University of South Carolina Scholar Commons

Theses and Dissertations

12-14-2015

Development of Ultra-Low Loading of Compressive PT Lattice Cathode Catalyst on Highly Stable Support for PEMFC Automotive Applications

Tianyuan Xie University of South Carolina - Columbia

Follow this and additional works at: http://scholarcommons.sc.edu/etd Part of the <u>Chemical Engineering Commons</u>

Recommended Citation

Xie, T.(2015). Development of Ultra-Low Loading of Compressive PT Lattice Cathode Catalyst on Highly Stable Support for PEMFC Automotive Applications. (Doctoral dissertation). Retrieved from http://scholarcommons.sc.edu/etd/3262

This Open Access Dissertation is brought to you for free and open access by Scholar Commons. It has been accepted for inclusion in Theses and Dissertations by an authorized administrator of Scholar Commons. For more information, please contact SCHOLARC@mailbox.sc.edu.

DEVELOPMENT OF ULTRA-LOW LOADING OF COMPRESSIVE PT LATTICE CATHODE CATALYST ON HIGHLY STABLE SUPPORT FOR PEMFC AUTOMOTIVE APPLICATIONS

by

Tianyuan Xie

Bachelor of Science Dalian University of Technology, 2010

Submitted in Partial Fulfillment of the Requirements

For the Degree of Doctor of Philosophy in

Chemical Engineering

College of Engineering and Computing

University of South Carolina

2015

Accepted by:

Branko N. Popov, Major Professor

Ralph E. White, Committee Member

Francis Gadala-Maria, Committee Member

Kevin Huang, Committee Member

Lacy Ford, Senior Vice Provost and Dean of Graduate Studies

© Copyright by Tianyuan Xie, 2015 All Rights Reserve

ACKNOWLEDGEMENTS

I would like to thank my advisor, Dr. Branko N. Popov for all the guidance and support he offered during the past five years. Every time I felt lost in my study, he helps me find way out. His knowledge in electrochemistry helps me become an experienced fuel cell researcher. His enthusiasm to work always cheers me up when I am out of energy. I also appreciated the opportunity he provided to give talks at the international conferences. I thank my committee members Dr. Ralph E. White, Dr. Francis Gadala-Maria and Dr. Kevin Huang for serving on my committee and providing valuable suggestions and advice.

Special thanks to my college Dr. Ganesan Prabhu, Taekeum Kim and Wonsuk Jung. As the only female in the group, I troubled them countless times in changing cylinders and other experimental work. Prabhu helps me a lot in both experiments and writing. TK has to bear all the food smell I took for lunch as my office neighbor.

I also thank all the professors taught me during my PhD study, besides all my committee members, Dr. Matthews and Dr. Heyden. I really learned a lot from the class. I want to acknowledge the help of various staff of the Chemical Engineering Department, especially Marcia, Loretta, Vernon and Carol.

Finally, I thank my family and friends for their moral supports over the years.

ABSTRACT

The major barriers in the commercialization of the fuel cell technology for automotive applications are the cost and durability of the Pt catalyst and the support stability at high potentials. The U.S. Department of Energy (DOE) targets direct hydrogen fuel cell systems for transportation to meet 65% peak-efficiency, 5,000 hour durability with a mass production cost of \$40/kW by 2020. Currently in 2015, the system can be operated at peak energy efficiency of 60% for 3,900 hours with cost of \$55/kW. To meet these targets, precious metal loadings must be greatly reduced without altering the catalyst stability.

The primary objective of this dissertation is to develop highly active and durable hybrid cathode catalysts (HCC) with ultra-low Pt loading for Proton Exchange Membrane Fuel Cells (PEMFC) through interaction of highly active and stable Pt and compressive Pt-lattice (Pt*) catalyst deposited on catalytically active and highly stable carbon composite catalyst (CCC) support and active carbon composite catalyst (A-CCC) support. The HCC activity is enhanced by by the synergistic effect of catalytic active sites for ORR present in the supports and those in Pt and Pt*. The stability of Pt-based catalyst can be greatly improved by doping with transition metal (TM), which weakens interactions between Pt and adsorbents such as OH_{ads} and H_{upd}. Highly active and durable HCC is developed in this study through: (i) synthesis of highly catalytically active and stable Co-containing CCC and A-CCC supports, (ii) surface functionalization and uniform Pt deposition on CCC and

A-CCC supports, (iii) performance optimization of Co-doped Pt catalysts by using protective coating to inhibit particle agglomeration and growth during the pyrolysis step, (iv) optimization of Pt/Co ratio and annealing temperature and (v) chemical leaching to remove excess metal used to dope the support. T The support stability has been enhanced through optimization of: (i) Brunauer-Emmett-Teller (BET) surface, (ii) the support structural properties (amorphous/crystalline ratio), and (iii) the hydrophilic/hydrophobic ratio of the supports. During the past five years, the performance and durability of the catalysts were continuously studied. Stability of the catalyst was tested under U. S. DRIVE Fuel Cell Tech Team suggested protocols (a) potential cycling between 0.6 and 1.0 V for 30,000 cycles, (b) potential holding at 1.2 V for 400 h, and (c) potential cycling between 1.0 and 1.5 V for 5,000 cycles. The mass activity, H₂-air polarization curve, ECSA, and power density were measured at regular intervals. Detailed results of this work will be discussed in this dissertation.

TABLE OF CONTENTS

ACKNOWLEDGEMENTSii
Abstract iv
LIST OF TABLESix
LIST OF FIGURES x
CHAPTER 1 INTRODUCTION
1.1 INTRODUCTION TO FUEL CELLS
1.2 PROTON EXCHANGE MEMBRANE FUEL CELL
1.3 CATHODE CATALYST FOR PEMFC
1.4 Objectives and Outline17
CHAPTER 2 EXPERIMENTAL
2.1 CARBON SUPPORT SYNTHESIS
2.2 CATALYST SYNTHESIS
2.3 MATERIALS CHARACTERIZATION
2.4 RRDE AND CV MEASUREMENTS
2.5 PEM FUEL CELL TESTING
2.6 Accelerated Stress Test
CHAPTER 3 EFFECT OF PLATINUM LOADING ON MASS ACTIVITY OF PEMFC
3.1 CHARACTERIZATION OF THE CATALYST
3.2 EFFECT OF PT LOADING ON THE ECSA IN PEMFC

3.3 Effect of Pt Loading on H_2 -O ₂ Polarization Curves in PEMFC33
3.4 EFFECT OF PT LOADING ON MASS ACTIVITY AND SPECIFIC ACTIVITY IN PEMFC
3.5 Physical Characterization of the MEAs
3.6 DEVELOPMENT OF THEORETICAL MODEL
3.7 CONCLUSION
CHAPTER 4 DEVELOPMENT OF HIGHLY ACTIVE HYBRID CATHODE CATALYSTS FOR PEMFC
4.1 Synthesis of Carbon Composite Catalyst
4.2 DEVELOPMENT OF HYBRID CATHODE CATALYST
4.3 Electrochemical Characterization
4.4 CATALYST STABILITY UNDER POTENTIAL CYCLING BETWEEN 0.6 AND 1.0 V57
4.5 Support Stability under Potential Holding at 1.2 V60
4.6 CONCLUSION
CHAPTER 5 DEVELOPMENT OF STABLE GRAPHITIC 2 ND AND 3 RD GENERATION CCC83
5.1 Synthesis of 2^{ND} and 3^{RD} Generation CCC
5.2 Synthesis of Pt on 2^{ND} and 3^{RD} Generation CCC
5.3 Electrochemical Characterization85
5.4 SUPPORT DURABILITY STUDIES OF PT ON CCC-2 ND AND CCC-3 RD CATALYSTS86
5.5 CATALYST DURABILITY STUDY ON CO-DOPED PT/CCC-3 RD CATALYST
5.6 Conclusion
CHAPTER 6 DEVELOPMENT OF ACTIVATED CARBON COMPOSITE CATALYST (A-CCS) AND PT/A-CCS CATALYST
6.1 SYNTHESIS OF A-CCS AND PT/A-CCS113
6.2 CATALYST STABILITY114

6.3 Support Durability under Potential Holding at 1.2 V115
6.4 Support Durability under Potential Cycling between 1.0 and 1.5 V116
6.5 CONCLUSION117
CHAPTER 7 DEVELOPMENT OF HIGHLY DURABLE HYBRID CATHODE CATALYST ON A-CCS FOR PEMFC
7.1 EFFECT OF PT TO CO RATIO ON ORR CATALYTIC ACTIVITY130
7.2 EFFECT OF ANNEALING TEMPERATURE ON ORR CATALYTIC ACTIVITY DURING CO-DOPED PT FORMATION132
7.3 CATALYST DURABILITY AND SUPPORT STABILITY STUDIES ON CO-DOPED PT/A-CCS CATALYSTS
7.4 CONCLUSION
REFERENCES

LIST OF TABLES

Table 1.1. Some characteristics of important fuel cells. 21
Table 3.1. Comparison of electrochemical properties for different Pt loadings
Table 3.2. Summary of the measured values and calculated mass and specific activities of the H ₂ -O ₂ fuel cells under DOE fuel cell testing conditions43
Table 3.3. Physical characterization of the pore structure of the CL at different Pt loadings
Table 4.1. Cobalt Concentration in carbon composite catalyst obtained after the chemical leaching in 0.5M H ₂ SO ₄ solution at 80 °C, determined by XPS and ICP62
Table 4.2. Comparison of cell potential, maximum power density, and mass activity of Co- doped Pt/CCC, L-Co-doped Pt/CCC, and commercial Pt/C catalysts before and after 30,000 cycles between 0.6 and 1.0 V in 25 cm ² MEAs under fuel cell testing conditions
Table 4.3. Compositions of the Pt/CCC, Co-doped Pt/CCC, L-Co-doped Pt/CCC (Initial) catalysts, determined by ICP-MS.
Table 4.4. Compositions of the Pt/CCC, Co-doped Pt/CCC, L-Co-doped Pt/CCC (initial and 30,000 cycles in fuel cell testing conditions ⁶⁸) catalysts, determined by XRF.
Table 4.5. Comparison of cell potential, maximum power density, ECSA and mass activity losses of 30% Co-doped Pt/CCC, 30% Pt/C and commercial 46% Pt/C catalysts before and after subjecting to 1.2 V potential holding experiment in 25 cm ² MEAs under fuel cell testing conditions
Table 5.1. Physical property of CCC subjected to different treatments, including XRD, BET and ICP.
Table 5.2. Comparison of particle size, mass activity, ECSA, cell potential losses of 30% Pt/CCC-2 nd , 30% Pt/CCC-3 rd and 30% Pt/C catalysts before and after subjecting

	to 1.2 V potential holding experiment in 25 cm ² MEAs under fuel cell tes conditions.	ting
Table 6.1	1. Summary of the fuel cell performance of Pt/A-CCS catalyst before and a catalyst and support AST.	after 118

 Table 7.1. Pt to Co ratio prepared by different Co to ligand amount.
 136

LIST OF FIGURES

Figure 1.1.	Fuel Cell working mechanism. 22
Figure 1.2.	PEMFC Stack Cost Breakdown23
Figure 3.1. ((a) XRD spectrum of the 46% Pt/C catalyst. Average particle size is 2.7 nm and (b) the HR-TEM image at 20 nm resolution
Figure 3.2.	The CV measurements in MEA at different loadings. Anode: 100 % H ₂ 200 ccm, Cathode: 100% N ₂ 75 ccm, cell temperature 80° C, 100% RH46
Figure 3.3.	Effects of Pt loading on the H ₂ -O ₂ fuel cell performance at high (a) and low current (b)47
Figure 3.4.	Effect of Pt loading on the (a) specific and (b) mass activity of MEAs under DOE fuel cell operating conditions
Figure 3.5 D	Differential pore volume at 0.05 (\blacktriangle) and 0.4 mg cm ⁻² (\blacksquare) Pt loadings CCM and the catalyst free Nafion (line)
Figure 4.1.	Schematic diagram of synthesize CCC and HCC67
Figure 4.2.	HRTEM images of (a) carbon black, and (b) CCC (The scale bar is 20 nm.)
Figure 4.3.	XRD patterns of carbon precursor, and CCC69
Figure 4.4.	Polarization curves for the oxygen reduction reaction on as-received carbon black, HNO_3 -oxidized carbon, and CCC in O_2 -saturated 0.1 M HClO ₄ at room temperature. Sweep rate: 5 mV s ⁻¹ ; rotation speed: 1600rpm; carbon loading: 120 µg cm ⁻²
Figure 4.5.	Comparison of Pt deposition on CCC support with and without surface activation

Figure 4.6.	XRD patterns of Pt/CCC and commercial Pt/C catalysts72
Figure 4.7.	Transmission electron microscopy image of (a) commercial Pt/C, and (b) Pt/CCC catalysts (The scale bar is 10 nm)73
Figure 4.8.	TEM images of Pt/CCC pyrolyzed with and without protective coating74
Figure 4.9.	XRD patterns of Pt/CCC, Co-doped Pt/CCC and L-Co-doped Pt/CCC catalysts
Figure 4.10	. Cyclic Voltammograms comparison between L-Co-doped Pt/CCC and Pt/C in RDE in N ₂ -saturated 0.1 M HClO ₄ at room temperature. Sweep rate: 50 mV s ⁻¹ ; rotation speed: 1600rpm; Pt loading: 20 μ g cm ⁻²
Figure 4.11	. (a) H ₂ -air polarization curves of the PEM fuel cells, and (b) the corresponding power density prepared with 30% Co-doped Pt/CCC, and 30% L-Co-doped Pt/CCC catalysts and compared with 30% Pt/C and commercial 46% Pt/C catalysts. The fuel cell operating conditions are: H ₂ /air (2.0/2.0), 80 °C, 50% RH, 170 kPa back pressure
Figure 4.12	. H ₂ -air polarization curves and the corresponding power density of the PEM fuel cells prepared with Co-doped Pt/CCC catalyst before and after 30,000 cycles. The fuel cell operating conditions are: H ₂ /air (2.0/2.0), 80 °C, 50% RH, 170 kPa back pressure
Figure 4.13	. H ₂ -air polarization curves and the corresponding power density of the PEM fuel cells prepared with L-Co-doped Pt/CCC catalyst before and after 30,000 cycles. The fuel cell operating conditions are: H ₂ /air (2.0/2.0), 80 °C, 50% RH, 170 kPa back pressure
Figure 4.14	. H ₂ -air polarization curves and the corresponding power density of the PEM fuel cells prepared with commercial 46% Pt/C catalyst before and after 30,000 cycles. The fuel cell operating conditions are: H ₂ /air (2.0/2.0), 80 °C, 50% RH, 170 kPa back pressure.
Figure 4.15	. XEDS elemental mapping of L-Co-doped Pt/CCC catalyst (a) before and (b) after 30,000 cycles81
Figure 4.16	. XEDS particle line-scan of L-Co-doped Pt/CCC catalyst (a) before and (b) after 30,000 cycles
Figure 5.1.	X-ray diffraction patterns of carbon black and CCC subjected to different treatment

Figure 5.2. TEM image	s of CCC treated a	t (a) 800°C, (b)	900°C, (c)	1100°C and (c	l) after
stabilization	n. The scale bar in	the TEM image	is 50 nm		95

Figure 5.3.	(a) Brunauer-Emmett-Teller (BET) isotherm and (b) Barrett-Joyner-Halenda (BJH) pore size distribution of carbon black and CCC subjected to different treatment
Figure 5.4.	X-ray diffractions of Pt/CCC-2 nd and Pt/CCC-3 rd catalysts97
Figure 5.5.	Transmission electron microscopy images of (a) Pt/CCC-2 nd and (b) Pt/CCC-3 rd catalysts (The scale bar is 10 nm)98
Figure 5.6.	H_2 -O ₂ polarization curve of Pt/CCC-2 nd , Pt/CCC-3 rd and commercial Pt/C catalysts. The fuel cell operating conditions are: H_2 -O ₂ (750/750 ml min ⁻¹), 80 °C, 100% RH
Figure 5.7.	Comparison of mass activities of Pt/CCC-2 nd , Pt/CCC-3 rd and commercial Pt/C catalysts. The fuel cell operating conditions are: H ₂ -O ₂ (2.0/9.5), 80 °C, 100% RH, 150kPa back pressure
Figure 5.8.	Comparison of H ₂ /air fuel cell performance of Pt/CCC- 2^{nd} , Pt/CCC- 3^{rd} and commercial Pt/C catalysts. The fuel cell operating conditions are: H ₂ -air (2.0/2.0), 80 °C, 40% RH, 150kPa back pressure101
Figure 5.9.	Mass Activity of (a) Pt/CCC- 2^{nd} , and (b) Pt/CCC- 3^{rd} cathode catalysts before and after the support stability test (1.2 V potential holding for 400 h). The fuel cell operating conditions are: H ₂ /O ₂ (2.0/9.5), 80 °C, 100% RH, 150kPa back pressure
Figure 5.10	9. Mass Activity of Pt/C cathode catalysts before and after the support stability test (1.2 V potential holding for 25 h). The fuel cell operating conditions are: H_2/O_2 (2.0/9.5), 80 °C, 100% RH, 150kPa back pressure103
Figure 5.11	. H ₂ -Air PEM fuel cell polarization curves of (a) Pt/CCC- 2^{nd} , and (b) Pt/CCC- 3^{rd} cathode catalysts before and after the support stability test (1.2 V potential holding for 400 h). The H ₂ -air polarization performances were measured under H ₂ /air (1.5/1.8 stoic.), 80 °C, 40% RH, and 150 kPa _{abs}
Figure 5.12	. H ₂ -Air PEM fuel cell polarization curves of Pt/C cathode catalyst before and after the support stability test (1.2 V potential holding for 25 h). The H ₂ -air polarization performances were measured under H ₂ /air (1.5/1.8 stoic.), 80 °C,

- Figure 5.13. Mass Activity of Pt/CCC-2nd, Pt/CCC-3rd and Pt/C cathode catalysts at 0.9 V before and after the support stability test (1.2 V potential holding for 400 h). The values are achieved from Figures 5.9 and 5.10......106

- Figure 5.17. H₂/air fuel cell performance of (a) Co-doped Pt/CCC-3rd and (b) L-Co-doped Pt/CCC-3rd before and after 30 k potential cycling between 0.6 and 1.0V (iR-corrected cell voltage vs. current density). The fuel cell operating conditions are: H₂/air (1.5/1.8), 80 °C, 40% RH, 150 kPa back pressure......110
- Figure 5.19. (a) Mass activity comparison at 0.9V of Co-doped Pt/CCC-3rd, L-Co-doped Pt/CCC-3rd, Pt/CCC-3rd, commercial Pt₃Co/C and Pt/C cathode catalysts (The values are achieved from Figures 5.18 and 5.20 a.) and (b) current density comparison at 0.6V of Co-doped Pt/CCC-3rd, L-Co-doped Pt/CCC-3rd Pt/CCC-3rd, commercial Pt₃Co/C and Pt/C cathode catalysts (The values are achieved from Figures 5.19 and 5.20 b.) before and after 30 k potential cycling between 0.6 and 1.0V.
- Figure 6.2. X-ray diffraction patterns of A-CCC support and Pt/A-CCC catalyst......120
- Figure 6.3. H₂-O₂ polarization curves of the PEM fuel cells prepared with (a) Pt/A-CCC and (b) commercial Pt/C catalysts before and after 30,000 cycles. The fuel cell

- Figure 6.4. Mass Activity of Pt/A-CCC and Pt/C catalysts before and after 30,000 potential cycling between 0.6 and 1.0V (iR-corrected cell voltage vs. current density). The fuel cell operating conditions are: H₂/O₂ (2.0/9.5), 80 °C, 100% RH, 150kPa back pressure.
- Figure 6.5. H₂-air polarization curves and the corresponding power density of the PEM fuel cells prepared with (a) Pt/A-CCC and (b) commercial Pt/C catalysts before and after 30,000 cycles. The fuel cell operating conditions are: H₂/air (2.0/2.0), 80 °C, 50% RH, 170 kPa back pressure.

- Figure 6.10. H₂-air polarization curves and the corresponding power density of the PEM fuel cells prepared with (a) Pt/A-CCC and (b) commercial Pt/C catalysts before and after 5,000 cycles between 1.0 and 1.5 V. The fuel cell operating conditions are: H₂/air (2.0/2.0), 80 °C, 50% RH, 170 kPa back pressure. ...128

Figure 7.2. XRD patterns of Co-doped Pt/A-CCS with different Pt to Co ratios......138

- Figure 7.7. (a) H₂-air polarization curves of the PEM fuel cells prepared with Pt to Co ratio of 2:1 at different annealing temperature (iR-corrected cell voltage vs. current density) and (b) current density at 0.6 V as a function of annealing temperature. The fuel cell operating conditions are: H₂/air (2.0/2.0), 80 °C, 50% RH, 170 kPa back pressure.
- Figure 7.9. Mass activity at 0.9 V as a function of cycle number of Co-doped Pt/A-CCS catalysts with Pt to Co ratio of 2:1 annealed at 800 °C and 850 °C.145
- Figure 7.10. H₂-air polarization curves of the PEM fuel cells prepared with Co-doped Pt/A-CCS catalysts with Pt to Co ratio of 2:1 annealed at (a) 800 °C and (b) 850 °C (iR-corrected cell voltage vs. current density) before and after 30,000 cycles between 0.6 and 1.0 V. The fuel cell operating conditions are: H₂/air (2.0/2.0), 80 °C, 50% RH, 170 kPa back pressure.

Figure 7.12. H2-air polarization curves of the PEM fuel cells prepared with Co-doped Pt/A-
CCS catalyst before and after 5,000 cycles between 1.0 and 1.5 V. The fuel
cell operating conditions are: H ₂ /air (2.0/2.0), 80 °C, 50% RH, 170 kPa back
pressure148
•

CHAPTER 1

INTRODUCTION

1.1 Introduction to Fuel Cells

Like battery, a fuel cell is an electrochemical device that converts chemical energy to electrical energy via a chemical reaction. However, a fuel cell can continuously provide electricity as long as the reactant are supplied from outside of the cell, while battery needs to be recharged when all the energy stored inside is consumed [1].

1.1.1 Composition and Working Mechanism

As shown in Figure 1.1, a fuel cell contains five parts from left to right: anode, anodic catalyst layer, electrolyte, cathodic catalyst layer and cathode. The reactions happen on the electrodes where catalysts facilitate the reactions' speed.

The basic fuel on the anode side is hydrogen. Methanol or other hydrocarbons can also be used as fuels. The oxidation reaction in a fuel cell when hydrogen fuel is used is:

$$H_2 \rightleftharpoons 2H^+ + 2e^-, e^0_{H_2/H^+} = 0V$$
(1.1)

When hydrogen enters from the anode side, it is catalyzed to form protons and electrons in the anodic catalyst layer. Protons go across electrolyte, which insulates electrons, and arrive at the cathode. Oxygen is fed into cathode as an oxidant. Electrons create electrical current by passing through the external circuit to the cathode to participate the oxygen reduction reaction (ORR) as follow:

$$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O, \ e^0_{O_2/H_2O} = 1.23V$$
(1.2)

The overall reaction is:

$$H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O, \ e_{total}^0 = 1.23V$$
 (1.3)

1.1.2 Advantages of Fuel Cells

With the limited fossil fuel storage and increased power demand, renewable energy is considered to be an alternative or at least supplemental to the current energy consumption mode. Among all, fuel cell offers high energy conversion efficiency as high as 60%, compared to the traditional energy and other renewable energy, such as reciprocating engine (35%) and wind turbine (25%) [2]. Fuel cells also show the superiority in zero emission, modularity, scalability, quick installation and cogeneration operations [2, 3].

1.1.3 Types of Fuel Cells

Fuel cells classification is determined by different types of electrolyte. They are named as proton exchange membrane fuel cells (PEMFC), direct methanol fuel cells (DMFC), phosphoric acid fuel cells (PAFC), molten carbonate fuel cells (MCFC) and solid oxide fuel cells (SOFC). Table 1.1 summarizes the major characteristics of different kinds of fuel cells [1]. With different stability of electrolyte, the fuel cells have to be operated at different temperatures. PEMFC, DMFC, AFC and PAFC have either polymer or liquid as electrolyte, so they are low temperature fuel cells. Since carbonate salt and ceramic are very stable, high temperature will help the electrochemical reaction occur in MCFC and SOFC, respectively. 1.1.4 Applications and Problems in Commercialization

PEMFC is suitable for automotive applications since the solid electrolyte will not leak and it can start up quickly at low temperatures. However, the cost of the Pt catalyst is too high to commercialize [4].

Similar as PEMFC, DMFC uses methanol as fuel. It could be used in portable electronics. Methanol reduced the fuel cost, but methanol will permeate through membrane and lower the cathode efficiency [5].

AFC is used in space vehicles and provides drinking water as well. It also uses Pt as catalyst and metal carbonate formation from the atmospheric CO_2 will decrease the electrolyte conductivity by the reaction between CO_2 and electrolyte [6].

With moderate operating temperature around 200 °C, PAFC is applied for stationary power instead of portable energy device. However, as all the low temperature fuel cells, the cost of Pt catalyst is the major drawback [4].

Both MCFC and SOFC are used for large stationary power applications. But their sulfur intolerant and slow start up remain to be the problem [6].

1.2 Proton Exchange Membrane Fuel Cell

As discussed above, due to advantages of PEMFC, like low operating temperature, high power density and easy scalability, it has great potential to be used in the next generation electric vehicles if the cost and durability issues are solved.

1.2.1 Current Status

According to the U.S. Department of Energy (DOE) targets, direct hydrogen fuel cell systems for transportation should meet 65% peak-efficiency, 5,000 hour durability

with a mass production cost of \$40/kW by 2020. Currently in 2015, the system can be operated at peak energy efficiency of 60% for 3,900 hours with cost of \$55/kW [7].

1.2.2 Research Focus

As shown in the cost breakdown in Figure 1.2 [7], nearly 3 quarters of the cost comes from the Membrane Electrode Assembly (MEA), which includes catalyst and application, gas diffusion layer (GDL), membrane, and MEA frames. Besides the cost, durability, the other barrier for PEMFC application, is also related to MEA degradation [8]. Thus, great deal of efforts needs to be put into the field of MEA study.

1.2.2.1 Catalyst Layer

Pt is commonly used as the electro-catalyst in PEMFC to facilitate hydrogen oxidation reaction (HOR) on the anode and oxygen reduction reaction (ORR) on the cathode by lower the activation energy. From Figure 1.2, we can see that catalyst and application occupies almost half of the cost. Carbon supported Pt was developed to increase the Pt utilization and lower Pt loading [9]. Solubilized ionomer is introduced as binder and proton conductor to the catalyst layer. Therefore, the normal catalyst ink composition contains catalyst, solvent and ionomer. The highly dispersed ink will be transferred to be a catalyst layer between membrane and GDL. Researchers at Los Alamos National Lab found that different solvent can contribute to different ionomer morphology which results in the variation of MEA stability under accelerated stress test (AST) [10, 11]. All these efforts lead the Pt loading to decrease from 3-4 mg/cm² to 0.4 mg/cm² with acceptable performance [12].

Since the electrochemical HOR is facile on Pt catalyst with an exchange-current density, i_0 , of the order of 10^{-3} A/cm² [13], anode loadings as low as 0.05 mg_{Pt}/cm² are

possible without significant cell voltage losses for fuel cell operation with pure H₂ [14]. To satisfy the 2020 DOE target of 0.125 mg_{PGM}/cm^2 loading total per MEA for automotive fuel cells, the major research focus draws on the decrease of cathode Pt catalyst loading or exploration of non-precious metal catalyst and improve the catalyst activity and durability. 1.2.2.2 Membrane

As a solid electrolyte, proton exchange membrane should offer high proton conductivity, high mechanical stability, zero electrical conductivity, high oxidation resistance, and low gas permeability [1]. Nafion[®] membrane from DuPont Company is the most outstanding commercialized PEM electrolyte. The backbone structure of polytetrafluoroethylene (PTFE) is responsible for the stability while the sulfonic acid groups (SO₃H) replace sulfonyl fluoride groups (SO₂F) on the side chain to provide proton conductivity. To further reduce the transfer resistance, thinner membrane is developed. However, the mechanical stability and H₂ cross-over affect the membrane lifetime [15]. Extensive research has been carried out to overcome these problems and to reduce cost, such as modification of Nafion[®] membrane with inorganic compound to increase the dimension stability and water uptake[16], and development of alternative membranes like hydrocarbon membranes with high temperature tolerance [17, 18].

1.2.2.3 Gas Diffusion Layer

GDL plays an important role in maintaining the three phase equilibrium in PEMFC. It allows gas reactants and proper amount of water to reach the catalyst layer. On the other hand, it avoids too much water accumulation with a PTFE coating to stop the electrochemical reaction. Therefore, better water management and cost reduction is required for GDL research by optimization of thickness, PTFE content, and morphology [19-21]. Since GDL is made from carbon paper, stability at high potentials (>1.2 V) also needs to be considered [15, 22, 23].

1.3 Cathode Catalyst for PEMFC

Due to the sluggish kinetics of ORR and high potential at the cathode side, the activity and durability of cathode catalyst restrict the PEMFC commercialization besides the high cost of Pt. Especially, for automotive applications, the cathode catalyst should be able to retain both the catalyst stability and support durability.

1.3.1 Catalyst Support

1.3.1.1 High Surface Area Carbon

High surface area (HSA) carbon like carbon black is widely used as the catalyst support to improve Pt utilization because of its good electric conductivity, pore structure for Pt anchorage, high surface area for uniform Pt particle dispersion and low cost [24]. Though carbon corrosion reaction starts above 0.207 V as follow in the presence of water,

$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-, e^0 = 0.207V$$
 (1.4)

carbon is inert material in acidic media, carbon corrosion rate is slow at relatively low temperature (60-80 °C) under normal PEMFC working conditions at 0.6-0.7 V [25]. However, for automotive PEMFC applications, local fuel cell starvation can cause water electrolysis and carbon oxidation on the anode and repetitive shutdown/startup may lead the cathode interfacial potential difference to nearly 1.5 V which accelerates carbon corrosion as well [26, 27]. Moreover, Pt on carbon speeds up the corrosion [28, 29]. Electrochemical oxidation of carbon supports results in carbon support loss which leads to Pt particle detachment, agglomeration and sintering and subsequent loss of electrochemical surface area (ECSA) of Pt-based catalysts [30-32]. Carbon oxidation can increase the hydrophilicity of the surface which results in higher mass transfer resistance [33]. Carbon support loss also causes a decrease in catalyst layer thickness which increases the cell resistance [34] due to poor electrical contact with the gas diffusion layer [35, 36]. The corrosion occurs much more on defects which is more present on high surface area carbon with high amorphicity [37].

1.3.1.2 Graphitic Carbon

Low surface area graphitic carbon has been taken into account for automotive application at high potentials for its larger average graphitic crystallites and less defects [38]. Carbon nanotube (CNT) [39, 40], carbon nanofiber (CNF) [40, 41], and graphene or graphene oxide [42, 43] have been proved with higher support stability comparing to HSA carbon by using both a rotating ring disk electrode (RRDE) and PEMFC. Andersen et al. [40] studied the thermal and electrochemical stability of CNF, CNT and Vulcan XC-72 and reported better durability of CNF and CNT, following the order that CNF>CNT>Vulcan XC-72. The electrochemical durability of single-walled carbon nanotube (SWNT) and multi-walled carbon nanotube (MWNT) is compared by cyclic voltammograms (CV) and X-ray photoelectron spectroscopy (XPS) before and after potentiostatic holding at 1.2V for 120 hours [39]. The results show lower oxygen content and better stability for MWNT than that for SWNT. Modified graphene exhibits 2-3 times higher durability than Pt/CNT and commercial Pt/C after potential step method (1.4 V 10 s to 0.85 V 5 s) for 44 hours [42].

Though the graphitic carbons improved the support stability at high potential operating conditions, the power density shows lower value compared to that of HSA carbons due to uneven Pt dispersion [40, 42]. Therefore, proper activation is necessary for

7

low surface area graphitic carbon support. The most common way for carbon activation is concentrated nitric acid oxidation to introduce carboxylic acid groups (COOH) into carbon surface which act as Pt anchorage sites. Jha et al. [44] activated SWNTs with varied amount of COOH groups by high temperature concentrate nitric acid oxidation. The Pt on functionalized SWNT shows better performance than that on Vulcan XC-72. Among all, the Pt on SWNT with low degree of functionalization illustrates best ORR activity with optimized BET surface area and amount of COOH groups. Ghosh et al. [45] synthesized graphene particles and functionalized the graphene with citric acid oxidation, there is chance to decrease the carbon electrical conductivity and corrosion resistance. Besides the chemical oxidation method to functionalize the support, support activation can also be carried out by coating with polymer [46, 47], covalent modification with ionic liquids [48, 49], and non-covalent functionalization by pi-pi interaction [50-52].

1.3.1.3 Non-carbonaceous Supports and Their Hybrid Support

To solve the support oxidation problem completely, non-carbonaceous material was studied as support for fuel cell. Titanium oxide (TiO_x) [53-58], tin oxide (SnO_x) [59-61], tungsten oxide (WO_x) [62-64] and tungsten carbide [63, 65, 66] supports are extensively explored on the performance and stability after Pt deposition. Wesselmark et al. [67] compared the polarization curve and electrochemical surface area (ECSA) of sole Pt and Pt on Sn, Ti, Zr, W and Ta before and after 1000 cycles between 0.6 and 1.2V. Only Pt on SnO_x exhibits initial activity higher than sole Pt. However, all Pt on metal oxide catalysts show lower performance than sole Pt after AST, except Pt on WO_x. The enhanced activity may be attributed to less oxide coverage on Pt surface.

Due to the low surface area and low electrical conductivity [68], the catalyst on non-carbonaceous support illustrates lower performance than that on carbon [59]. Doping metal oxide with n-type material can improve the electrical conductivity [69]. Huang et al. [54] synthesized Nb-doped Ti oxide with high conductivity of 1.11 S/cm. The Pt on this support shows similar performance as Pt/C. It also exhibits ten times higher activity after AST.

To combine the advantages of carbon and non-carbon supports, extensive research has been done on hybrid supports as well [70, 71]. Pt on N-doped carbon @ silica improves the electrical conductivity with N-doped carbon and can be self-humidified resulting from introduction of silica [72]. Liu et al. [73] prepared PtAu/C with different amounts of TiO_x. The PtAu/C durability is improved by the enhanced Pt-support interaction in the presence of TiO_x. Similar effect is found on SnO₂ on improvement of Pt/C durability [74].

1.3.2 Pt Catalyst

Platinum, due to its low overpotential and high catalytic activity, is currently used for hydrogen oxidation at the anode and oxygen reduction reaction (ORR) at the cathode in PEMFCs [75]. The requirements for fuel cell lifetime significantly vary for different applications; 5000 h for cars, 20,000 h for buses, and 40,000 h of continuous operation for stationary applications [76].

Platinum-based catalysts dissolve when the cathode is subjected to potential cycles during fuel cell operation. According to Pt Pourbaix diagrams, Pt dissolution can occur in a narrow potential and pH window near 1 V vs. RHE [77, 78]. A kinetic model developed by Darling and Meyers [79] indicated that platinum dissolution in PEMFC is fairly

negligible at low and high potentials but significantly large at intermediate potentials. The effect of potential on Pt dissolution was explained by considering three possible reactions:

$$Pt \to Pt^{2+} + 2e^{-} \tag{1.5}$$

$$Pt + H_2O \rightarrow PtO + 2H^+ + 2e^- \tag{1.6}$$

$$PtO + 2H^+ \to Pt^{2+} + H_2O \tag{1.7}$$

The model showed that the equilibrium concentration of dissolved Pt decreased between 1.1 and 1.5 V due to the formation of passivating oxides at high potentials [79].

Potential cycling is generally used for cleaning the catalyst surface and to activate the MEAs before evaluating the catalyst performance in PEMFC. As mentioned earlier, Pt dissolves at higher potential regions when subjected to potential cycling [77-80]. Platinum dissolution in phosphoric acid and sulfuric acid has been studied by Ota et al [81].

Improving the electrocatalytic activity and durability of Pt-based catalysts with low Pt content towards ORR is one of the main challenges in advancing the performance of PEMFCs. Different mechanisms for Pt dissolution and redeposition on the catalyst surface and Pt migration through the surface have been suggested to explain the increase of the catalyst particle size over exposure time. The thermodynamic driving force for agglomeration/sintering and Ostwald ripening is the reduction in surface energy accompanying particle growth [82]. This phenomenon leads to dissolution of smaller particles and growth of larger particles.

Accelerated durability test (ADT) has been used to evaluate the durability of Pt catalysts in a three-electrode cell employing either a rotating ring electrode (RDE) or a rotating ring disk electrode (RRDE). This procedure usually allows degradation in the catalyst activity to be observed within several days, rather than several weeks otherwise

required before any significant decrease in fuel cell performance is noticed [83]. Advances in the synthesis of porous and hollow Pt nanostructures as cathode catalysts for PEMFCs have been reported [84, 85]. Zhang et al. [85] showed extremely high activity and stability for porous dendritic Pt nanotubes under potential cycling between 0.6 and 1.2 V in O₂-saturated 0.5 M H₂SO₄. The porous dendritic Pt nanotubes exhibited 4.4 fold improved catalytic activity and 6.1 fold durability up to 4000 cycles when compared to a commercial Pt/C catalyst. Inaba [86] reviewed the durability and mechanisms of degradation of electrocatalysts in PEMFCs. The degradation phenomena of cathode catalysts using a square wave potential cycling protocol between 0.6 and 1.0 V indicated only Pt dissolution without affecting the carbon support. The square wave potential cycling significantly decreased the ECSA after 10,000 cycles.

However, the catalyst durability studies in three-electrode studies in flooded electrolyte is very different from the actual fuel cell operating conditions and provide only a fundamental understanding of Pt-based catalysts degradation under potential cycling conditions. A more reliable means of acquiring in-depth knowledge would be the performance evaluation of Pt catalysts in MEAs subjected to potential cycling experiment and measuring the decay in mass activity, ECSA, and H₂-air fuel cell performance [87-96].

The electrocatalyst durability under simulated automotive drive cycle by utilizing various simplified potential cycle profiles in a 25 cm² MEA was reported by Uchimura et al [94]. Based on the results a hypothesis was made to attribute the higher dissolution under higher anodic sweep rates to the lower coverage of Pt with oxides which exposed bare Pt to high potentials.

It has been reported that the square wave cycling (SWC) offers accelerated degradation when compared to triangular wave cycling (TWC) [78, 97]. The effect of TWC and SWC on the catalyst durability was studied by Marcu et al. [98]. The study showed that the number of cycles in SWC was responsible for the performance losses, while in TWC the transitional testing time is responsible for the loss.

The Pt/C catalyst stability in PEMFCs has been reported in the literature by measuring the fuel cell performance under H₂-air [87-89, 91, 95] or under H₂-O₂ [90, 93]. The fuel cell performances were evaluated after subjecting to TWC [87, 89, 90, 93, 95] or SWC [88, 91, 95]. The potential cycling experiments were performed either under H₂-N₂ [87, 89-91, 93, 95] or under H₂-air [88] supplied to the anode and cathode compartments, respectively.

A systematic study on the impact of Pt particle size and operating conditions on PEMFC cathode catalyst durability was carried out by Yang et al. [95] using MEAs with 0.2 mg cm⁻² Pt loading on both the anode and cathode. The results indicated that ~ 12 nm particles resulted in practically no change ECSA or mass activity up to10 k cycles with low fuel cell performance at high current density regions. The smaller Pt particles (~2 nm) showed very good initial performance and high losses of ECSA, mass activity, and potential loss at high current densities. The MEA prepared with ~7 nm Pt particle showed very good initial performance and very slow electrode decay characteristics. The fuel cell performance under constant flow of H₂ and air (1000/2000 sccm) at 80 °C and 150 kPa back pressure showed potential loss of 25-30 mV at 0.8 and 1.5 A cm⁻² after 30,000 cycles between 0.6 and 1.0 V. A very stable H₂-air fuel cell performance with less than 30 mV loss at 0.8 and 1.5 A cm⁻² was achieved when the MEA was cycled at low relative humidity

(RH) conditions (30% RH) up to 10,000 cycles. The slow decay for the 7 nm particle catalyst was attributed to the particle stability.

Arisetty et al [87] investigated the effect of Pt loading on Pt catalyst durability using commercial MEAs having 0.15 and 0.4 mg cm⁻² Pt loading at the cathode and 0.05 mg cm⁻² Pt at the anode. The authors observed high ECSA loss for the MEA with 0.15 mg cm⁻² Pt when compared to the MEA having 0.4 mg cm⁻² Pt. The authors concluded that 70% of the observed 54 mV cell voltage loss at 1.0 A cm⁻² after 30,000 cycles was resulted from the reduced mass transfer coefficient in the catalyst layer of the MEA with 0.15 mg cm⁻² Pt.

Kim et al. [89] have reported the effect of dispersing medium, such as water-2propanol mixture, N-methyl pyrrolidone (NMP), and glycerol, used for catalyst ink preparation, on the catalyst durability. The H₂-air fuel cell performance measured under constant flow (200/500 sccm H₂/air supplied to anode/cathode) at 30 psig back pressure exhibited only 20 mV for the catalyst ink prepared with glycerol and 178 mV loss for the commercial MEA at 0.8 A cm⁻² after 70,000 cycles. The authors have postulated that the microstructure of the electrode dictated by polymer-solvent interactions largely determines the durability rather than Pt particle growth.

The durability for 40% Pt/graphitic carbon catalyst under simulated fuel cell automotive operating conditions i.e. potential cycling under H₂/air atmosphere has been reported by Dhanushkodi et al. [88] SWC with 3 s at 0.6 followed by 3 s at 1.0 V was used to study Pt dissolution at 40, 60, and 80 °C. Significant loss in ECSA was observed during the first 1000 cycles at all the temperatures. Cell potential loss of ~ 30, 35, and 90 mV were observed at 1.7 A cm⁻² after 20,000 cycles at 40, 60, and 80 °C, respectively. The authors

have developed a diagnostic expression to estimate the kinetic activity losses using effective platinum surface area using cyclic voltammograms which indicated that the performance loss is mainly due to Pt loss.

Other durability studies have reported the H₂-O₂ fuel cell performance after performing potential cycling experiment on Pt nanostructure and Pt/C. However, these studies do not provide any useful information on the durability of Pt-based catalysts since PEMFCs for transportation applications are operated under H₂-air. The study of electrocatalytic activity and durability of carbon supported Pt nanodendrites showed H₂-O₂ fuel cell performance loss of 59.5% at 0.6 V after 20,000 cycles between 0.6 and 1.0 V [90]. The performance loss was attributed to the collapse of Pt nanodendrite structure due to potential cycling. The effect of operating conditions on Pt catalyst durability under 0.4-1.0 V potential cycling indicated the impact of cycle number on Pt agglomeration than the sweep rate and MEA size [93]. Ohyagi et al. [93] suggested that the Pt agglomeration degradation occurs in a flooding area in a cell plane under load change operating conditions.

1.3.3 Modified Pt Catalyst

In order to achieve high catalytic activity and to overcome the sluggish ORR kinetics at the cathode, well-defined alloys [99-102], core-shell type [103-109] and porous Pt nanostructure [84, 85] catalysts have been used as cathode catalysts in PEMFCs. However, the durability of Pt and Pt-based alloy catalysts still does not meet the demand from the automobile manufacturers [110].

A number of studies have been reported in the literature for the degradation of Pt and Pt-alloy cathode catalysts performance degradation using three-electrode cell [83, 86, 98, 110-119] and membrane electrode assembly (MEA) [87-96, 120]. The losses in catalyst mass activity (in A/mg_{Pt}), electrochemical surface area (ECSA, in m^2/g_{Pt}), and fuel cell performance under H₂-O₂ or H₂-air were used to evaluate the catalyst stability.

An ADT was used by Colon-Mercado et al. [83] to evaluate the durability of Pt₃Ni/C at various fixed potentials. Their study showed a direct correlation between performance degradation and Ni dissolution in 0.3 M H₂SO₄. A study of evaluation of stability and durability of Pt/C and Pt-Co/C catalysts showed that repetitive potential cycling (RPC) between 0.5 and 1.0 V resulted in Pt and Co dissolution and re-deposition of pure Pt on the Pt-Co particles [113]. The ORR activities of Pt and Pt-Co after RPC were found to be similar after 1000 cycles.

The effect of nanoporosity formation in PiNi₃ bimetallic catalyst during acid leaching on the catalytic activity and durability was studied by Gan et al. [114, 115]. The results indicated that O₂-free acid leaching enabled the suppression of nanoporosity which significantly increased the catalytic activity and catalyst durability up on potential cycling between 0.6 and 1.0 V. The PtNi₃ leached in the presence of N₂ showed a mass activity loss of 24% and a specific activity loss of 26% after 30,000 potential cycles in an RDE [114].

The catalytic activity and the durability of well-defined Pd@Pt core-shell nanoparticles with various shell thickness was evaluated by Choi et al. [116] in O₂-saturated 0.1 M HClO₄ at room temperature at a scan rate of 50 mV s⁻¹ using a potential cycle experiment between 0.6 and 1.2 V vs. RHE. The results indicated that the Pd@Pt nanoparticles with a shell thickness of 0.94 nm exhibited enhanced activity and stability up

to 20,000 cycles due to the lower OH_{ad} bonding strength when compared to pure Pt catalysts.

Pt monolayer (PtML) on electrodeposited Pd nanostructures such as Pd nanorods (Pd_{NR}) and Pd nanowires (Pd_{NW}) on oxidized carbon (Cox) support was used as an advanced electrocatalyst for PEMFCs [117]. The catalyst synthesis and the durability studies were performed in a three-electrode cell using glassy carbon RDE. Potential cycling studies indicated excellent stability for the $Pt_{ML}/Pd_{NW}/Cox$ catalyst with no negative shift in the polarization curve and 38% ECSA loss after 30k cycles. However, synthesis of Pt monolayer catalysts using RDE will yield a few milligram of the catalyst and is not feasible for large-scale production to meet the demand of automotive manufacturers.

Yu et al. [96] reported one of the earlier studies in evaluating the durability of PtCo/C cathode catalyst in a dynamic fuel cell environment with continuous water fluxing on the cathode. A potential cycling test between 0.87 and 1.2 V vs. RHE was applied to study the effect of cobalt or platinum dissolution on the cell performance. The results indicated that cobalt dissolution did not have any negative influence in terms of reduced cell voltage and the membrane conductance. Their study showed that the fuel cell performance enhancement of PtCo/C over Pt/C catalyst was sustained over 2400 cycles and the overall performance loss of the PtCo/C membrane electrode assemblies (MEAs) was less than that of the Pt/C MEA. The authors concluded that the potential cycle testing accelerated the cobalt dissolution which was supported by the observed catalyst activity loss in the first 400 potential cycles.

The impact of particle size and heat treatment on the durability of Pt and Pt-alloy catalysts under potential cycling (0.6-1.0 V) conditions was examined by Makharia et al.

16

[92]. The results indicated that poorly dispersed Pt/C catalyst with increased particle size showed reduced Pt surface area loss when compared to well-dispersed Pt/C. The authors observed similar ECSA loss after ~ 25,000 cycles for heat treated Pt/C and PtCo/C catalysts hiaving particle sizes of 4-5 nm. They assumed that the improved voltage-cycling stability of Pt-alloy catalyst is due to both its larger particle size and an intrinsically higher stability of the Pt-alloy catalyst when compared to pure Pt catalyst.

The catalyst durability is largely affected when subjected to SWC conditions [78, 88, 91, 97] Li et al. [91] studied the stability of Pt and PtPd hybrid catalysts supported on a nitrogen-modified carbon composite (NMCC) support by cycling the cathode between 0.7 for 30 s and 0.9 for 30 s under H₂-N₂ atmosphere. They have reported potential losses of 18.7, 5.3, and 1.2% for the Pt/C, Pt/NMCC, and Pt₃Pd₁/NMCC catalysts, respectively, at 0.8 A/cm². The higher stability for the Pt₃Pd₁/NMCC catalyst was attributed to the synergistic effect of NMCC and Pt by forming PtCo alloy during heat treatment, and the large particle sizes which are more resistant to Ostwald ripening and particle coalescence. A very high cell potential loss of ~210 mV at 0.8 A cm⁻² after 10,000 cycles has also been reported for a Pt/C catalyst when SWC between 0.4 V for 10 s and 1.05 V for 10 s was employed [95].

1.4 Objectives and Outline

Based on the catalyst durability studies available in the literature, it is evident that Pt-based catalysts are not stable under PEMFC operating conditions and Pt degradation occurs through Pt dissolution/re-deposition and Ostwald ripening mechanisms. Pt-based alloy catalysts appear to provide enhanced ORR activities. Formation of transition metal (TM) subsurface atoms in Pt-TM phases lead to weakened interactions between Pt and adsorbents such as OH_{ads} and H_{upd} . The altered Pt electronic structure decreases oxygen binding energy which not only increases the activity but also enhances the catalyst durability with less oxygenated intermediates covered on the Pt surface to induce Pt dissolution [121-125]. Consequently, Pt oxidation onset potential shifts to a higher value. The observed shift of the onset for Pt oxidation will increase kinetic mass activity due to less presence of Pt oxide on Pt at high potentials which has much lower exchange current density (i°= 1.7×10^{-10} A/cm²) compared to pure Pt (i°= 2.8×10^{-7} A/cm²). Since PtO₂ dissolves during potential cycling conditions according to the following reaction,

$$PtO_2 + 4H^+ + 2e^- \to Pt^{2+} + H_2O \tag{1.8}$$

Thus, less PtO₂ formation due to higher onset Pt oxidation potential alleviates Pt dissolution and enhances the catalyst stability.

However, due to galvanic corrosion and high anodic overvoltage for transition metal under operational conditions, the transition metal leaches out which results in contamination of the catalyst interface and the membrane. The un-leached Pt-alloy catalysts may show very good stability under potential cycling but low H₂/air fuel cell performance due to a protective passive layer on the Pt catalyst particles. Furthermore, the catalyst supports play an important role in determining the overall stability of the catalyst, since porous carbon supports is prone to corrode at low pH at the cathode interface, high temperature, and high anodic potentials (1.0-1.5V) at the cathode interface during start-up/shutdown cycles. Electrochemical oxidation of carbon at potentials between 1.0 and 1.5 V results in carbon loss leading to Pt agglomeration and sintering and subsequent loss of electrochemical surface area (ECSA). Carbon supports with high degree of graphitization as support materials is proved to be effective ways to improve the catalyst durability.
However, the durability studies of Pt and Pt-based alloy catalysts with ultra-low loading $(0.1-0.2 \text{ mg}_{Pt} \text{ cm}^{-2})$ in practical fuel cells are scarce. Most of the catalyst and support durability studies available in the literature do not fulfill the automotive PEM fuel cell requirements described by U.S. DRIVE Fuel Cell Tech Team in "Cell Component Accelerated Stress Test Protocols for PEM Fuel Cells." [126].

The objectives of the present investigation are to synthesize hybrid cathode catalysts (HCC) and metal-doped HCC using catalytically active and stable partially graphitized carbon composite catalyst (CCC) and graphitized activated carbon composite (A-CCC) supports and evaluate their performance using 0.1 mg_{Pt} cm⁻² loading according to U. S. DRIVE Fuel Cell Tech Team protocols [126]. The CCC and A-CCC supports show high activity for oxygen reduction reaction due to the presence of non-metallic active sites for ORR. The HCCs are a combination of Pt and CCC or A-CCC supports which show enhanced ORR activity through synergistic effect.

The support stability will be enhanced through optimization of: (i) Brunauer-Emmett-Teller (BET) surface, (ii) the support structural properties (amorphous/crystalline ratio), and (iii) the hydrophilic/hydrophobic ratio of the supports.

Highly active and durable hybrid cathode catalysts for PEM fuel cell was developed through: (i) synthesis of highly catalytically active and stable Co-containing CCC and activated carbon composite catalyst, A-CCC supports, (ii) surface functionalization and uniform Pt deposition on CCC and A-CCC supports, (iii) performance optimization of Co-doped Pt catalysts by using a protective coating to inhibit particle agglomeration and growth during the pyrolysis step, (iv) optimization of Pt/Co ratio and annealing temperature, and (v) chemical leaching to remove excess metal used to dope the support. The performance and durability of the catalyst was evaluated using RDE and 25 cm² membrane electrode assemblies (MEAs). Stability of the catalyst was tested under (a) potential cycling between 0.6 and 1.0 V for 30,000 cycles, (b) potential holding at 1.2 V for 400 h, and (c) potential cycling between 1.0 and 1.5 V for 5,000 cycles. The cell potential, ECSA, and power density was measured at regular intervals.

Table 1.1. Some characteristics of important fuel cells.

	PEMFC	DMFC	AFC	PAFC	MCFC	SOFC
Primary	Automotive and	Portable power	Space vehicles	Stationary	Stationary	Vehicle
applications	stationary power		and drinking	power	power	auxiliary power
			water			
Electrolyte	Polymer	Polymer	Concentrated	Concentrated	Molten	Yttrium-
	(plastic)	(plastic)	(30-50%) KOH	100%	Carbonate	stabilized
	membrane	membrane	in H ₂ O	phosphoric acid	retained in a	Zirkondioxide
					ceramic matrix	
					of LiAlO ₂	
Operation	50-100°C	0-60°C	50-200°C	150-220°C	600-700°C	700-1000°C
temperature						
range						
Charge carrier	H^+	H^+	OH-	H^+	$CO_3^=$	O ⁼
Prime cell	Carbon-based	Carbon-based	Carbon-based	Graphite-based	Stainless steel	Ceramic
components						
Catalyst	Pt	Pt-Pt/Ru	Pt	Pt	Ni	Perovskites
Primary fuel	H ₂	Methanol	H ₂	H ₂	H ₂ , CO, CH ₄	H ₂ , CO
Start-up time	Sec-min	Sec-min		Hours	Hours	Hours
Power density	3.8-6.5	~0.6	~1	0.8-1.9	1.5-2.6	0.1-1.5



Figure 1.1. Fuel Cell working mechanism.



Figure 1.2. PEMFC Stack Cost Breakdown.

CHAPTER 2

EXPERIMENTAL

2.1 Carbon Support Synthesis

2.1.1 Synthesis of Oxidized Carbon

6 g of the Ketjenblack EC-300J was refluxed with the mixture of 420 mL of 70% nitric acid and 180 mL of DI water for about 7 h at 85-90 °C. The solution was filtered and washed thoroughly with 2 L DI water. The sample was collected and dry in the vacuum oven overnight.

2.1.2 Synthesis of Carbon Composite Catalyst

Carbon composite catalyst, denoted as CCC, was synthesized by the drop-wise addition of Cobalt-N chelate complex onto the oxidized carbon dispersed in de-ionized water under vigorous stirring. The resulting CCC was subjected to heat-treatment in argon starting from 800 °C to 1100 °C, followed by leaching in 0.5M H₂SO₄ at 80 °C for 2 hours to remove excess Co on the carbon surface.

The CCC treated at 1100 °C was named as CCC-2nd to distinguish with the lower temperature heated CCC since the CCC-2nd support exhibits higher graphitization degree.

CCC-2nd was subjected to a purification and stabilization procedure to remove the electrochemically unstable amorphous carbon in the support [127, 128] and named as CCC-3rd.

2.1.3 Synthesis of Activated Carbon Composite Catalyst

Activated carbon composite catalyst (A-CCC) was synthesized using the same purification and stabilization procedure to remove the electrochemically unstable amorphous carbon with a different carbon base material.

Different weight percentages of Co were encapsulated into A-CCC by varying the ratio of Cobalt-N chelate complex and A-CCC to get different Pt to Co ratio in the Co-doped Pt/A-CCC catalysts.

The Co-doped CCC and A-CCC supports are used for Pt/CCC and Pt/A-CCC catalysts synthesis.

- 2.2 Catalyst Synthesis
- 2.2.1 Synthesis of Carbon Supported Pt Catalyst

A surface functionalization process to increase the hydrophilic property of CCC and A-CCC was developed using a bifunctional organic molecule containing aromatic hydrocarbon and acid groups. The surface modification process is necessary to control the Pt catalyst particle size as well as the uniform distribution of platinum over the support surface. The Pt/C and HCC were synthesized using a modified polyol method [59]. A desired amount of PtCl₄ was dissolved in 200 mL of ethylene glycol followed by dispersing carbon, CCC or A-CCC supports in the solution. 0.2 M NaOH was used to adjust the pH of the solution to 12. Next, the solution was refluxed at 160 °C for 3 h in an inert atmosphere. The resulting Pt/C, Pt/CCC or Pt/A-CCC catalysts were rinsed with de-ionized water and dried under vacuum at 80 °C for 12 hours.

2.2.2 Synthesis of Carbon Supported Co-doped Pt Catalyst

Co-doped Pt/CCC or Co-doped Pt/A-CCC catalyst was synthesized by encapsulating the Pt/CCC or Pt/A-CCC sample with a protective coating followed by heattreatment under reducing or inert atmosphere at 800 °C. During the controlled heating process, the Co incorporated in to the CCC support diffuses to the surface and forms the Co-doped Pt catalyst. In the final step, the Co-doped Pt/CCC catalyst treated in inert atmosphere was leached in 0.5M H₂SO₄ at 80 °C (named as L-Co-doped Pt/CCC). Commercial catalyst, a 46.4wt % Pt/C catalyst (TEC10E50E), purchased from Tanaka Kikinzoku Kogyo K.K, Japan was used to compare the performance and stability of the catalysts synthesized in this study.

2.3 Materials Characterization

X-ray diffraction (XRD, Rigaku 405S5) patterns were recorded to identify the crystalline structure of the supports and HCC catalysts. Brunauer-Emmett-Teller (BET, Quantachrome) was used to determine the surface area and pore-size distribution of the supports. X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD) was used to confirm the presence of pyridinic–type nitrogen active sites in the supports. High resolution transmission electron microscopy (HRTEM, Hitachi H9500) was used to determine the particle size and particle dispersion of the HCC catalysts. X-ray fluorescence spectroscopy (XRF, Fischer XDAL) was used to measure Pt and Co amounts in HCC (in wt. %) and the Pt loading (in mg_{Pt} cm⁻²) in the anode and cathode electrodes. Inductively coupled plasma (ICP, Perkin Elmer) analysis was used to determine the composition of the HCC catalysts. Energy-dispersive X-ray spectroscopy (XEDS) was used to analyze the Co-doped Pt structure in the HCC catalysts.

The porosity of the catalyst coated membrane (CCM) was measured by a mercury porosimeter (Micromeritics Autopore 9500). The cumulative pore volume as a function of pore diameter was determined from the mercury intrusion data, i.e. the volume of mercury penetrating into the pores versus the applied pressure. Under the assumption that all pores are cylindrical, the pore diameter d_p was calculated from the value of the applied pressure p using the capillary law [129].

$$d_p = \frac{4\gamma\cos\theta}{p} \tag{2.1}$$

where γ and θ denote the surface tension of mercury and the contact angle between mercury and the sample.

2.4 RRDE and CV Measurements

Electrochemical characterization studies were performed using a three-electrode cell and Pine bipotentiostat (Model AFCBP1). A rotating ring-disk electrode with a Pt ring and a glassy carbon disk (0.196 cm²) was used as the working electrode. Pt-mesh was used as the counter electrode, and an Ag/AgCl [0.255 V vs. reversible hydrogen electrode (RHE)] was used as the reference electrode. All the electrochemical characterization studies in three-electrode cell were performed in 0.1 M HClO₄. The catalyst ink was prepared by blending the catalyst powder (carbon, CCC, HCC or Pt/C) with ethanol in an ultrasonic bath. The carbon loading was 120 μ g_{Carbon} cm⁻² on the glassy carbon disk and Pt loading was 20 μ g_{Pt} cm⁻². 5 μ L of 0.25% Nafion[®] solution was added on top of the catalyst layer to minimize anion adsorption effects on the catalysts. Cyclic voltammograms (CVs) recorded in nitrogen at a scan rate of 50 mV s⁻¹ were used to obtain the background capacitive currents and electrochemical surface area (ECSA) of the Pt catalysts.

The ECSA of Pt-based catalysts was determined by charge integration under the hydrogen desorption peaks appearing between 0 and 0.35 V, by assuming a charge of 210 μ C cm⁻² for the electroactive Pt surface [130]. The specific ECSA was calculated based on the following equation:

$$Specific ECSA = \frac{Q_H}{m \times q_H}$$
(2.2)

where Q_H is the charge for hydrogen desorption, m is the Pt metal loading, and q_H is the charge required for desorbing a monolayer of hydrogen on Pt surface. After the ECSA measurements, the electrolyte was purged with oxygen for 30 min prior to the oxygen reduction reaction kinetics measurement using linear sweep voltammetry (LSV) at a scan rate of 5 mV s⁻¹. The oxygen reduction current was calculated from the difference between currents measured in the nitrogen- and oxygen-saturated electrolytes.

2.5 PEM Fuel Cell Testing

The catalyst inks for the anode and cathode were prepared by blending the catalysts (Pt/C or HCC) in isopropyl alcohol and Nafion[®] solution (5% solution, Alfa Aesar) in an ultrasonic bath. Commercially available carbon paper (SGL 10 BC) was used as the gas diffusion media for the anode preparation. The cathode catalysts were directly deposited onto the Nafion[®] NRE 212 membrane. The anode and cathode catalyst loading was fixed at 0.1 mg_{Pt} cm⁻² and confirmed using XRF. The catalyst-coated anode electrode was hot-pressed onto the blank side of the cathode catalyst-coated membrane at 140 °C for 3 min under 200 psi to form the membrane electrode assembly (MEA). A blank SGL 10 BC carbon paper was used as the gas diffusion media on the cathode side. Initially, the MEA was activated under the supply of H₂ and O₂ at 80 °C to the anode and cathode cataloge compartments, respectively with a flow rate of 750 mL min.⁻¹ and 100% relative humidity

(RH). The catalyst mass activity and polarization studies were performed under H_2/O_2 and H_2/air , respectively at 80 °C. Other fuel cell operating conditions are provided in respective figures.

2.6 Accelerated Stress Test

The electrochemical durability of the Pt/C and HCC cathode catalysts were examined using AST protocols suggested by U.S. DRIVE Fuel Cell Tech Team [126]. The tests were carried out in a single cell with an electrode area of 25 cm². During the experiment, pure hydrogen (200 cc min.⁻¹) and nitrogen (75 cc min.⁻¹) having 100% RH were supplied to the anode and cathode compartments, respectively.

To determine the stability of the carbon supported Pt catalyst, the cathode side of the cell is subjected to three different testing protocols: (i) 30,000 potential cycles between 0.6 and 1.0 V at 50 mV s⁻¹ at a cell temperature of 80 °C; (ii) applying 1.2 V constant potential to the cathode with respect to the anode for 400 h at a cell temperature of 80 °C under 150kPa_{abs} back pressure; (iii) 5,000 potential cycles between 1.0 and 1.5 V at 500 mV s⁻¹ at a cell temperature of 80 °C. Periodic measurements of polarization curve and ECSA were performed to determine the electrochemical stability of the Pt/C and HCC catalysts. The catalyst mass activity was evaluated under H₂/O₂ (2/9.5 stoic.) at 80 °C, 100% RH, and 150 kPa_{abs} back pressure. The polarization curves were recorded under H₂/air (2/2 stoic.) at 80 °C, 50% RH, and 170 kPa_{abs} back pressure.

CHAPTER 3

EFFECT OF PLATINUM LOADING ON MASS ACTIVITY OF PEMFC

If the use of PEMFC in transportation becomes a reality, the large required amount of Pt/C catalyst will cause an enormous increase of Pt demand that will result in a dramatic increase in platinum price. In the recent years, to alleviate this problem, research has been conducted at improving catalyst activity and durability while decreasing the catalyst cost through developing a catalyst with ultra-low platinum loading. The ultimate research goal is to develop a cathode catalyst with platinum group metal content (PGM) lower than 0.2 g PGM kW⁻¹ and approach 0.1 g PGM kW⁻¹. The parameters for catalyst activity at decreasing loading, however, have not yet been universally studied.

Gasteiger et al. [14] in their study of the dependence of polymer electrolyte membrane (PEM) fuel cell performance at three different Pt catalyst loadings (0.4, 0.24, and 0.15 mg_{Pt} cm⁻²), have concluded that mass activity (MA) and ECSA (utilization) in cathode catalyst membranes (CCMs) are essentially independent of Pt loading. Saha et al. [131] found that the utilization of a printed CCM layer decreased as the loading of the catalyst layer increased from 0.02 to 0.12 mg cm⁻². Lee et al. [132] observed that the mass activity measured in membrane electrode assemblies (MEAs) is only 10-30% of the ring disk electrode (RDE) mass activity, and increased as loading decreased while the utilization was held constant. They concluded that O₂ may access the catalyst particles more effectively when it exhibits thin layer geometry, or higher porosities at lower loadings.

Debe [133] concluded that the enhanced oxygen reduction reaction (ORR) activity of the Nano Structured Thin Film (NSTF) 3M catalysts is a result of asymmetrical surface area distribution. The asymmetrical surface area controls the gas velocity distributions in the Knudsen regime, which results in an additional pre-exponential scaling factor in the Butler-Volmer equation dependent on a distance metric describing the catalyst surface area distribution. The catalyst loading influenced the surface enhancement factor (SEF) and consequently the scaling factor.

Siddique et al. [134] developed catalyst layer microscopic model mimicking the experimental fabrication. The variation of the number of agglomerates varied the ECSA due to reduced connectivity and increased isolation. Large agglomerates correspond to insufficient mixing of ionomer and Pt/C and consequently limited triple phase boundaries. Too small agglomerate size may lead to the loss of connectivity or entanglement between them.

According to recent studies, the electrode fabrication method has a profound effect on optimal Pt loadings and utilization [110, 135-138], therefore the measurable mass activity also. Numerous studies were performed, but no final agreement has been achieved. Therefore, in this work we studied both (MA) and specific activity (SA) in detail for a better understanding of the effects of the catalyst loading on these parameters.

3.1 Characterization of the Catalyst

Figure 3.1 shows the XRD and TEM image of the Pt/C catalyst. It is shown, that the catalyst deposited uniformly on the surface of the carbon support. The particle's average diameter was calculated by using the Debeye-Scherrer equation. The average

31

particle diameter was found to be 2.7 nm. The thin layer-RDE method revealed that the ECSA is 85 m² g⁻¹, which is very close to the theoretically expected value.

3.2 Effect of Pt Loading on the ECSA in PEMFC

Figure 3.2 exhibits the hydrogen adsorption and desorption peaks in the cyclic voltammograms recorded for different cathode Pt loading in a 25 cm² MEAs. The total charge for the hydrogen adsorption/desorption increased as the Pt catalyst loading increased in the MEAs. As expected, the current in the double layer region also increased with an increase in the Pt loading. The specific electrochemical surface area of Pt was calculated using Equation 2.2 by integrating the charge under hydrogen desorption peaks appearing between 0.05 and 0.35 V (vs. Ag/AgCl). The ECSA was calculated by assuming a charge of 210 μ C cm⁻² required for the desorption of a monolayer of H⁺ on a smooth Pt planar electrode surface. The ECSA values given in Table 3.1 show a decrease in the ECSA with an increase in the Pt loading which indicates that A_{Pt,el} (ECSA) depends on the Pt loading. The increase in the ECSA at lower catalyst loading (0.05 mg_{Pt} cm⁻²) may be attributed to the fact that the Pt catalyst particles are uniformly distributed as a thin catalyst layer on the Nafion[®] membrane with minimum particle agglomeration. This increases the availability of Pt catalyst active sites for oxygen reduction resulting in maximum catalyst utilization. Table 3.1 also demonstrates that the catalyst utilization for different MEAs decreased from 82.56% to 48.33% when the Pt loading is increased from 0.05 to 0.4 mgPt cm⁻². The utilization of the Pt catalyst depends on how effectively the catalyst particles are connected to: (i) the ionic conductor Nafion[®] membrane and (ii) the electronic conductor gas diffusion layer (GDL). If the thickness of the catalyst layer increases, the probability of the percolation of the reactants through the catalyst layer may decrease. Hence, the reactants may not reach the Pt catalytic sites that are far away from the Nafion[®] membrane/GDL interface resulting in lower catalyst utilization at higher catalyst loadings.

3.3 Effect of Pt Loading on H₂-O₂ Polarization Curves in PEMFC

Figure 3.3 presents the effect of 46% Pt/C loading on the current density. The fuel cell was operated at 80 °C under H₂/O₂ (750/750 ml min⁻¹), 100% RH and ambient pressure to measure the initial performance of MEAs with different Pt loadings under H₂/O₂. The catalyst mass activity was determined using the experimental conditions suggested by the U.S. DRIVE Partnership, Fuel Cell Technical Team Cell Component Accelerated Stress Test and Polarization Curve Protocols for Polymer Electrolyte Membrane Fuel Cells. The fuel cell testing conditions are: 80 °C under H₂/O₂ (2/9.5 stoic.), 100% RH and 150 kPa_{abs}. The operating conditions are also given in the figures. The fuel cell performance was evaluated using MEAs prepared with Pt loadings of 0.05, 0.1, 0.2, 0.3 and 0.4 mg cm⁻², respectively. Both the high and low current increases as the loading increases, but the increase is more substantial when the loading increases from 0.05 to 0.2 mg cm⁻². As expected, the current density measured at 0.9 V (iR-corrected) decreases from 0.035 A cm⁻² to 0.012 A cm⁻² measured for Pt loadings between 0.4 mg cm⁻² and 0.05 mg cm⁻².

3.4 Effect of Pt Loading on Mass Activity and Specific Activity in PEMFC

Mass activity is defined as the normalized current density measured at 0.9 V (iR-corrected) divided by the cathode PGM loading in A mg_{PGM}^{-1} . The MA, catalyst loading (L), specific activity (SA), specific electrochemical surface area (ECSA), or surface enhancement factor (SEF) can be calculated if three of the five parameters are known by using the following equations:

$$MA = \frac{I_{0.9V}}{L}$$
(3.1)

$$SA = \frac{I_{0.9V}}{L \cdot ECSA_{MEA}}$$
(3.2)

$$SEF_{MEA} = ECSA_{MEA} \cdot L \tag{3.3}$$

where $i_{0.9V}$ is the current density measured at 0.9 V_{iR-free} and normalized to the geometrical surface area (A cm⁻²), here L is specifically the Pt loading (mg cm⁻²), SEF_{MEA} is the surface enhancement factor (cm_{Pt}² cm⁻²), SA is the specific activity (A cm_{Pt}⁻²) and MA is the mass activity (A mg_{Pt}⁻¹).

MA is evaluated by Tafel-equation. This equation is valid under the assumption that the surface area of the individual particles can be linearly added and is linearly proportional to the mass of the catalyst.

$$\eta = \text{TS}\log(j_{cell} + j_{\text{H}_2}) - \text{TS}\log(\text{ECSA} \cdot m_{\text{Pt}} j_0)$$
(3.4)

where TS is the Tafel slope, j_{cell} is the measured total cell current density (A cm⁻²), j_{H2} is the hydrogen crossover current density, which is measured to be a value of 3.3 mA cm⁻² according to literature [14]. m_{Pt} is the Pt cathode loading (mg_{Pt} cm⁻²).

Eq. (3.4) requires the polarization of the CCMs with different Pt loadings, and when

plotted the following should yield identical slopes: $E_{iR-free}$ vs. the $log(\frac{j_{cell} + j_{H_2}}{m_{p_t}})$ or $E_{iR-free}$ vs. log of mass activity A m_{Pt}^{-1} (the mass specific current density, j_m). With this

assumption, the cathode performance is controlled only by the ORR kinetics and the Ohmic losses (R_{Ω}) , or:

$$\left[\frac{\Delta E_{iR-free}}{\Delta \log(i_m)}\right]_{PO_2, PH_2, T, A_{Pt, el}} = -TS$$
(3.5)

Figure 3.4 shows the MA and SA at different loadings. An increase of MA up to 0.23 A mg_{Pt}⁻¹ was observed for 0.05 mg_{metal} cm⁻² loadings, compared with a MA of 0.085 A mg_{Pt}⁻¹ measured for Pt loadings of 0.4 mg cm⁻². However, as shown in Table 3.2 and the prediction of Eq. 3.4, the MA increases when the loading decreases which may be related to the increase in ECSA from 41.08 to 70.18 m² g⁻¹. The ECSA increase is a consequence of the catalyst utilization (Table 3.1) calculated from the ECSA of the thin-layer film RDE. The effect of the ECSA can be evaluated, by substituting the current density with the specific current. The result shows (Table 3.2) that the SA increased from 213 μ A cm⁻²Pt to $342 \,\mu\text{A cm}^{-2}\text{Pt}$ when the loading decreased from 0.4 mg cm⁻² to 0.05 mg cm⁻². The MA and SA increased by a factor of 2.7 and 1.6, respectively while, the ECSA increased to 1.7 times from its original value. This implies that the ECSA only partially accounted for the increase in MA. Consequently, the structure of the active layer or the reaction path may have also changed. Inaba et al. [139] showed that the increase of Pt loading altered the agglomeration of the Pt/C catalyst on RDE disk. Bonakdarpour [140] varied the loadings on nanostructured thin film catalysts (3M), and found that the reaction mechanism of the ORR changed. The lower loadings or increased catalyst agglomeration altered the reaction path of the ORR, which was attributed to the sparsely distributed active sites. The slopes of the log i_{Pt} -V and log i_m -V plots were almost identical to the theoretically expected values for the different Pt loadings, which indicate that the MEAs were kinetically controlled and the reaction path did not change. Consequently, the increased MA points out that the MA curves cannot be reasonably predicted by Eq. 3.4, therefore the polarization curves obtained in this study for 46% Pt/C catalyst cannot be fitted with Eq. 3.4.

According to the experimental results, the MA is controlled not only by R_{Ω} and the ORR kinetics, but also by the utilization of the Pt surface area which in turn depends on the cathode Pt loading shown in Table 3.1. The MA is also controlled by the morphology of the catalyst layer which depends on the self-assembled nature of the catalyst and how effectively it fills out the volume.

3.5 Physical Characterization of the MEAs

Table 3.3 shows the specific surface area, the average pore size, the porosity of the catalyst layer at different loadings. The data clearly shows that the loading highly influenced the physical properties of the catalyst layer. The specific surface area decreased from 754 to 212 m² g⁻¹ as the loading increases from 0.05 to 0.4 mg cm⁻². It suggests that the newly deposited particles stick to the previous ones and screen each other's surfaces.

The variation of the pore diameter is shown in Figure 3.5. At 0.05 mg cm⁻² loadings the pore size between the agglomerates is less than 10 nm, but at higher loadings (0.4 mg cm⁻²) it shifts to around 40 nm. Simultaneously, the pores smaller than 20 nm diminish. The porosity was almost the same between 39% and 42 % at 0.05 and 0.4 mg cm⁻¹ loadings, respectively. At 0.05 mg cm⁻² the porosity shows a higher value (39%) than 0.1 mg cm⁻² (31%), probably because the particles first coat the membrane and after 100% coverage they start to overlap with the previous layers. Above 0.1 mg cm⁻² a clear increasing trend is shown from 31% to 47% as the loading increases from 0.1 mg cm⁻² to 0.4 mg cm⁻².

3.6 Development of Theoretical Model

The results can be explained by taking into account that in PEM fuel cells, the catalyst forms triple phase boundaries (TPB) in a 3D structure of gas, catalyst, and electrolyte, which makes the experiments and the evaluation of the data more complex than

for simply flooded agglomerates [141]. Agglomerate and macro-homogeneous models have been developed to model the polarization curve. However they have no general solution, different asymptotic solutions have been derived. One of the first solutions was developed by Perry and Newman et al. [142]. When both diffusion and proton migration are not limiting (as in the kinetic region), the following expression can be derived:

$$i = -i_0 a_{P_t} \frac{c}{c_0} l_{CL} \exp\left(-\frac{\alpha F}{RT} \cdot \eta^c\right)$$
(3.6)

where a_{Pt} (cm² cm⁻³) is the area of the active catalyst per unit volume, i_0 (A cm⁻²) is the exchange current density, and l_{CL} (cm) is the catalyst layer thickness (theoretical value), α the symmetry factor of the charge transfer, c (mol cm⁻³) is the oxygen concentration at the catalyst interface, and c_0 (mol cm⁻³) is the reference concentration. This model, however, does not take the Pt loading into consideration.

Jaouen [143] et al. developed a spherical agglomerate model and also determined the asymptotic solutions. In the kinetic region it was found that:

$$i = -a_{Pt}i_0 l_{CL} \frac{c}{c_0} (1 - \varepsilon_1) (1 - \varepsilon_2) \exp\left(-\frac{\alpha F}{RT} \cdot \eta^C\right)$$
(3.7)

where ε_1 is the polymer volume fraction inside the agglomerate, and ε_2 is the gas-phase porosity (macroporosity), *T* is the temperature (K) and *R* is the universal gas constant. In his model the current depends on the structure of the active layer. The general theory of dimensionless analysis and asymptotic solutions were developed by Gyenge [144], but in the kinetic region he derived the same relationship as Eqs.3.4-3.5.

The Pt active area per unit volume is commonly determined by [145, 146]

$$a_{\rm Pt} = \frac{m_{\rm Pt} v_{\rm Pt} \rm ECSA_{\rm RDE}}{W_{\rm CL}}$$
(3.8)

where ECSA_{RDE} is the specific ECSA of the catalyst ($m^2 g^{-1}$), measured using thin-layer RDE and v_{Pt} is the catalyst utilization. The thickness, W_{CL} (cm), can be calculated by assuming the conservation of volume. This model indicates that the ECSA and the structure are independent of the loading, and consequently leads to the same linear scaling approach between loading and the volumetric specific surface area as the Tafel-approximation, i.e. *a*_{Pt} is independent of the loading. Contrarily, Gu et al. [12] concluded that Pt and C act as the structural element, while the ionomer essentially fills out the voids. Pt particles smaller than 1.7 nm are mainly incorporated into the pores, but bigger particles (3-5 nm) are mainly found on the surface [147]. Zhang et al. [148] also concluded that Pt particles are in the mesopores and Nafion primarily presents on the external surface, blocking the micropores but not the macropores. Gode et al. studied the effects of Nafion loading by using different porosimerty and simulation techniques [149]. First, they observed that the increase in Nafion ratio did not increase the layer thickness linearly. Second, Nafion first covered the micropores (<2 nm) and later the meso- and macropores. These result indicate, that the volume, and the thickness depend on how the catalyst layer formed and how the particles connect to eachother, and how they fill out the volume. Therefore Eq.3.8 should be precisely calculated as the quotient of the total surface area of the catalyst (A_{tot}) and the total volume of the catalyst layer (V_{tot}).

$$a_{\rm Pt} = \frac{A_{tot}}{V_{tot}} = \frac{ECSA \cdot M_{\rm Pt}}{V_{tot}} = ECSA(M_{\rm Pt})\rho_{\rm Pt}(M_{\rm Pt})$$
(3.9)

where M_{Pt} (mg) is the total Pt loading and $\rho_{\text{Pt}}(M_{\text{Pt}})$ (mg cm⁻³) is the loading dependent Pt density in the agglomerates or in the CL. Eq. 3.8 is valid only if the ECSA and the ρ_{Pt} are to be independent of the loading. However, the measured data shown in Table 3.1 indicate

that the ECSA depends on the loading. The catalyst density may also depend on the loading which were summarized previously according to [146-149]. Introducing a non-linear scaling factor, similar to the utilization of the ECSA (Table 3.1), Eq. 3.9 can be rewritten into the following form

$$a_{\rm Pt} = ECSA \cdot v_{\rm MEA} \rho_{\rm Pt} P_{\rm MEA} \tag{3.10}$$

where v_{MEA} is the catalyst utilization (%) of the MEA at different loadings and P_{MEA} is the non-linear scaling factor (%). While ρ_{Pt} now does not depend on the loading, it can be calculated by dividing it with the geometrical surface area:

$$\rho_{\rm Pt} = \frac{M_{\rm Pt}}{V_{\rm CL}} = \frac{m_{\rm Pt}}{W_{\rm CL}}$$
(3.11)

and Eq. 3.8 becomes

$$a_{\rm Pt} = ECSA \cdot v_{MEA} \frac{m_{\rm Pt}}{W_{CL}} P_{MEA}$$
(3.12)

where the W_{CL} is the average thickness predicted by the spherical agglomerate model. The real thickness of the catalyst layer is very difficult to determine by STEM measurement, because the surface of the CL is very rough (non-uniform).

The combination of the asymptotic solutions of the macro homogeneous and agglomerate models Eq. 3.6-3.7 and the new form of the surface area per unit volume of the cathode CL Eq. 3.12, renders the log i-V relationship with the following general form

$$\eta_0 = TS \ln \left[\frac{j_{cell}}{\text{ECSA} \cdot v_{\text{MEA}} i_0 P_{MEA} m_{\text{Pt}}} \left(\frac{c_{REF}^{O_2}}{c_{GDL}^{O_2}} \right)^{\gamma} \right]$$
(3.13)

Substituting $\frac{j_{cell}}{m_{Pt}} = i_m$ with the mass specific current and using the log identities we reach

$$\eta = TS \ln(i_m) - TS \ln\left(\text{ECSA} \cdot v_{\text{MEA}} i_0 P_{\text{MEA}} \left(\frac{c_{GDL}^{O_2}}{c_{REF}^{O_2}}\right)^{\gamma}\right),$$
(3.14)

Also including $\frac{j_{cell}}{ECSA \cdot v_{MEA}m_{Pt}} = i_{Pt}$ we reach

$$\eta = TS \ln(i_{P_t}) - TS \ln\left(i_0 P_{MEA} \left(\frac{c_{GDL}^{O_2}}{c_{REF}^{O_2}}\right)^{\gamma}\right)$$
(3.15)

which are both Tafel-type equations, however the constants are different from the original Tafel equation. It is evident that the non-linear scaling factor influences both the MA and SA.

3.7 Conclusion

Our experimental data showed that the electrochemical specific surface area (ECSA), MA, and SA all increase as the loading decreases. The increase of the ECSA is attributed to the increase of the utilization of the catalyst as they are closer to the membrane and to the GDL in a thinner layer. The increase of the ECSA indicates that the commonly applied Tafel-approximation cannot be fitted to our result, because the MA and SA are controlled not only by R_{Ω} and the ORR kinetics, but also by the utilization of the catalyst, which in turn depends on catalyst loading, and the structure of the catalyst layer, the degree of agglomeration, and screening of the catalyst particles.

A detailed and more precise definition of mass activity (MA) and specific activity (SA) was given to elucidate the variation of MA and SA with catalyst loading. The asymptotic solution of the agglomerate macro homogenous model has been applied in order to elucidate the dependence of MA and SA on catalyst loading. In the spherical agglomerate model, the surface area per unit volume is regarded as independent of the loading, however as in the case of the ECSA, it may also depend on the loading and the thickness of the CL. A new non-linear scaling factor has been introduced which considers the effect of the loading on the volumetric agglomerate density. The parameters of the semi-empirical function have been determined by non-linear fitting. The scaling factor was found to be exponentially dependent on the loading. Finally, the loading dependent Tafel equation has been derived. This model contains both the utilization and the non-linear scaling factor. First principle model will be developed in our future work which will explain quantitatively the dependence of mass activity on the loading.

Table 3.1.	Comparison	of electrochemica	al properties for	different Pt loadings.	

Pt loading	Current Density	ECSA	Utilization
/ mg cm ⁻²	@0.9V _{iR-free}	Fuel Cell/RDE	/ %
	/ A cm ⁻²	$/ m^2 g^{-1}$	
0.05	0.012	70/85	82
0.1	0.0185	68/85	80
0.2	0.03	64/85	75
0.3	0.0321	48/85	56
0.4	0.035	41/85	48

Table 3.2. Summary of the measured values and calculated mass and specific activities of the H_2 - O_2 fuel cells under DOE fuel cell testing conditions.

Pt loading	Tafel slope	Specific activity	Mass activity
/ mg cm ⁻²	/ V dec ⁻¹	$/ \mu A cm_{Pt}^{-2}$	/ mA mg ⁻¹
0.05	-0.065	343	240
0.1	-0.065	272	185
0.2	-0.063	234	150
0.3	-0.064	223	107
0.4	-0.063	213	87.5

Loading	Specific surface area	Pore diameter	Porosity
	$/ m^2 g^{-1}$	/ µm	/ %
0.05	754	0.012	39
0.1	557	0.011	31
0.3	244	0.044	34
0.4	212	0.0391	43

Table 3.3. Physical characterization of the pore structure of the CL at different Pt loadings.



Figure 3.1. (a) XRD spectrum of the 46% Pt/C catalyst. Average particle size is 2.7 nm and (b) the HR-TEM image at 20 nm resolution.



Figure 3.2. The CV measurements in MEA at different loadings. Anode: 100 % H_2 200 ccm, Cathode: 100% N_2 75 ccm, cell temperature 80°C, 100% RH.



Figure 3.3. Effects of Pt loading on the H_2 - O_2 fuel cell performance at (a) high and (b) low current.



Figure 3.4. Effect of Pt loading on the (a) specific and (b) mass activity of MEAs under DOE fuel cell operating conditions.



Figure 3.5 Differential pore volume at 0.05 (\blacktriangle) and 0.4 mg cm⁻² (\blacksquare) Pt loadings CCM and the catalyst free Nafion (line).

CHAPTER 4

DEVELOPMENT OF HIGHLY ACTIVE HYBRID CATHODE CATALYSTS FOR PEMFC

Stable and highly active hybrid cathode catalyst (HCC) has been developed by us at USC that shows higher fuel cell performance than the commercial Pt/C catalyst with low Pt loading of 0.4 mg cm⁻² [91, 150, 151]. Therefore, the objective of this work is to decrease the platinum loading in cathode electrodes through optimization of both the synergetic effect in the HCC catalyst and implementation of more active doped Pt catalyst. The goal is to maintain the high ORR activity with ultra-low Pt loading in fuel cells by combining the catalytic activity of the CCC used as support and Pt active sites. In this study, CCC is not only an ORR active support, but also a transition metal source to form Pt shell transition metal rich core catalyst to further improve the activity. The HCC is expected to show optimum performance at high potential (0.9 $V_{iR-free}$) under H₂/O₂ and at high current regions (0.6 $V_{iR-free}$) under H₂/air fuel cell operating conditions.

4.1 Synthesis of Carbon Composite Catalyst

Figure 4.1 illustrates the schematic diagram of the approach used to synthesize CCC and HCCs. Surface modification on the carbon support introduces oxygen and nitrogen groups on the surface. The metal-catalyzed pyrolysis increases the carbon graphitization degree in the presence of cobalt at high temperatures (800~900 °C), introduces Co in the carbon matrix, and introduces nonmetallic active sites on the carbon surface Next, the

chemical leaching removes excess of metal used to dope the support. Modified polylol process was used for uniform platinum deposition. After Pt deposition, the Co doped in the CCC diffuses to the surface to form Co-doped Pt catalysts during heat-treatment in the presence of polyaniline protective coating. The heat-treatment process was optimized to control the particle size between 3-5 nm, resulting in compressive Pt-lattice catalyst having Pt-shell/doped metal core structure with different metal doping content from 7-15%.

In our previous studies, partially graphitized CCC supports showing very good ORR activity were synthesized at relatively low temperatures [152]. Figure 4.2 (a) and (b) presents the HRTEM images of the carbon black and leached CCC, respectively. In Fig. 4.2 (a), carbon black exhibits the normal amorphous carbon structure. However, as a result of Co catalyzed pyrolysis, a nanostructured tube or fiber of graphitic carbon is formed, as shown in Fig. 4.2 (b). It is clear that Co particles are encapsulated by the graphitic carbon substrates even after chemical leaching.

Figure 4.3 illustrates the powder XRD patterns for the high surface area carbon black and the carbon composite catalyst. Co peaks are observed in the CCC support. The intensity of graphitic carbon peak (0 0 2) appearing at 26° is narrow and sharp for CCC support, which confirms the HRTEM results showing graphitic carbon morphology for the support. The formation of graphitic carbon increases both the electronic conductivity and the support stability in fuel cell operating conditions at high potentials, high humidity and low pH [153, 154]. The BET surface areas of CCC and A-CCC decreased from 800 m² g⁻¹ (carbon black) to 400 m² g⁻¹.

The ORR kinetics of as-received carbon (Ketjen black), oxidized Ketjen black and CCC are compared in Figure 4.4. The onset potential for ORR increases when the as-

received carbon is subjected to various surface modifications including oxidation in HNO₃ and incorporation of nitrogen and transition metals. The carbon composite catalyst showed an onset potential of 0.85 V vs. RHE and well-defined kinetic and mass transfer regions in 0.1 M HClO₄ electrolyte at room temperature.

Our previous studies have shown the formation of graphitic- and pyridinic- type nitrogen groups on the carbon surface by the X-ray photoelectron spectroscopy [155-160]. Although there is a disagreement on the active sites for the ORR in non-precious metal catalysts, it is generally believed that transition metal such as Fe or Co may introduce nitrogen groups (pyridinic-N, pyrrolic-N, and graphitic-N) on the carbon surface with a strong Lewis basicity [158, 161]. The increased electron-donor ability of the N-doped carbon weakens the O-O bond via the bonding between oxygen and nitrogen and/or the adjacent carbon atom and consequently increases the catalytic activity towards ORR [161]. Table 4.1 summarizes the cobalt concentration in the CCC support obtained after the chemical leaching in 0.5M H₂SO₄ solution at 80 °C determined by XPS and ICP-AES. XPS detected no metal traces from the leached carbon composite catalyst while ICP-AES analysis shows 12.7 wt.% Co. Since the escape depth of photoelectrons is a few nanometers, XPS analysis provides only the surface composition of the CCC [158, 162]. Therefore, it is evident that Co particles are removed from the CCC surface and exist only in the bulk of the carbon. The results obtained in this study are in agreement with our previously published work that the nitrogen-doped in the carbon matrix is presumably the primary active site for the ORR [155-160].

4.2 Development of Hybrid Cathode Catalyst

The HCC was synthesized by depositing Pt nanoparticles onto the CCC support to prepare the Pt/CCC catalyst. After the metal-catalyzed pyrolysis, the carbon surface becomes too hydrophobic due to the formation of graphitic nanostructures which do not facilitate uniform Pt deposition on the support. Therefore, a surface modification process was developed to control the Pt catalyst particle size within 3-5 nm and uniform distribution over the CCC supports. The most common method is oxidation of carbon supports in acid to increase the hydrophilicity [163]. However, strong acids will corrode the carbon support and increase the support acidity and CO_2 formation which will decrease the catalyst stability [112, 163]. In this study, we have used a non-covalent functionalization on carbon surface via π - π interaction. The non-covalent functionalization involves a bifunctional molecule which is adsorbed onto the inherently hydrophobic graphitized surfaces of the supports. The bifunctional molecule contains a pyrenyl group and a carboxylic acid functional group. The pyrenyl group, being highly aromatic in nature, is known to interact strongly with the basal plane of graphite via π - π interaction thus immobilizing the bifunctional molecule on the surface of carbon. Carboxylic acid functional groups attached to the pyrenyl group endow hydrophilic characterization with the graphitized carbon which is the same effect obtained from the acidic treatment. The grafting of oxygen-containing groups onto the CCC support surface endows a negative charge and creates the electrostatic stability required for a colloidal dispersion [163]. The effectiveness of surface functionalization on graphitic carbon supports is clearly seen in Figure 4.5. Without surface activation, half of the carbon surface is free of Pt particles and Pt aggregation is observed where Pt is deposited. After surface activation, Pt nanoparticles are uniformly disperse over the entire graphitic carbon surface.

Figure 4.6 compares the X-ray diffraction patterns of Pt/CCC and commercial Pt/C catalysts. The XRD patterns of the HCC catalysts show the characteristic diffraction peaks of the face centered cubic structure for Pt at $2\theta = 39.7$, 46.2, 67.8, 81.4° that correspond to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes, respectively. The particle sizes of the Pt/CCC and commercial Pt/C catalysts are calculated to be 2.2 and 2.0 nm, respectively, using the peak width of Pt (2 2 0) by Debye–Scherrer equation [53].

The HRTEM images shown in Figure 4.7 present the particle size distribution of commercial Pt/C and Pt/CCC catalysts, respectively. The particle size increases as the surface area of the carbon support decreases. Pt particles are dispersed uniformly on the partially graphitic CCC support due to the surface functionalization. The Pt particle size distribution shown in Figure 4.7 confirms the average particle sizes calculated using XRD data.

It has been reported that the Pt-alloy particle size can increase as high as 20 nm after heat-treatment at 800 °C [164]. In order to control the particle-size growth and inhibit particle agglomeration, a novel protective-coating methodology with polyaniline was developed for the synthesis of Co-doped Pt/CCC during high temperature pyrolysis process. In order to study the effectiveness of the polyaniline protective coating, the Pt/CCC catalyst was pyrolyzed at 800 °C for 60 min in the presence of protective coating and at 800 °C for 30 min without protective coating. The HRTEM images of these two catalysts are compared in Figure 4.8. It is important to note that the Pt/CCC catalyst heated for 30 min. in the absence of polyaniline protective coating resulted in particle

54
agglomeration and Pt particle size growth (5-8 nm). On the other hand, the catalyst obtained after pyrolysis at 800 °C for 60 min. with the polyaniline protective coating showed very uniform particle distribution with an average particle size of \sim 3.5 nm.

As described earlier, the novelty of the catalyst synthesis is to diffuse Co, which is already incorporated in to the graphitic carbon matrix, into Pt to form Co-doped Pt catalyst during heat-treatment as reported in our previous studies [91, 165]. This procedure is much simpler than the conventionally used impregnation method which uses excess amount of transition metal salts for impregnating Pt/C catalyst followed by heat-treatment to make PtM₃ (M = Cu, Co, Ni) catalyst [114, 115, 166-169]. The unreacted transition metals are then leached out in strong acids for longer duration [166-169]. In our studies, the chemical leaching was carried out for a shorter duration (~30 to 60 min) to remove excess transition metal particles from the surface to prepare leached Co-doped Pt/CCC (L-Co-doped Pt/CCC) catalyst.

Figure 4.9 compares the X-ray diffraction of fresh, heat-treated (Co-doped Pt/CCC), and leached (L-Co-doped Pt/CCC) catalysts. The XRD pattern of the fresh Pt/CCC catalyst shows the characteristic diffraction peaks of the face centered cubic structure at $2\theta = 39.7$, 46.2, 67.5, 81.4° that correspond to (111), (200), (220) and (311) planes, respectively. The diffraction peaks shift to higher Bragg angles, which illustrate a decreased lattice constant due to the formation of Co doped Pt catalysts. Moreover, the diffraction peaks became sharper after post treatment, indicating the increase in crystallite sizes. The particle sizes of the fresh Pt/CCC and treated catalysts are calculated to be 2.2 nm and 3.5 nm, respectively, using the peak width of Pt (220) by Debye–Scherrer equation.

4.3 Electrochemical Characterization

The mitigation of Pt dissolution mechanism is studied by comparing the CVs of L-Co-doped Pt/CCC and pure Pt/C catlysts. Pt surface structure tends to undergo modifications with sublayer transition metal leading to weakened interactions between Pt and adsorbates [121, 125]. A 60 mV shift of Pt oxidation peak is observed after Co-doping which indicates that the Pt compressive lattice catalyst experiences less electrochemical oxidation than pure Pt. Therefore, besides the oxidation potential shifts, the ECSA calculated by H desorption/adsorption also reduced 3 times.

Figure 4.11 (a and b) presents the H₂-air polarization curves and corresponding power density curves for 30% Pt/CCC, 30% Co-doped Pt/CCC, and 30% L-Co-doped Pt/CCC in comparison with in-house 30% Pt/C and commercial 46% Pt/C catalysts as cathodes with Pt loadings of 0.1 mg cm⁻² in single PEM fuel cells (25 cm² MEAs). The fuel cell was operated at 80 °C under H₂/air (2.0/2.0 stoic.), 50% RH and 170 kPa_{abs} back pressure. The current densities are 1420, 1370, 1730, 1200, 1200 mA cm⁻² at 0.6 V_{iR-free} with maximum power densities of 944, 857, 1050, 757, 746 mW cm⁻² for the Pt/A-CCC, Co-doped Pt/CCC, L-Co-doped Pt/CCC, Pt/C and commercial Pt/C, respectively. Figure 4.11 (a and b) indicates that all the HCCs perform better in H₂-air than in-house 30% Pt/C or commercial 46% Pt/C catalysts, especially in the mass transfer region. The enhancement in the performance proves the existence of synergistic effect between the catalytically active CCC support and Pt or doped-Pt catalysts. Moreover, after the removal of excess Co on the surface by chemical leaching, the L-Co-doped Pt/CCC displays the highest ORR activity due to the formation of altered Pt electronic structure by Co-doping [52, 170]. The other phenomena we observed is the activity increase at high potential for the L-Co-doped Pt is 2.4 times higher than Pt (0.47 A mg⁻¹ for L-Co-doped Pt vs. 0.18 a mg⁻¹ for Pt), but only 1.4 times (1730 mA cm⁻² for L-Co-doped Pt vs. 1200 mA cm⁻² for Pt) at low potential due to the fact that Pt oxide has less ORR catalytic activity compared to pure Pt. Due to less presence of Pt oxide at high potentials on the compressive Pt surface, the performance in the kinetic region increases as shown with higher mass activity at 0.9V. However, at 0.6 V where only pure Pt works as ORR catalyst, so the performance increase is not significant.

4.4 Catalyst Stability under Potential Cycling between 0.6 and 1.0 V

To investigate the Pt catalyst stability in PEM fuel cells under 100% RH and 80 °C cell temperature, potential cycling experiment (0.6-1.0 V for 30,000 cycles) was performed on the HCC and Pt/C catalysts [126]. Figures 4.12, 4.13 and 4.14 present the polarization curves of Co-doped Pt/CCC and L-Co-doped Pt/CCC and commercial Pt/C catalysts before and after 30,000 cycles under H₂-air (2.0/2.0 stoic.) operating conditions. The stability of the Co-doped catalysts is better than commercial Pt/C catalyst. After 30,000 potential cycles between 0.6 and 1.0 V, the Co-doped Pt/CCC and L-Co-doped Pt/CCC catalysts showed 40 and 65 mV loss, respectively at 800 mA cm⁻². It has been reported that the altered Pt electronic structure decreases oxygen binding energy which not only increases the activity but also enhances the catalyst durability with less oxygenated intermediates covered on the Pt surface to induce Pt dissolution [170].

Table 4.2 summarizes the catalyst stability results such as cell potential loss, power density loss, and mass activity loss of the catalysts synthesized in this investigation in comparison with commercial Pt/C. The calculation of loss of mass activity and the

degradation rate are outlined in Table 4.2. The mass activity in the kinetic region shows values higher than 0.44 A mg_{Pt}⁻¹ for Co-doped Pt/CCC indicating higher ORR catalytic activity than Pt/C catalyst due to the change in Pt electronic structure [52, 170]. The initial and final mass activities of Co-doped Pt/CCC catalyst are 0.44 and 0.25 A mg_{Pt}⁻¹ (43% mass activity loss), respectively. The activity and stability of mass activity for this catalyst meet the 2017 DOE technical targets (initial value ≥ 0.44 A mg_{Pt}⁻¹ and final value ≥ 0.26 A mg_{Pt}^{-1}). Under the same condition, the commercial catalyst showed 0.18 and 0.08 A mg_{Pt}^{-1} (55% mass activity loss) before and after AST, respectively. On the other hand, the mass activity degradation rate per cycle of Co-doped Pt/CCC is 6.33×10^{-6} A mg_{Pt}⁻¹ cycle⁻¹, while that of Pt/C is 3.33×10^{-6} A mg_{Pt}⁻¹ cycle⁻¹. The Co-doped Pt/CCC catalyst exhibits the highest cell voltage at 800 mA cm⁻² (666 mV) value after 30,000 cycles with a maximum power density (initial) of 857 mW cm⁻². The L-Co-doped Pt/CCC demonstrates the highest maximum power density values before and after potential cycling (decreased from 1054 to 820 mW cm⁻² after 30,000 cycles) since more Pt skin is exposed during acid leaching due to the removal of excess Co [166-169].

The fresh and cycled L-Co-doped Pt/CCC catalysts were selected for elemental mapping and line-scan XEDS studies post-test analysis to confirm the formation and retention of doped-metal core and Pt-shell type catalyst structure. The elemental mapping and line-scan of XEDS results of fresh and after 30,000 potential cycles of L-Co-doped Pt/CCC catalyst are shown in Figure 4.15 and 4.16, respectively. The XEDS elemental mapping results indicate that Pt and Co are homogeneously mixed as seen in Figure 4.15. Most of the Co particles that are incorporated into the CCC support diffused during controlled heat-treatment process to form the Co-doped Pt catalysts and only a small

amount is remaining in the support. After 30,000 cycles, Pt dissolved and re-deposited to form larger particles. The Co is partially removed accompanied by Pt dissolution and the remaining one is protected by a thicker Pt film as shown in Figure 4.16. The Pt shell thickness increases from 0.8 nm to as high as 2.4 nm. From density functional theory simulations, it has been postulated that the optimized Pt skin thickness is 2 to 3 monolayers which is equal to 0.50 - 0.75 nm [106, 171]. Thus, the initial high activity is related to the compressive Pt strain [52]. After cycling, with the thicker Pt skin formation due to Pt dissolution/re-deposition, the electronic effect between Pt and Co is reduced [106], which may be one of the reasons for the activity loss besides the well-explained Pt particle agglomeration effect [126].

Tables 4.3 and 4.4 summarize the compositions for Pt/CCC, Co-doped Pt/CCC and L-Co-doped Pt/CCC (initial and after 30,000 cycles) catalysts determined by ICP-MS and XRF, respectively. The Pt concentration in the fresh Pt/CCC catalyst is 28.02% (Table 4.3), which is close to that of the target 30% Pt concentration. After heat-treatment, Pt concentration is increased in the heat-treated (Co-doped Pt/CCC) and leached (L-Co-doped Pt/CCC) samples due to the loss of carbon support during heat-treatment. The difference in Co amount in Pt/CCC and Co-doped Pt/CCC is due to the fact that some of the Co is lost during protective coating process performed in acidic solution. Since XRF detects only the weight ratio of Pt and Co, it is easier to illustrate the Co composition variation using the data presented in Table 4.4. After leaching, XRF analysis indicates that ~45% Co remains in the L-Co-doped Pt/CCC catalyst with a Pt to Co ratio of 1:0.42. Approximately one third of initial Co amount from the core of the catalyst is dissolved during potential cycling between 0.6 and 1. 0 V leading to Pt to Co ratio of 1:0.29 after cycling.

4.5 Support Stability under Potential Holding at 1.2 V

Besides the normal fuel cell operating conditions between 0.6 and 1.0 V, the cathode catalysts should be stable upon fuel starvation and start-up/shutdown conditions when the cathode potential exceeds 1.2 V and reaches as high as 1.5V. Thus, potential holding at 1.2 V was used to evaluate the support stability to meet the requirements of automotive fuel cells.

In our previous study, Co-doped Pt/CCC cathode catalyst was subjected to 1.2 V constant potential for 400 h to study their support stability in comparison with commercial Pt/C catalyst [128]. The results are summarized in Table 4.5. The commercial Pt/C catalyst which uses high surface area carbon as support lost its activity completely after 400 h potential holding. The Co-doped Pt/CCC showed 201 mV loss at 800 mA cm⁻². It has been reported that carbon corrodes at 0.207 V vs. RHE; however, it is not detected during fuel cell operation (0.6-1.0 V) due to its sluggish kinetics [92]. According to Young et al. [172], potentials above 1.2 V accelerates the carbon corrosion rate and cause severe structural degradation of catalyst layer on both commercial Pt/C and doped-Pt/CCC catalysts.

4.6 Conclusion

Catalytically active CCC was synthesized from commercial Ketjen black carbon by subjecting to various processes including surface modification with mineral acids, treatment with nitrogen-containing organic compounds, transition metal catalyzed pyrolysis, and chemical leaching. A novel controlled pyrolysis with polianiline protective coating was used to prevent the Pt particle agglomeration and sintering during Co-doped Pt/CCC catalyst synthesis. X-ray diffraction study indicated the formation of Co-doped Pt particles with an average particle size of 3.5 nm which was confirmed by HRTEM studies. The fuel cell studies indicated significant performance improvements for the HCCs in both kinetic and mass transfer regions of the polarization curve when compared to a commercial Pt/C catalyst. The improvement in the fuel cell performance of the HCCs with ultra-low Pt loading (0.1 mg_{Pt} cm⁻²) is attributed to the synergistic effect of catalytically active CCC support and Pt or compressive Pt-lattice catalysts. The HCCs, namely, Co-doped Pt/CCC, and L-Co-doped Pt/CCC showed enhanced maximum power densities of 857, 1050 mW cm⁻², respectively, when compared to commercial Pt/C (746 mW cm⁻²). The Co-doped Pt/CCC, and L-Co-doped Pt/CCC catalysts showed maximum power density loss of 16, and 22% after 30,000 cycles between 0.6 and 1.0 V which is much less than that for a commercial Pt/C (63% loss). However, due to the corrosion of CCC support at 1.2 V, this catalyst is cannot be used for automotive applications.

Table 4.1. Cobalt Concentration in carbon composite catalyst obtained after the chemical leaching in 0.5M H₂SO₄ solution at 80 °C, determined by XPS and ICP-AES.

Analytical technique	Co Concentration / wt.%
XPS	0
ICP	12.7%

Table 4.2. Comparison of cell potential, maximum power density, and mass activity of Co-doped Pt/CCC, L-Co-doped Pt/CCC, and commercial Pt/C catalysts before and after 30,000 cycles between 0.6 and 1.0 V in 25 cm² MEAs under fuel cell testing conditions.

Sample	H ₂ -air performance		Maximum power		Mass Activity					
	at 800 mA cm ^{-2}		density		at 0.9V _{iR-free}					
	/ mV _{iR-free}			$/ \mathrm{mW} \mathrm{cm}^{-2}$			$/ \mathrm{A} \mathrm{mg_{pt}}^{-1}$			
	Initial	30,000	Loss* / mV	Initial	30,000	Loss /%	Initial	30,000	Loss** / %	Degradation rate *** / A mg _{Pt} ⁻¹ cycle ⁻¹
Co-doped Pt/CCC	706	666	40	857	721	16	0.44	0.25	43	6.33×10 ⁻⁶
L-Co-doped Pt/CCC	724	659	65	1054	820	22	0.47	0.16	66	10.33×10 ⁻⁶
Commercial Pt/C	696	0	696	746	274	63	0.18	0.08	56	3.33×10 ⁻⁶

* FY 2017 US DOE technical targets for electrocatalysts after 30,000 potential cycles between 0.6 and 1.0 V. The catalyst performance evaluation metrics are: \leq 30 mV cell potential loss at 800 mA cm⁻² and \leq 40% mass activity loss after 30,000 cycles.

** Mass activity loss = $\frac{Initial - 30,000}{Initial} \times 100\%$ *** Degradation rate = $\frac{Initial - 30,000}{30,000}$

Sample	Co	oncentration / wt	Pt to Co ratio	
	Pt	Со	С	/ molar ratio
Pt/CCC	28.02	8.37	66.61	Pt : Co = 1:1
Co-doped Pt/CCC	30.88	7.82	61.30	Pt : Co = 1:0.85
L-Co-doped Pt/CCC	30.60	3.92	65.48	Pt : Co = 1:0.43

Table 4.3. Compositions of the Pt/CCC, Co-doped Pt/CCC, L-Co-doped Pt/CCC (Initial) catalysts, determined by ICP-MS.

Sample	Concentration / wt. %		Pt to Co ratio
	Pt	Со	/ molar ratio
Pt/CCC	78.4	21.6	Pt : Co = 1:0.93
Co-doped Pt/CCC	80.1	19.9	Pt : Co = 1:0.81
L-Co-doped Pt/CCC (Initial)	88.8	11.2	Pt : Co = 1:0.42
L-Co-doped Pt/CCC (30,000)	91.7	8.1	Pt : Co = 1:0.29

Table 4.4. Compositions of the Pt/CCC, Co-doped Pt/CCC, L-Co-doped Pt/CCC (initial and 30,000 cycles in fuel cell testing conditions⁶⁸) catalysts, determined by XRF.

Table 4.5. Comparison of cell potential, maximum power density, ECSA and mass activity losses of 30% Co-doped Pt/CCC, 30% Pt/C and commercial 46% Pt/C catalysts before and after subjecting to 1.2 V potential holding experiment in 25 cm² MEAs under fuel cell testing conditions.

	Potential loss	Maximum		Mass activity	
Sample	In H ₂ -air at 800	power density	ECSA loss	Loss	
	$mA cm^{-2}$	loss	/ %	at 0.9 V _{iR-free}	
	/ mV _{iR-free}	/ %		/ %	
30% Co-doped Pt/CCC	201	54	60	50	
30% Pt/C (25 h)	685	91	-	58	
Commercial 46% Pt/C	696	85	71	72	



Figure 4.1. Schematic diagram of synthesize CCC and HCC.



Figure 4.2. HRTEM images of (a) carbon black, and (b) CCC (The scale bar is 20 nm.).



Figure 4.3. XRD patterns of carbon precursor, and CCC.



Figure 4.4. Polarization curves for the oxygen reduction reaction on as-received carbon black, HNO₃-oxidized carbon, and CCC in O₂-saturated 0.1 M HClO₄ at room temperature. Sweep rate: 5 mV s⁻¹; rotation speed: 1600rpm; carbon loading: 120 μ g cm⁻².



Figure 4.5. Comparison of Pt deposition on CCC support with and without surface activation.



Figure 4.6. XRD patterns of Pt/CCC and commercial Pt/C catalysts.



Figure 4.7. Transmission electron microscopy image of (a) commercial Pt/C, and (b) Pt/CCC catalysts (The scale bar is 10 nm).



Figure 4.8. TEM images of Pt/CCC pyrolyzed with and without protective coating.



Figure 4.9. XRD patterns of Pt/CCC, Co-doped Pt/CCC and L-Co-doped Pt/CCC catalysts.



Figure 4.10. Cyclic Voltammograms comparison between L-Co-doped Pt/CCC and Pt/C in RDE in N₂-saturated 0.1 M HClO₄ at room temperature. Sweep rate: 50 mV s⁻¹; rotation speed: 1600rpm; Pt loading: 20 μ g cm⁻².



Figure 4.11. (a) H₂-air polarization curves of the PEM fuel cells, and (b) the corresponding power density prepared with 30% Co-doped Pt/CCC, and 30% L-Co-doped Pt/CCC catalysts and compared with 30% Pt/C and commercial 46% Pt/C catalysts. The fuel cell operating conditions are: H₂/air (2.0/2.0), 80 °C, 50% RH, 170 kPa back pressure.



Figure 4.12. H₂-air polarization curves and the corresponding power density of the PEM fuel cells prepared with Co-doped Pt/CCC catalyst before and after 30,000 cycles. The fuel cell operating conditions are: H₂/air (2.0/2.0), 80 °C, 50% RH, 170 kPa back pressure.



Figure 4.13. H₂-air polarization curves and the corresponding power density of the PEM fuel cells prepared with L-Co-doped Pt/CCC catalyst before and after 30,000 cycles. The fuel cell operating conditions are: H₂/air (2.0/2.0), 80 °C, 50% RH, 170 kPa back pressure.



Figure 4.14. H₂-air polarization curves and the corresponding power density of the PEM fuel cells prepared with commercial 46% Pt/C catalyst before and after 30,000 cycles. The fuel cell operating conditions are: H₂/air (2.0/2.0), 80 °C, 50% RH, 170 kPa back pressure.



Figure 4.15. XEDS elemental mapping of L-Co-doped Pt/CCC catalyst (a) before and (b) after 30,000 cycles.



Figure 4.16. XEDS particle line-scan of L-Co-doped Pt/CCC catalyst (a) before and (b) after 30,000 cycle

CHAPTER 5

DEVELOPMENT OF STABLE GRAPHITIC 2ND AND 3RD GENERATION CCC

Besides the normal fuel cell operating conditions between 0.6 and 1.0 V, the cathode catalysts should be stable during fuel starvation and start-up/shutdown conditions when the cathode interfacial potential difference exceeds 1.2 V and reaches as high as 1.5 V [92]. This high potential together with other favorable conditions such as presence of Pt, low pH, high oxygen and water contents, and high temperature accelerates the carbon corrosion according to reaction 1.4.

The kinetics of carbon oxidation reaction is very slow at the actual cathode potential under PEMFC operating conditions [92]. However, the corrosion reactions are significantly accelerated under high potential conditions, such as OCV (~1.0 V) and potential excursions (~1.5 V) under startup/shutdown cycles [26] or local fuel starvation [92, 173], which lead to fuel cell performance degradation. Therefore, durability of the catalyst support is extremely important for automotive fuel cell applications, since approximately 30,000 startup/shutdown cycles without any significant loss of voltage are required over 5,500 h of operation [126]. According to our previous study, the Pt/CCC catalyst showed an iR-free cell voltage of 699 mV at 800 mA cm⁻² which decreased to 498 mV after 400 h potential holding at 1.2 V resulting in total cell potential loss of 201 mV. The mass activity and ECSA losses after 400 h testing are 50% and 60%, respectively. The

high cell potential loss for the Pt/CCC catalyst may be attributed to the oxidation of nongraphitic carbon initiated by the surface defects on the partially graphitized CCC. Thus, the objective of the chapter is to develop CCC with different graphitization degree and to study their stability using a potential holding experiment (1.2 V for 400 h) by comparing the potential loss at 800 mA cm⁻² under H₂-air fuel cell operating conditions. The 2nd generation CCC, named as CCC-2nd, is achieved by annealing CCC precursor at 1100 °C in the presence of Co, followed by acid leaching. To further increase the graphitic support purity, a purification and stabilization step is carried out to treat the CCC-2nd. The new material is the 3rd generation CCC, named as CCC-3rd.

5.1 Synthesis of 2nd and 3rd Generation CCC

Figure 5.1 shows the XRD patterns of carbon black and CCC treated at different temperatures. The sharp peak at 26° confirms the formation of highly graphitic carbon for CCC-2nd and CCC-3rd, which were treated at 1100 °C. The sample with or without purification shows no difference in XRD, which means the graphitic carbon remains in the support. Only CCC annealed below 900 °C exhibits obvious Co peaks at 44 at 52°. Table 5.1 summarizes the Co content achieved by ICP analysis and the lattice parameters calculated from XRD for different CCC. ICP analysis proves that CCC treated at 800 and 900 °C contains 12.7 and 4.8% Co in the support, respectively. However, less than 1% Co exist in the CCC-2nd pyrolyzed at 1100 °C since most of the Co was diffused to the surface during heat-treatment which was then leached out in 0.5 M H₂SO₄. HRTEM images of different CCCs in Figure 5.2 prove the above assumptions. Compared to the CCC heat-treated at lower temperature (Fig 5.2 a & b) in chapter 4, CCC-2nd illustrates much more

clear graphitic structure (Fig. 5.2 c). As can be seen in Figure 5.2 d, the amorphous carbon has been successfully removed and only graphitic carbon exists after purification step.

Brunauer-Emmett-Teller (BET) isotherm and the corresponding Barrett-Joyner-Halenda (BJH) pore size distribution of the carbon black and CCC supports subjected to different treatment showed large hysteresis between adsorption and desorption, as well as sharp increase/decrease in high relative pressure which indicates the presence of mesopores in both the supports (Figure 5.3). After stabilization, the pore volume of CCC-3rd decreased by half compared with CCC-2nd. Furthermore, the BET surface area of CCC-2nd and CCC-3rd are 250 and 140 m² g⁻¹, respectively due to the removal of high surface area amorphous carbon.

5.2 Synthesis of Pt on 2nd and 3rd Generation CCC

X-ray diffraction studies of Pt/CCC-2nd and Pt/CCC-3rd catalysts and Pt crystallite size calculation using Debye–Scherrer equation indicated particle size of 2.5 and 2.7 nm, respectively (Figure 5.4). Besides the Pt peaks, prominent graphite (002) peak is also detected at 26°. The TEM image shown in Fig. 5.5 confirms the XRD particle size calculations and particle sizes between 2.0 and 3.0 nm are observed for the Pt/CCC-2nd and Pt/CCC-3rd catalysts. The micrograph shows that the Pt particles are uniformly distributed on to the supports and Pt/CCC-3rd has more clear graphite structure than Pt/CCC-2nd.

5.3 Electrochemical Characterization

The fuel cell performances of the Pt/CCC- 2^{nd} , Pt/CCC- 3^{rd} and commercial Pt/C catalysts were evaluated in a 25 cm² cell. Nafion NRE 212 membrane was used as the electrolyte. First, the fuel cell was operated at 80 °C under H₂-O₂ (750/750 ml min⁻¹) and 100% RH. Fig. 5.6 indicates that the performance of the catalyst increases as the CCC

support surface area decreases and Pt/CCC-3rd achieves highest activity with lowest support surface area and highest graphitization degree.

The mass activities of the Pt/CCC-2nd, Pt/CCC-3rd and commercial Pt/C catalysts are compared in Fig. 5.7. The experiment was carried out under the following DOE suggested conditions: 80 °C under H₂/O₂ (2/9.5 stoic.), 100% RH and 150 kPa_{abs.} As can be seen from Fig. 5.7, the mass activities of Pt/CCC-2nd, Pt/CCC-3rd and commercial Pt/C catalysts are 0.227, 0.29 and 0.18 A mg_{Pt}⁻¹, respectively. The trend is the same as the whole polarization curve shown in Fig. 5.6. The mass activity of the heated sample increased to 0.29 A mg_{Pt}⁻¹ even without forming the alloy. The higher mass activity of Pt/CCC-3rd is attributed to the synergetic effect of CCC support and Pt catalyst.

Figure 5.8 depicts the H₂-air fuel cell performance of Pt/CCC-2nd, Pt/CCC-3rd and commercial Pt/C catalysts. The cell was operated at 80 °C with 40% RH and 150 kPa_{abs} back pressure. Similar to the H₂/O₂ and mass activity performance, Pt/CCC shows higher activity than Pt/C commercial catalyst in high current region. The performance at high current density region under H₂/air for the Pt/CCC-3rd catalyst (1.2 A/cm² at 0.6 V_{iR-free}) is much better than that of commercial Pt/C (0.85 A/cm² at 0.6 V_{iR-free}). Pt deposited on stabilized highly graphitic CCC support shows better performance than that on CCC prepared without stabilization.

5.4 Support Durability Studies of Pt on CCC-2nd and CCC-3rd Catalysts

The support durability test was evaluated for the Pt/CCC-2nd and Pt/CCC-3rd catalysts. Pt/CCC-2nd, Pt/CCC-3rd and commercial Pt/C catalysts were tested under support stability conditions suggested by U.S. DRIVE Partnership/Fuel Cell Technical Team. The

test conditions are given in the experimental section. The mass activity and H₂/air fuel cell performance were measured at regular intervals.

Figure 5.9 and 5.10 compare the mass activity of Pt/CCC-2nd, Pt/CCC-3rd catalysts (before and after potential holding for 400 h) with that of Pt/C (before and after potential holding for 25 h) obtained under H₂/O₂ according to the testing protocol suggested by the U.S. DRIVE Partnership/Fuel Cell Technical Team. The details of operating conditions are given in the graph. The mass activity of Pt/CCC-2nd decreased from 0.22 to 0.11 A mg_{Pt}^{-1} (50% loss) after 400 hours holding at 1.2V while the mass activity of Pt/CCC-3rd decreased from 0.29 to 0.20 A mg⁻¹ (31% loss). On the other hand, the commercial Pt/C showed 58.2% loss of mass activity from 0.182 to 0.076 A mg_{Pt}⁻¹ decay after 25 h potential holding at 1.2 V. Furthermore, the loss in ECSA for the Pt/CCC-2nd and Pt/CCC-3rd catalysts is 64 and 34.7%, respectively after 400 h potential holding test. The 1.2 V potential holding test revealed that the Pt/CCC-2nd and Pt/CCC-3rd catalysts show higher initial mass activity and excellent support stability than the Pt/C which clearly indicates the importance of CCC supports' stability and catalytic activity at high potentials.

The H₂-Air fuel cell performances of Pt/CCC-2nd and Pt/CCC-3rd catalysts are compared in Figure 5.11. Both the catalysts showed current densities of ~1.2 A cm⁻² at 0.6 $V_{iR-free}$. In the case of Pt/CCC-2nd, the iR-free cell voltage loss is 128 mV (from 671 mV to 543 mV) and the cell voltage loss is 118 mV. For the Pt/CCC-3rd catalyst, the whole polarization curve remains the same until 200 h potential holding at 1.2 V and the iR-free voltage loss is 66 mV while the cell voltage loss is 76 mV. The potential loss is higher than the 2017 DOE target (30 mV loss after 400 h). However, Pt/C catalyst showed a drastic

decrease in H_2 -air performance after 25 h potential holding at 1.2 V due to the severe carbon corrosion (Fig. 5.12).

Figure 5.13 and Figure 5.14 compare the activity of Pt/CCC-2nd, Pt/CCC-3rd and Pt/C cathode catalysts at high potential, and high current regions before and after the support stability test, respectively. At high potential of 0.9V, both CCC supports exhibits good support stability after holding at 1.2V (Figure 5.13). However, as the current increases, the drop in voltage becomes higher and higher. At 800 mA cm⁻², doubled voltage loss is observed (Figure 5.14 a). When the current increases to 1200 mA cm⁻², Pt/CCC-3rd shows 115 mV voltage after stability test. Both Pt/CCC-2nd and Pt/C both show no activity at that current density. The huge power density loss at high current region is due to carbon oxidation during the AST. The water formation at low current region is limited. As the current increases, more water is produced on the cathode side during ORR. However, it cannot be efficiently removed from the catalyst layer due to increased hydrophilicity caused by carbon oxidation. Most of the Pt active sites are covered by water and oxygen cannot penetrate to participate in the reaction, which causes the mass transfer limitation to occur at much earlier stage during ORR.

The present study showed that the graphitic structure increases the support stability when compared to the high surface area carbon support which is generally used in commercial Pt/C catalyst. The improved support stability is solely attributed to the high degree of graphitization of the CCC-2nd. It has been reported that the extent of graphitization of carbon supports plays an important role on the support stability, with more graphitic carbons being more thermally and electrochemically stable [174-176]. However, the cell potential loss of 128 mV is significantly high for practical use in automotive PEM

fuel cell stacks. Since Pt deposition is non-selective or more favorable on amorphous carbon, the CCC-2nd leads to a poor stability under high potentials. By removal of amorphous carbon without changing the graphitic structure in CCC-2nd, CCC-3rd further improves the corrosion resistance and support stability.

5.5 Catalyst Durability Study on Co-doped Pt/CCC-3rd Catalyst

The Co-doped Pt/CCC-3rd catalyst was prepared by impregnating Co salt into the Pt/CCC-3rd catalyst in the presence of an in-house developed coating, followed by high temperature pyrolysis. As shown by XRD in Figure 5.15, the shift of all the peaks for the PtCo catalyst illustrates the Pt-Pt bond distance is decreased compared to the fresh catalyst. The particle size of Co-doped Pt/CCC-3rd catalyst grows to 4.0 nm from 2.5 nm after high temperature pyrolysis.

To improve the high current density activity, the Co-doped Pt/CCC-3rd is leached to remove the excess Co on the surface. The leached sample is named as L-Co-doped Pt/CCC-3rd.

The catalyst durability was evaluated by cycling the potential between 0.6 and 1.0 V at 50 mV s⁻¹ scan rate. The durability test conditions are described in the experimental section. Figure 5.16 and Figure 5.17 illustrates the mass activity at high potentials measured in H₂-O₂ and H₂-air polarization curves of the Co-doped Pt/CCC-3rd and the L-Co-doped Pt/CCC-3rd catalysts, respectively. The Co-doped Pt/CCC-3rd shows initial mass activity (0.42 A mg_{Pt}⁻¹) and mass activity after 30k cycles (0.20 A mg_{Pt}⁻¹) in H₂/O₂ corresponding to a loss of 52%. The ECSA decreased from 23.2 to 19.8 m² g⁻¹ after 30 k cycles. The Co-doped Pt/CCC-3rd catalyst exhibited an initial H₂/air performance of 800 mA cm⁻² at 0.607 V_{iR-free} and the iR-free potential decreased to 0.561 V after 30 k cycles

(loss of 46 mV). The cell potential loss is 53 mV after 30 k cycles. The loss in cell potential is slightly higher than the 2017 DOE target of 30 mV loss after 30 k cycles. On the other hand, the leached catalyst exhibits higher initial activity in both high potential (mass activity of 0.44 A mg⁻¹ at 0.9V) and high current regions (cell voltage of 690 mV at 800 mA cm⁻²). However, after cycling, there is a significant activity decrease due to Pt dissolution. As a comparison, the catalyst durability results of commercial Pt₃Co on graphitic carbon support is presented in Figure 18.

Figure 5.19 a summarizes the mass activity comparison (at 0.9V) of Co-doped Pt/CCC-3rd, L-Co-doped Pt/CCC-3rd Pt/CCC-3rd, commercial Pt₃Co/C and Pt/C cathode catalysts (The values are obtained from Figures 5.16 and 5.18 a.). Fig. 5.19 b summarizes the current density comparison (at 0.6V) of Co-doped Pt/CCC-3rd, L-Co-doped Pt/CCC-3rd Pt/CCC-3rd, commercial Pt₃Co/C and Pt/C cathode catalysts (The values are achieved from Figures 5.17 and 5.18 b.) before and after 30 k potential cycling between 0.6 and 1.0V. Figure 5.19 a shows that all the Co-doped catalysts have initial high mass activity than pure Pt. The mass activities are 0.42, 0.44 and 0.39 for Co-doped, L-Co-doped catalyst and commercial Pt₃Co/C, respectively. After 30k cycles, both Pt/CCC-3rd and Pt/C catalysts have final mass activity of 0.08 A/mg. With Pt compressive lattice formation, the final mass activity of Co-doped Pt/CCC-3rd is 0.2, which is 2.5 times higher than that of pure Pt. However, this catalyst lost the stable structure after leaching, showing the same final mass activity as Pt. The whole polarization curve in H₂-air illustrates that the current obtained for the Co-doped Pt/CCC-3rd at 0.6V is stable but not high enough to achieve desired power density. High mass activity at high potential does not always transform to better performance at high current in H₂-air, but the stability of mass activity is
representative for the catalyst system. Therefore, the unstable mass activity can indicate the poor durability of L-Co-doped Pt/CCC-3rd. The other phenomenon observed is that the leached catalyst is not as stable on CCC-3rd as on the 1st generation CCC. One major difference is that we used two different Co doping method. That is, the compressive Pt lattice on CCC-3rd is formed by Co doping from outside the Pt particles (conventional impregnation method), while that on CCC is formed through Co diffusion from the CCC support. After acid leaching, conventionally (impregnation method) prepared compressive Pt structure has more pores on the surface. The increase of roughness contributes to the decrease in catalyst durability [52]. The other reason is that the CCC-3rd has 3-time smaller BET surface area and smoother surface which also affects the Pt-C interaction.

5.6 Conclusion

Cobalt catalyzed the support graphitization and aided the formation of carbon nanotubes at 1100 °C. Graphitic carbon has better support corrosion-resistance due to less presence of surface defects which act as oxidation etching sites. A support purification and stabilization procedure was developed to remove the electrochemically unstable amorphous carbon from the CCC-2nd which resulted in a highly stable CCC-3rd with improved support stability. At high temperatures above 900 °C, the Co embedded within the support diffused towards the surface and formed compressive Pt lattice catalyst. The compressive lattice structure prepared by the conventional impregnation method showed less ORR activity with the Co-rich surface compared to the in-house developed doping method. After removal of excess Co by chemical leaching, the stability of the compressive lattice structure is reduced due to increase of surface roughness.

Table 5.1 Physical property of CCC subjected to different treatments, including XRI),
BET and ICP.	

Sample	Pyrolysis	L _c	BET	Со
	temperature	from XRD	surface area	from ICP
	/ °C	/ nm	$/ m^2 g^{-1}$	/ %
Carbon black	-	1.1	780	0
CCC	800	3.6	350	12.7
CCC-900 °C	900	3.8	380	5
CCC-2 nd	1100	7.3	250	0.5
CCC-3 rd	1100 &	7.4	140	0.3
	purification			

Table 5.2. Comparison of particle size, mass activity, ECSA, cell potential losses of 30% Pt/CCC-2nd, 30% Pt/CCC-3rd and 30% Pt/C catalysts before and after subjecting to 1.2 V potential holding experiment in 25 cm² MEAs under fuel cell testing conditions.

Sample	Particle size / nm	Mass activity Loss at 0.9 V _{iR-free} / %	Potential loss in H ₂ -air at 800 mA cm ⁻² / mV _{iR-free}	ECSA loss / %
30% Pt/CCC-2 nd	2.5	50	128	64
30% Pt/CCC-3 rd	2.7	31	66	22
30% Pt/C (25 h)	2.2	58	620	-



Figure 5.1. X-ray diffraction patterns of carbon black and CCC subjected to different treatment.



Figure 5.2. TEM images of CCC treated at (a) 800°C, (b) 900°C, (c) 1100°C and (d) after stabilization. The scale bar in the TEM image is 50 nm.



Figure 5.3. (a) Brunauer-Emmett-Teller (BET) isotherm and (b) Barrett-Joyner-Halenda (BJH) pore size distribution of carbon black and CCC subjected to different treatment.



Figure 5.4. X-ray diffraction of Pt/CCC-2nd and Pt/CCC-3rd catalysts.



Figure 5.5. Transmission electron microscopy images of (a) $Pt/CCC-2^{nd}$ and (b) $Pt/CCC-3^{rd}$ catalysts (The scale bar is 10 nm).



Figure 5.6. H₂-O₂ polarization curve of Pt/CCC- 2^{nd} , Pt/CCC- 3^{rd} and commercial Pt/C catalysts. The fuel cell operating conditions are: H₂-O₂ (750/750 ml min⁻¹), 80 °C, 100% RH.



Figure 5.7. Comparison of mass activities of Pt/CCC- 2^{nd} , Pt/CCC- 3^{rd} and commercial Pt/C catalysts. The fuel cell operating conditions are: H₂-O₂ (2.0/9.5), 80 °C, 100% RH, 150kPa back pressure.



Figure 5.8. Comparison of H_2/air fuel cell performance of Pt/CCC-2nd, Pt/CCC-3rd and commercial Pt/C catalysts. (a) iR-corrected cell voltage vs. current density, (b) cell voltage vs. current density.



Figure 5.9. Mass Activity of (a) Pt/CCC- 2^{nd} , and (b) Pt/CCC- 3^{rd} cathode catalysts before and after the support stability test (1.2 V potential holding for 400 h). The fuel cell operating conditions are: H₂/O₂ (2.0/9.5), 80 °C, 100% RH, 150kPa back pressure.



Figure 5.10. Mass Activity of Pt/C cathode catalysts before and after the support stability test (1.2 V potential holding for 25 h). The fuel cell operating conditions are: H_2/O_2 (2.0/9.5), 80 °C, 100% RH, 150kPa back pressure.



Figure 5.11. H₂-Air PEM fuel cell polarization curves of (a) Pt/CCC- 2^{nd} , and (b) Pt/CCC- 3^{rd} cathode catalysts before and after the support stability test (1.2 V potential holding for 400 h). The H₂-air polarization performances were measured under H₂/air (1.5/1.8 stoic.), 80 °C, 40% RH, and 150 kPa_{abs}.



Figure 5.12. H₂-Air PEM fuel cell polarization curves of Pt/C cathode catalyst before and after the support stability test (1.2 V potential holding for 25 h). The H₂-air polarization performances were measured under H₂/air (1.5/1.8 stoic.), 80 °C, 40% RH, and 150 kPa_{abs}.



Figure 5.13. Mass Activity of Pt/CCC-2nd, Pt/CCC-3rd and Pt/C cathode catalysts at 0.9 V before and after the support stability test (1.2 V potential holding for 400 h). The values are achieved from Figures 5.9 and 5.10.



Figure 5.14. IR-corrected cell voltage at (a) 800 mA cm⁻² and (b) 1200 mA cm⁻² of Pt/CCC- 2^{nd} , Pt/CCC- 3^{rd} and Pt/C cathode catalysts before and after the support stability test (1.2 V potential holding for 400 h). The values are achieved from Figures 5.11 and 5.12.



Figure 5.15. X-ray diffraction patterns of Pt/CCC-3rd and Co-doped Pt/CCC-3rd catalysts.



Figure 5.16. Mass Activity of (a) Co-doped Pt/CCC- 3^{rd} and (b) L-Co-doped Pt/CCC- 3^{rd} before and after 30k potential cycling between 0.6 and 1.0V. The fuel cell operating conditions are: H₂/O₂ (2.0/9.5), 80 °C, 100% RH, 150kPa back pressure.



Figure 5.17. H₂/air fuel cell performance of (a) Co-doped Pt/CCC- 3^{rd} and (b) L-Co-doped Pt/CCC- 3^{rd} before and after 30 k potential cycling between 0.6 and 1.0V (iR-corrected cell voltage vs. current density). The fuel cell operating conditions are: H₂/air (1.5/1.8), 80 °C, 40% RH, 150kPa back pressure.



Figure 5.18. Fuel cell performance of commercial Pt_3Co on graphitic carbon before and after 30 k potential cycling between 0.6 and 1.0V (a) Mass activity. The fuel cell operating conditions are: H_2/O_2 (2.0/9.5), 80 °C, 100% RH, 150kPa back pressure. (b) H_2/air . The fuel cell operating conditions are: H_2/air (1.5/1.8), 80 °C, 40% RH, 150kPa back pressure.



Figure 5.19. (a) Mass activity comparison at 0.9V of Co-doped Pt/CCC-3rd, L-Co-doped Pt/CCC-3rd Pt/CCC-3rd, commercial Pt₃Co/C and Pt/C cathode catalysts (The values are achieved from Figures 5.18 and 5.20 a.) and (b) current density comparison at 0.6V of Co-doped Pt/CCC-3rd, L-Co-doped Pt/CCC-3rd Pt/CCC-3rd, commercial Pt₃Co/C and Pt/C cathode catalysts (The values are achieved from Figures 5.19 and 5.20 b.) before and after 30 k potential cycling between 0.6 and 1.0V. (Pt-1: Pt/CCC-3rd, Pt*-2: Co-doped Pt/CCC-3rd, Pt*-3: L-Co-doped Pt/CCC-3rd.)

CHAPTER 6

DEVELOPMENT OF ACTIVATED CARBON COMPOSITE CATALYST (A-CCS) AND PT/A-CCS CATALYST

6.1 Synthesis of A-CCS and Pt/A-CCS

In order to further improve the support stability at high potentials (1-1.5 V), The A-CCC was synthesized by the same two-step stabilization process described in Chapter 5 from a different carbon precursor. The A-CCC with a BET surface area of 200 m² g⁻¹ was used to synthesize 30% Pt/A-CCC catalyst. The HRTEM images shown in Fig. 6.1 revealed that the Pt particles are uniformly distributed over the A-CCC support with an average particle size of ~3.1 nm. Figure 6.2 exhibits the XRD patterns of A-CCC and Pt/A-CCC. It has been reported that higher L_c value of (002) peak at 26° implies higher degree of graphitization, which can be calculated by Scherrer formula [177, 178]. The L_c value for A-CCC is only 2.8 while that for Ketjen black, CCC and CCC-2nd is 1.1, 3.6 and 7.3, respectively. Compared to CCC, A-CCC did not show significant graphitic structures. However, due to difference in the carbon precursors' nature, A-CCC exhibits improved hydrophobicity.

From Chapter 5, we know that highly graphitic carbon was not friendly for Pt anchorage due to its small BET surface area and smooth surface. Therefore, the catalyst after 30,000 potential cycles between 0.6 and 1.0V exhibits poor catalytic performance. Thus, it is very important to study the Pt-C interaction on A-CCS to see the increase of

surface area and decrease of graphitic nature can help to improve the catalyst-support interaction and further enhance the catalyst durability.

6.2 Catalyst Stability

To investigate the Pt catalyst stability in PEM fuel cells under 100% RH and 80 °C cell temperature, potential cycling experiment (0.6-1.0 V for 30,000 cycles) was performed on the Pt/A-CCC and Pt/C catalysts. Figures 6.3, 6.4, and 6.5 present the polarization curves of Pt/A-CCC and commercial Pt/C catalysts before and after 30,000 cycles under H_2-O_2 (constant flow 750/750 mL min⁻¹ and stoic 2.0/9.5) and H_2 -air (2.0/2.0 stoic.) operating conditions, respectively. As shown in Figure 6.3 a, when the cathode reactant is sufficiently supplied for ORR at 100% RH, the Pt/A-CCC catalyst maintains the activity before and after 30,000 cycles. However, the performance loss of the commercial Pt/C catalyst is much more significant after 30,000 cycles (Figure 6.3 b). At kinetic region in Figure 6.4, when fuel supply is limited, mass activity losses of 50 and 61% are noticed for Pt/A-CCC and Pt/C, respectively. In the case of air with reduced humidity (50% RH), the performance decrease is observed in both the catalysts. In the case of Pt/A-CCC catalyst (Figure 6.5 a), the V_{iR-free} loss is 72 mV (cell voltage decreased from 715 to 643 mV after 30,000 cycles between 0.6 and 1.0 V) at 800 mA cm⁻². Furthermore, the Pt/A-CCC catalyst showed initial maximum power density of 944 mW cm⁻² and 703 mW cm⁻² after 30,000 cycles (26% loss). The Pt/C (Figure 6.5 b) showed no activity at that current density and the maximum power density drops from 746 mW cm⁻² to 274 mW cm⁻² (63% loss). The increased stability can be attributed to strong π -bond in the A-CCC due to enhanced graphitic nature, which acts as anchoring sites (sp2-hybridized carbon) for Pt [179, 180]. The ECSA change during potential cycling shown in Figure 6.6 also supports the above explanation. The ECSA of commercial catalyst experienced significant loss from 65 to 13 $m^2 g^{-1}$ while that of Pt/A-CCC is much more stable during the cycling test with only 41% loss (from 39 to 23 $m^2 g^{-1}$). As shown in Figure 6.6 (c), the normalized ECSA remained at around 60% of its initial value for the Pt/A-CCC catalyst when compared to 80% ECSA loss for the commercial Pt/C catalyst which is consistent with the results obtained from the polarization curves.

With improved catalyst durability, it is also crucial to investigate the support stability at high potentials in order to be a promising candidate for automotive applications.

6.3 Support Durability under Potential Holding at 1.2 V

The initial H₂-air polarization curve and polarization curves obtained after 100 h, 200 h, and 400 h potential holding at 1.2 V for the 30% Pt/A-CCC catalyst are compared in Figure 6.7. The 30% Pt/A-CCC catalyst showed an initial potential of 689 mV and 662 mV after 400 h potential holding with a potential loss of 27 mV. The initial peak power density is 1098 mW cm⁻² which decreased to 958 mW cm⁻² after 400 h stability tests corresponding to a loss of only 13%. Besides, there is a mass activity loss of only 32% as shown in Fig. 6.8. Figure 6.9 (a) and Figure 6.9 (b) compare the ECSA loss in the fuel cell for the commercial 46.7% Pt/C and 30% Pt/A-CCC catalysts, respectively. The commercial Pt/C showed an initial ECSA of 52 m² g_{Pt}⁻¹ which drastically decreased to 15 m² g_{Pt}⁻¹ (71% loss) after 25 h due to severe carbon corrosion. Conversely, the 30% Pt/A-CCC showed much lower ECSA loss of only 30% with initial and final ECSA values of 40 and 28 m² g_{Pt}⁻¹, respectively.

All the fuel cell polarization results together with kinetic activity loss and ECSA loss data clearly indicate that graphitic carbon-support offers better corrosion resistance

during potential holding. Furthermore, significantly low potential loss of 27 mV at 800 mA cm⁻² after 400 h potential holding experiment obtained for the 30% Pt/A-CCCS catalyst is also attributed to the increased hydrophobicity of the support [181] and a relatively stronger catalyst-support interaction [180] when compared to other Pt catalysts investigated in this study.

6.4 Support Durability under Potential Cycling between 1.0 and 1.5 V

In order to further evaluate the support stability of Pt/A-CCC under very severe corroding conditions, AST [126] between 1.0 and 1.5 V for 5,000 cycles at 500 mV s⁻¹ sweep rate was performed under H₂/N₂ at 80 °C and 100% RH and the results are compared with that of commercial Pt/C catalyst in Figure 6.10 (a and b). The Pt/A-CCC catalyst showed no potential loss up to 2,000 cycles and only 24 mV loss cycles at 1500 mA cm⁻² after 5,000 which satisfies the DOE targets for support stability [126]. The maximum initial power density is 970 mW cm⁻² and the loss is only 3% after 5,000 cycles which shows that the A-CCC support in Pt/A-CCC catalyst is highly stable under severe corroding conditions. However, the commercial Pt/C catalyst showed drastic performance degradation after only 500 cycles and showed poor activity after 2,000 cycles due to severe carbon support corrosion at high potentials. These results clearly indicate that the A-CCC support offers better resistance to corrosion at high potentials between 1.0 and 1.5 V, which may be attributed to the increased hydrophobicity when compared to commercial high surface area supported Pt catalyst.

Fig. 6.11 (a) and (b) shows the BSEM image of the cross-section of the fresh and post-cell test of the MEAs, which contains Pt/C or Pt/A-CCC catalyst on the cathode side. Five distinct layers can be identified: the anode GDL, the commercial Pt anode, the Nafion

membrane, the cathode catalyst layer and the cathode GDL. From the change in the contrast provided by the BSEM, it is obvious to distinguish the cathode catalyst layer of commercial catalyst is corroded completely, as shown in Figure 6.10 (a). However, after 5,000 cycles between 1.0 to 1.5 V, the cathode side of Pt/A-CCC maintained its catalyst layer structure under highly corrosion environment (Figure 6.11 b).

6.5 Conclusion

A-CCC support was synthesized using purification and stabilization process with a different carbon precursor as a starting material. The A-CCS support is less graphitic but more hydrophobic in nature compared to CCC-3rd. The Pt on A-CCC support exhibits improved Pt catalyst stability due to modified pore size distribution and graphitization of the support. On the other hand, the Pt/A-CCC catalyst exhibited only 27 mV loss at 800 mA cm⁻² after 400-hour potential holding at 1.2 V and 35 mV loss at 1500 mA cm⁻² after 5,000 potential cycles between 1.0 and 1.5 V. The enhanced support stability is attributed to high surface hydrophobicity which repels water that is produced during high current operation and slows down carbon corrosion. These studies suggest that the Pt/A-CCC catalyst can be a promising cathode candidate material for transportation applications.

Table 6.1. Summary of the fuel cell performance of Pt/A-CCS catalyst before and after catalyst and support AST.

				DOE			
Metric	Units	Pt/A-CCS	Pt/C				
				target			
	Initial Mass Acti	vitv					
miniai mass Activity							
Initial Mass activity	A/mg _{PGM} @ 0.9 V	0.22~0.26	0.18	≥0.44			
Catalyst Stability (30,000 cycles between 0.6 and 1.0 V)							
Loss in catalyst activity	% loss after AST	50%	68%	≤40%			
Loss in ECSA	% loss after AST	41%	80%	≤40%			
Potential loss @ 0.8 A/cm ²	mV loss after AST	72 mV	620	≤30 mV			
Support Stability (400 h holding at 1.2 V)							
Loss in catalyst activity	% loss after AST	32%	72%	≤40%			
Loss in ECSA	% loss after AST	6%	71%	≤40%			
Potential loss @ 0.8 A/cm ²	mV loss after AST	18 mV	620	≤30 mV			
Support Stability (5,000 cycles between 1.0 and 1.5 V)							
Loss in catalyst activity	% loss after AST	41%	56%	≤40%			
Loss in ECSA	% loss after AST	-	-	≤40%			
Potential loss @ 1.5 A/cm ²	mV loss after AST	36 mV	620	≤30 mV			
PGM Content and PGM Loading							
PGM total content	g _{PGM} /kW (rated)	0.18	0.3	≤0.125			
PGM total loading	mg _{PGM} /cm ² _{geo}	0.2	0.2	≤0.125			



Figure 6.1. Transmission electron microscopy image of Pt/A-CCC catalyst (The scale bar is 10 nm).



Figure 6.2. X-ray diffraction patterns of A-CCC support and Pt/A-CCC catalyst.



Figure 6.3. H₂-O₂ polarization curves of the PEM fuel cells prepared with (a) Pt/A-CCC and (b) commercial Pt/C catalysts before and after 30,000 cycles. The fuel cell operating conditions are: H_2/O_2 (750/750 sccm), 80 °C, 100% RH, no back pressure.



Figure 6.4. Mass Activity of Pt/A-CCC and Pt/C catalysts before and after 30,000 potential cycling between 0.6 and 1.0V (iR-corrected cell voltage vs. current density). The fuel cell operating conditions are: H_2/O_2 (2.0/9.5), 80 °C, 100% RH, 150kPa back pressure.



Figure 6.5. H₂-air polarization curves and the corresponding power density of the PEM fuel cells prepared with (a) Pt/A-CCC and (b) commercial Pt/C catalysts before and after 30,000 cycles. The fuel cell operating conditions are: H₂/air (2.0/2.0), 80 °C, 50% RH, 170 kPa back pressure.



Figure 6.6. CVs of (a) Pt/A-CCC and (b) commercial Pt/C catalysts during 30,000 cycles; (c) normalized ECSA change as a function of potential cycles.



Figure 6.7. Mass activity of Pt/A-CCC and Pt/C catalysts before and after 400h potential holding at 1.2 V (iR-corrected cell voltage vs. current density). The fuel cell operating conditions are: H_2/O_2 (2.0/9.5), 80 °C, 100% RH, 150kPa back pressure.



Figure 6.8. H₂-air polarization curves and the corresponding power density of the PEM fuel cells prepared with Pt/A-CCC catalyst before and after 400 hours potential holding at 1.2 V. The fuel cell operating conditions are: H₂/air (2.0/2.0), 80 °C, 50% RH, 170 kPa back pressure.


Figure 6.9. CVs of (a) commercial Pt/C and (b) Pt/A-CCC catalysts before and after 400 hours potential holding at 1.2 V; (c) normalized ECSA change as a function of potential holding time.



Figure 6.10. H₂-air polarization curves and the corresponding power density of the PEM fuel cells prepared with (a) Pt/A-CCC and (b) commercial Pt/C catalysts before and after 5,000 cycles between 1.0 and 1.5 V. The fuel cell operating conditions are: H₂/air (2.0/2.0), 80 °C, 50% RH, 170 kPa back pressure.



Figure 6.11. BSEM images of the cross-section of the MEAs containing (a) Pt/A-CCC and (b) commercial Pt/C catalysts on the cathode side before and after 5,000 potential cycles between 1.0 and 1.5 V.

CHAPTER 7

DEVELOPMENT OF HIGHLY DURABLE HYBRID CATHODE CATALYST DEPOSITED ON A-CCS FOR PEMFC

The pure Pt on A-CCS presents high support stability and enhanced catalyst durability compared to Pt/CCC-3rd catalyst. To further improve the durability, Co should be doped into Pt to have the lattice contraction to slow down Pt dissolution. However, doping Pt with too much Co can decrease the ORR activity with excess Co coverage on Pt active sites, while smaller Co ratio may not be effectively to provide the compressed Pt strain. Therefore, Pt to Co ratio plays a significant role in catalyst development and Pt to ratio needs to be optimized to achieve the highly active and durable catalyst.

7.1 Effect of Pt to Co Ratio on ORR Catalytic Activity

Initially Co-doped A-CCS was synthesized by mixing A-CCS with Co precursor and nitrogen containing organic compound followed by annealing at 800°C for 1 hour in inert atmosphere. The final product, which is leached in 0.5M H_2SO_4 for 4 hours to remove the excess of Co on the surface, is named as A-CCS. Table 7.1 summarizes the ACCS composition for the starting materials of carbon, Co and ligand compound and the final Co weight percentage in the support and Pt to Co ratio after 30% Pt deposition. From the table, we can see that the Co amount included in the support can be varied by modifying the cobalt to ligand ratio. The role of ligand is to form Co-N chelate compound. Therefore, the amount of Co incorporated into A-CCS is only related to carbon to Co ratio. XRD patterns of A-CCSs with different Co concentration are compared in Figure 7.1. The presence of Co metal is confirmed by the peak appearing at 44°. The Co peak intensity increases as the Co concentration in the support increases. The graphitic (002) peak at 26° for the sample with less Co is higher due to less ligand inclusion, which may be attributed to formation of more amorphous carbon with more ligand.

30% Pt is first deposited on the supports having different Co concentrations and PtCo alloy catalysts with the Pt to Co ratio between 1:1 and 3:1 are formed using the methodologies described in Chapter 2. The heat-treated catalysts are named as Co-doped Pt/A-CCS. The XRD is shown in Figure 7.2. After annealing at 800 °C, all the Pt peaks shift to higher angle indicating a lattice contraction caused by the substitution of the smaller Co metal atoms for the larger Pt atoms. The higher the amount of Co doping into Pt, the higher the peak shift observed in XRD. Among various PtCo catalysts, Pt₁Co₁ exhibits clear ordered fct structure with extra peak formation by show additional superlattice reflections such as (100) reflection at 33°.

The effect of Pt to Co ratio on ORR catalytic activity are compared in PEMFC with Pt loadings of 0.1 mg cm⁻² on both anode and cathode in a single PEM fuel cell (25 cm² MEA).

The mass activity is measured at high potential region under the condition: H_2/O_2 (2.0/9.5 stoic.), 100% RH and 150 kPa_{abs} back pressure, 80°C cell temperature. As shown in Figure 7.3, at 0.9V, the mass activities are 0.220, 0.298, 0.311, 0.356, 0.420 and 0.383A mg⁻¹ for pure Pt, Pt₃Co₁, Pt_{2.5}Co₁, Pt₂Co₁, Pt_{1.5}Co₁ and Pt₁Co₁ catalysts, respectively. From Figure 7.3 b, we can see that the mass activity increases as the Co to Pt ratio increases, following a linear fit, except for Pt₁Co₁. The lower mass activity achieved with Pt₁Co₁ is

due to the formation of ordered fct structure. It has been reported by Koh [182] that ordered PtCo fct structure is more corrosion resistant but less active for ORR.

The polarization curves are obtained under H_2/air (2.0/2.0 stoic.), 50% RH and 170 kPa_{abs} back pressure, 80°C cell temperature. As discussed in chapter 5, higher mass activity at high potentials does not always translate to a high performance in high current regions. Due to more surface coverage of Pt with excess Co in the case of catalysts with high Co to Pt ratio, the current density decreases as the Co amount increases. The best performance is achieved with Pt to Co ratio of 3:1.

7.2 Effect of Annealing Temperature on ORR Catalytic Activity

Since Co is chemically and electrochemically not stable in acidic media especially in the presence of Pt, it is important to have maximum amount of Co in the Pt structure to keep the compressive lattice strain as long as possible during potential cycling between 0.6 and 1.0 V. The purpose of studying the effect of Pt to Co ratio is to include maximum possible Co in the structure without decreasing the performance very much. Pt to Co ratios between 2:1 and 3:1 give higher activity than pure Pt at 0.6 V. Therefore, Pt to Co ratio 2:1 is selected to be optimized the annealing temperature to have better Pt Co interaction.

As reported in the literature, when the annealing temperature is increased, more ordered PtCo structure with lower activity is form [182]. At 650 °C, most of the catalyst shows disordered structure. In this study, 700 °C is chosen to be the lowest annealing temperature. All the catalysts show peak shift in XRD after subjected to annealing (Figure 7.5). Furthermore, the catalyst annealed at higher temperature exhibits higher shift in 2 Θ angle indicating more compressive Pt lattice formation.

The effect of annealing temperature on ORR catalytic activity is compared in PEMFC with Pt loadings of 0.1 mg cm⁻² on both anode and cathode in a single PEM fuel cell (25 cm² MEA). From the mass activity study results shown in Figure 7.6 a & b, at 0.9V, the highest mass activity of 0.356 A mg⁻¹ is obtained for the Pt₂Co catalyst heat-treated at 800 °C. Figure 7.6 b shows that above 800 °C, the mass activity decreases as temperature increases. The H₂/air polarization curves shown in Figure 7.7 a & b presents the similar tendency as the mass activity study. The observed phenomenon is due to more ordered structure formation at high temperature which decreases the activity. Besides, high temperature also contributes to Pt particle growth and agglomeration. Therefore, the compressive Pt-lattice catalyst development is a trade-off between the catalyst activity and durability. At 0.6V, the catalysts pyrolyzed between 700 and 850°C show better ORR activity than pure Pt, as shown in Figure 7.7 b. Based on these studies, the catalysts annealed at 800 and 850°C are chosen for catalyst durability studies.

7.3 Catalyst Durability and Support Stability Studies of Co-doped Pt/A-CCS Catalysts

To investigate the catalyst stability in PEM fuel cell under 100% RH and 80 °C cell temperature, potential cycling experiment (0.6-1.0 V for 30,000 cycles) was performed on the 800 and 850°C treated Co-doped Pt/A-CCS catalysts. Figures 7.8 a & b and Figure 7.10 a & b present the Tafel plot of voltage versus mass activity and whole polarization curves of the 800 and 850°C treated Pt₂Co₁ catalysts before and after each 10,000 cycles under H₂-O₂ and H₂-air operating conditions, respectively. The mass activity values at 0.9V versus cycle number or these two catalysts are compared in Figure 7.9. Both the catalysts showed huge performance decay at 0.9 V after first 10,000 cycles at 0.9V which is similar to the results reported for pure Pt [11]. The performance decay is caused due to removal of Co

from the PtCo catalyst together with Pt dissolution and re-deposition. Once a thick Pt shell is formed due to Pt dissolution/re-deposition process, the catalyst becomes more stable. However, the catalyst treated at 850°C presents improved durability but with lower initial ORR activity. Similar phenomenon is also shown in H₂-air polarization curves. At 0.6V, as shown in Figure 7.11, the initial current densities are 1430 and 1360 mA cm⁻² for 800 and 850 °C treated catalysts, respectively. After the first 10,000 cycles, both the catalysts show the same current density value of 1190 mA cm⁻². From then on, the higher temperature annealed catalyst exhibits enhanced durability upon cycling with the same power output at 0.6 V. On the other hand, the lower temperature annealed catalyst shows gradual decrease of current density at the same potential during catalyst durability test (0.6-1.0 V cycling). The enhanced durability is attributed to more ordered structure formation at 850 °C.

To determine if the support stability is affected by Co doping, the Pt_2Co_1 cathode catalyst was cycled between 1.0 and 1.5 V for 5,000 times under the AST conditions: the anode and cathode were under H_2 and N_2 atmosphere at 80 °C and 100% inlet RH. The polarization curve measured in H_2 -air shows no decrease of ORR activity after 5,000 cycles. Instead, there is a 10 mV gain at 1500 mA cm⁻². This is because Co is leached out from the structure both chemically (due to low pH at the cathode/electrolyte interface) and electrochemically (due to high overpotential during 1.0-1.5V cycling) and expose more Pt surface active sites. However, at moderate cycling condition such as the one between 0.6 and 1.0 V, Pt dissolution occurs through Pt oxidation and Pt-oxide reduction process and the activity increase is not observed. But during high potential cycling, Pt is passivated by Pt oxide film, so the activity increase shows up.

7.4 Conclusion

To avoid the leaching step during Co-doped Pt catalyst synthesis, the effect of Pt to Co ratio on the ORR activity in PEMFC has been investigated. With the increase of Co to Pt ratio from 0 to 0.67:1, the mass activity at high potential increases while the H₂-air performance at low potential decreases. Co to Pt ratio of 0.5:1 was selected to further analyze the annealing temperature effect on the activity and stability of the catalyst. Low temperature treated catalyst exhibits better activity while high temperature treated catalyst shows higher catalyst stability under moderate potential cycling conditions. Therefore, it is a trade-off between the catalyst activity and durability. The final optimized Co-doped Pt catalyst is achieved with Pt₂Co₁ ratio annealed at 850°C. The A-CCS support also shows high corrosion-resistance in the presence of Co-doped Pt during potential cycling between 1.0 and 1.5V.

Table 7.1 Pt to Co ratio prepared by different Co to ligand amount.

C : Co : ligand	Co wt.	Pt to Co	Pt to Co
/ wt. ratio	percentage in A-	/ wt. ratio	/ atomic ratio
	CCS		
	/ %		
4:1:20	13%	77:23	1:1
4:1:10	14%	75:25	1:1.1
4:1:5	13%	77:23	1:1
4:0.5:5	6.4%	87:13	1:0.50
4:0.5:2.5	6.4%	87:13	1:0.50
4:0.33:3.33	4.3%	91:9	1:0.33



Figure 7.1. XRD patterns of A-CCSs with different Co concentrations.



Figure 7.2. XRD patterns of Co-doped Pt/A-CCS with different Pt to Co ratios.



Figure 7.3. (a) Mass Activity Tafel plot of Co-doped Pt/A-CCS catalysts with different Co to Pt ratio (iR-corrected cell voltage vs. mass activity) (b) mass activity at 0.9V as a function of Co to Pt ratio. The fuel cell operating conditions are: H_2/O_2 (2.0/9.5), 80 °C, 100% RH, 150kPa back pressure.



Figure 7.4. H₂-air polarization curves of the PEM fuel cells prepared with Co-doped Pt/A-CCS catalysts with different Co to Pt ratio (iR-corrected cell voltage vs. current density). The fuel cell operating conditions are: H₂/air (2.0/2.0), 80 °C, 50% RH, 170 kPa back pressure.



Figure 7.5. XRD patterns of Pt₂Co₁ annealed at different temperatures.



Mass Activity / A mg_{Pt}⁻¹



Figure 7.6. (a) Mass Activity Tafel plot of Co-doped Pt/A-CCS catalysts with Pt to Co ratio of 2:1 at different annealing temperature (iR-corrected cell voltage vs. mass activity) (b) mass activity at 0.9V as a function of annealing temperature. The fuel cell operating conditions are: H_2/O_2 (2.0/9.5), 80 °C, 100% RH, 150kPa back pressure.



Figure 7.7. (a) H₂-air polarization curves of the PEM fuel cells prepared with Pt to Co ratio of 2:1 at different annealing temperature (iR-corrected cell voltage vs. current density) and (b) current density at 0.6 V as a function of annealing temperature. The fuel cell operating conditions are: H₂/air (2.0/2.0), 80 °C, 50% RH, 170 kPa back pressure.



Figure 7.8. Mass Activity Tafel plot of Co-doped Pt/A-CCS catalysts with Pt to Co ratio of 2:1 annealed at (a) 800 °C and (b) 850 °C (iR-corrected cell voltage vs. mass activity) before and after 30,000 cycles between 0.6 and 1.0 V. The fuel cell operating conditions are: H_2/O_2 (2.0/9.5), 80 °C, 100% RH, 150kPa back pressure.



Figure 7.9. Mass activity at 0.9 V as a function of cycle number of Co-doped Pt/A-CCS catalysts with Pt to Co ratio of 2:1 annealed at 800 $^{\circ}$ C and 850 $^{\circ}$ C.



Figure 7.10. H₂-air polarization curves of the PEM fuel cells prepared with Co-doped Pt/A-CCS catalysts with Pt to Co ratio of 2:1 annealed at (a) 800 °C and (b) 850 °C (iR-corrected cell voltage vs. current density) before and after 30,000 cycles between 0.6 and 1.0 V. The fuel cell operating conditions are: H₂/air (2.0/2.0), 80 °C, 50% RH, 170 kPa back pressure.



Figure 7.11. Comparison of current density before and after each 10k cycles measured at 0.6 V for Co-doped Pt/A-CCS catalysts with Pt to Co ratio of 2:1 annealed at 800 $^{\circ}$ C and 850 $^{\circ}$ C.



Figure 7.12. H₂-air polarization curves of the PEM fuel cells prepared with Co-doped Pt/A-CCS catalyst before and after 5,000 cycles between 1.0 and 1.5 V. The fuel cell operating conditions are: H₂/air (2.0/2.0), 80 °C, 50% RH, 170 kPa back pressure.

REFERENCES

[1] S. Basu, Recent Trends in Fuel Cell Science and Technology, Springer2007.

[2] H. Xu, L. Kong, X. Wen, Fuel cell power system and high power DC-DC converter, Power Electronics, IEEE Transactions on, 19 (2004) 1250-1255.

[3] A. Kirubakaran, S. Jain, R.K. Nema, A review on fuel cell technologies and power electronic interface, Renewable and Sustainable Energy Reviews, 13 (2009) 2430-2440.

[4] Fuel Cell Basics. http://americanhistory.si.edu/fuelcells/basics.htm

[5] B.L. García, V.A. Sethuraman, J.W. Weidner, R.E. White, R. Dougal, Mathematical Model of a Direct Methanol Fuel Cell, Journal of Fuel Cell Science and Technology, 1 (2004) 43-48.

[6] M. Farooque, H.C. Maru, Fuel cells-the clean and efficient power generators, Proceedings of the IEEE, 89 (2001) 1819-1829.

[7] D. Papageorgopoulos, Fuel Cells overview, 2015 U.S. Department of Energy (DOE) Hydrogen and Fuel Cells Program and Vehicle Technologies Office Annual Merit Review and Peer Evaluation MeetingWashington D.C., 2015.

[8] S. Zhang, X. Yuan, H. Wang, W. Mérida, H. Zhu, J. Shen, S. Wu, J. Zhang, A review of accelerated stress tests of MEA durability in PEM fuel cells, International Journal of Hydrogen Energy, 34 (2009) 388-404.

[9] E.A. Ticianelli, J.G. Beery, S. Srinivasan, DEPENDENCE OF PERFORMANCE OF SOLID POLYMER ELECTROLYTE FUEL-CELLS WITH LOW PLATINUM LOADING ON MORPHOLOGICAL-CHARACTERISTICS OF THE ELECTRODES, Journal of Applied Electrochemistry, 21 (1991) 597-605.

[10] C. Welch, A. Labouriau, R. Hjelm, B. Orler, C. Johnston, Y.S. Kim, Nafion in Dilute Solvent Systems: Dispersion or Solution?, ACS Macro Letters, 1 (2012) 1403-1407.

[11] Y.S. Kim, C.F. Welch, N.H. Mack, R.P. Hjelm, E.B. Orler, M.E. Hawley, K.S. Lee, S.D. Yim, C.M. Johnston, Highly durable fuel cell electrodes based on ionomers dispersed in glycerol, Phys Chem Chem Phys, 16 (2014) 5927-5932.

[12] H.A. Gasteiger, W. Gu, R. Makharia, M.F. Mathias, B. Sompalli, Beginning-of-life MEA performance — efficiency loss contributions, Handbook of Fuel Cells, John Wiley & Sons, Ltd2010.

[13] N.M. Marković, B.N. Grgur, P.N. Ross, Temperature-Dependent Hydrogen Electrochemistry on Platinum Low-Index Single-Crystal Surfaces in Acid Solutions, The Journal of Physical Chemistry B, 101 (1997) 5405-5413.

[14] H.A. Gasteiger, J.E. Panels, S.G. Yan, Dependence of PEM fuel cell performance on catalyst loading, Journal of Power Sources, 127 (2004) 162-171.

[15] R. Borup, J. Meyers, B. Pivovar, Y.S. Kim, R. Mukundan, N. Garland, D. Myers, M. Wilson, F. Garzon, D. Wood, P. Zelenay, K. More, K. Stroh, T. Zawodzinski, J. Boncella, J.E. McGrath, M. Inaba, K. Miyatake, M. Hori, K. Ota, Z. Ogumi, S. Miyata, A. Nishikata, Z. Siroma, Y. Uchimoto, K. Yasuda, K.-i. Kimijima, N. Iwashita, Scientific Aspects of

Polymer Electrolyte Fuel Cell Durability and Degradation, Chemical Reviews, 107 (2007) 3904-3951.

[16] A.K. Sahu, G. Selvarani, S. Pitchumani, P. Sridhar, A.K. Shukla, A Sol-Gel Modified Alternative Nafion-Silica Composite Membrane for Polymer Electrolyte Fuel Cells, Journal of The Electrochemical Society, 154 (2007) B123-B132.

[17] Q. Li, J.O. Jensen, R.F. Savinell, N.J. Bjerrum, High temperature proton exchange membranes based on polybenzimidazoles for fuel cells, Progress in Polymer Science, 34 (2009) 449-477.

[18] S. Atkinson, Membranes for fuel cells compared in real time, Membrane Technology, 2005 (2005) 5-7.

[19] L.R. Jordan, A.K. Shukla, T. Behrsing, N.R. Avery, B.C. Muddle, M. Forsyth, Diffusion layer parameters influencing optimal fuel cell performance, Journal of Power Sources, 86 (2000) 250-254.

[20] Z. Qi, A. Kaufman, Improvement of water management by a microporous sublayer for PEM fuel cells, Journal of Power Sources, 109 (2002) 38-46.

[21] M. Mortazavi, K. Tajiri, Effect of the PTFE content in the gas diffusion layer on water transport in polymer electrolyte fuel cells (PEFCs), Journal of Power Sources, 245 (2014) 236-244.

[22] G. Chen, H. Zhang, H. Ma, H. Zhong, Electrochemical durability of gas diffusion layer under simulated proton exchange membrane fuel cell conditions, International Journal of Hydrogen Energy, 34 (2009) 8185-8192.

[23] X. Wang, H. Zhang, J. Zhang, H. Xu, X. Zhu, J. Chen, B. Yi, A bi-functional microporous layer with composite carbon black for PEM fuel cells, Journal of Power Sources, 162 (2006) 474-479.

[24] (!!! INVALID CITATION !!! [24, 25]).

[25] L.M. Roen, C.H. Paik, T.D. Jarvic, Electrocatalytic corrosion of carbon support in PEMFC cathodes, Electrochem. Solid State Lett., 7 (2004) A19-A22.

[26] C.A. Reiser, L. Bregoli, T.W. Patterson, J.S. Yi, J.D. Yang, M.L. Perry, T.D. Jarvi, A Reverse-Current Decay Mechanism for Fuel Cells, Electrochemical and Solid-State Letters, 8 (2005) A273-A276.

[27] F. Xu, M.X. Wang, Q. Liu, H.F. Sun, S. Simonson, N. Ogbeifun, E.A. Stach, J.A. Xie, Investigation of the Carbon Corrosion Process for Polymer Electrolyte Fuel Cells Using a Rotating Disk Electrode Technique, Journal of the Electrochemical Society, 157 (2010) B1138-B1145. [28] S. Maass, F. Finsterwalder, G. Frank, R. Hartmann, C. Merten, Carbon support oxidation in PEM fuel cell cathodes, Journal of Power Sources, 176 (2008) 444-451.

[29] N. Linse, L. Gubler, G.G. Scherer, A. Wokaun, The effect of platinum on carbon corrosion behavior in polymer electrolyte fuel cells, Electrochimica Acta, 56 (2011) 7541-7549.

[30] Y.Y. Shao, G.P. Yin, Y.Z. Gao, P.F. Shi, Durability study of Pt/C and Pt/CNTs catalysts under simulated PEM fuel cell conditions, Journal of the Electrochemical Society, 153 (2006) A1093-A1097.

[31] Y.Y. Shao, G.P. Yin, J. Zhang, Y.Z. Gao, Comparative investigation of the resistance to electrochemical oxidation of carbon black and carbon nanotubes in aqueous sulfuric acid solution, Electrochimica Acta, 51 (2006) 5853-5857.

[32] B. Avasarala, R. Moore, P. Haldar, Surface oxidation of carbon supports due to potential cycling under PEM fuel cell conditions, Electrochimica Acta, 55 (2010) 4765-4771.

[33] M. Fowler, J.C. Amphlett, R.F. Mann, B.A. Peppley, P.R. Roberge, Issues associated with voltage degradation in a PEMFC, J. New Mat.Electrochem. Syst., 5 (2002) 255-262.

[34] E. Guilminot, A. Corcella, M. Chatenet, F. Maillard, F. Charlot, G. Berthomé, C. Iojoiu, J.-Y. Sanchez, E. Rossinot, E. Claude, Membrane and Active Layer Degradation upon PEMFC Steady-State Operation: I. Platinum Dissolution and Redistribution within the MEA, Journal of The Electrochemical Society, 154 (2007) B1106-B1114.

[35] C. He, S. Desai, G. Brown, S. Bollepalli, PEM fuel cell catalysts: Cost, performance, and durability, Interface-Electrochemical Society, 14 (2005) 41-46.

[36] M.K. Debe, A. Schmoeckel, S. Hendricks, G. Vernstrom, G. Haugen, R. Atanasoski, Durability Aspects of Nanostructured Thin Film Catalysts for PEM Fuel Cells, ECS Transactions, 1 (2006) 51-66.

[37] S.V. Selvaganesh, P. Sridhar, S. Pitchumani, A.K. Shukla, Pristine and graphitized-MWCNTs as durable cathode-catalyst supports for PEFCs, Journal of Solid State Electrochemistry, 18 (2014) 1291-1305.

[38] F. Forouzandeh, D.W. Banham, F.X. Feng, X.A. Li, S.Y. Ye, V. Birss, Corrosion Study of Mesoporous Carbon Supports for Use in PEM Fuel Cells, in: H.A. Gasteiger, A. Weber, K. Shinohara, H. Uchida, S. Mitsushima, T.J. Schmidt, S.R. Narayanan, V. Ramani, T. Fuller, M. Edmundson, P. Strasser, R. Mantz, J. Fenton, F.N. Buchi, D.C. Hansen, D.L. Jones, C. Coutanceau, K. SwiderLyons, K.A. Perry (Eds.) Polymer Electrolyte Fuel Cells 13, Electrochemical Soc Inc, Pennington, 2013, pp. 1739-1749.

[39] J. Wang, G. Yin, Y. Shao, Z. Wang, Y. Gao, Electrochemical durability investigation of single-walled and multi-walled carbon nanotubes under potentiostatic conditions, Journal of Power Sources, 176 (2008) 128-131.

[40] S.M. Andersen, M. Borghei, P. Lund, Y.-R. Elina, A. Pasanen, E. Kauppinen, V. Ruiz, P. Kauranen, E.M. Skou, Durability of carbon nanofiber (CNF) & amp; carbon nanotube (CNT) as catalyst support for Proton Exchange Membrane Fuel Cells, Solid State Ionics, 231 (2013) 94-101.

[41] J. Jung, B. Park, J. Kim, Durability test with fuel starvation using a Pt/CNF catalyst in PEMFC, Nanoscale Res Lett, 7 (2012).

[42] Y. Shao, S. Zhang, C. Wang, Z. Nie, J. Liu, Y. Wang, Y. Lin, Highly durable graphene nanoplatelets supported Pt nanocatalysts for oxygen reduction, Journal of Power Sources, 195 (2010) 4600-4605.

[43] J.H. Jung, H.J. Park, J. Kim, S.H. Hur, Highly durable Pt/graphene oxide and Pt/C hybrid catalyst for polymer electrolyte membrane fuel cell, Journal of Power Sources, 248 (2014) 1156-1162.

[44] N. Jha, P. Ramesh, E. Bekyarova, X. Tian, F. Wang, M.E. Itkis, R.C. Haddon, Functionalized Single-Walled Carbon Nanotube-Based Fuel Cell Benchmarked Against US DOE 2017 Technical Targets, Sci. Rep., 3 (2013).

[45] A. Ghosh, S. Basu, A. Verma, Graphene and Functionalized Graphene Supported Platinum Catalyst for PEMFC, Fuel Cells, 13 (2013) 355-363.

[46] Y.L. Hsin, K.C. Hwang, C.-T. Yeh, Poly(vinylpyrrolidone)-Modified Graphite Carbon Nanofibers as Promising Supports for PtRu Catalysts in Direct Methanol Fuel Cells, Journal of the American Chemical Society, 129 (2007) 9999-10010.

[47] H.-S. Oh, K. Kim, H. Kim, Polypyrrole-modified hydrophobic carbon nanotubes as promising electrocatalyst supports in polymer electrolyte membrane fuel cells, International Journal of Hydrogen Energy, 36 (2011) 11564-11571.

[48] Z. Wang, Q. Zhang, D. Kuehner, X. Xu, A. Ivaska, L. Niu, The synthesis of ionicliquid-functionalized multiwalled carbon nanotubes decorated with highly dispersed Au nanoparticles and their use in oxygen reduction by electrocatalysis, Carbon, 46 (2008) 1687-1692.

[49] B. Wu, D. Hu, Y. Kuang, B. Liu, X. Zhang, J. Chen, Functionalization of Carbon Nanotubes by an Ionic-Liquid Polymer: Dispersion of Pt and PtRu Nanoparticles on Carbon Nanotubes and Their Electrocatalytic Oxidation of Methanol, Angewandte Chemie International Edition, 48 (2009) 4751-4754.

[50] H.-S. Oh, H. Kim, Efficient Synthesis of Pt Nanoparticles Supported on Hydrophobic Graphitized Carbon Nanofibers for Electrocatalysts Using Noncovalent Functionalization, Advanced Functional Materials, 21 (2011) 3954-3960.

[51] S. Wang, X. Wang, S.P. Jiang, PtRu Nanoparticles Supported on 1-Aminopyrene-Functionalized Multiwalled Carbon Nanotubes and Their Electrocatalytic Activity for Methanol Oxidation, Langmuir, 24 (2008) 10505-10512.

[52] V.R. Stamenkovic, B.S. Mun, K.J.J. Mayrhofer, P.N. Ross, N.M. Markovic, Effect of Surface Composition on Electronic Structure, Stability, and Electrocatalytic Properties of Pt-Transition Metal Alloys: Pt-Skin versus Pt-Skeleton Surfaces, Journal of the American Chemical Society, 128 (2006) 8813-8819.

[53] S.-Y. Huang, P. Ganesan, B.N. Popov, Titania supported platinum catalyst with high electrocatalytic activity and stability for polymer electrolyte membrane fuel cell, Applied Catalysis B: Environmental, 102 (2011) 71-77.

[54] S.-Y. Huang, P. Ganesan, B.N. Popov, Electrocatalytic activity and stability of niobium-doped titanium oxide supported platinum catalyst for polymer electrolyte membrane fuel cells, Applied Catalysis B: Environmental, 96 (2010) 224-231.

[55] M. Wang, D.-j. Guo, H.-l. Li, High activity of novel Pd/TiO2 nanotube catalysts for methanol electro-oxidation, Journal of Solid State Chemistry, 178 (2005) 1996-2000.

[56] D.-H. Lim, W.-J. Lee, N.L. Macy, W.H. Smyrl, Electrochemical Durability Investigation of Pt/TiO2 Nanotube Catalysts for Polymer Electrolyte Membrane Fuel Cells, Electrochemical and Solid-State Letters, 12 (2009) B123-B125.

[57] N. Rajalakshmi, N. Lakshmi, K.S. Dhathathreyan, Nano titanium oxide catalyst support for proton exchange membrane fuel cells, International Journal of Hydrogen Energy, 33 (2008) 7521-7526.

[58] A. Ignaszak, C. Song, W. Zhu, J. Zhang, A. Bauer, R. Baker, V. Neburchilov, S. Ye, S. Campbell, Titanium carbide and its core-shelled derivative TiC@TiO2 as catalyst supports for proton exchange membrane fuel cells, Electrochimica Acta, 69 (2012) 397-405.

[59] P. Zhang, S.-Y. Huang, B.N. Popov, Mesoporous Tin Oxide as an Oxidation-Resistant Catalyst Support for Proton Exchange Membrane Fuel Cells, Journal of The Electrochemical Society, 157 (2010) B1163.

[60] S.M. Andersen, C.F. Nørgaard, M.J. Larsen, E. Skou, Tin Dioxide as an Effective Antioxidant for Proton Exchange Membrane Fuel Cells, Journal of Power Sources, 273 (2015) 158-161.

[61] M. Dou, M. Hou, D. Liang, W. Lu, Z. Shao, B. Yi, SnO2 nanocluster supported Pt catalyst with high stability for proton exchange membrane fuel cells, Electrochimica Acta, 92 (2013) 468-473.

[62] H. Chhina, S. Campbell, O. Kesler, Ex situ Evaluation of Tungsten Oxide as a Catalyst Support for PEMFCs, Journal of The Electrochemical Society, 154 (2007) B533-B539.

[63] M. Perchthaler, T. Ossiander, V. Juhart, J. Mitzel, C. Heinzl, C. Scheu, V. Hacker, Tungsten materials as durable catalyst supports for fuel cell electrodes, Journal of Power Sources, 243 (2013) 472-480.

[64] A.J. Martín, A.M. Chaparro, L. Daza, Single cell study of electrodeposited cathodic electrodes based on Pt–WO3 for polymer electrolyte fuel cells, Journal of Power Sources, 196 (2011) 4187-4192.

[65] J. Bernard d'Arbigny, G. Taillades, J. Rozière, D. Jones, M. Marrony, High Surface Area Tungsten Carbide with Novel Architecture and High Electrochemical Stability, ECS Transactions, 41 (2011) 1207-1213.

[66] J.B. d'Arbigny, G. Taillades, M. Marrony, D.J. Jones, J. Roziere, Hollow microspheres with a tungsten carbide kernel for PEMFC application, Chemical Communications, 47 (2011) 7950-7952.

[67] M. Wesselmark, B. Wickman, C. Lagergren, G. Lindbergh, Electrochemical performance and stability of thin film electrodes with metal oxides in polymer electrolyte fuel cells, Electrochimica Acta, 55 (2010) 7590-7596.

[68] S. Sharma, B.G. Pollet, Support materials for PEMFC and DMFC electrocatalysts— A review, Journal of Power Sources, 208 (2012) 96-119.

[69] D. Morris, Y. Dou, J. Rebane, C.E.J. Mitchell, R.G. Egdell, D.S.L. Law, A. Vittadini, M. Casarin, Photoemission and STM study of the electronic structure of Nb-doped ${\rm Metr}_{2}$, Physical Review B, 61 (2000) 13445-13457.

[70] D. Eder, Carbon Nanotube–Inorganic Hybrids, Chemical Reviews, 110 (2010) 1348-1385.

[71] S. Guo, S. Dong, E. Wang, Gold/Platinum Hybrid Nanoparticles Supported on Multiwalled Carbon Nanotube/Silica Coaxial Nanocables: Preparation and Application as Electrocatalysts for Oxygen Reduction, The Journal of Physical Chemistry C, 112 (2008) 2389-2393.

[72] S. Seok, I. Choi, K.G. Lee, B.G. Choi, K.J. Park, J.Y. Park, O.J. Kwon, S.J. Lee, D.H. Kim, Dopamine-induced Pt and N-doped carbon@silica hybrids as high-performance anode catalysts for polymer electrolyte membrane fuel cells, RSC Advances, 4 (2014) 42582-42584.

[73] C.-W. Liu, C.-M. Lai, J.-N. Lin, L.-D. Tsai, K.-W. Wang, Highly effective oxygen reduction activity and durability of titanium oxide modified PtAu/C electrocatalysts, RSC Advances, 4 (2014) 15820-15824.

[74] Y. Chen, J. Wang, X. Meng, Y. Zhong, R. Li, X. Sun, S. Ye, S. Knights, Pt–SnO2/nitrogen-doped CNT hybrid catalysts for proton-exchange membrane fuel cells (PEMFC): Effects of crystalline and amorphous SnO2 by atomic layer deposition, Journal of Power Sources, 238 (2013) 144-149.

[75] B.C.H. Steele, A. Heinzel, Materials for fuel-cell technologies, Nature, 414 (2001) 345-352.

[76] J.F. Wu, X.Z. Yuan, J.J. Martin, H.J. Wang, J.J. Zhang, J. Shen, S.H. Wu, W. Merida, A review of PEM fuel cell durability: Degradation mechanisms and mitigation strategies, Journal of Power Sources, 184 (2008) 104-119.

[77] M. Pourbaix, Atlas of electrochemical equilibria in aqueous solutions, 1st English ed., Pergamon Press, Oxford, New York,, 1966.

[78] M. Uchimura, S.S. Kocha, The Impact of Cycle Profile on PEMFC Durability, ECS Transactions, 11 (2007) 1215-1226.

[79] R.M. Darling, J.P. Meyers, Kinetic Model of Platinum Dissolution in PEMFCs, Journal of The Electrochemical Society, 150 (2003) A1523-A1527.

[80] K. Kinoshita, J.T. Lundquist, P. Stonehart, Potential cycling effects on platinum electrocatalyst surfaces, Journal of Electrocanalytical Chemistry and Interfacial Electrochemistry, 48 (1973) 157-166.

[81] D.C. Johnson, D.T. Napp, S. Bruckenstein, A ring-disk electrode study of the current/potential behaviour of platinum in 1.0 M sulphuric and 0.1 M perchloric acids, Electrochimica Acta, 15 (1970) 1493-1509.

[82] Z. Chen, M. Waje, W. Li, Y. Yan, Supportless Pt and PtPd Nanotubes as Electrocatalysts for Oxygen-Reduction Reactions, Angewandte Chemie International Edition, 46 (2007) 4060-4063.

[83] H.R. Colón-Mercado, H. Kim, B.N. Popov, Durability study of Pt3Ni1 catalysts as cathode in PEM fuel cells, Electrochemistry Communications, 6 (2004) 795-799.

[84] A. Takai, Y. Yamauchi, K. Kuroda, Fabrication of mesoporous Pt nanotubes utilizing dual templates under a reduced pressure condition, Chemical Communications, (2008) 4171-4173.

[85] G. Zhang, S. Sun, M. Cai, Y. Zhang, R. Li, X. Sun, Porous Dendritic Platinum Nanotubes with Extremely High Activity and Stability for Oxygen Reduction Reaction, Scientific Reports, 3 (2013) 1526.

[86] M. Inaba, Durability of Electrocatalysts in Polymer Electrolyte Fuel Cells, ECS Transactions, 25 (2009) 573-581.

[87] S. Arisetty, X. Wang, R.K. Ahluwalia, R. Mukundan, R. Borup, J. Davey, D. Langlois, F. Gambini, O. Polevaya, S. Blanchet, Catalyst Durability in PEM Fuel Cells with Low Platinum Loading, Journal of The Electrochemical Society, 159 (2012) B455-B462.

[88] S.R. Dhanushkodi, S. Kundu, M.W. Fowler, M.D. Pritzker, Study of the effect of temperature on Pt dissolution in polymer electrolyte membrane fuel cells via accelerated stress tests, Journal of Power Sources, 245 (2014) 1035-1045.

[89] Y.S. Kim, C.F. Welch, N.H. Mack, R.P. Hjelm, E.B. Orler, M.E. Hawley, K.S. Lee, S.D. Yim, C.M. Johnston, Highly durable fuel cell electrodes based on ionomers dispersed in glycerol, Physical Chemistry Chemical Physics, 16 (2014) 5927-5932.

[90] W.H. Lee, H. Kim, Electrocatalytic activity and durability study of carbon supported Pt nanodendrites in polymer electrolyte membrane fuel cells, International Journal of Hydrogen Energy, 38 (2013) 7126-7132.

[91] X. Li, S. Park, B.N. Popov, Highly stable Pt and PtPd hybrid catalysts supported on a nitrogen-modified carbon composite for fuel cell application, Journal of Power Sources, 195 (2010) 445-452.

[92] R. Makharia, S. Kocha, P. Yu, M.A. Sweikart, W. Gu, F. Wagner, H.A. Gasteiger, Durable PEM Fuel Cell Electrode Materials: Requirements and Benchmarking Methodologies, Ecs Transactions, 1 (2006) 3-18.

[93] S. Ohyagi, T. Matsuda, Y. Iseki, T. Sasaki, C. Kaito, Effects of operating conditions on durability of polymer electrolyte membrane fuel cell Pt cathode catalyst layer, Journal of Power Sources, 196 (2011) 3743-3749.

[94] M. Uchimura, S. Sugawara, Y. Suzuki, J. Zhang, S.S. Kocha, Electrocatalyst Durability under Simulated Automotive Drive Cycles, ECS Transactions, 16 (2008) 225-234.

[95] Z. Yang, S. Ball, D. Condit, M. Gummalla, Systematic Study on the Impact of Pt Particle Size and Operating Conditions on PEMFC Cathode Catalyst Durability, Journal of The Electrochemical Society, 158 (2011) B1439-B1445.

[96] P. Yu, M. Pemberton, P. Plasse, PtCo/C cathode catalyst for improved durability in PEMFCs, Journal of Power Sources, 144 (2005) 11-20.

[97] A. Ohma, K. Shinohara, A. Iiyama, T. Yoshida, A. Daimaru, Membrane and Catalyst Performance Targets for Automotive Fuel Cells by FCCJ Membrane, Catalyst, MEA WG, ECS Transactions, 41 (2011) 775-784.

[98] A.A.-M. Marcu, G. Toth, P. Pietrasz, Cathode Catalysts Degradation Mechanism from Liquid Electrolyte to Polymer Electrolyte Membrane Fuel Cells, ECS Transactions, 50 (2013) 1523-1532.

[99] N.M. Marković, T.J. Schmidt, V. Stamenković, P.N. Ross, Oxygen Reduction Reaction on Pt and Pt Bimetallic Surfaces: A Selective Review, Fuel Cells, 1 (2001) 105-116.

[100] S.-I. Choi, R. Choi, S.W. Han, J.T. Park, Synthesis and characterization of Pt9Co nanocubes with high activity for oxygen reduction, Chemical Communications, 46 (2010) 4950-4952.

[101] S.-I. Choi, R. Choi, S.W. Han, J.T. Park, Shape-Controlled Synthesis of Pt3Co Nanocrystals with High Electrocatalytic Activity toward Oxygen Reduction, Chemistry – A European Journal, 17 (2011) 12280-12284.

[102] Y. Kang, C.B. Murray, Synthesis and Electrocatalytic Properties of Cubic Mn–Pt Nanocrystals (Nanocubes), Journal of the American Chemical Society, 132 (2010) 7568-7569.

[103] P. Strasser, S. Koh, T. Anniyev, J. Greeley, K. More, C. Yu, Z. Liu, S. Kaya, D. Nordlund, H. Ogasawara, M.F. Toney, A. Nilsson, Lattice-strain control of the activity in dealloyed core–shell fuel cell catalysts, Nat Chem, 2 (2010) 454-460.

[104] A.R. Malheiro, J. Perez, E.I. Santiago, H.M. Villullas, The Extent on the Nanoscale of Pt-Skin Effects on Oxygen Reduction and Its Influence on Fuel Cell Power, The Journal of Physical Chemistry C, 114 (2010) 20267-20271.

[105] Y. Chen, Z. Liang, F. Yang, Y. Liu, S. Chen, Ni–Pt Core–Shell Nanoparticles as Oxygen Reduction Electrocatalysts: Effect of Pt Shell Coverage, The Journal of Physical Chemistry C, 115 (2011) 24073-24079.

[106] C. Wang, M. Chi, D. Li, D. Strmcnik, D. van der Vliet, G. Wang, V. Komanicky, K.-C. Chang, A.P. Paulikas, D. Tripkovic, J. Pearson, K.L. More, N.M. Markovic, V.R. Stamenkovic, Design and Synthesis of Bimetallic Electrocatalyst with Multilayered Pt-Skin Surfaces, Journal of the American Chemical Society, 133 (2011) 14396-14403.

[107] M. Shao, K. Shoemaker, A. Peles, K. Kaneko, L. Protsailo, Pt Monolayer on Porous Pd–Cu Alloys as Oxygen Reduction Electrocatalysts, Journal of the American Chemical Society, 132 (2010) 9253-9255.

[108] J. Zhang, M.B. Vukmirovic, Y. Xu, M. Mavrikakis, R.R. Adzic, Controlling the Catalytic Activity of Platinum-Monolayer Electrocatalysts for Oxygen Reduction with Different Substrates, Angewandte Chemie, 117 (2005) 2170-2173.

[109] K.A. Kuttiyiel, K. Sasaki, Y. Choi, D. Su, P. Liu, R.R. Adzic, Nitride Stabilized PtNi Core–Shell Nanocatalyst for high Oxygen Reduction Activity, Nano Letters, 12 (2012) 6266-6271.

[110] H.A. Gasteiger, S.S. Kocha, B. Sompalli, F.T. Wagner, Activity benchmarks and requirements for Pt, Pt-alloy, and non-Pt oxygen reduction catalysts for PEMFCs, Applied Catalysis B: Environmental, 56 (2005) 9-35.

[111] J. Wang, G. Yin, Y. Shao, S. Zhang, Z. Wang, Y. Gao, Effect of carbon black support corrosion on the durability of Pt/C catalyst, Journal of Power Sources, 171 (2007) 331-339.

[112] C. Grolleau, C. Coutanceau, F. Pierre, J.M. Léger, Effect of potential cycling on structure and activity of Pt nanoparticles dispersed on different carbon supports, Electrochimica Acta, 53 (2008) 7157-7165.

[113] S.C. Zignani, E. Antolini, E.R. Gonzalez, Evaluation of the stability and durability of Pt and Pt–Co/C catalysts for polymer electrolyte membrane fuel cells, Journal of Power Sources, 182 (2008) 83-90.

[114] L. Gan, M. Heggen, R. O'Malley, B. Theobald, P. Strasser, Understanding and Controlling Nanoporosity Formation for Improving the Stability of Bimetallic Fuel Cell Catalysts, Nano Letters, 13 (2013) 1131-1138.

[115] L. Gan, C. Cui, S. Rudi, P. Strasser, Core–Shell and Nanoporous Particle Architectures and Their Effect on the Activity and Stability of Pt ORR Electrocatalysts, Top Catal, 57 (2014) 236-244.

[116] R. Choi, S.-I. Choi, C.H. Choi, K.M. Nam, S.I. Woo, J.T. Park, S.W. Han, Designed Synthesis of Well-Defined Pd@Pt Core–Shell Nanoparticles with Controlled Shell Thickness as Efficient Oxygen Reduction Electrocatalysts, Chemistry – A European Journal, 19 (2013) 8190-8198.

[117] S.T. Bliznakov, M.B. Vukmirovic, L. Yang, E.A. Sutter, R.R. Adzic, Pt Monolayer on Electrodeposited Pd Nanostructures: Advanced Cathode Catalysts for PEM Fuel Cells, Journal of The Electrochemical Society, 159 (2012) F501-F506.

[118] K.S. Mason, K.C. Neyerlin, M.-C. Kuo, K.C. Horning, K.L. More, A.M. Herring, Investigation of a Silicotungstic Acid Functionalized Carbon on Pt Activity and Durability for the Oxygen Reduction Reaction, Journal of The Electrochemical Society, 159 (2012) F871-F879.

[119] J.Y. Kim, S. Lee, T.-Y. Kim, H.-T. Kim, A Simple Diazonium Coupling Reaction Enhances Durability of Modified Graphitic Carbons Used as Catalyst Supports for Polymer Electrolyte Membrane Fuel Cell, Electrochimica Acta, 134 (2014) 418-425.

[120] F.T. Wagner, H.A. Gasteiger, R. Makharia, K.C. Neyerlin, E.L. Thompson, S.G. Yan, Catalyst Development Needs and Pathways for Automotive PEM Fuel Cells, ECS Transactions, 3 (2006) 19-29.

[121] V.R. Stamenkovic, B.S. Mun, M. Arenz, K.J. Mayrhofer, C.A. Lucas, G. Wang, P.N. Ross, N.M. Markovic, Trends in electrocatalysis on extended and nanoscale Pt-bimetallic alloy surfaces, Nat Mater, 6 (2007) 241-247.

[122] C. Chen, Y. Kang, Z. Huo, Z. Zhu, W. Huang, H.L. Xin, J.D. Snyder, D. Li, J.A. Herron, M. Mavrikakis, M. Chi, K.L. More, Y. Li, N.M. Markovic, G.A. Somorjai, P. Yang, V.R. Stamenkovic, Highly crystalline multimetallic nanoframes with three-dimensional electrocatalytic surfaces, Science, 343 (2014) 1339-1343.

[123] C. Wang, D. van der Vliet, K.L. More, N.J. Zaluzec, S. Peng, S. Sun, H. Daimon, G. Wang, J. Greeley, J. Pearson, A.P. Paulikas, G. Karapetrov, D. Strmcnik, N.M. Markovic, V.R. Stamenkovic, Multimetallic Au/FePt3 nanoparticles as highly durable electrocatalyst, Nano Lett, 11 (2011) 919-926.

[124] V.R. Stamenkovic, B. Fowler, B.S. Mun, G. Wang, P.N. Ross, C.A. Lucas, N.M. Markovic, Improved oxygen reduction activity on Pt3Ni(111) via increased surface site availability, Science, 315 (2007) 493-497.

[125] C. Wang, M. Chi, D. Li, D. Strmcnik, D. van der Vliet, G. Wang, V. Komanicky, K.C. Chang, A.P. Paulikas, D. Tripkovic, J. Pearson, K.L. More, N.M. Markovic, V.R. Stamenkovic, Design and synthesis of bimetallic electrocatalyst with multilayered Pt-skin surfaces, J Am Chem Soc, 133 (2011) 14396-14403.

[126] Hydrogen, Fuel Cells & Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan, 2010.

[127] T. Xie, W. Jung, T. Kim, P. Ganesan, B.N. Popov, Development of Highly Active and Durable Hybrid Cathode Catalysts for Polymer Electrolyte Membrane Fuel Cells, Journal of the Electrochemical Society, 161 (2014) F1489-F1501.

[128] T. Kim, T.Y. Xie, W. Jung, F. Gadala-Maria, P. Ganesan, B.N. Popov, Development of catalytically active and highly stable catalyst supports for polymer electrolyte membrane fuel cells, J Power Sources, 273 (2015) 761-774.

[129] A.J. Bard, L.R. Faulkner, Electrochemical methods : fundamentals and applications, 2. ed., John Wiley, New York, 2001.

[130] J.O.M. Bockris, B.E. Conway, E.B. Yeager, R.E. White, S. Srinivasan, Comprehensive treatise of electrochemistry, Plenum, New York, 1980.

[131] M.S. Saha, D. Malevich, E. Halliop, J.G. Pharoah, B.A. Peppley, K. Karan, Electrochemical Activity and Catalyst Utilization of Low Pt and Thickness Controlled Membrane Electrode Assemblies, Journal of the Electrochemical Society, 158 (2011) B562-B567.

[132] M. Lee, M. Uchida, D.A. Tryk, H. Uchida, M. Watanabe, The effectiveness of platinum/carbon electrocatalysts: Dependence on catalyst layer thickness and Pt alloy catalytic effects, Electrochimica Acta, 56 (2011) 4783-4790.

[133] M.K. Debe, Effect of Electrode Surface Area Distribution on High Current Density Performance of PEM Fuel Cells, Journal of The Electrochemical Society, 159 (2011) B53-B66.

[134] N.A. Siddique, F. Liu, Process based reconstruction and simulation of a threedimensional fuel cell catalyst layer, Electrochimica Acta, 55 (2010) 5357-5366. [135] M. Yuasa, A. Yamaguchi, H. Itsuki, K. Tanaka, M. Yamamoto, K. Oyaizu, Modifying Carbon Particles with Polypyrrole for Adsorption of Cobalt Ions as Electrocatatytic Site for Oxygen Reduction, Chemistry of Materials, 17 (2005) 4278-4281.

[136] D. Villers, X. Jacques-Bédard, J.-P. Dodelet, Fe-Based Catalysts for Oxygen Reduction in PEM Fuel Cells: Pretreatment of the Carbon Support, Journal of The Electrochemical Society, 151 (2004) A1507-A1515.

[137] P. Mani, R. Srivastava, P. Strasser, Dealloyed Pt–Cu Core–Shell Nanoparticle Electrocatalysts for Use in PEM Fuel Cell Cathodes, The Journal of Physical Chemistry C, 112 (2008) 2770-2778.

[138] F.T. Wagner, B. Lakshmanan, M.F. Mathias, Electrochemistry and the Future of the Automobile, The Journal of Physical Chemistry Letters, 1 (2010) 2204-2219.

[139] M. Inaba, H. Yamada, J. Tokunaga, A. Tasaka, Effect of Agglomeration of Pt/C Catalyst on Hydrogen Peroxide Formation, Electrochemical and Solid-State Letters, 7 (2004) A474-A476.

[140] A. Bonakdarpour, T.R. Dahn, R.T. Atanasoski, M.K. Debe, J.R. Dahn, H2O2 Release during Oxygen Reduction Reaction on Pt Nanoparticles, Electrochemical and Solid-State Letters, 11 (2008) B208-B211.

[141] K. Kinoshita, Electrochemical Oxygen Technology, 1992.

[142] M.L. Perry, J. Newman, E.J. Cairns, Mass Transport in Gas-Diffusion Electrodes: A Diagnostic Tool for Fuel-Cell Cathodes, Journal of The Electrochemical Society, 145 (1998) 5-15.

[143] F. Jaouen, G. Lindbergh, G. Sundholm, Investigation of Mass-Transport Limitations in the Solid Polymer Fuel Cell Cathode: I. Mathematical Model, Journal of The Electrochemical Society, 149 (2002) A437-A447.

[144] E.L. Gyenge, Dimensionless numbers and correlating equations for the analysis of the membrane-gas diffusion electrode assembly in polymer electrolyte fuel cells, Journal of Power Sources, 152 (2005) 105-121.

[145] Á. Kriston, G. Inzelt, I. Faragó, T. Szabó, Simulation of the transient behavior of fuel cells by using operator splitting techniques for real-time applications, Computers & Chemical Engineering, 34 (2010) 339-348.

[146] S. Litster, N. Djilali, Mathematical modelling of ambient air-breathing fuel cells for portable devices, Electrochimica Acta, 52 (2007) 3849-3862.

[147] L. Gan, H.-d. Du, B.-h. Li, F.-y. Kang, The effect of particle size on the interaction of Pt catalyst particles with a carbon black support, New Carbon Materials, 25 (2010) 53-59.

[148] J.Z. Zhang, K. Hongsirikarn, J.G. Goodwin Jr, Effect and siting of Nafion® in a Pt/C proton exchange membrane fuel cell catalyst, Journal of Power Sources, 196 (2011) 7957-7966.

[149] P. Gode, F. Jaouen, G. Lindbergh, A. Lundblad, G. Sundholm, Influence of the composition on the structure and electrochemical characteristics of the PEFC cathode, Electrochimica Acta, 48 (2003) 4175-4187.

[150] B.N. Popov, X. Li, G. Liu, J.-W. Lee, Power source research at USC: Development of advanced electrocatalysts for polymer electrolyte membrane fuel cells, International Journal of Hydrogen Energy, 36 (2011) 1794-1802.

[151] X. Li, H.c.R. Colón-Mercado, G. Wu, J.-W. Lee, B.N. Popov, Development of Method for Synthesis of Pt–Co Cathode Catalysts for PEM Fuel Cells, Electrochemical and Solid-State Letters, 10 (2007) B201.

[152] (!!! INVALID CITATION !!! [153-158]).

[153] X. Yu, S. Ye, Recent advances in activity and durability enhancement of Pt/C catalytic cathode in PEMFC: Part II: Degradation mechanism and durability enhancement of carbon supported platinum catalyst, Journal of Power Sources, 172 (2007) 145-154.

[154] Y. Shao, J. Sui, G. Yin, Y. Gao, Nitrogen-doped carbon nanostructures and their composites as catalytic materials for proton exchange membrane fuel cell, Applied Catalysis B: Environmental, 79 (2008) 89-99.

[155] G. Liu, X. Li, J.-W. Lee, B.N. Popov, A review of the development of nitrogenmodified carbon-based catalysts for oxygen reduction at USC, Catalysis Science & Technology, 1 (2011) 207.

[156] X. Li, G. Liu, B.N. Popov, Activity and stability of non-precious metal catalysts for oxygen reduction in acid and alkaline electrolytes, Journal of Power Sources, 195 (2010) 6373-6378.

[157] V. Nallathambi, J.-W. Lee, S.P. Kumaraguru, G. Wu, B.N. Popov, Development of high performance carbon composite catalyst for oxygen reduction reaction in PEM Proton Exchange Membrane fuel cells, Journal of Power Sources, 183 (2008) 34-42.

[158] G. Liu, X. Li, P. Ganesan, B.N. Popov, Development of non-precious metal oxygenreduction catalysts for PEM fuel cells based on N-doped ordered porous carbon, Applied Catalysis B: Environmental, 93 (2009) 156-165.

[159] N.P. Subramanian, X. Li, V. Nallathambi, S.P. Kumaraguru, H. Colon-Mercado, G. Wu, J.-W. Lee, B.N. Popov, Nitrogen-modified carbon-based catalysts for oxygen reduction reaction in polymer electrolyte membrane fuel cells, Journal of Power Sources, 188 (2009) 38-44.

[160] X. Li, B.N. Popov, T. Kawahara, H. Yanagi, Non-precious metal catalysts synthesized from precursors of carbon, nitrogen, and transition metal for oxygen reduction in alkaline fuel cells, Journal of Power Sources, 196 (2011) 1717-1722.

[161] R.A. Sidik, A.B. Anderson, N.P. Subramanian, S.P. Kumaraguru, B.N. Popov, O2 Reduction on Graphite and Nitrogen-Doped Graphite: Experiment and Theory, The Journal of Physical Chemistry B, 110 (2006) 1787-1793.

[162] G. Liu, X. Li, P. Ganesan, B.N. Popov, Studies of oxygen reduction reaction active sites and stability of nitrogen-modified carbon composite catalysts for PEM fuel cells, Electrochimica Acta, 55 (2010) 2853-2858.

[163] H.-S. Oh, K. Kim, Y.-J. Ko, H. Kim, Effect of chemical oxidation of CNFs on the electrochemical carbon corrosion in polymer electrolyte membrane fuel cells, International Journal of Hydrogen Energy, 35 (2010) 701-708.

[164] C. Wang, G. Wang, D. van der Vliet, K.-C. Chang, N.M. Markovic, V.R. Stamenkovic, Monodisperse Pt3Co nanoparticles as electrocatalyst: the effects of particle size and pretreatment on electrocatalytic reduction of oxygen, Physical Chemistry Chemical Physics, 12 (2010) 6933-6939.

[165] X. Li, H.R. Colón-Mercado, G. Wu, J.-W. Lee, B.N. Popov, Development of Method for Synthesis of Pt – Co Cathode Catalysts for PEM Fuel Cells, Electrochemical and Solid-State Letters, 10 (2007) B201-B205.

[166] C. Chen, Y. Kang, Z. Huo, Z. Zhu, W. Huang, H.L. Xin, J.D. Snyder, D. Li, J.A. Herron, M. Mavrikakis, M. Chi, K.L. More, Y. Li, N.M. Markovic, G.A. Somorjai, P. Yang, V.R. Stamenkovic, Highly Crystalline Multimetallic Nanoframes with Three-Dimensional Electrocatalytic Surfaces, Science, 343 (2014) 1339-1343.

[167] P. Mani, R. Srivastava, P. Strasser, Dealloyed binary PtM3 (M = Cu, Co, Ni) and ternary PtNi3M (M = Cu, Co, Fe, Cr) electrocatalysts for the oxygen reduction reaction: Performance in polymer electrolyte membrane fuel cells, Journal of Power Sources, 196 (2011) 666-673.

[168] K.C. Neyerlin, R. Srivastava, C. Yu, P. Strasser, Electrochemical activity and stability of dealloyed Pt–Cu and Pt–Cu–Co electrocatalysts for the oxygen reduction reaction (ORR), Journal of Power Sources, 186 (2009) 261-267.

[169] R. Yang, J. Leisch, P. Strasser, M.F. Toney, Structure of Dealloyed PtCu3 Thin Films and Catalytic Activity for Oxygen Reduction, Chemistry of Materials, 22 (2010) 4712-4720.

[170] E. Antolini, J.R.C. Salgado, M.J. Giz, E.R. Gonzalez, Effects of geometric and electronic factors on ORR activity of carbon supported Pt–Co electrocatalysts in PEM fuel cells, International Journal of Hydrogen Energy, 30 (2005) 1213-1220.

[171] X. Tuaev, J.P. Paraknowitsch, R. Illgen, A. Thomas, P. Strasser, Nitrogen-doped coatings on carbon nanotubes and their stabilizing effect on Pt nanoparticles, Physical Chemistry Chemical Physics, 14 (2012) 6444-6447.

[172] A.P. Young, J. Stumper, E. Gyenge, Characterizing the Structural Degradation in a PEMFC Cathode Catalyst Layer: Carbon Corrosion, J Electrochem Soc, 156 (2009) B913-B922.

[173] T.W. Patterson, R.M. Darling, Damage to the Cathode Catalyst of a PEM Fuel Cell Caused by Localized Fuel Starvation, Electrochemical and Solid-State Letters, 9 (2006) A183-A185.

[174] B.J. Eastwood, P.A. Christensen, R.D. Armstrong, N.R. Bates, Electrochemical oxidation of a carbon black loaded polymer electrode in aqueous electrolytes, J Solid State Electrochem, 3 (1999) 179-186.

[175] Y. Shao, G. Yin, Y. Gao, Understanding and approaches for the durability issues of Pt-based catalysts for PEM fuel cell, Journal of Power Sources, 171 (2007) 558-566.

[176] D.A. Stevens, M.T. Hicks, G.M. Haugen, J.R. Dahn, Ex Situ and In Situ Stability Studies of PEMFC Catalysts: Effect of Carbon Type and Humidification on Degradation of the Carbon, Journal of The Electrochemical Society, 152 (2005) A2309-A2315.

[177] T. Hyeon, S. Han, Y.-E. Sung, K.-W. Park, Y.-W. Kim, High-Performance Direct Methanol Fuel Cell Electrodes using Solid-Phase-Synthesized Carbon Nanocoils, Angewandte Chemie International Edition, 42 (2003) 4352-4356.

[178] Y.A. Zhu, Z.J. Sui, T.J. Zhao, Y.C. Dai, Z.M. Cheng, W.K. Yuan, Modeling of fishbone-type carbon nanofibers: A theoretical study, Carbon, 43 (2005) 1694-1699.

[179] M. Cerro-Alarcón, A. Maroto-Valiente, I. Rodríguez-Ramos, A. Guerrero-Ruiz, Further insights into the Ru nanoparticles–carbon interactions and their role in the catalytic properties, Carbon, 43 (2005) 2711-2722.

[180] S. Vinod Selvaganesh, G. Selvarani, P. Sridhar, S. Pitchumani, A.K. Shukla, Graphitic Carbon as Durable Cathode-Catalyst Support for PEFCs, Fuel Cells, 11 (2011) 372-384.

[181] H.-S. Oh, J.-G. Oh, S. Haam, K. Arunabha, B. Roh, I. Hwang, H. Kim, On-line mass spectrometry study of carbon corrosion in polymer electrolyte membrane fuel cells, Electrochemistry Communications, 10 (2008) 1048-1051.

[182] S. Koh, J. Leisch, M.F. Toney, P. Strasser, Structure-Activity-Stability Relationships of Pt–Co Alloy Electrocatalysts in Gas-Diffusion Electrode Layers, The Journal of Physical Chemistry C, 111 (2007) 3744-3752.