

**DIAGNOSIS AND MITIGATION OF WATER
ACCUMULATION AND CARBON MONOXIDE POISONING
IN PROTON EXCHANGE MEMBRANE FUEL CELL**

HARIKRISHNAN N.



**DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI
JANUARY 2019**

© Indian Institute of Technology Delhi (IITD), New Delhi, 2019

**DIAGNOSIS AND MITIGATION OF WATER
ACCUMULATION AND CARBON MONOXIDE POISONING
IN PROTON EXCHANGE MEMBRANE FUEL CELL**

by

HARIKRISHNAN N.

Department of Chemical Engineering

Submitted

in fulfilment of the requirements of the degree of Doctor of Philosophy
to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI

JANUARY 2019

Dedicated to my family

Certificate

This is to certify that the thesis entitled “**Diagnosis and Mitigation of Water Accumulation and Carbon Monoxide Poisoning in Proton Exchange Membrane Fuel Cell**” submitted by **Mr. Harikrishnan N.** to the Indian Institute of Technology Delhi, for the award of degree of doctor of philosophy, is a record of the original bonafide research work carried out by him. He has worked under my supervision and has fulfilled the requirements, which to my knowledge, has reached the requisite standard for the submission of this thesis. The results contained in this thesis have not been submitted in part or full to any University or Institute for the award of any degree or diploma.

Date:

New Delhi

Dr. Suddhasatwa Basu

Professor

Department of Chemical Engineering

Indian Institute of Technology Delhi

Hauz Khas, New Delhi - 110016

India

Acknowledgments

There are number of people without whom this thesis might not have been written, and to whom I am greatly indebted for their part in my success. It is pleasant aspect that I now have the opportunity to express my gratitude for all of them.

First of all I would like to express my special thanks of gratitude to my professor and supervisor **Dr. Suddhasatwa Basu**. This work would not have been possible without his guidance, support and encouragement. He has given me full liberty to pursue my research work. Under his guidance I successfully overcame many difficulties and learned a lot.

I am also thankful to **Head of the Department** of Department of Chemical Engineering Indian Institute of Technology, Delhi. I would also like to thank my thesis committee members and all the faculty members of the Department of Chemical Engineering. I am thankful to all the administrative and technical staff members Department of Chemical Engineering, Indian Institute of Technology, Delhi for their help and cooperation. I am also thankful to all the members of Nanoscale Research Facility (NRF) for providing me with the facilities to carry out my research work.

I also gratefully acknowledge Council of Scientific and Industrial Research (CSIR), Ministry of Electronics and Information Technology (MeitY) and Department of Science and Technology (DST), India for the financial support which made my Ph.D. work possible without the tension of earning my living.

I express my special thanks to my respected seniors and juniors Dr. Pankaj, Dr. Varagunapandiyam, Dr. Rajalakshmi, Dr. Gurpreet, Dr. Rahul, Dr. Ayan, Dr. Kapil, Dr. Merajul, Dr. Sankalpita, Dr. Amandeep, Dr. Debabrata, Ms. Neetu, Ms. Ieeba, Ms. Ayushi, Mr. Ravi, Mr. Aditya, Mr. Nimai, Mr. Baijnath, Mr. Shahid, Mr. Biswajit and Mr. Ramji for

their time to time outstanding scientific guidance and for making lab environment cordial. I also thank Mr. Sundar for making the lab during PhD more easily accessible and fun.

I would like to specially acknowledge my friends Richa, Shruti, Snigdha, Namrata, Jawad, Rajesh, Rami, Vinay, Brajesh, Deepika, Ketan, Steven, Avinash, Nidhi, Bhawna, Simrjit, Deepanshu and Sandeep for their moral support and motivation.

But most of all, I would like to thank those whom I deeply love, respect and admire, and whom I dedicate this thesis– my family. I express my heartfelt gratitude to my parents for their unconditional love, encouragement and blessings. I also wish to express my feelings for my fiancée Deepthi and brother Arun for listening to my problems and providing perspective. I also want to express my sincere thanks to all those who directly and indirectly helped me at various stage of the work but I could not mention their name due to shortage of the space.

At last thanks to the almighty God who has given me the spiritual support and courage to carry out this work.

Harikrishnan N.

Abstract

In order to make proton exchange membrane fuel cell (PEMFC) more economically viable, researchers have been developing non-noble metal catalyst to replace platinum catalyst, redesigning PEMFC to increase its efficiency and studying various performance loss causing issues like water accumulation, poisoning of catalyst, membrane electrode assembly (MEA) degradation. In the present work, the focus has been on diagnosing and mitigating performance loss causing issues like water accumulation in cathode channel and CO poisoning of anode electro-catalyst. Mathematical modelling and simulation has also been carried out to better understand the mechanism behind CO poisoning of anode electro-catalyst and its regeneration process.

A single channel PEMFC with bends at the entrance and exit has been used to investigate effects on the performance of PEMFC due water accumulation in cathode channel. For this purpose, MEAs with reversible hydrogen electrodes (RHE) are placed in a series of sub cells and current-voltage (i-V) characteristics and electrochemical impedance spectroscopy (EIS) data are collected for anode and cathode separately. By comparing i-V characteristics and EIS data between different sub cells, a dip in i-V curve is found to follow cathode polarization loss from sub cell 1 to 5. The increase in charge transfer resistance at the cathode and dip in i-V curve attributed to product water accumulation in subsequent sub cells. However, no dip in i-V characteristics and increase in cathode charge transfer resistance is observed when single sub cells operated at different locations, i.e., close to entry, middle and exit of the channel. Further, in sub cell 5, accumulation of product water at the cathode and in the exit bend leads to drastic reduction in the limiting current density due to high concentration over-potential.

In case of CO poisoning study of anode electro-catalyst, an experimental procedure is developed based on break-in procedure and dilute KMnO_4 solution is used to regenerate the

CO poisoned Pt black anode electro-catalyst of a PEMFC. Also to understand the effect of operating temperature on extent of CO poisoning and regeneration of CO poisoned Pt black anode electro-catalyst, PEMFC is operated at 30 °C, 50 °C and 70 °C. At 50 °C and 70 °C, break-in procedure contributes towards recovering the initial performance i.e. 74.6 % and 78.8 % of the initial current density at 0.2 V respectively and rest is regenerated by use of dilute KMnO_4 solution. Later, in order to restrict the usage of dilute KMnO_4 solution, the experimental procedure is further modified by increasing the number of activation cycle.

In order to better understand the actual mechanism being followed during CO poisoning and regeneration of CO poisoned electro-catalyst, a single cell PEMFC mathematical model coupled with surface coverage equations are simulated. Hydrogen oxidation reaction (HOR) are assumed to follow Heyrovsky-Volmer mechanism “before CO poisoning” and “after activation cycle” and Tafel-Volmer mechanisms “after CO poisoning” stage of operations. During CO poisoning, surface coverage variation for CO and H_2 clearly shows that adsorption of CO hinders adsorption of H_2 and eventually decreases the cell performance. The above mentioned diagnostics and regeneration procedures followed for water accumulation and CO poisoning can be used extend to large scale PEMFC stacks, which may facilitate PEMFC commercialisation.

सार

प्रोटॉन एक्सचेंज मेम्ब्रेन फ्यूल सेल (PEMFC) को अधिक आर्थिक रूप से व्यवहार्य बनाने के लिए, शोधकर्ताओं ने प्लैटिनम उत्प्रेरक को बदलने के लिए नॉन-नोबल मेटल उत्प्रेरक विकसित किया है, इसकी दक्षता बढ़ाने के लिए PEMFC को फिर से डिज़ाइन किया गया है और जल संचय, उत्प्रेरक की विषाक्तता के कारण विभिन्न प्रदर्शन हानि का अध्ययन किया है।, झिल्ली इलेक्ट्रोड असेंबली (MEA) की गिरावट। वर्तमान कार्य में, प्रदर्शन हानि को कम करने और कैथोड चैनल में जल संचय और एनोड इलेक्ट्रो-उत्प्रेरक के सीओ विषाक्तता जैसे मुद्दों का कारण बनता है। एनोड इलेक्ट्रो-उत्प्रेरक और इसके पुनर्जनन प्रक्रिया के सीओ विषाक्तता के पीछे के तंत्र को बेहतर ढंग से समझने के लिए गणितीय मॉडलिंग और सिमुलेशन भी किया गया है।

प्रवेश द्वार पर झुकता हुआ एक एकल चैनल PEMFC और कैथोड चैनल में पानी के जमाव के कारण PEMFC के प्रदर्शन पर पड़ने वाले प्रभावों की जांच करने के लिए उपयोग किया गया है। इस प्रयोजन के लिए, प्रतिवर्ती हाइड्रोजन इलेक्ट्रोड (RHE) वाले MEAs को उप कोशिकाओं की एक श्रृंखला में रखा जाता है और वर्तमान-वोल्टेज (i-V) विशेषताओं और विद्युत रासायनिक प्रतिबाधा स्पेक्ट्रोस्कोपी (EIS) डेटा को अलग से एनोड और कैथोड के लिए एकत्र किया जाता है। विभिन्न उप कोशिकाओं के बीच आईवी विशेषताओं और ईआईएस डेटा की तुलना करके, आईवी वक्र में एक डुबकी उप सेल 1 से 5. से कैथोड ध्रुवीकरण नुकसान का पालन करने के लिए पाया जाता है। कैथोड में प्रभारी स्थानांतरण प्रतिरोध में वृद्धि और उत्पाद जल संचय के लिए जिम्मेदार iV वक्र में डुबकी। बाद के उप कक्षों में। हालांकि, आई-वी विशेषताओं और कैथोड चार्ज ट्रांसफर प्रतिरोध में कोई गिरावट नहीं देखी जाती है, जब विभिन्न स्थानों पर एकल उप कोशिकाओं को संचालित किया जाता है, अर्थात्, चैनल के प्रवेश, मध्य और निकास के करीब। इसके अलावा, उप सेल 5 में, कैथोड पर और निकास मोड़ पर उत्पाद के पानी का संचय उच्च सांद्रता क्षमता के कारण सीमित घनत्व में भारी कमी की ओर जाता है।

एनोड इलेक्ट्रो-उत्प्रेरक के सीओ विषाक्तता अध्ययन के मामले में, एक प्रायोगिक प्रक्रिया ब्रेक-इन प्रक्रिया के आधार पर विकसित की जाती है और एक पीईएमएफसी के सीओ जहर पीटी काले एनोड इलेक्ट्रो-उत्प्रेरक को पुनः उत्पन्न करने के लिए KMnO_4 समाधान का उपयोग किया जाता है। सीओ विषाक्तता की सीमा पर ऑपरेटिंग तापमान के प्रभाव को समझने के लिए और सीओ जहर वाले पं। काले एनोड इलेक्ट्रो-उत्प्रेरक के पुनर्जनन को समझने के लिए, पीईएमएफसी को 30 °C, 50 °C और 70 °C पर संचालित किया जाता है। 50 °C और 70 °C पर, ब्रेक-इन प्रक्रिया प्रारंभिक प्रदर्शन यानी 74.6% और 78.8% के प्रारंभिक वर्तमान घनत्व को क्रमशः 0.2 V पर पुनर्प्राप्त करने की दिशा में योगदान करती है और पतला KMnO_4 समाधान के उपयोग से पुनर्जीवित होती है। बाद में, पतला KMnO_4 समाधान के उपयोग को प्रतिबंधित करने के लिए, सक्रियण चक्र की संख्या में वृद्धि करके प्रयोगात्मक प्रक्रिया को और संशोधित किया गया है।

सीओ विषाक्तता और सीओ जहर इलेक्ट्रो-उत्प्रेरक के उत्थान के दौरान पीछा किए जाने वाले वास्तविक तंत्र को बेहतर ढंग से समझने के लिए, सतह कवरेज समीकरणों के साथ मिलकर एक एकल सेल पीईएमएफसी गणितीय मॉडल को सिमुलेटेड किया जाता है। हाइड्रोजन ऑक्सीकरण प्रतिक्रिया (HOR) को माना जाता है कि हेओरोव्स्की-वोल्मर तंत्र "सीओ विषाक्तता से पहले" और "सक्रियण चक्र के बाद" और टाफेल-वोल्मर तंत्र "सीओ विषाक्तता के बाद" संचालन के चरण का पालन करें। सीओ विषाक्तता के दौरान, सीओ और एच 2 के लिए सतह कवरेज भिन्नता स्पष्ट रूप से दिखाती है कि सीओ का सोखना एच 2 के सोखना में बाधा डालता है और अंततः सेल के प्रदर्शन को कम करता है। पानी के संचय और CO विषाक्तता के लिए उपर्युक्त निदान और पुनर्जनन प्रक्रियाओं का उपयोग बड़े पैमाने पर PEMFC स्टैक तक किया जा सकता है, जो PEMFC व्यावसायीकरण की सुविधा प्रदान कर सकता है।

Table of Contents

	Page No.
<i>Certificate</i>	i
<i>Acknowledgement</i>	iii
<i>Abstract</i>	v
<i>Table of contents</i>	ix
<i>List of figures</i>	xiii
<i>List of tables</i>	xix
Chapter 1: Introduction	1-16
1.1 Background of PEMFC	1
1.2 Various degradations in PEMFC	3
1.2.1 GDL degradation	3
1.2.2 Electro-catalyst degradation	5
1.2.3 Membrane degradation	7
1.2.4 Bipolar plate degradation	10
1.2.5 Sealing gasket degradation	10
1.3 Diagnosis of degradation in PEMFC	11
1.3.1 Cyclic voltammetry/Linear sweep voltammetry	11
1.3.2 Electrochemical impedance spectroscopy	13
1.3.3 Current/Temperature mapping	14
1.3.4 Visualisation technique	16
Chapter 2: Literature Review: Degradation and Diagnosis	17-28
2.1 Introduction	17
2.2 Water accumulation study	17

2.3 CO poisoning study	21
2.4 Mathematical modelling of CO poisoning	24
2.5 Motivation and objective of the present work	26
2.5.1 Gap in literature/Motivation	26
2.5.2 Objective of thesis	26
2.6 Thesis organization	27
Chapter 3: Experimental	29-40
3.1 Introduction	29
3.2 Water accumulation - Diagnostics	29
3.2.1 Methodology	29
3.2.1.1 Cell design	29
3.2.1.2 Membrane electrode assembly (MEA) fabrication	32
3.2.1.3 Reference electrode (RE) arrangement	33
3.2.2 PEMFC diagnostics	34
3.3 CO poisoning – Diagnosis and Mitigation	36
3.3.1 Methodology	36
3.3.1.1 Membrane electrode assembly (MEA) fabrication	36
3.3.1.2 Experimental setup and procedure	37
Chapter 4: Simple diagnostic tool to determine water accumulation	41-52
4.1 Introduction	41
4.2 Validation of reference electrode positioning	41
4.3 Entry effect: comparison between SC1-5 and SC1	43
4.4 Mid region: comparison between SC3-5 and SC3	46
4.5 Exit effect: comparison between SC5-5 and SC5	48
4.6 Summary	50

Chapter 5: Diagnosis and mitigation of CO poisoned Pt Anode catalyst	53-64
5.1 Introduction	53
5.2 Before CO poisoning	53
5.3 After CO poisoning	55
5.4 After activation cycle (break-in procedure)	57
5.5 After KMnO ₄ treatment	60
5.6 Summary	62
Chapter 6: Surface coverage modelling of CO poisoning	65-84
6.1 Introduction	65
6.2 Mathematical Modelling of CO poisoning	65
6.2.1 Modelling equations for PEMFC	65
6.2.2 Surface coverage equations	68
6.2.2.1 Before CO poisoning	68
6.2.2.2 After CO poisoning	70
6.2.2.3 After activation cycle (break-in procedure)	72
6.3 i-V characteristics simulation	73
6.4 Surface coverage with pure H ₂ as fuel	76
6.5 Surface coverage with “100 ppm CO + H ₂ ” as fuel	77
6.6 Surface coverage during activation cycle	79
6.7 Summary	83
Chapter 7: Conclusion and Future Direction	85-90
7.1 Water accumulation	85
7.2 CO poisoning	86
7.3 Surface coverage modelling	87
7.4 Future direction	89

References	91-108
Curriculum Vitae	109-110

List of Figures

Figure No.	Title	Page No.
Fig. 1.1	Schematic of Proton Exchange Membrane Fuel Cell	2
Fig. 1.2	Carbon corrosion mechanism in a fuel starved Proton Exchange Membrane Fuel Cell	5
Fig. 1.3	Electro-catalyst and support degradation after prolonged usage	6
Fig. 1.4	CV plot showing H ₂ adsorption and desorption (just for representation)	11
Fig. 1.5	LSV plot showing H ₂ desorption and crossover current (just for representation)	12
Fig. 1.6	Nyquist plot of a Proton Exchange Membrane Fuel Cell under a load (just for representation)	14
Fig. 1.7	Equivalent circuit of Nyquist plot of a Proton Exchange Membrane Fuel Cell	14
Fig. 1.8	Photograph of a) printed circuit board with serpentine flow channels and current collector, b) reverse side of the printed circuit board showing the current and voltage sense points	15
Fig. 1.9	Photograph of anode plate showing embedded thermocouple for temperature sensing	15
Fig. 3.1	Schematic of Proton Exchange Membrane Fuel Cell design with reference electrode	30
Fig. 3.2	Dimensions of anode side channel with reference electrode	31
Fig. 3.3	a) MEA and b) Original image of PEMFC with reference electrode	31

Fig. 3.4	Schematic of Membrane Electrode Assembly fabrication	32
Fig. 3.5	Schematic of Reference electrode arrangement	33
Fig. 3.6	Schematic of in house measurement arrangement	35
Fig. 3.7	a) 5 cm ² Proton Exchange Membrane Fuel Cell and b) Fuel cell test station	37
Fig. 3.8	Flowchart showing the experimental procedure followed at an operating temperature in reviving CO poisoned Pt black anode of a Proton Exchange Membrane Fuel Cell	38
Fig. 4.1	Nyquist plot of individual anode and cathode electrodes along with sub cell, SC3, Summation of anode and cathode contribution at 300 mV of SC3; (●) Cell SC3 measured, (■) Cathode SC3, (▲) Anode SC3, (○) Cell SC3 calculated	42
Fig. 4.2	Variation in anode potential with respect to Reversible Hydrogen Electrode at sub cell 3, SC3	43
Fig. 4.3	Current-voltage characteristics of anode, cathode and the cell of SC1-5 and SC1; (●) Cell SC1, (■) Cathode SC1, (▲) Anode SC1, (○) Cell SC1-5, (□) Cathode SC1-5, (Δ) Anode SC1-5	44
Fig. 4.4	Nyquist plot of anode and cathode of SC1-5 and SC1 at 600 mV; (■) Cathode SC1, (▲) Anode SC1, (□) Cathode SC1-5, (Δ) Anode SC1-5	45
Fig. 4.5	Nyquist plot of anode and cathode of SC1-5 and SC1 at 300 mV; (■) Cathode SC1, (▲) Anode SC1, (□) Cathode SC1-5, (Δ) Anode SC1-5	45

Fig. 4.6	Current-voltage characteristics of anode, cathode and the cell of SC3-5 and SC3; (●) Cell SC3, (■) Cathode SC3, (▲) Anode SC3, (○) Cell SC3-5, (□) Cathode SC3-5, (Δ) Anode SC3-5	46
Fig. 4.7	Nyquist plot of anode and cathode of SC3-5 and SC3 at 600 mV; (■) Cathode SC3, (▲) Anode SC3, (□) Cathode SC3-5, (Δ) Anode SC3-5	47
Fig. 4.8	Nyquist plot of anode and cathode of SC3-5 and SC3 at 300 mV; (■) Cathode SC3, (▲) Anode SC3, (□) Cathode SC3-5, (Δ) Anode SC3-5	48
Fig. 4.9	Current-voltage characteristics of anode, cathode and the cell of SC5-5 and SC5; (●) Cell SC5, (■) Cathode SC5, (▲) Anode SC5, (○) Cell SC5-5, (□) Cathode SC5-5, (Δ) Anode SC5-5	49
Fig. 4.10	Nyquist plot of anode and cathode of SC5-5 and SC5 at 600 mV; (■) Cathode SC5, (▲) Anode SC5, (□) Cathode SC5-5, (Δ) Anode SC5-5	49
Fig. 5.1	i-V and i-P plots before “CO poisoning” of Pt black anode of a Proton Exchange Membrane Fuel Cell at 30 °C, 50 °C and 70 °C temperature	54
Fig. 5.2	Nyquist plot (0.6 V) before “CO poisoning” of Pt black anode of a Proton Exchange Membrane Fuel Cell at 30 °C, 50 °C and 70 °C temperature	54
Fig. 5.3	Bode plot (0.6 V) before “CO poisoning” of Pt black anode of a Proton Exchange Membrane Fuel Cell at 30 °C, 50 °C and 70 °C temperature	55

Fig. 5.4	i-V and i-P plots after “CO poisoning” of Pt black anode of a Proton Exchange Membrane Fuel Cell at 30 °C, 50 °C and 70 °C temperature	56
Fig. 5.5	Nyquist plot (0.6 V) after “CO poisoning” of Pt black anode of a Proton Exchange Membrane Fuel Cell at 30 °C, 50 °C and 70 °C temperature	56
Fig. 5.6	Bode plot (0.6 V) after “CO poisoning” of Pt black anode of a Proton Exchange Membrane Fuel Cell at 30 °C, 50 °C and 70 °C temperature	57
Fig. 5.7	i-V and i-P plots after “break-in procedure” of Pt black anode of a Proton Exchange Membrane Fuel Cell at 30 °C, 50 °C and 70 °C temperature	58
Fig. 5.8	Nyquist plot (0.6 V) after “break-in procedure” of Pt black anode of a Proton Exchange Membrane Fuel Cell at 30 °C, 50 °C and 70 °C temperature	58
Fig. 5.9	Bode plot (0.6 V) after “break-in procedure” of Pt black anode of a Proton Exchange Membrane Fuel Cell at 30 °C, 50 °C and 70 °C temperature	59
Fig. 5.10	i-V and i-P plots after “KMnO ₄ treatment” of Pt black anode of a Proton Exchange Membrane Fuel Cell at 30 °C, 50 °C and 70 °C temperature	61
Fig. 5.11	Nyquist plot (0.6 V) after “KMnO ₄ treatment” of Pt black anode of a Proton Exchange Membrane Fuel Cell at 30 °C, 50 °C and 70 °C temperature	61

Fig. 5.12	Bode plot (0.6 V) after “KMnO ₄ treatment” of Pt black anode of a Proton Exchange Membrane Fuel Cell at 30 °C, 50 °C and 70 °C temperature	62
Fig. 5.13	Effect of CO poisoning, break-in procedure and dilute KMnO ₄ solution treatment on percentage regeneration of Pt black anode of Proton Exchange Membrane Fuel Cell	62
Fig. 6.1	Experimental and simulated i-V characteristics of Proton Exchange Membrane Fuel Cell at 30 °C with a) 10 min, b) 30 min and c) 60 min of CO poisoning	75
Fig. 6.2	x_{H_2O} variation during Proton Exchange Membrane Fuel Cell operation ‘  ’ before CO poisoning, ‘  ’ after CO poisoning, ‘  ’ after activation cycle at a) 30 °C, b) 50 °C and c) 70 °C	76
Fig. 6.3	a) θ_H variation and b) $\frac{d\theta_H}{dV}$ variation versus anode over-potential during pure H ₂ /O ₂ supply at different operating temperatures.	77
Fig. 6.4	θ_H and θ_{CO} during 100 ppm CO + H ₂ supply at anode a) 30 °C, b) 50 °C and c) 70 °C	79
Fig. 6.5	Variation in θ_{CO} during activation cycling at various operating temperature after a) 10 min, b) 30 min and c) 60 min of CO poisoning	81
Fig. 6.6	Variation in θ_H during activation cycling at various operating temperature after a) 10 min, b) 30 min and c) 60 min of CO poisoning	83

List of Tables

Table No.	Title	Page No.
Table 3.1	Schematic representation of the Sub cells occupied with MEA for different cases.	34
Table 6.1	Parameters used for Proton Exchange Membrane Fuel Cell simulation	65
Table 6.2	Kinetic parameters used for surface coverage simulations	69
Table 6.3	Initial values of CO and H ₂ surface coverage used for simulation	72
Table 6.4	Absolute values of x_{H_2O} during various stages of Proton Exchange Membrane Fuel Cell operation	74