on the cathode leads to an increase in water permeation from cathode to anode due to its function as a water barrier. This is reflected in increased anodic mass-transport overpotential, decreased ohmic losses and decreased cathode mass-transport losses, especially in the cathode electrode. It also improves the ohmic resistance which can be attributed to an improved contact resistance between transport layer and CL.

### 6.3 Future Work and Recommendation

This work inspired several ongoing research projects based on the here presented methods. The results of the designed experiments presented in Chapter 4 are applied to
characterize novel, ultra-thin catalyst materials in cooperation with Dr. Marc Secanell, University of Alberta, established through the CARPE network. Our methods allow reducing the testing time and required number of samples while enabling a direct comparison to commercially available materials. It is recommended to employ designed experiments when characterizing and validating new materials and hardware in order to avoid the masking of effects and falsifying results due to systematic errors. These methods will also increase the testing efficiency and hence allowing for more cost effective material development.

This work employs 2-level factorial designs that feature each factor at two levels. This was chosen in order to include a large number of factors in order to determine the sparsity of effects while still maintaining efficient test numbers. As the fit of the model equations within the design space chosen for this thesis work was sufficient, the 2-level design was applied. Future efforts employing DoE to map PEMFC performance, especially in the mass-transport region of the polarization curve, should consider reducing the number of tested factors to those factors determined relevant in this work and increasing the levels for each individual factor in order to capture curvature effects of the responses in more detail. This will require the transition to a multi-level design, for an example a response surface design as reported here. These designs work with additional star and center points in order to improve the accuracy of the model equations. This may also be relevant when studying the kinetic regions or the transitions between kinetic and ohmic region of the polarization curve. While the model equations based on multi-level designs may have a better fit over the design space, they do require more test points increasing cost and test duration.
Ongoing and future works that were initiated as a result of this research include the voltage loss breakdown with reference electrodes as presented here for a segmented cell in order to create a comprehensive, spatially resolved performance and loss mapping as a function of inlet distance. Current plans include the elimination of geometric effects by applying same sized electrodes for RE and CE.

Current efforts also include the use of the improved reference electrode system in combination with Alternate Current (AC) Impedance measurements. Initial results were submitted for publication here.\textsuperscript{46}

In order to improve the voltage loss breakdown, it is recommended to use the here presented method to quantify and analyze the anodic overpotential during non-favorable conditions, like drying and flooding. In order to distinguish between mass-transport losses in the anode CL and anode GDL/MPL an analysis employing a mixture of helium and hydrogen could be used to derive a mathematical approach to separate these losses based on polarization data via reference electrode system. The VLB tool could also be coupled with additional in-situ diagnostic measurements featuring different operating strategies and cell configurations to further the study of the role of the anode PTL regarding the product water removal. The structure of the Matlab tool will allow for straightforward implementation and extension of the model.
Bibliography

7. J. Larminie and A. Dicks.,


Appendices

Appendix A

A.1 Experimental

This section features further information and drawing regarding the experimental set-up and diagnostic tools.

Figure A.1: Humidity and temperature sensor mount with heating capability
Figure A.2: Drawing for humidity and temperature sensor mount
Sensor Performance

Relative Humidity

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Condition</th>
<th>min</th>
<th>typ</th>
<th>max</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resolution1</td>
<td>0.04</td>
<td>0.05</td>
<td>0.03</td>
<td>%RH</td>
<td></td>
</tr>
<tr>
<td>Accuracy2</td>
<td>SHT71 typ</td>
<td>±3.0</td>
<td>%RH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Accuracy2</td>
<td>SHT71 max</td>
<td>see Figure 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Accuracy2</td>
<td>SHT73 typ</td>
<td>±1.8</td>
<td>%RH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Accuracy2</td>
<td>SHT73 max</td>
<td>see Figure 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Repeatability</td>
<td>max</td>
<td>±0.1</td>
<td>%RH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hygrosopic</td>
<td>max</td>
<td>±1</td>
<td>%RH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nonlinearity</td>
<td>max</td>
<td>±3</td>
<td>%RH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Response time1</td>
<td>max</td>
<td>8</td>
<td>s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Operating Range</td>
<td>max</td>
<td>0</td>
<td>100</td>
<td>%RH</td>
<td></td>
</tr>
<tr>
<td>Long term drift1</td>
<td>max</td>
<td>&lt;0.5</td>
<td>%RH/°C</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Temperature

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Condition</th>
<th>min</th>
<th>typ</th>
<th>max</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resolution1</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td>°C</td>
<td></td>
</tr>
<tr>
<td>Accuracy1</td>
<td>SHT71 typ</td>
<td>±6.4</td>
<td>°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Accuracy1</td>
<td>SHT73 max</td>
<td>see Figure 3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Repeatability</td>
<td>max</td>
<td>±6.3</td>
<td>°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Operating Range</td>
<td>max</td>
<td>-40</td>
<td>125.8</td>
<td>°F</td>
<td></td>
</tr>
<tr>
<td>Response time2</td>
<td>max</td>
<td>5</td>
<td>s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Long term drift1</td>
<td>max</td>
<td>&lt;0.04</td>
<td>°C/°C</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![Graph 1: Relative Humidity vs. RH]

Figure 2: Maximal RH-tolerance at 25°C per sensor type.

![Graph 2: Temperature vs. Temperature]

Figure 3: Maximal T-tolerance per sensor type.

Electrical and General Items

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Condition</th>
<th>min</th>
<th>typ</th>
<th>max</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source Voltage</td>
<td>2.4</td>
<td>3.3</td>
<td>5.5</td>
<td>V</td>
<td></td>
</tr>
<tr>
<td>Power Consumption5</td>
<td>Sleep</td>
<td>2</td>
<td>μW</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Measuring</td>
<td>3</td>
<td>mW</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>90</td>
<td>μW</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Communication</td>
<td>Digital 2 wire interface, see Communication</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Storage</td>
<td>10 – 50°C (0 – 80°C peak), 20 – 60% RH</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Packaging Information

<table>
<thead>
<tr>
<th>Sensor Type</th>
<th>Packaging</th>
<th>Quantity</th>
<th>Order Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>SHT71</td>
<td>Tape Strips</td>
<td>50</td>
<td>1-100952-04</td>
</tr>
<tr>
<td>SHT73</td>
<td>Tape Strips</td>
<td>50</td>
<td>1-100971-04</td>
</tr>
</tbody>
</table>

This datasheet is subject to change and may be amended without prior notice.

---

1 The default measurement resolution is ±1.5% for temperature and ±3% for humidity. It can be reduced to ±0.8% by command to status register.
2 Accuracies are labeled at Calibing Quality Control at 25°C (77°F) and 3.3V.
3 Values exhibit hygroscopic and are only applicable to non-condensing environments.
4 Time for reaching 63% of a step function, valid at 25°C and 1% RH, follow.
5 Values may be higher in environments with low contents of volatile organic compounds. See Section 1.2 of User Guide.
6 Values for VDD=3.3V at 25°C, average value at one 125Hz measurement per second.
7 Response time depends on load capacity of and thermal resistance to sensor substrate.

www.sensirion.com

Version 5 – December 2011

Z12

Figure A.3: Sensirion SHT75 datasheet, Source: ww.sensirion.com
## Technical Data

**Performance**

<table>
<thead>
<tr>
<th>Variable</th>
<th>Range</th>
<th>Accuracy (including non-linearity, hysteresis, and repeatability)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative Humidity</td>
<td>0...100%RH</td>
<td>±1.7% (30...100%RH) at 20°C (2...77°F)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>±1.0% (20...50%RH) at 0...+40°C (32...104°F)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>±0.5% (0...95%RH) at -20...+50°C (4...122°F)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>±0.5% RH (0...95%RH) at -20...+50°C (4...122°F)</td>
</tr>
</tbody>
</table>

(Defined as ±2 standard deviation limits. Small variations possible; see also calibration certificate.)

Response time (90%) at 25°C (77°F): 4±17 seconds with grid filter

**Temperature**

<table>
<thead>
<tr>
<th>Variable</th>
<th>Range</th>
<th>Accuracy at 20°C (68°F)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>±0.2°C (±0.36°F)</td>
</tr>
</tbody>
</table>

Accuracy over temperature range (measurement range exceeds on model)

---

**Inputs and Outputs**

- **Operating voltage**: 10...30 VDC, 24 VAC, ±5%
- **with optional power supply module**: 100...240 VAC, 50/60 Hz
- **Power consumption at 20°C**: U_{in} 24 VDC; U_{out} 5 V...10 V; 20 mA
- **during chemical range**: max. 110 mA
- **during probe heating (HMT337)**: max. 120 mA

**Analog outputs** (2 standard, 4 optional)

- **current output**: 0...20 mA, 4...20 mA
- **voltage output**: 0...5 V, 0...10 V

**Temperature dependence of the analog outputs**: ±0.03% of full scale

** Accuracy of analog outputs at 25°C**: ±0.05% full scale

- **Stranded wires recommended**

**Digital outputs**: RS232, RS485 (optional)

**Protocols**: ASCII commands, MODBUS RTU

**Service connection**: RS232, USB

**Relay outputs (optional)**: 0.3 A, 220 VAC

**Ethernet interface (optional)**

- **Supported standards**: 10BASE-T, 100BASE-TX
- **Connector**: RJ45
- **IP address assignment**: DHCP (automatically), static

**WLAN interface (optional)**

- **Supported standards**: 802.11b
- **Antenna connector type**: RP-SMA
- **IP address assignment**: DHCP (automatically), static

**Protocols**: Telnet, MODBUS/TCP

**Security**: WEP04/128, WPA2/802.11i

**Authentication / Encryption (WLAN)**

- **Open / no encryption**
- **Open / WEP**
- **WPA PreShared key / TKIP**
- **WPA PreShared key / CCMP (a.k.a. WPA2)**

**Optional data logger with real-time clock**

- **Logged parameters**: max. four with min/max values
- **Logging interval**: 10 sec. (preset)
- **Max. logging period**: 4 years, 5 months
- **Battery lifetime**: 13.7 million points per parameter
- **Display**: LCD with backlight, graphical trend display of any parameter

**Menu languages**: English, Chinese, Russian, German, Japanese, Russian, Spanish, Swedish

---

Figure A.4: Vaisala HMT 337 datasheet, source: vaisala.com
A.2 Materials

Table A.1: Properties of GDL material used for the ex-situ pressure drop experiments

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness / µm</th>
<th>Areal weight / g m²</th>
<th>PTFE loading / wt.%</th>
<th>MPL / yes or no</th>
</tr>
</thead>
<tbody>
<tr>
<td>SGL 24 BC</td>
<td>235 ± 20</td>
<td>100 ± 10</td>
<td>5</td>
<td>yes</td>
</tr>
<tr>
<td>SGL 24 BA</td>
<td>190 ± 30</td>
<td>54 ± 10</td>
<td>5</td>
<td>no</td>
</tr>
<tr>
<td>SGL 24 EC</td>
<td>235 ± 30</td>
<td>120 ± 10</td>
<td>30</td>
<td>yes</td>
</tr>
<tr>
<td>SGL 24 EA</td>
<td>190 ± 30</td>
<td>75 ± 12</td>
<td>30</td>
<td>no</td>
</tr>
</tbody>
</table>
A.3 Diagnostic Tools

Figure A.6: Drift of the measured potentials over time at 75 °C and 100 % RH at OCV
Figure A.7: Signal of the measured potentials over time at 75 °C and 100 % RH at 60 A
Figure A.8: Potentials stability of the RHE versus cathode over time at constant load of 20 A for varying reference section flow rates. Standard deviations are shown in error bars.
Appendix B

B.1 Response Selection

The lasting imprint from the flow field on the GDL can in some cases be quantified using profilometry. Figure B.1(a) shows the profiles for beginning and end-of-life 24 EA GDL. The trace for BoL is highly irregular and shows no discernable repeating patterns. After compression, repetitive features with a peak-to-peak distance that roughly corresponds to the flowfield dimensions, 1.5 mm channel + 0.8 mm land width, are observed with a height of approximately 30 µm. For 24 BA (Figure B.1(b)) the imprint is much clearer near the edge but the profilometry trace is much more irregular than that of the 24 EA material. Peak-to-peak distance is, however,
regular at 2.3 mm. Closer to the center of the GDL, the profilometry trace shows no discernable
features.

Figure B.2 and Figure B.3 display the pressure drop as a function of the anode / cathode flow
during a cycling experiment where the clamping pressure was cycled between 75 psi and 120 psi
multiple times. The hysteresis remains constant and there is a slight increase in pressure drop
when the material is compressed to 120 psi for a second time (cycle 3), indicating an increase in
channel intrusion due to GDL fibers protruding. When the sample is relaxed to 75 psi for the
third time (cycle 4) a difference to the first relaxed measurements (cycle 2) is observed. This
difference is consistent with the delta between cycle 1 and cycle 3, resulting in an almost constant
hysteresis. This behavior is consistent with the measurements on the anode side for the same
experiment shown in Figure B.3. Notably, the second increase to 120 psi (cycle 3) here leads to
a more consistent trend in the pressure drop curve, while some non-linear behavior can be
observed for cycle 1.

Figure B.2: Hysteresis after the clamping pressure was cycled from 75 psi to 120 psi and back twice on the
cathode side.
Figure B.3: Hysteresis after the clamping pressure was cycled from 75 psi to 120 psi and back twice on the anode side.

B.2 Split-plot Designs

ANOVA: Whole plot of Split-plot design 1
Response 1 Voltage @ 1.0 A/cm²
These Rows Were Ignored for this Analysis.
12, 39, 13, 2

ANOVA for selected factorial model

Error term includes A, D, AB, AC, AD, AE, AF, BD, BE, CD, CE, DE, DF, EF, ABD, ABE, ACE, ACF, ADE, ADF, AEF, BCD, BCE, BCF, BDE, BDF, BEF, CDE, CDF, CEF, DEF, Lack Of Fit

Terms set aside are G AG BG CG DG EG FG ACG AEG AFG BCG BDG BEG BFG CDG CEG CFG DEG DFG EFG

SS: 0.482122 df: 20

Analysis of variance table [Partial sum of squares - Type III]

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of squares</th>
<th>df</th>
<th>Mean Square</th>
<th>F</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>0.44</td>
<td>7</td>
<td>0.062</td>
<td>163.63</td>
<td>&lt; 0.0001 significant</td>
</tr>
<tr>
<td>B-Stoich. Cathode</td>
<td>0.093</td>
<td>1</td>
<td>0.093</td>
<td>245.92</td>
<td>&lt; 0.0001</td>
</tr>
</tbody>
</table>
C-Temperature & 0.15 & 1 & 0.15 & 404.2 & < 0.0001  
E-Cathode RH & 0.016 & 1 & 0.016 & 43.11 & < 0.0001  
F-Pressure & 0.074 & 1 & 0.074 & 195.05 & < 0.0001  
BC & 0.039 & 1 & 0.039 & 101.76 & < 0.0001  
BF & 7.22E-03 & 1 & 7.22E-03 & 18.98 & 0.0001  
CF & 0.021 & 1 & 0.021 & 54.98 & < 0.0001  
Residual & 0.012 & 32 & 3.80E-04 &  
Cor Total & 0.45 & 39 &  

The Model F-value of 163.63 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case B, C, E, F, BC, BF, CF are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

| Std. Dev. | 0.019 | R-Squared | 0.9728 |
| Mean | 0.49 | Adj R-Squared | 0.9669 |
| C.V. % | 3.95 | Pred R-Squared | 0.9027 |
| PRESS | 0.044 | Adeq Precision | 38.133 |

The "Pred R-Squared" of 0.9027 is in reasonable agreement with the "Adj R-Squared" of 0.9669.

Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 38.133 indicates an adequate signal. This model can be used to navigate the design space.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Standard Factor</th>
<th>Estimate</th>
<th>95% CI df</th>
<th>Error</th>
<th>95% CI Low</th>
<th>95% CI High</th>
<th>VIF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td></td>
<td>0.49</td>
<td>1</td>
<td>2.60E-03</td>
<td>0.48</td>
<td>0.49</td>
<td></td>
</tr>
<tr>
<td>B-Stoich. Cathode</td>
<td>0.04</td>
<td>1</td>
<td>2.57E-03</td>
<td>0.035</td>
<td>0.046</td>
<td>1.04</td>
<td></td>
</tr>
<tr>
<td>C-Temperature</td>
<td>0.052</td>
<td>1</td>
<td>2.57E-03</td>
<td>0.046</td>
<td>0.057</td>
<td>1.04</td>
<td></td>
</tr>
<tr>
<td>E-Cathode RH</td>
<td>0.017</td>
<td>1</td>
<td>2.57E-03</td>
<td>0.012</td>
<td>0.022</td>
<td>1.04</td>
<td></td>
</tr>
<tr>
<td>F-Pressure</td>
<td>0.036</td>
<td>1</td>
<td>2.57E-03</td>
<td>0.031</td>
<td>0.041</td>
<td>1.04</td>
<td></td>
</tr>
<tr>
<td>BC</td>
<td>-0.026</td>
<td>1</td>
<td>2.60E-03</td>
<td>-0.031</td>
<td>-0.021</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>BF</td>
<td>0.011</td>
<td>1</td>
<td>2.60E-03</td>
<td>6.02E-03</td>
<td>0.017</td>
<td>1.02</td>
<td></td>
</tr>
<tr>
<td>CF</td>
<td>0.019</td>
<td>1</td>
<td>2.60E-03</td>
<td>0.014</td>
<td>0.025</td>
<td>1.06</td>
<td></td>
</tr>
</tbody>
</table>

Final Equation in Terms of Coded Factors:
Voltage @ 1.0 A/cm^2 =
0.49
0.04 * B
0.052 * C
0.017 * E
0.036 * F
-0.026 * B * C
0.011 * B * F
0.019 * C * F

Final Equation in Terms of Actual Factors:

Voltage @ 1.0 A/cm^2 =
9.63E-03
0.12904 * Stoich. Cathode
4.89E-03 * Temperature
1.00E-03 * Cathode RH
-3.95E-04 * Pressure
-1.77E-03 * Stoich. Cathode * Temperature
1.11E-04 * Stoich. Cathode * Pressure
9.30E-06 * Temperature * Pressure

ANOVA: Whole plot of Split-plot design 1
Response 2 Voltage @ 1.4 A/cm^2
These Rows Were Ignored for this Analysis.
12, 39, 13, 2

ANOVA for selected factorial model

Error term includes A, D, E, AB, AC, AD, AE, AF, BD, BE, BF, CD, CE, DE, DF, EF,
ABC, ABD, ABE, ABF, ACD, ACE, ACF, ADE, ADF, AEF, BCD, BCE, BCF, BDE, BDF, CDE, CEF, DEF

Terms set aside are G AG BG CG DG EG FG ABG ACG ADG AEG AFG BCG BDG BEG BFG CDG
CFG DFG EFG
SS: 0.667689 df: 20

Analysis of variance table [Partial sum of squares - Type III]

<table>
<thead>
<tr>
<th>Sum of squares</th>
<th>Mean F</th>
<th>p-value</th>
</tr>
</thead>
</table>

161
<table>
<thead>
<tr>
<th>Source</th>
<th>Squares</th>
<th>df</th>
<th>Square</th>
<th>Value</th>
<th>Prob &gt; F</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>0.7</td>
<td>5</td>
<td>0.14</td>
<td>46.45</td>
<td>&lt; 0.0001</td>
<td>significant</td>
</tr>
<tr>
<td>B-Stoich Cathode</td>
<td>0.18</td>
<td>1</td>
<td>0.18</td>
<td>57.9</td>
<td>&lt; 0.0001</td>
<td></td>
</tr>
<tr>
<td>C-Temperature</td>
<td>0.22</td>
<td>1</td>
<td>0.22</td>
<td>71.5</td>
<td>&lt; 0.0001</td>
<td></td>
</tr>
<tr>
<td>F-Pressure</td>
<td>0.13</td>
<td>1</td>
<td>0.13</td>
<td>43.38</td>
<td>&lt; 0.0001</td>
<td></td>
</tr>
<tr>
<td>BC</td>
<td>0.062</td>
<td>1</td>
<td>0.062</td>
<td>20.45</td>
<td>&lt; 0.0001</td>
<td></td>
</tr>
<tr>
<td>CF</td>
<td>0.077</td>
<td>1</td>
<td>0.077</td>
<td>25.37</td>
<td>&lt; 0.0001</td>
<td></td>
</tr>
<tr>
<td>Residual</td>
<td>0.1</td>
<td>34</td>
<td>3.03E-03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cor Total</td>
<td>0.81</td>
<td>39</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The Model F-value of 46.45 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case B, C, F, BC, CF are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

<table>
<thead>
<tr>
<th>Std. Dev.</th>
<th>0.055</th>
<th>R-Squared</th>
<th>0.8723</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>0.36</td>
<td>Adj R-Squared</td>
<td>0.8535</td>
</tr>
<tr>
<td>C.V. %</td>
<td>15.29</td>
<td>Pred R-Squared</td>
<td>0.6037</td>
</tr>
<tr>
<td>PRESS</td>
<td>0.32</td>
<td>Adeq Precision</td>
<td>15.977</td>
</tr>
</tbody>
</table>

Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 15.977 indicates an adequate signal. This model can be used to navigate the design space.

<table>
<thead>
<tr>
<th>Coefficient Factor</th>
<th>Standard Estimate</th>
<th>95% CI df</th>
<th>Error</th>
<th>95% CI</th>
<th>95% CI</th>
<th>VIF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>0.35</td>
<td>1</td>
<td>7.28E-03</td>
<td>0.34</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td>B-Stoich Cathode</td>
<td>0.055</td>
<td>1</td>
<td>7.23E-03</td>
<td>0.04</td>
<td>0.07</td>
<td>1.03</td>
</tr>
<tr>
<td>C-Temperature</td>
<td>0.061</td>
<td>1</td>
<td>7.23E-03</td>
<td>0.046</td>
<td>0.076</td>
<td>1.03</td>
</tr>
<tr>
<td>F-Pressure</td>
<td>0.048</td>
<td>1</td>
<td>7.23E-03</td>
<td>0.033</td>
<td>0.062</td>
<td>1.03</td>
</tr>
<tr>
<td>BC</td>
<td>-0.033</td>
<td>1</td>
<td>7.28E-03</td>
<td>-0.048</td>
<td>-0.018</td>
<td>1.08</td>
</tr>
<tr>
<td>CF</td>
<td>0.037</td>
<td>1</td>
<td>7.28E-03</td>
<td>0.022</td>
<td>0.051</td>
<td>1.02</td>
</tr>
</tbody>
</table>

Final Equation in Terms of Coded Factors:

Voltage @ 1.4 A/cm^2 = 0.35
Final Equation in Terms of Actual Factors:

\[
\text{Voltage @ 1.4 A/cm}^2 = -0.1567 + 0.19971 \times \text{Stoich Cathode} + 4.51 \times 10^{-3} \times \text{Temperature} - 5.94 \times 10^{-4} \times \text{Pressure} - 2.32 \times 10^{-3} \times \text{Stoich Cathode} \times \text{Temperature} + 1.95 \times 10^{-5} \times \text{Temperature} \times \text{Pressure}
\]

ANOVA: Whole plot of Split-plot design 1

Response 3 Voltage @ 1.6 A/cm^2
These Rows Were Ignored for this Analysis.
12, 39, 13, 2

ANOVA for selected factorial model

Error term includes A, D, E, AB, AC, AD, AE, AF, BC, BD, BE, BF, CD, CE, DE, DF, EF, ABC, ABE, ABF, ACD, ACE, ACF, ADE, ADF, BCD, BCE, BCF, BDE, BDF, BEF, CDE, CDF, CEF, DEF

Terms set aside are G AG BG CG DG EG FG ABG AEG AFG BCG BDG BEG BFG CDG CEG CFG DEG DFG EFG

SS: 0.619352 df: 20

Analysis of variance table [Partial sum of squares - Type III]

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>Mean Square</th>
<th>F Value</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>0.82</td>
<td>0.21</td>
<td>32.27</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>B-Stoich Cathode</td>
<td>0.23</td>
<td>0.23</td>
<td>35.94</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>C-Temperature</td>
<td>0.093</td>
<td>0.093</td>
<td>14.6</td>
<td>0.0005</td>
</tr>
<tr>
<td>F-Pressure</td>
<td>0.28</td>
<td>0.28</td>
<td>43.38</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>CF</td>
<td>0.16</td>
<td>0.16</td>
<td>25.63</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>Residual</td>
<td>0.22</td>
<td>6.35E-03</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Cor Total 1.04 39

The Model F-value of 32.27 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case B, C, F, CF are significant model terms.

Std. Dev. 0.08 R-Squared 0.7867
Mean 0.29 Adj R-Squared 0.7623
C.V. % 27.52 Pred R-Squared 0.3584
PRESS 0.67 Adeq Precision 11.345

Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 11.345 indicates an adequate signal. This model can be used to navigate the design space.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Standard Error</th>
<th>95% CI Low</th>
<th>95% CI High</th>
<th>VIF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>0.29</td>
<td>0.27</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td>B-Stoich Cathode</td>
<td>0.063</td>
<td>0.041</td>
<td>0.084</td>
<td>1.03</td>
</tr>
<tr>
<td>C-Temperature</td>
<td>0.04</td>
<td>0.019</td>
<td>0.061</td>
<td>1.03</td>
</tr>
<tr>
<td>F-Pressure</td>
<td>0.069</td>
<td>0.048</td>
<td>0.09</td>
<td>1.03</td>
</tr>
<tr>
<td>CF</td>
<td>0.053</td>
<td>0.032</td>
<td>0.074</td>
<td>1.08</td>
</tr>
</tbody>
</table>

Final Equation in Terms of Coded Factors:

Voltage @ 1.6 A/cm^2 =
0.29
0.063  * B
0.04  * C
0.069  * F
0.053  * C * F

Final Equation in Terms of Actual Factors:

Voltage @ 1.6 A/cm^2 =
0.19933
0.076116  * Stoich Cathode
-4.04E-03  * Temperature
-9.84E-04  * Pressure
3.00E-05  * Temperature * Pressure

**ANOVA: Sub- lot of Split-plot design 1**

Voltage @ 1.0

Response 1  A/cm^2

These Rows Were Ignored for this Analysis.
12, 39, 13, 2

ANOVA for selected factorial model

Error term includes AG, BG, DG, EG, FG, ABC, ABG, ACD, ACG, AFG, BCG, BEG,
BFG, CEG, CFG, DEG, DFG, EFG, Lack Of Fit

Terms set aside are A B C D E F AB AC AD AE AF BC BD BE BF CD CE CF DE DF EF
ABD ABE ACE ACF ADE ADF AEF BCD BCE BCF BDE BDF BEF CDE CDF CEF DEF

SS:  0.480427  df:  38

Analysis of variance table [Partial sum of squares - Type III]

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>df</th>
<th>Mean Square</th>
<th>F</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>0.34</td>
<td>2</td>
<td>0.17</td>
<td>31.01</td>
<td>&lt; 0.0001 significant</td>
</tr>
<tr>
<td>G-Type of GDL</td>
<td>0.21</td>
<td>1</td>
<td>0.21</td>
<td>37.51</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>CG</td>
<td>0.12</td>
<td>1</td>
<td>0.12</td>
<td>21.94</td>
<td>0.0002</td>
</tr>
<tr>
<td>Residual</td>
<td>0.11</td>
<td>19</td>
<td>5.55E-03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cor Total</td>
<td>0.45</td>
<td>21</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The Model F-value of 31.01 implies the model is significant. There is only
a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.
In this case G, CG are significant model terms.
Values greater than 0.1000 indicate the model terms are not significant.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Standard Factor</th>
<th>95% CI</th>
<th>95% CI</th>
<th>95% CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>0.49</td>
<td>1</td>
<td>0.011</td>
<td>0.47</td>
</tr>
<tr>
<td>G-Type of GDL</td>
<td>-0.06</td>
<td>1</td>
<td>9.84E-03</td>
<td>-0.081</td>
</tr>
<tr>
<td>CG</td>
<td>0.047</td>
<td>1</td>
<td>0.01</td>
<td>0.026</td>
</tr>
</tbody>
</table>

Final Equation in Terms of Coded Factors:

\[ \text{Voltage @ 1.0 A/cm}^2 = 0.49 - 0.06 \cdot G + 0.047 \cdot C \cdot G \]

Final Equation in Terms of Actual Factors:

Type of GDL: MPL

\[ \text{Voltage @ 1.0 A/cm}^2 = 0.71473 \]

Type of GDL: No MPL

\[ \text{Voltage @ 1.0 A/cm}^2 = 0.26752 \]

ANOVA: Sub- lot of Split-plot design 1

<table>
<thead>
<tr>
<th>Response</th>
<th>2 A/cm^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voltage @ 1.4 A/cm^2</td>
<td></td>
</tr>
</tbody>
</table>

These Rows Were Ignored for this Analysis.

12, 39, 13, 2
ANOVA for selected factorial model

Error term includes AG, EG, ABG, ACG, ADG, AEG, AFG, BDG, BEG, BFG, CDG, CFG, DFG, EFG

Terms set aside are A B C D E F FAB AC AD AE AF BD BE BF CD CE CF DE DF DG EF ABC ABD ABE ABF ACD ACE ACF ADE ADF AEG AFG BCD BCE BCF BDE BDF CDE CDF CEF DEF

SS: 0.89446 df: 40

Analysis of variance table [Partial sum of squares - Type III]

<table>
<thead>
<tr>
<th>Source</th>
<th>Squares</th>
<th>df</th>
<th>Square</th>
<th>Value</th>
<th>F</th>
<th>p-value</th>
<th>Prob &gt; F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>0.56</td>
<td>5</td>
<td>0.11</td>
<td>80.57</td>
<td>&lt; 0.0001</td>
<td>significant</td>
<td></td>
</tr>
<tr>
<td>G-Type of GDL</td>
<td>0.18</td>
<td>1</td>
<td>0.18</td>
<td>131.82</td>
<td>&lt; 0.0001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BG</td>
<td>0.034</td>
<td>1</td>
<td>0.034</td>
<td>24.49</td>
<td>0.0002</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CG</td>
<td>0.27</td>
<td>1</td>
<td>0.27</td>
<td>196.44</td>
<td>&lt; 0.0001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FG</td>
<td>0.068</td>
<td>1</td>
<td>0.068</td>
<td>48.58</td>
<td>&lt; 0.0001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BCG</td>
<td>0.054</td>
<td>1</td>
<td>0.054</td>
<td>38.51</td>
<td>&lt; 0.0001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Residual</td>
<td>0.02</td>
<td>14</td>
<td>1.39E-03</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cor Total</td>
<td>0.58</td>
<td>19</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The Model F-value of 80.57 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Std. Dev. 0.037 R-Squared 0.9664
Mean 0.36 Adj R-Squared 0.9544
C.V. % 10.37 Pred R-Squared 0.3792
PRESS 0.36 Adeq Precision 18.036

Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 18.036 indicates an adequate signal. This model can be used to navigate the design space.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Standard Error</th>
<th>95% CI Low</th>
<th>95% CI High</th>
<th>VIF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor Estimate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intercept</td>
<td>0.35</td>
<td>5.28E-03</td>
<td>0.34</td>
<td>0.36</td>
</tr>
<tr>
<td>G-Type of GDL</td>
<td>-0.058</td>
<td>5.04E-03</td>
<td>-0.069</td>
<td>-0.047</td>
</tr>
<tr>
<td>BG</td>
<td>0.026</td>
<td>5.35E-03</td>
<td>0.015</td>
<td>0.038</td>
</tr>
<tr>
<td>CG</td>
<td>0.075</td>
<td>5.35E-03</td>
<td>0.063</td>
<td>0.086</td>
</tr>
<tr>
<td>FG</td>
<td>-0.037</td>
<td>5.35E-03</td>
<td>-0.049</td>
<td>-0.026</td>
</tr>
<tr>
<td>BCG</td>
<td>-0.031</td>
<td>5.04E-03</td>
<td>-0.042</td>
<td>-0.02</td>
</tr>
</tbody>
</table>
Final Equation in Terms of Coded Factors:

Voltage @ 1.4 A/cm² =

0.35
-0.058 * G
0.026 * B * G
0.075 * C * G
-0.037 * F * G
-0.031 * B * C * G

Final Equation in Terms of Actual Factors:

Not available, because this model is not hierarchical.
Only hierarchical models are scale independent and can be translated into actual units.

ANOVA: Sub-lot of Split-plot design 1

These Rows Were Ignored for this Analysis.
12, 39, 13, 2

ANOVA for selected factorial model

Error term includes AG, DG, EG, ABG, AEG, AFG, BDG, BEG, BFG, CDG, CEG, CFG, DEG, DFG, EFG

Terms set aside are A B C D E F AB AC AD AE AF BC BD BE BF CD CE CF DE DF EF ABC ABE ABF ACD ACE ACF ADE ADF BCD BCE BCF BDF BEF CDE CDF CEF DEF

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>df</th>
<th>Mean Square</th>
<th>F Value</th>
<th>Prob &gt; F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>0.49</td>
<td>5</td>
<td>0.099</td>
<td>66.26</td>
<td>&lt; 0.0001 significant</td>
</tr>
<tr>
<td>G-Type of GDL</td>
<td>0.1</td>
<td>1</td>
<td>0.1</td>
<td>70.54</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>BG</td>
<td>3.67E-03</td>
<td>1</td>
<td>3.67E-03</td>
<td>2.47</td>
<td>0.1371</td>
</tr>
<tr>
<td>CG</td>
<td>0.27</td>
<td>1</td>
<td>0.27</td>
<td>180.51</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>FG</td>
<td>0.075</td>
<td>1</td>
<td>0.075</td>
<td>50.45</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>BCG</td>
<td>0.059</td>
<td>1</td>
<td>0.059</td>
<td>39.43</td>
<td>&lt; 0.0001</td>
</tr>
</tbody>
</table>
Residual 0.022 15 1.49E-03
Cor Total 0.52 20

The Model F-value of 66.26 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Std. Dev. 0.039 R-Squared 0.9567
Mean 0.29 Adj R-Squared 0.9422
C.V. % 13.32 Pred R-Squared 0.272
PRESS 0.38 Adeq Precision 16.361

Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 16.361 indicates an adequate signal. This model can be used to navigate the design space.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Standard Estimate</th>
<th>95% CI df</th>
<th>Error</th>
<th>95% CI Low</th>
<th>95% CI High</th>
<th>VIF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>0.28</td>
<td>1</td>
<td>5.62E-03</td>
<td>0.27</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>G-Type of GDL</td>
<td>-0.043</td>
<td>1</td>
<td>5.16E-03</td>
<td>-0.054</td>
<td>-0.032</td>
<td>1.21</td>
</tr>
<tr>
<td>BG</td>
<td>8.58E-03</td>
<td>1</td>
<td>5.46E-03</td>
<td>-3.06E-03</td>
<td>0.02</td>
<td>1.39</td>
</tr>
<tr>
<td>CG</td>
<td>0.073</td>
<td>1</td>
<td>5.46E-03</td>
<td>0.062</td>
<td>0.085</td>
<td>1.39</td>
</tr>
<tr>
<td>FG</td>
<td>-0.039</td>
<td>1</td>
<td>5.46E-03</td>
<td>-0.05</td>
<td>-0.027</td>
<td>1.24</td>
</tr>
<tr>
<td>BCG</td>
<td>-0.032</td>
<td>1</td>
<td>5.16E-03</td>
<td>-0.043</td>
<td>-0.021</td>
<td>1.39</td>
</tr>
</tbody>
</table>

Final Equation in Terms of Coded Factors:

Voltage @ 1.6 A/cm^2  =

0.28
-0.043 * G
8.58E-03 * B * G
0.073 * C * G
-0.039 * F * G
-0.032 * B * C * G

Final Equation in Terms of Actual Factors:

Not available, because this model is not hierarchical.
Only hierarchical models are scale independent and can be translated into actual units.
ANOVA: Final Split-plot 1
Response 1 Voltage @ 1.0 A/cm^2
These Rows Were Ignored for this Analysis.
12, 39, 13, 2

ANOVA for selected factorial model
Analysis of variance table [Partial sum of squares - Type III]

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>df</th>
<th>Mean Square</th>
<th>Mean</th>
<th>F</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>0.79</td>
<td>8</td>
<td>0.099</td>
<td>37.24</td>
<td>&lt; 0.0001</td>
<td>significant</td>
</tr>
<tr>
<td>B-Cathode</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stoichiometry</td>
<td>0.091</td>
<td>1</td>
<td>0.091</td>
<td>34.32</td>
<td>&lt; 0.0001</td>
<td></td>
</tr>
<tr>
<td>C-Temperature</td>
<td>0.15</td>
<td>1</td>
<td>0.15</td>
<td>56.93</td>
<td>&lt; 0.0001</td>
<td></td>
</tr>
<tr>
<td>E-Cathode RH</td>
<td>0.018</td>
<td>1</td>
<td>0.018</td>
<td>6.91</td>
<td>0.0113</td>
<td></td>
</tr>
<tr>
<td>F-Pressure</td>
<td>0.079</td>
<td>1</td>
<td>0.079</td>
<td>29.72</td>
<td>&lt; 0.0001</td>
<td></td>
</tr>
<tr>
<td>G-Type of GDL</td>
<td>0.22</td>
<td>1</td>
<td>0.22</td>
<td>81.27</td>
<td>&lt; 0.0001</td>
<td></td>
</tr>
<tr>
<td>BC</td>
<td>0.035</td>
<td>1</td>
<td>0.035</td>
<td>13.31</td>
<td>0.0006</td>
<td></td>
</tr>
<tr>
<td>CF</td>
<td>0.018</td>
<td>1</td>
<td>0.018</td>
<td>6.85</td>
<td>0.0117</td>
<td></td>
</tr>
<tr>
<td>CG</td>
<td>0.16</td>
<td>1</td>
<td>0.16</td>
<td>58.87</td>
<td>&lt; 0.0001</td>
<td></td>
</tr>
<tr>
<td>Residual</td>
<td>0.14</td>
<td>51</td>
<td>2.66E-03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cor Total</td>
<td>0.93</td>
<td>59</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The Model F-value of 37.24 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case B, C, E, F, G, BC, CF, CG are significant model terms.

Std. Dev. 0.052 R-Squared 0.8538
Mean 0.49 Adj R-Squared 0.8309
C.V. % 10.47 Pred R-Squared 0.7976
PRESS 0.19 Adeq Precision 21.253

The "Pred R-Squared" of 0.7976 is in reasonable agreement with the "Adj R-Squared" of 0.8309.

Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 21.253 indicates an adequate signal. This model can be used to navigate the design space.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Standard Error</th>
<th>95% CI Low</th>
<th>95% CI High</th>
<th>VIF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>0.49</td>
<td>6.73E-03</td>
<td>0.48</td>
<td>0.5</td>
</tr>
<tr>
<td>B-Cathode</td>
<td>0.039</td>
<td>6.74E-03</td>
<td>0.026</td>
<td>0.053</td>
</tr>
</tbody>
</table>
Stoichiometry

<table>
<thead>
<tr>
<th>Factor</th>
<th>Coefficient</th>
<th>Power of</th>
<th>Coefficient</th>
<th>Power of</th>
<th>Coefficient</th>
<th>Power of</th>
<th>Coefficient</th>
<th>Power of</th>
<th>Coefficient</th>
<th>Power of</th>
<th>Coefficient</th>
<th>Power of</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-Temperature</td>
<td>0.051</td>
<td>1</td>
<td>6.74E-03</td>
<td>0.037</td>
<td>0.064</td>
<td>1.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E-Cathode RH</td>
<td>0.018</td>
<td>1</td>
<td>6.74E-03</td>
<td>4.19E-03</td>
<td>0.031</td>
<td>1.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F-Pressure</td>
<td>0.037</td>
<td>1</td>
<td>6.74E-03</td>
<td>0.023</td>
<td>0.05</td>
<td>1.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G-Type of GDL</td>
<td>-0.06</td>
<td>1</td>
<td>6.68E-03</td>
<td>-0.074</td>
<td>-0.047</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BC</td>
<td>-0.025</td>
<td>1</td>
<td>6.73E-03</td>
<td>-0.038</td>
<td>-0.011</td>
<td>1.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF</td>
<td>0.018</td>
<td>1</td>
<td>6.73E-03</td>
<td>4.10E-03</td>
<td>0.031</td>
<td>1.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CG</td>
<td>0.051</td>
<td>1</td>
<td>6.69E-03</td>
<td>0.038</td>
<td>0.065</td>
<td>1.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Final Equation in Terms of Coded Factors:

Voltage @ 1.0
A/cm^2  =
0.49
0.039  * B
0.051  * C
0.018  * E
0.037  * F
-0.06  * G
-0.025 * B * C
0.018  * C * F
0.051  * C * G

Final Equation in Terms of Actual Factors:

Type of GDL
MPL
Voltage @ 1.0
A/cm^2  =
0.17974
0.16016 * Cathode Stoichiometry
2.17E-03 * Temperature
8.86E-04 * Cathode RH
-2.11E-04 * Pressure
-1.87E-03 * Cathode Stoichiometry * Temperature
1.01E-05 * Temperature * Pressure

Type of GDL
No MPL
Voltage @ 1.0
A/cm^2  =
-0.27787
0.16016  * Cathode Stoichiometry
8.03E-03  * Temperature
8.86E-04  * Cathode RH
-2.11E-04  * Pressure
-1.87E-03  * Cathode Stoichiometry * Temperature
1.01E-05  * Temperature * Pressure

ANOVA: Final Split-plot 1
Response 2  Voltage @ 1.4 A/cm^2
These Rows Were Ignored for this Analysis.
12, 39, 13, 2

ANOVA for selected factorial model
Analysis of variance table [Partial sum of squares - Type III]

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>df</th>
<th>Mean Square</th>
<th>F Value</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>1.35</td>
<td>10</td>
<td>0.14</td>
<td>54.27</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>B-Cathode Stoichiometry</td>
<td>0.18</td>
<td>1</td>
<td>0.18</td>
<td>71.05</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>C-Temperature</td>
<td>0.22</td>
<td>1</td>
<td>0.22</td>
<td>87.8</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>F-Pressure</td>
<td>0.13</td>
<td>1</td>
<td>0.13</td>
<td>53.91</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>G-Type of GDL</td>
<td>0.19</td>
<td>1</td>
<td>0.19</td>
<td>74.45</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>BC</td>
<td>0.065</td>
<td>1</td>
<td>0.065</td>
<td>25.95</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>BG</td>
<td>0.043</td>
<td>1</td>
<td>0.043</td>
<td>17.42</td>
<td>0.0001</td>
</tr>
<tr>
<td>CF</td>
<td>0.08</td>
<td>1</td>
<td>0.08</td>
<td>32.16</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>CG</td>
<td>0.34</td>
<td>1</td>
<td>0.34</td>
<td>135.26</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>FG</td>
<td>0.085</td>
<td>1</td>
<td>0.085</td>
<td>34.06</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>BCG</td>
<td>0.051</td>
<td>1</td>
<td>0.051</td>
<td>20.57</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>Residual</td>
<td>0.12</td>
<td>49</td>
<td>2.49E-03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cor Total</td>
<td>1.48</td>
<td>59</td>
<td>0.9172</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The Model F-value of 54.27 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case B, C, F, G, BC, BG, CF, CG, FG, BCG are significant model terms.

Std. Dev. 0.05  R-Squared 0.9172
Mean 0.36  Adj R-Squared 0.9003
C.V. % 13.87  Pred R-Squared 0.8735
PRESS 0.19  Adeq Precision 25.836

The "Pred R-Squared" of 0.8735 is in reasonable agreement with the "Adj R-Squared" of 0.9003.

Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 25.836 indicates an adequate signal. This model can be used to navigate the design space.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Standard Estimate</th>
<th>95% CI Low</th>
<th>95% CI High</th>
<th>VIF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>0.35</td>
<td>0.34</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td>B-Cathode Stoichiometry</td>
<td>0.055</td>
<td>0.042</td>
<td>0.068</td>
<td>1.02</td>
</tr>
<tr>
<td>C-Temperature</td>
<td>0.061</td>
<td>0.048</td>
<td>0.074</td>
<td>1.02</td>
</tr>
<tr>
<td>F-Pressure</td>
<td>0.048</td>
<td>0.035</td>
<td>0.061</td>
<td>1.02</td>
</tr>
<tr>
<td>G-Type of GDL</td>
<td>-0.056</td>
<td>-0.069</td>
<td>-0.043</td>
<td>1.01</td>
</tr>
<tr>
<td>BC</td>
<td>-0.033</td>
<td>-0.046</td>
<td>-0.02</td>
<td>1.01</td>
</tr>
<tr>
<td>BG</td>
<td>0.027</td>
<td>0.014</td>
<td>0.04</td>
<td>1.02</td>
</tr>
<tr>
<td>CF</td>
<td>0.037</td>
<td>0.024</td>
<td>0.05</td>
<td>1.01</td>
</tr>
<tr>
<td>CG</td>
<td>0.076</td>
<td>0.063</td>
<td>0.089</td>
<td>1.02</td>
</tr>
<tr>
<td>FG</td>
<td>-0.038</td>
<td>-0.051</td>
<td>-0.025</td>
<td>1.02</td>
</tr>
<tr>
<td>BCG</td>
<td>-0.029</td>
<td>-0.042</td>
<td>-0.016</td>
<td>1.01</td>
</tr>
</tbody>
</table>

Final Equation in Terms of Coded Factors:

\[
\text{Voltage @ 1.4 A/cm}^2 =
\]
\[
0.35 + 0.055 \times B + 0.061 \times C + 0.048 \times F - 0.056 \times G - 0.033 \times B \times C + 0.027 \times B \times G + 0.037 \times C \times F + 0.076 \times C \times G - 0.038 \times F \times G - 0.029 \times B \times C \times G
\]

Final Equation in Terms of Actual Factors:
Type of GDL  MPL
Voltage @ 1.4 A/cm^2  =
  0.41005
  0.053198 * Cathode Stoichiometry
  -4.42E-03 * Temperature
  -3.54E-04 * Pressure
  -2.82E-04 * Cathode Stoichiometry * Temperature
  2.11E-05 * Temperature * Pressure

Type of GDL  No MPL
Voltage @ 1.4 A/cm^2  =
  -0.7903
  0.38346 * Cathode Stoichiometry
  0.014319 * Temperature
  -1.11E-03 * Pressure
  -4.77E-03 * Cathode Stoichiometry * Temperature
  2.11E-05 * Temperature * Pressure

ANOVA: Final Split-plot 1
Response  3  Voltage @ 1.6 A/cm^2
These Rows Were Ignored for this Analysis.
  12, 39, 13, 2

  ANOVA for selected factorial model
  Analysis of variance table [Partial sum of squares - Type III]

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>Mean Square</th>
<th>F</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>1.45</td>
<td>0.15</td>
<td>33.63</td>
<td>&lt; 0.0001 significant</td>
</tr>
<tr>
<td>B-Cathode Stoichiometry</td>
<td>0.22</td>
<td>0.22</td>
<td>50.2</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>C-Temperature</td>
<td>0.085</td>
<td>0.085</td>
<td>19.68</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>F-Pressure</td>
<td>0.29</td>
<td>0.29</td>
<td>67.95</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>G-Type of GDL</td>
<td>0.11</td>
<td>0.11</td>
<td>24.97</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>BC</td>
<td>0.041</td>
<td>0.041</td>
<td>9.58</td>
<td>0.0032</td>
</tr>
<tr>
<td>BG</td>
<td>7.22E-03</td>
<td>7.22E-03</td>
<td>1.67</td>
<td>0.2019</td>
</tr>
<tr>
<td>CF</td>
<td>0.19</td>
<td>0.19</td>
<td>43.92</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>CG</td>
<td>0.34</td>
<td>0.34</td>
<td>78.65</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>FG</td>
<td>0.1</td>
<td>0.1</td>
<td>23.28</td>
<td>&lt; 0.0001</td>
</tr>
</tbody>
</table>
The Model F-value of 33.63 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case B, C, F, G, BC, CF, CG, FG, BCG are significant model terms.

The "Pred R-Squared" of 0.8069 is in reasonable agreement with the "Adj R-Squared" of 0.8469.

Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 19.277 indicates an adequate signal. This model can be used to navigate the design space.

Final Equation in Terms of Coded Factors:

\[
\text{Voltage @ 1.6 A/cm}^2 = \]
0.28
0.061 * B
0.038 * C
0.071 * F
-0.043 * G
-0.026 * B * C
0.011 * B * G
0.057 * C * F
0.076 * C * G
-0.041 * F * G
-0.032 * B * C * G

Final Equation in Terms of Actual Factors:

Type of GDL | MPL
---|---
Voltage @ 1.6 A/cm^2 | =
0.50137
0.043204 * Cathode Stoichiometry
-9.54E-03 * Temperature
-7.44E-04 * Pressure
3.99E-04 * Cathode Stoichiometry * Temperature
3.24E-05 * Temperature * Pressure

Type of GDL | No MPL
---|---
Voltage @ 1.6 A/cm^2 | =
-0.60925
0.35067 * Cathode Stoichiometry
0.010005 * Temperature
-1.57E-03 * Pressure
-4.43E-03 * Cathode Stoichiometry * Temperature
3.24E-05 * Temperature * Pressure
B.3 General Blocked Factorial

Figure B.4: Pareto Chart for 25 BC at 1.4 A cm$^{-2}$

Figure B.5: Pareto Chart for 25 BA at 1.4 A cm$^{-2}$
Figure B.6: Pareto Chart for 25 BC at 1.6 A cm$^{-2}$

Figure B.7: Pareto Chart for 25 BA at 1.6 A cm$^{-2}$
ANOVA: General blocked design : MPL
Response 1 Voltage @ 1.0 A/cm^2
ANOVA for selected factorial model
Analysis of variance table [Partial sum of squares - Type III]

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>df</th>
<th>Mean Square</th>
<th>F Value</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>0.12</td>
<td>1</td>
<td>0.12</td>
<td>76.75</td>
<td>&lt; 0.0001 significant</td>
</tr>
<tr>
<td>F-Pressure</td>
<td>0.12</td>
<td>1</td>
<td>0.12</td>
<td>76.75</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>Residual</td>
<td>0.047</td>
<td>30</td>
<td>1.57E-03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cor Total</td>
<td>0.17</td>
<td>31</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The Model F-value of 76.75 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Std. Dev. 0.04 R-Squared 0.719
Mean 0.54 Adj R-Squared 0.7096
C.V. % 7.28 Pred R-Squared 0.6802
PRESS 0.054 Adeq Precision 12.389

The "Pred R-Squared" of 0.6802 is in reasonable agreement with the "Adj R-Squared" of 0.7096.

Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 12.389 indicates an adequate signal. This model can be used to navigate the design space.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Standard Error</th>
<th>95% CI Low</th>
<th>95% CI High</th>
<th>VIF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor</td>
<td>Estimate</td>
<td>df</td>
<td>Error</td>
<td></td>
</tr>
<tr>
<td>Intercept</td>
<td>0.54</td>
<td>1</td>
<td>7.01E-03</td>
<td>0.56</td>
</tr>
<tr>
<td>F-Pressure</td>
<td>0.061</td>
<td>1</td>
<td>7.01E-03</td>
<td>0.076</td>
</tr>
</tbody>
</table>

Final Equation in Terms of Coded Factors:

\[
\text{Voltage @ 1.0 A/cm}^2 = 0.54 + 0.061 \times F
\]

Final Equation in Terms of Actual Factors:

\[
\text{Voltage @ 1.0 A/cm}^2 = 0.42191
\]
ANOVA: General blocked design : MPL

Response 2 Voltage @ 1.4 A/cm^2

ANOVA for selected factorial model

Analysis of variance table [Partial sum of squares - Type III]

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>Mean Square</th>
<th>F Value</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>0.29</td>
<td>0.29</td>
<td>39.2</td>
<td>&lt; 0.0001 significant</td>
</tr>
<tr>
<td>F-Pressure</td>
<td>0.29</td>
<td>0.29</td>
<td>39.2</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>Residual</td>
<td>0.22</td>
<td>7.38E-03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cor Total</td>
<td>0.51</td>
<td></td>
<td>7.38E-03</td>
<td></td>
</tr>
</tbody>
</table>

The Model F-value of 39.20 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.
In this case F are significant model terms.

<table>
<thead>
<tr>
<th>Std. Dev.</th>
<th>0.086</th>
<th>R-Squared</th>
<th>0.5665</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>0.4</td>
<td>Adj R-Squared</td>
<td>0.552</td>
</tr>
<tr>
<td>C.V. %</td>
<td>21.39</td>
<td>Pred R-Squared</td>
<td>0.5067</td>
</tr>
<tr>
<td>PRESS</td>
<td>0.25</td>
<td>Adeq Precision</td>
<td>8.854</td>
</tr>
</tbody>
</table>

The "Pred R-Squared" of 0.5067 is in reasonable agreement with the "Adj R-Squared" of 0.5520.

Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 8.854 indicates an adequate signal. This model can be used to navigate the design space.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Standard 95% CI</th>
<th>95% CI</th>
<th>95% CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor</td>
<td>Estimate df</td>
<td>Error Low</td>
<td>0.37</td>
</tr>
<tr>
<td>Intercept</td>
<td>0.4</td>
<td>1</td>
<td>0.015</td>
</tr>
<tr>
<td>F-Pressure</td>
<td>0.095</td>
<td>1</td>
<td>0.015</td>
</tr>
</tbody>
</table>

Final Equation in Terms of Coded Factors:

Voltage @ 1.4 A/cm^2 = 0.4
Final Equation in Terms of Actual Factors:

\[
\text{Voltage @ 1.4 A/cm}^2 = 0.21138 \times 9.51 \times 10^{-4} \times \text{Pressure}
\]

**ANOVA: General blocked design : MPL**

ANOVA for selected factorial model

Analysis of variance table [Partial sum of squares - Type III]

<table>
<thead>
<tr>
<th>Source</th>
<th>Squares</th>
<th>df</th>
<th>Mean Square</th>
<th>F Value</th>
<th>Prob &gt; F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>0.44</td>
<td>1</td>
<td>0.44</td>
<td>34.46</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>F-Pressure</td>
<td>0.44</td>
<td>1</td>
<td>0.44</td>
<td>34.46</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>Residual</td>
<td>0.38</td>
<td>30</td>
<td>0.013</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cor Total</td>
<td>0.82</td>
<td>31</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The Model F-value of 34.46 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Std. Dev. 0.11 R-Squared 0.5346

Mean 0.32 Adj R-Squared 0.5191

C.V. % 35.35 Pred R-Squared 0.4705

PRESS 0.44 Adeq Precision 8.302

The "Pred R-Squared" of 0.4705 is in reasonable agreement with the "Adj R-Squared" of 0.5191.

Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 8.302 indicates an adequate signal. This model can be used to navigate the design space.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Standard Estimate</th>
<th>95% CI df Error</th>
<th>95% CI Low</th>
<th>High</th>
<th>VIF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>0.32</td>
<td>1 0.02</td>
<td>0.28</td>
<td>0.36</td>
<td></td>
</tr>
<tr>
<td>F-Pressure</td>
<td>0.12</td>
<td>1 0.02</td>
<td>0.077</td>
<td>0.16</td>
<td>1</td>
</tr>
</tbody>
</table>
Final Equation in Terms of Coded Factors:

\[
\text{Voltage @ 1.6 A/cm}^2 = 0.32 - 0.12 \times F
\]

Final Equation in Terms of Actual Factors:

\[
\text{Voltage @ 1.6 A/cm}^2 = 0.085188 + 1.17 \times 10^{-3} \times \text{Pressure}
\]

ANOVA: General blocked design : No MPL

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>df</th>
<th>Mean Square</th>
<th>F</th>
<th>p-value</th>
<th>Prob &gt; F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>0.66</td>
<td>6</td>
<td>0.11</td>
<td>11.99</td>
<td>&lt; 0.0001</td>
<td>significant</td>
</tr>
<tr>
<td>B-Cathode</td>
<td>0.077</td>
<td>1</td>
<td>0.077</td>
<td>8.44</td>
<td>0.0076</td>
<td></td>
</tr>
<tr>
<td>Stoichiometry</td>
<td>0.23</td>
<td>1</td>
<td>0.23</td>
<td>25.31</td>
<td>&lt; 0.0001</td>
<td></td>
</tr>
<tr>
<td>C-Temperature</td>
<td>0.037</td>
<td>1</td>
<td>0.037</td>
<td>4.1</td>
<td>0.0537</td>
<td></td>
</tr>
<tr>
<td>F-Pressure</td>
<td>0.17</td>
<td>1</td>
<td>0.17</td>
<td>18.38</td>
<td>0.0002</td>
<td></td>
</tr>
<tr>
<td>BC</td>
<td>0.063</td>
<td>1</td>
<td>0.063</td>
<td>6.84</td>
<td>0.0149</td>
<td></td>
</tr>
<tr>
<td>BF</td>
<td>0.081</td>
<td>1</td>
<td>0.081</td>
<td>8.85</td>
<td>0.0064</td>
<td></td>
</tr>
<tr>
<td>CF</td>
<td>0.23</td>
<td>25</td>
<td>9.14E-03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Residual</td>
<td>0.23</td>
<td>25</td>
<td>9.14E-03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cor Total</td>
<td>0.89</td>
<td>31</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The Model F-value of 11.99 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case B, C, BC, BF, CF are significant model terms.

Std. Dev. 0.096 R-Squared 0.7421
The "Pred R-Squared" of 0.5774 is in reasonable agreement with the "Adj R-Squared" of 0.6802.

Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 10.225 indicates an adequate signal. This model can be used to navigate the design space.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Standard Estimate</th>
<th>95% CI Error</th>
<th>95% CI Low</th>
<th>95% CI High</th>
<th>VIF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>0.4</td>
<td>0.017</td>
<td>0.36</td>
<td>0.43</td>
<td></td>
</tr>
<tr>
<td>B-Cathode Stoichiometry</td>
<td>0.049</td>
<td>0.017</td>
<td>0.014</td>
<td>0.084</td>
<td>1</td>
</tr>
<tr>
<td>C-Temperature</td>
<td>0.085</td>
<td>0.017</td>
<td>0.05</td>
<td>0.12</td>
<td>1</td>
</tr>
<tr>
<td>F-Pressure</td>
<td>0.034</td>
<td>0.017</td>
<td>-5.92E-04</td>
<td>0.069</td>
<td>1</td>
</tr>
<tr>
<td>BC</td>
<td>-0.072</td>
<td>0.017</td>
<td>-0.11</td>
<td>-0.038</td>
<td>1</td>
</tr>
<tr>
<td>BF</td>
<td>0.044</td>
<td>0.017</td>
<td>9.41E-03</td>
<td>0.079</td>
<td>1</td>
</tr>
<tr>
<td>CF</td>
<td>0.05</td>
<td>0.017</td>
<td>0.015</td>
<td>0.085</td>
<td>1</td>
</tr>
</tbody>
</table>

Final Equation in Terms of Coded Factors:

\[
\text{Voltage @ 1.0 A/cm}^2 = 0.4 + 0.049 \times B + 0.085 \times C + 0.034 \times F - 0.072 \times B \times C + 0.044 \times B \times F + 0.05 \times C \times F
\]

Final Equation in Terms of Actual Factors:

\[
\text{Voltage @ 1.0 A/cm}^2 = -0.21412 + 0.26502 \times \text{Cathode Stoichiometry} + 0.011536 \times \text{Temperature} - 2.64E-03 \times \text{Pressure} - 5.52E-03 \times \text{Cathode Stoichiometry} \times \text{Temperature}
\]
ANOVA: General blocked design: No MPL
Response 2 Voltage @ 1.4 A/cm²
ANOVA for selected factorial model
Analysis of variance table [Partial sum of squares - Type III]

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>df</th>
<th>Mean Square</th>
<th>F Value</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>0.94</td>
<td>5</td>
<td>0.19</td>
<td>20</td>
<td>&lt; 0.0001 significant</td>
</tr>
<tr>
<td>B-Cathode Stoichiometry</td>
<td>0.10</td>
<td>1</td>
<td>0.10</td>
<td>10.72</td>
<td>0.003</td>
</tr>
<tr>
<td>C-Temperature</td>
<td>0.39</td>
<td>1</td>
<td>0.39</td>
<td>41.66</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>F-Pressure</td>
<td>0.041</td>
<td>1</td>
<td>0.041</td>
<td>26.13</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>BC</td>
<td>0.09</td>
<td>1</td>
<td>0.09</td>
<td>4.31</td>
<td>0.0479</td>
</tr>
<tr>
<td>CF</td>
<td>0.16</td>
<td>1</td>
<td>0.16</td>
<td>17.17</td>
<td>0.0003</td>
</tr>
<tr>
<td>Residual</td>
<td>0.25</td>
<td>26</td>
<td>0.0009</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cor Total</td>
<td>1.19</td>
<td>31</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The Model F-value of 20.00 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.
In this case B, C, F, BC, CF are significant model terms.

| Std. Dev. | R-Squared | 0.7936 |
| Mean      | Adj R-Squared | 0.7539 |
| C.V. %    | Pred R-Squared | 0.6874 |
| PRESS     | Adeq Precision | 12.827 |

The "Pred R-Squared" of 0.6874 is in reasonable agreement with the "Adj R-Squared" of 0.7539.

Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 12.827 indicates an adequate signal. This model can be used to navigate the design space.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Standard Error</th>
<th>95% CI Low</th>
<th>95% CI High</th>
<th>VIF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>0.27</td>
<td>0.017</td>
<td>0.24</td>
<td>0.31</td>
</tr>
<tr>
<td>B-Cathode Stoichiometry</td>
<td>0.056</td>
<td>0.017</td>
<td>0.021</td>
<td>0.092</td>
</tr>
<tr>
<td>C-Temperature</td>
<td>0.11</td>
<td>0.017</td>
<td>0.076</td>
<td>0.15</td>
</tr>
<tr>
<td>F-Pressure</td>
<td>0.036</td>
<td>0.017</td>
<td>3.57E-04</td>
<td>0.071</td>
</tr>
</tbody>
</table>
Final Equation in Terms of Coded Factors:

Voltage @ 1.4 A/cm^2  =

0.27
0.056 * B
0.11 * C
0.036 * F
-0.088 * B * C
0.071 * C * F

Final Equation in Terms of Actual Factors:

Voltage @ 1.4 A/cm^2  =

-0.72825
* Cathode Stoichiometry
0.45952
* Temperature
0.01325
* Pressure
-1.98E-03
* Cathode Stoichiometry * Temperature
-6.69E-03
* Temperature * Pressure
4.07E-05
* Temperature * Pressure

ANOVA: General blocked design : No MPL
Response 3 Voltage @ 1.6 A/cm^2
ANOVA for selected factorial model
Analysis of variance table [Partial sum of squares - Type III]

<table>
<thead>
<tr>
<th>Source</th>
<th>Squares</th>
<th>df</th>
<th>Mean Square</th>
<th>F</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>0.84</td>
<td>5</td>
<td>0.17</td>
<td>25.76</td>
<td>&lt; 0.0001 significant</td>
</tr>
<tr>
<td>B-Cathode Stoichiometry</td>
<td>0.091</td>
<td>1</td>
<td>0.091</td>
<td>13.96</td>
<td>0.0009</td>
</tr>
<tr>
<td>C-Temperature</td>
<td>0.29</td>
<td>1</td>
<td>0.29</td>
<td>44.83</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>F-Pressure</td>
<td>0.073</td>
<td>1</td>
<td>0.073</td>
<td>11.31</td>
<td>0.0024</td>
</tr>
<tr>
<td>BC</td>
<td>0.18</td>
<td>1</td>
<td>0.18</td>
<td>27.62</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>CF</td>
<td>0.2</td>
<td>1</td>
<td>0.2</td>
<td>31.09</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>Residual</td>
<td>0.17</td>
<td>26</td>
<td>6.49E-03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cor Total</td>
<td>1</td>
<td>31</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The Model F-value of 25.76 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case B, C, F, BC, CF are significant model terms.

<table>
<thead>
<tr>
<th>Std. Dev.</th>
<th>R-Squared</th>
<th>Adj R-Squared</th>
<th>Pred R-Squared</th>
<th>Adeq Precision</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.081</td>
<td>0.8321</td>
<td>0.7998</td>
<td>0.7456</td>
<td>14.311</td>
</tr>
</tbody>
</table>

The "Pred R-Squared" of 0.7456 is in reasonable agreement with the "Adj R-Squared" of 0.7998.

Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 14.311 indicates an adequate signal. This model can be used to navigate the design space.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Standard Error</th>
<th>95% CI Low</th>
<th>95% CI High</th>
<th>VIF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>0.22</td>
<td>0.19</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>B-Cathode Stoichiometry</td>
<td>0.053</td>
<td>0.024</td>
<td>0.082</td>
<td>1</td>
</tr>
<tr>
<td>C-Temperature</td>
<td>0.095</td>
<td>0.066</td>
<td>0.12</td>
<td>1</td>
</tr>
<tr>
<td>F-Pressure</td>
<td>0.048</td>
<td>0.019</td>
<td>0.077</td>
<td>1</td>
</tr>
<tr>
<td>BC</td>
<td>-0.075</td>
<td>-0.1</td>
<td>-0.046</td>
<td>1</td>
</tr>
<tr>
<td>CF</td>
<td>0.079</td>
<td>0.05</td>
<td>0.11</td>
<td>1</td>
</tr>
</tbody>
</table>

Final Equation in Terms of Coded Factors:

\[
\text{Voltage @ 1.6 A/cm}^2 = 0.22 + 0.053 \times B + 0.095 \times C + 0.048 \times F - 0.075 \times B \times C + 0.079 \times C \times F
\]

Final Equation in Terms of Actual Factors:

\[
\text{Voltage @ 1.6 A/cm}^2 = -0.561
\]
0.39867 * Cathode Stoichiometry
9.20E-03 * Temperature
-2.13E-03 * Pressure
-5.70E-03 * Cathode Stoichiometry * Temperature
4.54E-05 * Temperature * Pressure
Appendix C

C.1 Exemplary Voltammetry Results

Figure C.1: Exemplary CV results for 25 BA sample
Figure C.2: Exemplary LSV result for 25 BA sample
C.2 Voltage Loss Breakdown

Figure C.3: Baseline polarization data for GDL material 25 BA, including the standard deviation of the signal in error bars.

Figure C.4: iR-corrected polarization results at baseline conditions for 25 BA
Figure C.5: VLB at baseline conditions for 25 BA

Figure C.6: VLB at 100 kPa, 75 °C and 100% RH for 25 BC
Figure C.7: VLB at 100 kPa, 75 °C and 100% RH for 25 BA

Figure C.8: VLB at 100 kPa, 40 °C and 100% RH for 25 BC
Figure C.9: VLB at 100 kPa, 40 °C and 100% RH for 25 BA

Figure C.10: VLB at 300 kPa, 40 °C and 100% RH for 25 BC
Figure C.11: VLB at 300 kPa, 40 °C and 100% RH for 25 BA

Figure C.12: VLB at 300 kPa, 75 °C and 100% RH for 25 BC
Figure C.13: VLB at 300 kPa, 75 °C and 100% RH for 25 BA