Investigation of electrode processes in proton exchange membrane fuels cells : a self-assembly approach

Liu, Zengcai

2007

Liu, Z. C. (2007). Investigation of electrode processes in proton exchange membrane fuels cells : a self-assembly approach. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/6071>

<https://doi.org/10.32657/10356/6071>

Nanyang Technological University

Downloaded on 26 Apr 2023 14:19:39 SGT

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**AN INVESTIGATION OF ELECTRODE PROCESSES IN
PROTON EXCHANGE MEMBRANE FUEL CELLS:
A SELF-ASSEMBLY APPROACH**

LIU ZENGCAI

SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

2007

**An Investigation of Electrode Processes in
Proton Exchange Membrane Fuel Cells:
A Self-Assembly Approach**

Liu Zengcai

School of Mechanical and Aerospace Engineering

A thesis submitted to the Nanyang Technological University
in fulfilment of the requirement for the degree of
Doctor of Philosophy

2007

ACKNOWLEDGEMENTS

I would like to express my sincere and grateful thanks to my supervisor Professor Jiang San Ping for his invaluable advice and guidance, and his continuous encouragement throughout this work. I would also like to sincerely thank Professor Chan Siew Hwa, the Director of Fuel Cell Laboratory, for his generous help and inspiring discussion on this work.

The thanks are extended to Dr Xia Zetao, Mr. Han Ming, Dr Leng Yongjun, Dr Chen Xiaojun and Dr Tian Zhiqun for their kind assistance in conducting the experiments and helpful discussions. Thanks are also extended to my colleagues: Mr Wang Wei, Mr. Zhen Yongda, Mr. Liu Qinglin, Ms Xu Jianhong, Mr. Ding Ovi Lian, Mr. Tun Win Aung and other research students and post doctoral fellows, for their supports and unforgettable friendship.

Acknowledgements are also extended to all technicians in Fuel Cell Laboratory, Energy systems Laboratory, Materials Laboratory A, CNC Laboratory, and Thermodynamics Laboratory: Ms Ho Agnes, Ms Yong Mei Yoke, Ms Chow Shiau Kee, and Mr. Leong Kwok Phui for their supports.

I would also like to acknowledge the receipt of a studentship from Nanyang Technological University and financial support.

Table of Content

Table of Content	I
List of Abbreviations	V
List of Figures	VI
List of Tables	XIII
ABSTRACT.....	XIV
 <i>CHAPTER 1</i> Introduction	 1
1.1 Basic Principles and Types of Fuel Cells	1
1.2 Proton Exchange Membrane and Direct Methanol Fuel Cell.....	4
1.2.1 Proton Exchange Membrane Fuel Cell	4
1.2.1 Direct Methanol Fuel Cell (DMFC)	5
1.3 Project Objectives	7
1.4 Scopes	7
1.5 Thesis Layout.....	8
<i>CHAPTER 2</i> Literature Review	10
2.1 General Introduction to PEMFC	10
2.2 Components of PEMFC	12
2.2.1 Bipolar Plates	13
2.2.2 Proton exchange membrane and methanol crossover	13
2.2.3 Electrodes.....	16
2.3 Electrochemical Reaction in PEM Fuel Cells.....	21
2.3.1 Oxygen Reduction Reaction	21
2.3.2 Hydrogen Oxidation.....	24
2.3.3 Methanol Oxidation	25
2.4 Synthesis of Pt and Pt alloys nanoparticles.....	26
2.5 Deposition Techniques.....	32
2.6 Self-assembly and Layer-by-Layer Technique.....	34
2.7 Ionic Conductivity of the Membrane	37
2.8 Summary	43
<i>CHAPTER 3</i> Experimental Procedures.....	45

Table of Content

3.1 Chemicals.....	45
3.2 Synthesis of platinum nanoparticle colloidal solutions	46
3.3 Electrode preparation	47
3.3.1 Rotating disk electrode (RDE).....	47
3.3.2 Gas diffusion electrode and catalyst layer	47
3.3.3 Self-assembled Pt/Nafion membrane.....	48
3.3.4 Layer-by-layer self-assembled polyelectrolyte/Nafion membrane.....	49
3.3.5 Membrane electrode assembly.....	50
3.4 Electrochemical Characterization	51
3.4.1 Rotating disk electrode (RDE) system.....	51
3.4.2 Half-Cell Testing System.....	51
3.4.3 Full Cell Testing System.....	52
3.4.4 Polarisation	53
3.4.5 Cyclic Voltammetry	54
3.4.6 Electrochemical Impedance Spectroscopy (EIS).....	55
3.4.7 Through-plane conductivity measurement	58
3.5 Physical Characterization.....	61
3.5.1 UV-visible Spectroscopy	61
3.5.2 Transmission Electronic Microscopy (TEM)/Energy Dispersive Spectroscopy (EDS).....	62
3.5.3 Atomic Force Microscopy (AFM)	63
3.5.4 X-ray Diffraction (XRD)	63
3.5.5 X-ray Photoelectron Spectrum (XPS).....	64
CHAPTER 4 Electrochemical Characterization of Pt/C Catalysts	65
4.1 Experimental	65
4.2 Results and Discussions	66
4.2.1 Oxygen Reduction Reaction on Pt/C	66
4.2.2 Methanol Oxidation Reaction on Pt/C	75
4.3 Summary	78
CHAPTER 5 Synthesis and Characterization of PDDA Stabilized Pt Nanoparticles.....	80
5.1 Experimental	80
5.2 Results and Discussions	81
5.2.1 Synthesis of the Pt nanoparticles	81
5.2.2 TEM images of Pt nanoparticles	83

Table of Content

5.2.3 Electron Diffraction and XRD patterns of PDDA-Pt nanoparticles	86
5.2.4 XPS analysis of Pt nanoparticles	88
5.2.5 Oxygen reduction reaction	89
5.2.6 Oxygen reduction reaction in the presence of methanol	92
5.2.7 Methanol Oxidation Reaction	94
5.3 Summary	98
CHAPTER 6 Synthesis and Characterization of Polymer Stabilized Pt Nanoparticles	99
6.1 Experimental	99
6.2 Results and Discussions	100
6.2.1 Synthesis of Nafion-Pt nanoparticles	100
6.2.2 TEM images of Nafion-Pt nanoparticles	107
6.2.3 Electron Diffraction and XRD patterns of Pt nanoparticles	110
6.2.4 XPS analysis of Pt nanoparticles	113
6.2.5 Oxygen reduction reaction on Nafion-Pt	114
6.2.6 Oxygen reduction reaction in the presence of methanol	116
6.2.7 Methanol oxidation reaction on Nafion-Pt	118
6.2.8 Effect of polymer on the electrocatalytic activity	121
6.3 Summary	129
CHAPTER 7 Self-Assembled PDDA-Pt/Nafion Interface	131
7.1 Experimental	131
7.2 Results and Discussion	132
7.2.1 TEM images of self-assembled nanoparticles	132
7.2.2 EDS analysis of self-assembled nanoparticles	133
7.2.3 PDDA-Pt/Nafion interface	134
7.2.4 Cell performance of self-assembled MEA	139
7.3 Summary	142
CHAPTER 8 Self-assembly Monolayer of PDDA-Pt Nanoparticles for Direct	
Methanol Fuel Cells	143
8.1 Experimental details	143
8.2 Results and Discussions	144
8.2.1 XPS analysis of PDDA-Pt nanoparticles self-assembled Nafion membrane	144
8.2.2 Methanol crossover current measurement	145
8.2.3 Cell performance	147

Table of Content

8.3 Summary	152
<i>CHAPTER 9</i> Layer-by-Layer Self-Assembly of Poly- electrolyte for DMFCs	154
9.1 Experimental	154
9.2 Results and discussions	155
9.3 Summary	163
<i>CHAPTER 10</i> Measurement of Through-Plane Ionic Conductivity of Polymer Electrolyte Membrane.....	164
10.1 Experimental	164
10.2 Results and Discussion	164
10.2.1 Determination of current used	164
10.2.2 Measurement of membrane conductivity.....	166
10.3 Summary	171
<i>CHAPTER 11</i> Conclusions and Recommendations.....	172
11.1 Conclusions.....	172
11.2 Major achievements	175
11.3 Recommendations.....	177
List of Publications	179
Reference:	181

List of Abbreviations

AC	Alternating Current
AFM	Atomic Force Microscopy
CCT	Cathodic Current Treatment
CE	Counter Electrode
CV	Cyclic Voltammetry/Voltammogram
DC	Direct Current
DMFC	Direct Methanol Fuel Cell
EDS	Energy Dispersive Spectroscopy
EIS	Electrochemical Impedance Spectroscopy/Spectrum
ESA	Electrochemical Surface Area
FRA	Frequency Response Analysis
GC	Glassy Carbon
GDE	Gas Diffusion Electrode
GDL	Gas Diffusion Layer
HOR	Hydrogen Oxidation Reaction
HRTEM	High Resolution Transmission Electronic Microscopy
LBL	Layer-by-Layer
MEA	Membrane Electrode Assembly
MOR	Methanol Oxidation Reaction
OCP	Open Circuit Potential
OSP	Onset Potential
ORR	Oxygen Reduction Reaction
PAZO	poly(1-(4-(3-carboxy- 4-hydroxyphenylazo) benzene sulfonmido)-1,2-ethanediyl, sodium salt
PDDA	Poly(diallyldimethylammonium Chloride)
PEM	Polymer Electrolyte Membrane/ Proton Exchange Membrane
PVP	poly(vinylpyrrolidone)
PSS	Poly(Sodium Styrenesulfonate)
PTFE	Polytetrafluoroethylene
RDE	Rotating Disk Electrode
RE	Reference Electrode
RRDE	Rotating Ring Disk Electrode
SA	Specific Area
SAM	Self-Assembled Monolayer
SCE	Saturated Calomel Electrode
TEM	Transmission Electronic Microscopy
UV-visible	Ultraviolet-visible
WE	Working Electrode
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

List of Figures

Fig 1.1 Principle diagram for PEMFC	4
Fig 1.2 Schematic diagram of a direct methanol fuel cell	5
Fig 1.3 Polarization curves for a DMFC and its constituent electrodes.	7
Fig 2.1 diagram of a DMFC with Pt-Membrane	16
Fig 2.2 Molecular structure of polymers	29
Fig 2.3 Schematic diagram of self-assembly polycation on the negatively charged substrate.....	35
Fig 2.4 Schematic diagram of the LBL self-assembly of oppositely charged polycation and polyanion on negatively charged substrate.....	36
Fig 2.5 Cell used for determination of the in-plane membrane conductivity: (1) Kel-F block; (2) thumbscrew; (3) open area to allow equilibration; (4) membrane sample; (5) blackened Pt foil; (6) Pt ribbon lead. Reproduced from Zawodzinski et al. [1991].....	39
Fig 2.6 Schematic diagram of the experimental setup for the in-plane proton conductivity measurements. C1, C2: Pt mesh electrode; R1, R2: saturated calomel electrodes: B1, B2: Luggin capillary. Reproduced from Tricoli et al. [1998]	40
Fig 2.7 Schematic illustration of a conductivity cell for Nafion® membranes: (1) graphite current collectors; (2) carbon paper electrodes; (3) membrane; (4) electric connection; (5) beaker filled with deionized water and (6) thermocouple. Reproduced from Silva et al. [2004].....	40
Fig 2.8 Schematic diagram of the four-electrode glass cell used for conductivity measurements on a circular sample (1 cm^2) of membrane, using a steady state linear sweep galvanodynamic technique. Reproduced from Slade et al., [2002].....	41
Fig 2.9 Sketch of the conductivity cell: main body is stainless-steel, two center blocks are Kel-F® with platinum foil used for electrical contact: l is the length between the two platinum foils. Four different conductivity measurements were performed: (1-2) longitudinal top, (3-4) longitudinal bottom, (1-4) transversal 1 and (2-3) transversal 2. Reproduced from Nouel et al. [1998].....	42
Fig 3.1 Molecular structure of polymers	45
Fig 3.2 Schematic diagram of the synthesis process.	46
Fig 3.3 Nafion 1135 membrane (a) before and (b) after self-assembly process in Pt-PDDA colloid solution and cleaning process.....	49
Fig 3.4 Schematic diagram of (a) the membrane electrode with the self-assembled PDDA-Pt nanoparticles on one side and (b) two sides of Nafion membrane	50
Fig 3.5 Schematic diagram for the rotating disk electrode (RDE) system. RE: reference electrode; WE: working electrode; CE: counter electrode.	51

List of Figures

Fig 3.6 Experimental setup for half cell testing. GDE: gas diffusion electrode, WE: working electrode, RE: reference electrode, CE: counter electrode.	52
Fig 3.7 Schematic setup for DMFC measurement	53
Fig 3.8 CV (100mV/s) at 25°C on PTFE-bonded Pt/C electrode in the potential range 0-1.4V vs SHE in 1M H ₂ SO ₄ saturated with nitrogen, Q' and Q'' represent the amounts of charge exchanged during the electro-adsorption and desorption of hydrogen on Pt sites and the shaded area is the contribution of double layer charge.....	55
Fig 3.9 An example impedance curve for oxygen reduction reaction on PTFE-bonded electrode measured at 0.9V in oxygen. Pt loading and PTFE content of the electrode was 0.4mg/cm ² and 10wt%, respectively.	58
Fig 3.10 Equivalent circuit for fitting impedance in Fig 3.9	58
Fig 3.11 Schematic of a four-probe cell for conductivity measurements. W1, W2 Platinum Foil Electrodes; C1, C2: Saturated Calomel Electrodes; M: Nafion Membrane; L: Luggin Capillaries; P1, P2: Perspex plates with a centered circular hole of 1cm ²	59
Fig 3.12 Typical curves measured for the cell with and without membrane, current: 100mA.	60
Fig 3.13 The range of electromagnetic radiation. [Denney, <i>et al.</i> , 1987]	61
Fig 4.1 Polarisation curves of Pt/C in O ₂ -saturated 1 M H ₂ SO ₄ under a scan rate of 5 mVs ⁻¹ at 25°C using RDE at different rotating speeds. Pt loadings were 56µgcm ⁻²	66
Fig 4.2 Polarisation curves of Pt/C and Pt disk electrode in O ₂ -saturated 1M H ₂ SO ₄ under a scan rate of 5mVs ⁻¹ at 25°C using RDE. RDE was rotated at 3000rpm.	67
Fig 4.3 Current density @ 0.7V and the limiting current density for oxygen reduction reaction as a function of Pt loading	68
Fig 4.4 Cyclic voltammograms of Pt/C and Pt disk electrode in N ₂ -saturated 1M H ₂ SO ₄ under a scan rate of 100 mVs ⁻¹ at 25°C using RDE under static condition	68
Fig 4.5 Polarisation curves for oxygen reduction on Pt/C in O ₂ -saturated 1 M H ₂ SO ₄ + 0.5M CH ₃ OH under a scan rate of 5 mVs ⁻¹ at 25°C using RDE as a function of rotating speed. Pt loading was 56µgcm ⁻²	70
Fig 4.6 Plots of limiting current density for oxygen reduction reaction on Pt RDE and Pt/C electrode in oxygen saturated 1M H ₂ SO ₄ (Fig 4.1) and 1M H ₂ SO ₄ + 0.5M CH ₃ OH (Fig 4.3). The Pt loading was 56µgcm ⁻²	71
Fig 4.7 Polarisation curves for oxygen reduction on Pt/C and Pt RDE in O ₂ -saturated 1M H ₂ SO ₄ + 0.5M CH ₃ OH under a scan rate of 5 mVs ⁻¹ at 25°C using RDE. The RDE was rotated at 3000rpm.	73
Fig 4.8 Current density @ 0.6V, limiting current density, onset potential for ORR, and peak current density for MOR in N ₂ -saturated 1M H ₂ SO ₄ + 0.5M CH ₃ OH as a function of Pt loading. The RDE was rotated at 3000rpm.	73

List of Figures

Fig 4.9 Cyclic voltammograms of Pt/C and Pt RDE in 1M H ₂ SO ₄ + 0.5M CH ₃ OH under a scan rate of 100 mVs ⁻¹ at 25°C	74
Fig 4.10 ESA for Pt/C electrode with different platinum loading and Pt RDE obtained from CV measurements.....	75
Fig 4.11 Polarisation curves for methanol oxidation on Pt/C electrode in nitrogen saturated 1M H ₂ SO ₄ + 2M CH ₃ OH at 25°C as a function of rotating speed. The scan rate was 5mv s ⁻¹ . The platinum loading was 5.6µg cm ⁻²	76
Fig 4.12 Polarisation curves for methanol oxidation on Pt/C electrode with different Pt loading in N ₂ -saturated 1M H ₂ SO ₄ at 25°C as a function of methanol concentration. The scan rate was 5mv s ⁻¹	77
Fig 4.13 Current density at 0.7V, peak current density, and the onset potential for MOR as a function of Pt loading	78
Fig 5.1 UV-visible spectrum for PDDA, H ₂ PtCl ₆ and the mixture of PDDA and H ₂ PtCl ₆ solutions.....	81
Fig 5.2 UV-visible spectrum of the PDDA-H ₂ PtCl ₆ -alcohol-water system as a function of reflux time, PDDA:Pt=5:1, [Pt]=10 ⁻⁴ M. The inset graph is the absorbance at 500nm vs reflux time.....	82
Fig 5.3 TEM images and size distribution histograms of PDDA-Pt synthesized at the different molar ratio, (a) 1:1, (b) 3:1, (c) 5:1, (d) 15:1	84
Fig 5.4 High resolution TEM image of PDDA-Pt nanoparticles, PDDA:Pt =5:1	86
Fig 5.5 The electron diffraction patterns of PDDA-Pt nanoparticles, PDDA:Pt =5:1.....	87
Fig 5.6 XRD patterns of PDDA-Pt synthesized with the different molar ratio of PDDA to Pt, (1) 1:1, (2) 3:1, (3) 5:1, (4) 8:1 and (5) 15:1	87
Fig 5.7 X-ray photoelectron spectra of Pt 4f for PDDA-Pt nanoparticles, PDDA:Pt=5:1	88
Fig 5.8 Polarisation curves of Pt/C and PDDA-Pt nanoparticle colloids in O ₂ -saturated 1M H ₂ SO ₄ under a scan rate of 5 mVs ⁻¹ at 25°C, using RDE. The RDE was rotated at 3000rpm. The Pt loading was 5.6 µg cm ⁻²	89
Fig 5.9 Cyclic voltammograms of the Pt/C and PDDA-Pt nanoparticles synthesized with various PDDA/Pt molar ratios in N ₂ -saturated 1 M H ₂ SO ₄ at 25°C on a RDE. The enlarged hydrogen desorption peaks in the 0.0 to 0.08 V range were shown as inset. The scan rate was 100 mV s ⁻¹	91
Fig 5.10 Polarisation curves for oxygen reduction on Pt/C and PDDA-Pt nanoparticle colloids in O ₂ -saturated 1 M H ₂ SO ₄ + 0.5M CH ₃ OH under a scan rate of 5 mVs ⁻¹ at 25°C, using RDE. The RDE was rotated at 3000rpm. The Pt loading was 5.6 µg cm ⁻²	93
Fig 5.11 Cyclic voltammograms of Pt/C and PDDA-Pt nanoparticle colloids in 1M H ₂ SO ₄ + 0.5M CH ₃ OH saturated with nitrogen at 25°C on a RDE. The scan rate was 100 mV s ⁻¹ . The Pt loading was 5.6 µg cm ⁻²	93

List of Figures

Fig 5.12 Cyclic voltammograms of PDDA-Pt nanoparticles with different molar ratios in N ₂ -saturated 1M H ₂ SO ₄ + 2M CH ₃ OH at 25°C on a RDE. The platinum loading was 56µgcm ⁻² . (a) The single scan. The scan rate was 5 mV s ⁻¹ . (b) The cyclic scan. The scan rate was 100 mV s ⁻¹ .	95
Fig 5.13 Current vs time plot of Pt/C and PDDA-Pt nanoparticles in N ₂ -saturated 1M H ₂ SO ₄ + 2M CH ₃ OH at 25°C on a RDE. The applied potential was 0.7V. The platinum loading was 56µgcm ⁻² .	96
Fig 6.1 UV-visible spectrum of Nafion, H ₂ PtCl ₆ and the mixture of H ₂ PtCl ₆ and Nafion, 10 ⁻⁴ M Pt ⁴⁺ , Nafion:Pt=2:1	100
Fig 6.2 UV-visible spectrum of the Nafion- H ₂ PtCl ₆ -ethanol-water system as a function of reflux time, 10 ⁻⁴ M Pt ⁴⁺ , Nafion:Pt=(a) 1:2, (b) 1:1, (c) 4:1, and (d) 8:1.	101
Fig 6.3 UV absorbance @ 260nm (Pt ⁴⁺) and 500nm (Pt ⁰) as a function of reflux time during the formation of Nafion-Pt at different Nafion/Pt ratios, 10 ⁻⁴ M Pt ⁴⁺	102
Fig 6.4 UV-visible spectrum at (a) 82°C, (b) 75°C, (c) 65°C and the absorbance @ 260nm (Pt ⁴⁺) and 500nm (Pt ⁰) (d) as a function of reflux time during the formation of Nafion-Pt nanoparticles at different temperatures. Nafion:Pt=2:1, 10 ⁻⁴ M Pt ⁴⁺	103
Fig 6.5 UV-visible spectrum of (a) PSS, H ₂ PtCl ₆ , the mixture of H ₂ PtCl ₆ and PSS, (b) the mixture and (c) the absorbance @ 261nm (Pt ⁴⁺) and 500nm (Pt ⁰) during the formation of PSS-Pt nanoparticles as a function of reflux time. 10 ⁻⁴ M Pt ⁴⁺ , the PSS/Pt molar ratio was 4:1.	105
Fig 6.6 UV-visible spectrum of (a) PVP, H ₂ PtCl ₆ , the mixture of H ₂ PtCl ₆ and PVP, (b) the mixture and (c) the absorbance @ 261nm (Pt ⁴⁺) and 500nm (Pt ⁰) during the formation of PVP-Pt nanoparticles as a function of reflux time. 10 ⁻⁴ M Pt ⁴⁺ . The PVP/Pt molar ratio was 4:1.	106
Fig 6.7 TEM image of Nafion-stabilized platinum nanoparticles with different molar ratio of Nafion to Pt, (a) 1:2, (b) 2:1, (c) 4:1, (d) 8:1	107
Fig 6.8 TEM images of Nafion-Pt synthesized at different reflux temperatures, (a) 65°C, (b) 75°C, and (c) 82°C. Nafion:Pt=2:1	108
Fig 6.9 TEM images of Pt nanoparticles (a) Nafion-Pt (4:1), (b) PDDA-Pt (3:1), (c) PVP-Pt (4:1), (d) PSS-Pt (4:1)	109
Fig 6.10 The electron diffraction patterns of Nafion-Pt nanoparticles, Nafion:Pt=2:1	111
Fig 6.11 XRD patterns of Nafion-Pt nanoparticles synthesized (a) with different molar ratio of Nafion to Pt at 82°C, pH=8.5. (1) 1:2, (2) 1:1, (3) 2:1, (4) 4:1, (5) 8:1; and (b) at different temperatures, Nafion:Pt=2:1, pH=8.5. (1) 65°C, (2) 75°C, (3) 82°C.	112
Fig 6.12 X-ray photoelectron spectra of Pt 4f for Nafion-Pt nanoparticles prepared with Nafion/Pt ratio of 2:1	114

List of Figures

Fig 6.13 Polarization curves of Pt/C and Nafion-Pt nanoparticles in O ₂ -saturated 1M H ₂ SO ₄ under a scan rate of 5 mVs ⁻¹ at 25°C, using RDE. The RDE was rotated at 3000rpm. The Pt loading was 5.6 µg cm ⁻²	115
Fig 6.14 Cyclic voltammograms of Pt/C and Nafion-Pt nanoparticles in 1M H ₂ SO ₄ saturated with nitrogen at 25°C on a RDE. The scan rate was 100 mV s ⁻¹ . The Pt loading was 5.6 µg cm ⁻²	115
Fig 6.15 Polarization curves of Pt/C and Nafion-Pt nanoparticle colloids in O ₂ -saturated 1 M H ₂ SO ₄ + 0.5M CH ₃ OH under a scan rate of 5 mVs ⁻¹ at 25°C, using RDE. The RDE was rotated at 3000rpm. The Pt loading was 5.6µg cm ⁻²	117
Fig 6.16 Cyclic voltammograms of Pt/C and Nafion-Pt nanoparticle colloids in 1M H ₂ SO ₄ + 0.5M CH ₃ OH saturated with nitrogen at 25°C on a RDE. The scan rate was 100mV s ⁻¹ . The Pt loading was 5.6 µg cm ⁻²	117
Fig 6.17 Cyclic voltammograms of and Nafion-Pt nanoparticles in N ₂ -saturated 1M H ₂ SO ₄ + 2M CH ₃ OH at 25°C on a RDE, (a) single scan at potential range of 0.2 – 1.0 V. The scan rate was 5 mV s ⁻¹ . (b) Cyclic scan between potential range of 0.2 – 1.2 V. The scan rate was 100 mV s ⁻¹ . Pt loading was 56µgcm ⁻²	119
Fig 6.18 Current vs time plot of Pt/C and Nafion-Pt nanoparticles in N ₂ -saturated 1M H ₂ SO ₄ + 2M CH ₃ OH at 25°C on a RDE. The applied potential was 0.7V vs SHE. The platinum loading was 56µgcm ⁻²	120
Fig 6.19 Polarization curves for oxygen reduction reaction on different polymer-Pt nanoparticles in O ₂ -saturated 1M H ₂ SO ₄ . The RDE was rotated at 3000rpm. The scan rate was 5mV s ⁻¹ . The Pt loading was 5.6 µg cm ⁻²	121
Fig 6.20 Tafel curves for oxygen reduction reaction on different polymer-Pt nanoparticles in O ₂ -saturated 1M H ₂ SO ₄ . The RDE was rotated at 3000rpm. The scan rate was 5mV s ⁻¹ . The Pt loading was 5.6 µg cm ⁻²	122
Fig 6.21 Polarization curves for oxygen reduction reaction on different polymer-Pt nanoparticles in N ₂ -saturated 1M H ₂ SO ₄ . The RDE was kept under static condition. The scan rate was 100mV s ⁻¹ . The Pt loading was 5.6 µg cm ⁻²	123
Fig 6.22 Polarization curves for oxygen reduction reaction on different polymer-Pt nanoparticles in O ₂ -saturated 1M H ₂ SO ₄ + 0.5M CH ₃ OH. The RDE was rotated at 3000rpm. The scan rate was 100mV s ⁻¹ . The Pt loading was 5.6 µg cm ⁻²	124
Fig 6.23 Cyclic voltammograms for different polymer-Pt nanoparticles in N ₂ -saturated 1M H ₂ SO ₄ + 0.5M CH ₃ OH. The RDE was kept under static condition. The scan rate was 100mV s ⁻¹ . The Pt loading was 5.6 µg cm ⁻²	125
Fig 6.24 Polarization curves for methanol oxidation reaction on different polymer-Pt nanoparticles in O ₂ -saturated 1M H ₂ SO ₄ + 2M CH ₃ OH. The RDE was kept static. The scan rate was 5mV s ⁻¹ . The Pt loading was 56 µg cm ⁻²	125

List of Figures

Fig 6.25 Cyclic voltammograms for Pt/C and Pt nanoparticles stabilized by different polymers measured in N ₂ -saturated 1M H ₂ SO ₄ + 2M CH ₃ OH. The RDE was kept under static condition. The scan rate was 100mvs-1. The Pt loading was 56µgcm ⁻²	126
Fig 6.26 Current vs time plot of Pt/C and Nafion-Pt nanoparticles in N ₂ -saturated 1M H ₂ SO ₄ + 2M CH ₃ OH at 25°C on a RDE. The applied potential was 0.7V vs SHE. The platinum loading was 56µgcm ⁻²	127
Fig 6.27 The current densities for ORR at 0.6V (1) in the absence and (2) in the presence of methanol and (3) MOR at 0.7V and (4) MOR at 0.7V after 1hrs on different polymer stabilized Pt nanoparticles	127
Fig 7.1 TEM images of the self-assembled PDDA-Pt nanoparticle colloids on the thin Nafion film cast on the copper grid. The PDDA-Pt nanoparticle colloids were synthesized with (a) PDDA:Pt = 1:1, (b) PDDA:Pt = 5:1 and (c) PDDA:Pt = 15:1.....	133
Fig 7.2 EDS spectrum for PDDA-Pt nanoparticles self-assembled on Nafion thin film. PDDA:Pt =5:1	134
Fig 7.3 Cyclic voltammograms of the membrane electrodes prepared by the self-assembly of PDDA-Pt nanoparticles with various PDDA to Pt ratios in 1M H ₂ SO ₄ saturated with N ₂ at 25°C. The scanning rate was 100mV s ⁻¹	135
Fig 7.4 Polarization curves of self-assembled PDDA-Pt nanoparticles membrane electrodes prepared in the presence of different molar ratios of PDDA to Pt. The curves were measured in 1M H ₂ SO ₄ saturated with O ₂ at 25°C under scanning rate of 5mVs ⁻¹	136
Fig 7.5 Impedance behavior for the O ₂ reduction on the self-assembled PDDA-Pt nanoparticles membrane electrodes prepared with different molar ratios of PDDA to Pt. The curves were measured in 1M H ₂ SO ₄ saturated with O ₂ at 0.3V (i.e., under dc bias of 0.6 V). Symbols are the measured results and lines are the fitted results. Numbers are frequencies in Hz. The inset graph is the equivalent circuit for the fitting.	137
Fig 7.6 Impedance curves of the membrane electrode self-assembled in the PDDA-Pt colloid solution with PDDA:Pt=1:1, measured under different dc bias.	138
Fig 7.7 Schematic diagram of the self-assembly process of (a) the PDDA-Pt nanoparticles and (b) the PDDA-Pt nanoparticle agglomerates to the Nafion surface.	139
Fig 7.8 Cell performance of MEA self-assembled by PDDA-Pt nanoparticles with different PDDA/Pt molar ratio. The Cell was fed with H ₂ /O ₂ and operated at 30°C.....	140
Fig 8.1 A typical XPS spectrum for PDDA-Pt nanoparticles self-assembled Nafion membrane	145
Fig 8.2 Methanol crossover current curves in a membrane-electrode-assembly (MEA) with the self-assembly monolayer of PDDA-Pt nanoaprticles on N-1135 membrane as a function of self-assembly time. The measurements were carried out at 30°C.	146

List of Figures

Fig 8.3 Methanol crossover current curves in a membrane-electrode-assembly (MEA) with the self-assembly monolayer of PDDA-Pt nanoparticles on N-1135 membrane at 30oC as a function of PDDA/Pt molar ratio.....	147
Fig 8.4 Polarization curves and power output of DMFC using pure N-1135 membrane and self-assembly monolayer of PDDA-Pt nanoparticles on N-1135 membrane measured at 30°C.....	148
Fig 8.5 Polarization curves and power output of DMFC using pure N-1135 membrane and self-assembly monolayer of PDDA-Pt nanoparticles on N-1135 membrane measured at 30°C.....	149
Fig 8.6 Schematic diagram of the self-assembly process between the Nafion membrane and the PDDA-Pt nanoparticle colloidal solution.....	152
Fig 9.1 UV-visible spectra of the Nafion 1135 membrane as a function of LBL self-assembled (a) PDDA/PSS and (b) PDDA/PAZO bilayers.....	156
Fig 9.2 AFM images of (a) glass substrate, (b) monolayer of PDDA and (c) 4 PDDA/PSS bilayers on glass substrate.....	157
Fig 9.3 Polarisation curves for methanol crossovered through the membrane as a function of PDDA/PSS bilayer measured at 30°C	159
Fig 9.4 Polarisation curves and power output of DMFC using N-1135 membrane as a function of self-assembled PDDA/PSS layer measured at 30°C	161
Fig 9.5 Schematic diagram of the structure of the LbL self-assembly of oppositely charged polycation and polyanion on Nafion electrolyte membrane, showing the blocking of the methanol crossover.....	162
Fig 10.1 Potential curves for the cell without the membrane as a function of current, (a) 1mA, (b) 10mA, (c) 100mA and (d) 1000mA. The measurement was conducted at 25°C.....	165
Fig 10.2 Membrane area resistance as a function of hydrated membrane thickness measured in 1M H ₂ SO ₄ at 25°C, the inserted are the equation and R-squared value obtained by linear simulation.....	167
Fig 10.3 Membrane conductivity as a function of hydrated membrane thickness measured in 1M H ₂ SO ₄ at 25°C	168

List of Tables

Table 1.1 Major types of fuel cells classified by electrolyte	2
Table 2.1 Market Segmentation of Potential Non-Vehicular Fuel Cell Applications	12
Table 4.1 ESA for Pt/C electrode with different platinum loading and Pt RDE obtained from CV measurements	69
Table 4.2 Oxygen diffusion coefficient calculated based on Fig 4.6	72
Table 5.1 Particle size and surface area obtained from TEM images and XRD measurements ...	85
Table 5.2 ESA for Pt/C and PDDA-Pt with the different molar ratio obtained from CV measurements in 1M H ₂ SO ₄ and 1M H ₂ SO ₄ + 0.5M CH ₃ OH saturated with nitrogen. The platinum loading was 5.6µg cm ⁻²	91
Table 6.1 Particle sizes obtained from XRD and ESA from CV for Nafion-Pt nanoparticles synthesized at various conditions	113
Table 6.2 ESA for Pt/C and Nafion-Pt with the different molar ratio obtained from CV measurements in 1 M H ₂ SO ₄ and 1 M H ₂ SO ₄ + 0.5M CH ₃ OH saturated with nitrogen. The platinum loading was 5.6µg cm ⁻²	116
Table 6.3 Tafel slopes for oxygen reduction reaction on different polymer-Pt nanoparticles obtained from Fig 6.20	122
Table 6.4 ESA for different Pt nanoparticles based on cyclic voltammetry measurements	123
Table 7.1 Atomic compositions and atomic ratio of S/Pt for PDDA-Pt nanoparticles self- assembled on copper grid precoated with Nafion	134
Table 7.2 Fitting results of EIS in Fig 7.5	137
Table 8.1 Atomic compositions for PDDA-Pt nanoparticles with various molar ratios self- assembled Nafion membrane	145
Table 8.2 Open circuit potential, methanol crossover limiting current and maximum power density of DMFC prepared by un-modified N-1135 and N-1135 modified by the self-assembly monolayer of PDDA-Pt nanoparticles at 30°C	148
Table 8.3 Open circuit potential, methanol crossover limiting current and maximum power density of DMFC prepared by un-modified N-1135 and N-1135 modified by the self-assembly monolayer of PDDA-Pt nanoparticles at 30°C	150
Table 9.1 The proton conductivity, limiting methanol crossover current, and maximum power density of Nafion 1135 membrane as a function of number of PDDA/PSS bilayer ...	158
Table 10.1 Cell (without membrane) resistance obtained using different current	166
Table 10.2 Nominal thickness and fully hydrate membrane thickness of Nafion membranes ...	166

ABSTRACT

The polymer stabilized Pt nanoparticles were synthesized via alcohol reduction in the presence of polymers, PDDA, PVP, PSS and Nafion. These particles show fcc structure and the particle sizes are in the range of 2~4nm, depending on the synthesis conditions. Interestingly, PDDA-Pt nanoparticles show high catalytic activity for the oxygen reduction reaction in the absence and presence of methanol, but low catalytic activity for methanol oxidation reaction. This indicates that PDDA-Pt may be a potential methanol resistant cathode catalyst. On the other hand, PSS-Pt nanoparticles are catalytically very active for both oxygen reduction and methanol oxidation reactions. Thus, PSS-Pt nanoparticles show very low activity for oxygen reduction in the presence of methanol due to the direct chemical reaction between the oxygen and methanol. However, PVP-Pt nanoparticles show very low activity for all the reactions investigated here. This indicates that PVP has a significant shielding effect on the catalytic activity of Pt nanoparticles. The relative low activity of Nafion-Pt nanoparticles is mainly due to the agglomeration and the additional diffusion resistance caused by excessive Nafion. These results show that different polymers may exhibit different selectivity to Pt nanoparticles

Since PDDA is a polycation, PDDA-Pt nanoparticles are positively charged. As-synthesized PDDA-Pt nanoparticles can be self-assembled on the Nafion membrane due to the electrostatic interaction between positively charged PDDA-Pt nanoparticle and negatively charged SO_3^- on the surface of Nafion membrane. A monolayer of PDDA-Pt nanoparticles was obtained for the well-dispersed PDDA-Pt nanoparticles. This is a useful technique that can be used to study the Pt/Nafion interface. The self-

assembled membrane electrode assembly gave a maximum power output of 2.1 mW cm^{-2} , corresponding to 955 W per g_{Pt} .

Inspired by the methanol tolerance of PDDA-Pt nanoparticles, the PDDA-Pt self-assembled Nafion membrane was also used to reduce the methanol crossover through the Nafion membrane in DMFC. The results shows that modified Nafion membrane reduced the methanol crossover, and the cell performance increased by about 34% compared to that using the unmodified Nafion membrane.

Self-assembled multilayer of PDDA/PSS on Nafion membrane was also found to reduce the methanol crossover effectively. The proton conductivity was sacrificed at the same time since PDDA is not a proton conductor. The thickness of the multilayer can be tailored by simply changing the number of layers to obtain a compromise between the reduction in the methanol crossover and the decrease in the proton conductivity. Therefore, the optimal cell performance can be obtained. Methanol crossover was reduced by 18%, and the cell performance was increased by 39% for the Nafion membrane with 4 layers of PDDA/PSS compared with the unmodified Nafion membrane. Self-assembly was proven to be a useful, flexible technique to study the electrochemical interface and to modify the Nafion membrane in polymer electrolyte fuel cells.

Through-plane conductivity of Nafion membrane reflects the real direction of proton transportation in the fuel cells, but the in-plane conductivity does not. Therefore, it is necessary and urgent to design a cell for the measurement of the through-plane conductivity especially when the membrane is modified to have a layered structure, such as by self-assembly and layer-by-layer techniques. In this work, a modified method to measure the through-plane conductivity of the polymer electrolyte membranes was developed in house. The through-plane conductivity for

Abstract

Nafion membranes is about $0.120 \pm 0.002 \text{ Scm}^{-1}$, which is independent of the Nafion membrane thickness.

Key words: Polymer stabilized, Charged Pt nanoparticles, Self-assembly, Layer-by-layer, Pt/Nafion interface, Reduction of methanol crossover

CHAPTER 1 Introduction

1.1 Basic Principles and Types of Fuel Cells

Fuel cells are galvanic cells, in which the free energy of a chemical reaction is converted into electrical energy (or electrical current). The Gibbs free energy of a chemical reaction is related to the cell voltage via:

$$\Delta G = -nFE \quad (1.1)$$

where n is the number of electrons involved in the reaction, F is the Faraday constant, and E is the cell voltage under thermodynamic equilibrium in the absence of a current flow. The anode reaction in fuel cells is either the direct oxidation of hydrogen or the oxidation of hydrocarbons. An indirect oxidation via a reforming step can also occur. The cathode reaction in fuel cells is oxygen reduction. In most cases oxygen comes from air.

In the case of hydrogen/oxygen fuel cells, the overall reaction is:

Therefore, an equilibrium cell voltage for standard conditions at 25°C is:

$$E = \frac{-\Delta G}{nF} = 1.23\text{V} \quad (1.3)$$

The cell voltage is the difference of the electrode potentials between the cathode and the anode, which are determined by the electrochemical reaction taking place at the respective electrodes.

Based on the electrolyte used, fuel cells can be classified into five different systems. They are proton exchange membrane fuel cell (PEMFC), alkaline fuel cell (AFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC) and

solid oxide fuel cell (SOFC). The comparisons of these five fuel cells are listed in Table 1.1.

Table 1.1 Major types of fuel cells classified by electrolyte

Type	AFC	PAFC	MCFC	SOFC	PEMFC
Operating temp. (°C)	<100	160-220	600-800	800-1000 (500-600)	~80
Anode reaction	$\text{H}_2 + 2\text{OH}^- = 2\text{H}_2\text{O} + 2\text{e}^-$	$\text{H}_2 = 2\text{H}^+ + 2\text{e}^-$	$\text{H}_2 + \text{CO}_3^{2-} = \text{H}_2\text{O} + \text{CO}_2 + 2\text{e}^-$	$\text{H}_2 + \text{O}^{2-} = \text{H}_2\text{O} + 2\text{e}^-$	$\text{H}_2 = 2\text{H}^+ + 2\text{e}^-$
Cathode reaction	$1/2\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- = 2\text{OH}^-$	$1/2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- = \text{H}_2\text{O}$	$1/2\text{O}_2 + \text{CO}_2 + 2\text{e}^- = \text{CO}_3^{2-}$	$1/2\text{O}_2 + 2\text{e}^- = \text{O}^{2-}$	$1/2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- = \text{H}_2\text{O}$
Electrolyte	KOH	H_3PO_4	Molten $\text{Li}_2\text{CO}_3 + \text{K}_2\text{CO}_3$	$\text{ZrO}_2 + \text{Y}_2\text{O}_3$	Proton exchange membrane
Charge carrier	OH^-	H^+	CO_3^{2-}	O^{2-}	H^+

Alkaline fuel cell (AFC) was first developed in 1932 by Francis T. Bacon of Cambridge University. The technology was also investigated by Allis-Chalmers of Milwaukee, Wisconsin, who demonstrated an alkaline fuel cell powered a farm tractor in 1959. AFC was later chosen for the Appolo space missions. AFC designs proved to be more durable and reliable than PEM fuel cell of that time but they required very pure hydrogen and oxidant streams. Their high sensitivity to CO_2 (which degrades the alkaline electrolyte) necessitates expensive reforming and air cleanup processors.

Phosphoric acid fuel cell (PAFC) is considered at this moment as a well developed system for near-term applications. A moderate temperature (200°C) device is reasonably tolerant to impurities in the fuel stream and do not face the challenges of materials and durability of the high temperature cells. Aside from inherent bulkiness and poor prospects for mass-production cost reduction, PAFC faces serious issues due to its high operating temperature, typically 200°C, creating startup problems for transportation applications.

Molten carbonate fuel cell (MCFC) has been investigated for the stationary cogeneration of electrical power and heat. The operating temperature of about 650°C allows the electrochemical conversion process to take place at the electrodes without any precious metal catalysts. It is also possible to reform conventional fuel gases using the heat generated by the fuel cell. In addition, the operating temperature is low enough for conventional metallic materials to be used in the construction of both the cell structure and the peripheral equipment. Thanks to internal reforming, the fuel cell system can be greatly simplified and its efficiency significantly increased. However, high operational temperature entails significant time lags to bring the thermal mass up to the operating temperature and is an inhibitor for their use as vehicle engines.

SOFCs, besides for stationary use like MCFC, are being studied for some mobile applications, such as auxiliary power units for heavy-duty vehicles, where startup time is less of a problem. SOFCs have already demonstrated more than 10,000 hours of durability in prototype stationary applications. Although this lifetime is too short for power generation, it is sufficient for mobile application. Compared with low-temperature operation of PEMFCs, the high-temperature operation of SOFCs permits the use of a reformat from gasoline without expensive catalytic clean up requirements, while maintaining a traditional engine for propulsion. However, the downsides of high-temperature operation are startup and thermal cycling problems, which make SOFCs less suitable as an engine replacement.

PEMFCs have become the focus for automotive propulsion efforts because of its low operational temperature and potential for low-cost mass production. Currently, the hydrogen and direct methanol PEM fuel cell are studied extensively in automotive programs. Work is also underway to find catalysts that might enable direct use of

other fuels, such as ethanol. For the foreseeable future, DMFCs seem more promising for portable power application than high-power applications such as motor vehicles.

1.2 Proton Exchange Membrane and Direct Methanol Fuel Cell

1.2.1 Proton Exchange Membrane Fuel Cell

Fig 1.1 shows a schematic diagram of a PEMFC. Typical cell components within a PEMFC include: 1) the proton exchange membrane, 2) an electrically conductive porous backing layer, 3) a catalyst layer (the electrodes) sandwiched between the backing layer and the membrane, and 4) bipolar plate that delivers the fuel and oxidant to the reactive sites via flow channels.

Fig 1.1 Principle diagram for PEMFC

Platinum is the most active catalyst for both hydrogen oxidation reaction (HOR) at the anode and oxygen reduction reaction (ORR) at the cathode. It has been known that major loss of performance is due to the slow ORR and mass transport limitations especially when air is used. Many efforts are on the way to develop platinum alloy catalysts to increase the kinetics of ORR and to tailor the electrode structure to

decrease transport limitations. When hydrogen is obtained from reformed gas, significant power losses may arise due to platinum poisoned by tracer amount of CO in reformed gas. Therefore, another challenge is to develop CO resistant catalyst for HOR.

1.2.2 Direct Methanol Fuel Cell (DMFC)

Although the power efficiencies of hydrogen PEMFCs continue to show steady improvements, problems remain with the use of hydrogen as the active fuel because hydrogen is not a primary fuel and must be obtained from in-situ reformation of solid or liquid hydrocarbons (petroleum, coal, methanol) or be pre-purified and stored as pressurized gas (or in the form of an admixture with a metal alloy, carbon or some other absorbent). In all cases, either a considerable weight penalty or increased engineering complexity adds to the cost.

Direct methanol fuel cell (DMFC), shown schematically in Fig 1.2, oxidizes liquid methanol at the anode according to the reaction:

Fig 1.2 Schematic diagram of a direct methanol fuel cell

where SHE stands for the standard hydrogen electrode.

The cathode reaction in a DMFC proceeds as

Accordingly, the net cell reaction in a DMFC is

Methanol possesses a number of advantages as a fuel, such as it being a liquid and therefore can be easily transported, stored, dispensed within the current refueling network. Methanol is cheap and plentiful, and the only products of the reaction are CO₂ and water. Above all, the use of methanol as a fuel highly simplifies the engineering problems at the front end of the fuel cells, driving down complexity and cost.

However, owing to the high degree of irreversibility of the oxygen reduction reaction, even under open circuit conditions, the overpotential at the oxygen electrode in a PEM hydrogen/air fuel cell is about 0.2V. This represents a loss of about 20% from the theoretical maximum efficiency. The situation has become worse with the DMFCs. The thermodynamic potential for a DMFC is 1.21 V under standard conditions (Eq. 1.6), which is only 20 mV less than that for a PEM hydrogen/air fuel cell. But in a DMFC, both the methanol oxidation and oxygen-reduction reactions are highly irreversible and thus there is a loss of about 0.2V at the anode under open-circuit conditions, and an additional loss of about 0.1 V or more at the oxygen electrode because of the crossover of methanol from the anode to the cathode (Fig 1.3). Experimentally, this problem can be tackled by seeking alternative oxygen-reduction catalysts and substantially increasing the platinum loading. Consequently, many efforts have been made to develop alternative membranes with low methanol

permeability and high proton conductivity, and to modify the Nafion membranes to reduce the methanol crossover through the membranes.

Fig 1.3 Polarization curves for a DMFC and its constituent electrodes.

1.3 Project Objectives

The objectives of this study are to develop novel self-assembly and layer-by-layer techniques for the PEMFCs and DMFCs. The electrocatalytic activity of the polyelectrolyte stabilized Pt nanoparticles and the self-assembled Pt nanoparticles/Nafion membrane interface will be studied. The reduction in methanol crossover through the layer-by-layer self-assembled Nafion membrane will also be investigated in DMFCs.

1.4 Scopes

The scopes of the project are as follows:

- Synthesis and characterization of polyelectrolyte stabilized Pt nanoparticles, in particular
 - Synthesis and characterization of positively charged Pt nanoparticles

- Synthesis and characterization of negatively charged Pt nanoparticles
- Study of the self-assembled Pt/Nafion membrane interface
 - The self-assembled positively charged Pt nanoparticle/Nafion membrane interface
 - The self-assembled negatively charged Pt nanoparticle/positively charged polyelectrolyte/Nafion membrane interface
- Reduction of methanol crossover by self-assembled charged nanoparticles
 - Fabrication of the self-assembled Nafion membrane with charged nanoparticles
 - Methanol crossover measurement of the self-assembled Nafion membrane
 - Cell performance with the self-assembled Nafion membrane
- Reduction of methanol crossover by multilayer of polyelectrolytes via layer-by-layer technique
 - Fabrication of the self-assembled multilayer of polyelectrolytes on the Nafion membrane
 - Methanol crossover measurement of the self-assembled Nafion membrane
 - Cell performance evaluation with the self-assembled Nafion membrane

1.5 Thesis Layout

Chapter 2 is the literature review, including the components of the PEM fuel cell systems, catalysts employed, synthesis of nanoparticles, self-assembly and layer-by-layer techniques. Chapter 3 describes the experimental methods and the characterization methods. Chapter 4 presents the work on the studying the

electrochemical activity of the commercial Pt/C catalysts and the parameters for the investigation of the polymer stabilized Pt nanoparticles. Chapters 5 and 6 contain the synthesis and characterization of polymer stabilized Pt nanoparticles. In Chapter 7, the self-assembled Pt nanoparticles/Nafion membrane interface is studied. Chapters 8 and 9 present the reduction of the methanol crossover of the modified Nafion membrane and the cell performance of DMFC. Chapter 10 presents an ex situ method to improve the accuracy for measuring the through-plane proton conductivity of Nafion membrane. Finally in chapter 11, the conclusions are drawn together with the summarized major achievements in this project and the recommendations for future work.

CHAPTER 2 Literature Review

2.1 General Introduction to PEMFC

Fuel cells were invented by a UK amateur scientist, Sir William Grove, about 160 years ago. It has been taken so long for fuel cells to come to the forefront of energy and environmental considerations. It was not so much because their environmental attributes were not known or indeed promoted, but more as a result of the technical challenges to be met in developing a viable power system. On the one hand, it was the competition from the internal combustion engines and steam turbines. On the other hand, it was the limited current density produced by the Grove cell because of the small effective area of the Pt electrodes in the cell.

It was Mond and Langer who, in 1889, were the first to take up the challenge of increasing the “surface of action”. Their cells operated on hydrogen and oxygen at 0.73V and a current density of $3.5\text{mA}/\text{cm}^2$ was generated by using porous electrode structures. It was not until 1933 that Bacon developed a fuel cell delivering power density of $1000\text{mA}/\text{cm}^2$ at 0.8V by using hydrogen and oxygen at elevated pressure. The alkaline fuel cell, commonly referred to as the “Bacon Cell”, not only provided, after adaptation by Pratt and Whitney, the on-board power system for the Apollo lunar missions, but also stimulated the start of the current interest in fuel cell technology for sustainable stationary and mobile power generation.

It was during the 1960s that the other four fuel cell systems were originally conceived. They are the proton exchange membrane fuel cell (PEMFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC) and solid oxide fuel cell (SOFC).

Among these five types fuel cells, PEMFC has been considered the most potential power source for transportation application due to its high efficiency, free or very low pollution, low temperature operation, quick startup, and potential for low-cost mass production [Freire, *et al.*, 2001].

The most dramatic research and development advances for stack have been made during the past decades. Through the mid-1980s, the energy and power densities of stack were so low and the necessary platinum catalysts loading was so high that most commercial applications, let alone automotive use, seemed out of the question. Platinum requirements for the General Electric stack in 1960s were on the order of 100g/kW, costing \$1400/kW [Appleby, *et al.*, 1986]. Costs appeared prohibitive because of both expensive membranes and especially the high platinum catalyst loading. In 1983, Ballard started its research and development work on PEM stack. Ballard's work was the first serious engineering effort with PEM technology since General Electric's efforts two decades earlier. The company was able to address membrane, electrode, flow field, and other issues adequately, to the point of where major performance improvements were achieved by 1986. Announcement of these results at a LANL fuel cell conference that year sparked broader attention to the potential of PEM technology. Even as of 1990s, the quantity of platinum catalysts required for a stack cost was on the order of \$75/kW [Srinivasan, *et al.*, 1988]. Then, largely through the continuing efforts at Ballard, platinum cost was decreased by an order of magnitude within a few short years, to \$6/kW by 1993. Based on laboratory demonstrations of improved catalyst deposition techniques, platinum catalyst cost levels of \$2-3/kW now appear possible.

Direct methanol proton exchange membrane fuel cell (DMFC) is another promising power source especially for portable applications due to its easy handling and availability.

PEM fuel cells will, in the future, be used not only in the automotive industry and also in the distributed power supply. Due to its excellent dynamic characteristics, PEM fuel cells can be used as emergency generating set for users, who have special requirements for their critical equipment in case of power failure. Table 2.1 shows the market segmentation of potential non-vehicular fuel cell applications [Maceda, 1999].

Table 2.1 Market Segmentation of Potential Non-Vehicular Fuel Cell Applications

Scale	Power (kW)	Life (hrs)	Cost (\$/kW)	Fuels	Applications
Micro	<0.1	<2000	<2500	H ₂ , CH ₃ OH	Battery replacement in portable electronics, instrumentation
Small	0.1-1	1000	1500	H ₂	Small portable generation sets, communications robotics
Medium	1-40	2000-20000	100-1000	H ₂ , HCs	Large generation sets, communications, submersibles, backup power
Large	>100	>50000	300-500	H ₂ , CH ₄ , HCs	Distributed electricity generation, peaking, reliability, etc.

CH₄=Natural gas or biogas, including landfill methane.

HCs: liquid hydrocarbons, including alcohols.

Thus, PEMFCs have a very broad use, including vehicular and non-vehicular applications.

2.2 Components of PEMFC

A fuel cell may comprise a single-cell, or a multi-cell stack. In either case, it includes: 1) the proton exchange membrane, 2) the electrode composed of an electrically conductive porous backing layer and a catalyst layer, 3) the bipolar plate that delivers the fuel and oxidant to the reactive sites via flow channels.

2.2.1 Bipolar Plates

Bipolar plates function as current collectors providing electrical continuity between the fuel cell voltage terminals and electrodes. Additionally, the plates provide mechanical support for the MEA and distribute the reactants and water across the active area of the electrodes, which is accomplished by a flow field embedded into the side of each plate in direct contact with the electrodes of the MEA [Besmann, *et al.*, 2000].

Bipolar plates, accounting for the bulk of the stack, are desirable to have the smallest dimensions in order to improve their power output per unit weight or volume. Traditionally, carbon based materials have been chosen for bipolar plates, as these materials are chemically stable and electronically conductive in a fuel cell environment. However, the lack of mechanical strength inherent with carbon limits the size and hence the volumetric power density. The alternatives to graphite can be classified under three categories: carbon-carbon composites [Besmann, *et al.*, 2000], carbon-polymer composites [Busick, *et al.*, 1998] and metals [Makkus, *et al.*, 2000; Hodgson, *et al.*, 2001].

2.2.2 Proton exchange membrane and methanol crossover

The membrane presently available for fuel cell application can be divided into two general classes, perfluorosulfonic acid (PFSA)-based membranes (e.g. Nafion) and aromatic sulfonic acid moieties-based membranes. PFSA have been considered as the most suitable membranes for PEMFCs. PFSA-based membranes include the following types: 1) Nafion membranes developed by DuPont with the thickness ranging from 25 μ m to 175 μ m; 2) XUS-B204 membranes developed by Dow; 3)

Aciplex developed by Asahi in Japan; 4) C membranes developed by Chlorine engineers in Japan; 5) BAM membranes developed by Ballard Co. in Canada.

Among these membranes, Nafion membranes have been widely used in polymer electrolyte fuel cells due to their high chemical and electrochemical stability, reasonable mechanical strength, extremely low permeability to gas reactant species, selective and high ionic conductivity, and their ability to provide electronic insulation [Savadogo, 1998].

However, when fed with hydrogen-rich reformat containing small amount of carbon monoxide (CO), the performance will drop severely due to poisoning of platinum anode catalysts. High temperature operation of a PEMFC (above 120°C) has been investigated to reduce the effects of CO adsorption onto the platinum electrocatalyst [Malhotra, *et al.*, 1997]. In addition to increasing the tolerable CO concentration in the anode fuel, higher temperature operation is adopted to improve thermal management and heat utilization of the fuel cell stack, increase reaction rates at the anode and cathode, and potentially simplify fuel cell water management. Therefore, it is necessary to develop alternative membranes with high proton conductivity under high temperature operation [Doyle, *et al.*, 2000] and to modify the present membranes to maintain sufficient hydration [Yang, *et al.*, 2001].

On the other hand, when methanol is used as fuel in anode, methanol crossover causes a significant reduction of both the cathode potential and of the fuel utilization. There are continuing efforts in the modification of Nafion-based membranes in addition to the development of alternative electrolyte membranes with aims to achieve low methanol permeability and high conductivity [Arico, *et al.*, 2001; Kreuer, 2001]. Jia *et al.* [2000] impregnated Nafion membrane with poly(1-methylpyrrole) by in situ polymerization. The impregnation reduced the methanol crossover but also decreased

the proton conductivity. Composite membranes such as sol-gel derived Nafion/silica [Miyake, *et al.*, 2001], Nafion/zirconium phosphate [Yang, *et al.*, 2001], and Nafion/cesium ions [Tricoli, 1998] have also been investigated. To achieve significant reduction in the methanol permeability, oxide content has to be high (e.g., 20wt% silica in the case of Nafion/silica composite [Miyake, *et al.*, 2001]). This in turn affects the proton conductivity and other properties such as mechanical stability. Using Pd thin films sandwiched between Nafion membranes [Pu, *et al.*, 1995] and deposition of Pd nanoparticles through ion exchange and chemical reduction [Kim, *et al.*, 2004a] were shown to reduce the methanol crossover. Unfortunately, the Pd film increased the overall cell resistance. The dispersed Pd particles through ion-exchange and reduction alter the microstructure of the Nafion membrane, resulting in the reduced cell performance and stability. Kim *et al.* [2004b] reported the performance of the Nafion/polyvinylidene fluoride (PVdF)/Nafion laminated membrane for DMFC. The middle PVdF layer blocks the methanol crossover but at the same time reduces the conductivity significantly due to the non-conducting properties of PVdF. Casting non-conducting polymers such as polyvinyl alcohol (PVA) onto Nafion membrane can also reduce the methanol crossover [Shao, *et al.*, 2002]. However, casting an additional film causes the significant decrease of the proton conductivity of the Nafion membrane, similar to that of sandwiched Nafion/PVdF/Nafion approach. It was also found that Pt-dispersed PEM, when applied to a direct methanol fuel cell, would result in the effective recombination of the cross-overed methanol and oxygen at the catalytic sites. This is schematically shown in Fig 2.1. The cathode potential was increased resulting from the reduced amount of methanol reaching the cathode [Uchida, *et al.*, 2000].

Fig 2.1 A diagram of a DMFC with Pt-Membrane

2.2.3 Electrodes

Electrode structures of PEMFC can be classified as two-layer or three-layer structure. Dual-layer electrodes consist of a hydrophobic support layer and a porous electrocatalyst layer formed by Pt on carbon (Pt/C) as a catalyst with polytetrafluoroethylene (PTFE) and/or polyperfluorosulphonic acid (Nafion). Three-layer electrodes are made by a porous support layer, a diffusion layer consisting of carbon particles and PTFE, and a catalyst layer formed by Pt/C, PTFE and/or Nafion. The performances of the electrodes depend on various parameters including [Maoka, 1988; Arico, et al., 1993]: (1) support (carbon paper or carbon cloth) and its characteristics (porosity and thickness); (2) catalyst (Pt black, Pt alloy, Pt/C, Pt amount, Pt particle size, type of carbon support); (3) PTFE content; (4) Nafion content; (5) thermal treatment; (6) thickness of diffusion layer and catalyst layer; and (7) fabrication process. Both diffusion layer and catalyst layers can be fabricated by different techniques.

2.2.3.1 Support layer

Support layer functions as the current collector and the backing of catalyst layer. There are two types of support layer: carbon paper and carbon cloth. They not only

offer the passage for reactant (hydrogen and oxygen from air) and product (water), but also for the electrons. Therefore, the support layer must be hydrophobic, permeable to gas and electrically conductive. The hydrophobicity can be achieved by proper control of the PTFE content, while permeability and electrical conductivity are related to its microstructure and thickness. Wilson [1995] evaluated the effect of support layer on the performance of Pt/C electrodes. The results showed that carbon cloth has better performance as compared to carbon paper. Qi et al. [2002] reported that different batches of carbon paper exhibit different performances. To reduce the effect of support layer on the gas diffusion, a diffusion layer consisting of carbon powder and PTFE was introduced between the support layer and the catalyst layer.

2.2.3.2 PTFE and Nafion Content

The incorporation of PTFE into the diffusion layer or catalyst layer serves two purposes: binding the high surface carbon particles into a cohesive layer and introducing some hydrophobic property to the layer. It has been suggested that PTFE in the catalyst layer offers a passage for gas access and thus reduces mass transportation polarization. At the same time, it also increases the ohmic polarization of the electrodes due to the insulation nature of PTFE [Mahlendorf, et al., 1995].

Incorporating Nafion into catalyst layer has been used widely since Raistrick [1989] discovered that three-phase interface of electrode can be extended by impregnating Nafion into the catalyst layer. The content and distribution of Nafion in the catalyst layer play important roles on the electrochemical reaction. It not only increases the utilization of catalyst due to the increased active area of the electrode, but also promotes proton transportation in the catalyst layer. On the other hand, Taylor [1992] indicated that Nafion could be used as a binder and proton conductor to replace PTFE. Some Nafion will lose its sulfonic acid group during the heat treatment

and function as PTFE. Ochida [1995] considered that Nafion could completely replace PTFE without using heat treatment to degrade Nafion to PTFE. It has been shown [Ticianelli 1988] that there is an optimized content of Nafion in the catalyst layer. The optimum Nafion/(Nafion+Pt+C) was 0.36 (w/w). This is because that Nafion plays two different roles on the electrode: it increases both the active area of the catalyst and the gas diffusion resistance in the catalyst layer.

2.2.3.3 Electrocatalysts

There are various electrochemical reactions in PEMFCs: hydrogen oxidation reaction (HOR) or methanol oxidation reaction (MOR) on anode and oxygen reduction reaction (ORR) on cathode. To accelerate the reactions, the electrocatalysts must be used in the electrodes. Platinum, a precious metal, has high electrocatalytic activity for both reactions. However, its wide applications are limited by the high cost. There are two general directions in the research and development of electrocatalysts: one is to increase the utilization of Pt-based catalyst; the other is to develop alternative catalysts other than precious metals.

The first PEM fuel cells used in the Gemini Space Program had a loading of 4-10mgPt/cm² [Appleby, *et al.*, 1986]. The cost of the electrodes was drastically reduced when pure colloidal Pt black was replaced by Pt supported on carbon (Pt/C) with a content of 0.4mg/cm² [Srinivasan, *et al.*, 1988]. Since then, many studies have been aimed further lowering the Pt loading. Today, Pt loading reported for oxygen reduction reaction is in the range of 0.05-0.1mg/cm² [Taylor, *et al.*, 1992; Kumar, *et al.*, 1995]. It is also possible to reduce Pt loading within the 0.1mg/cm² range at the cathode by using carbon-based catalysts containing Pt inclusions [Fournier, *et al.*, 1997]. The interests have also been focused on developing methanol resistant oxygen reduction reaction catalysts in direct methanol fuel cells [Shukla, *et al.*, 2003].

Arico et al. [2002] suggested that if the particle size of a platinum electrocatalyst for oxygen reduction is very small or the platinum electrocatalyst is amorphous, the methanol chemisorption energy would be lower and the cathode would be less likely to be poisoned. Various preparatory routes have been reported to synthesize platinum and platinum-alloy electrocatalysts with finer particle size [Petrov, et al., 1976]. Maillard et al. [2002] reported that the mass activity of platinum (A/g Pt) toward oxygen reduction increases continuously with a decrease in particle size from 4.6 to 2.3 nm, whereas mass activity is independent of size in methanol-free electrolyte when the platinum particle size is less than 3.5 nm. The effects of adding a second metal to platinum have also been investigated. Although both Pt-Co/C and Pt-Fe/C have been reported to be methanol-resistant oxygen-reduction catalysts, Pt-Fe/C were found to exhibit higher activity than Pt-Co/C [Shukla, et al., 2003].

Iron tetramethoxyphenylporphyrin (FeTMPP) has been reported to be the most active catalyst among transition-metal porphyrins [Chu, et al., 2001]. However, it was arguable that the organic linkages around the iron atom help to prevent iron atoms from oxidation, which is similar to its catalytic activity for oxygen reduction reaction [Bron, et al., 2002].

Another category of the catalysts consists mainly of Ru-Mo-S, RuS, and RuSe [Sebastian, et al., 1999; Bron, et al., 2001; Le Rhan, et al., 2000; Tributsch, et al., 2001]. Among these, RuSe exhibits the best activity as a selective oxygen-reduction catalyst. RuSe was obtained by reacting a mixture of ruthenium dodecacarbonyl ($\text{Ru}_3(\text{CO})_{12}$) with sulfur or selenium at about 140°C, with xylene in nitrogen under refluxing conditions, followed by washing the resultant mass with triethyl ether [Bron, et al., 2001]. These catalysts were deposited onto a Vulcan XC-72R carbon powder as oxygen-reduction electrodes. Bron et al. [2001] reported that ruthenium, even after

refluxing in a selenium-containing solution, shows little change in its XRD pattern. However, RuSe exhibits higher catalytic activity than ruthenium metal. According to Bron et al. [2001], the activity enhancement by selenium was related to an interfacial effect due to the binary structure of the catalyst. It is noteworthy that the RuSe/C catalyst is different from a metallic ruthenium surface, and its activity towards oxygen reduction is substantially higher. Because the RuSe/C catalyst is loaded with organic compound made up of carbonyl or carboxylic groups, its high catalytic activity is probably due to an interaction of nanocrystalline ruthenium and carbon ligands.

For anodic catalysts, the most challenging task is to develop catalysts resistant to CO-poisoning. Pt is easily poisoned by CO at lower temperature, and significant power losses may arise when H₂ is obtained from the reforming of alcohols or hydrocarbons. Even 10 ppm of CO in the H₂ feed stream has a detrimental effect on the fuel cell performance [Gottesfeld, et al., 1997].

Binary electrocatalysts have been used with some success to alleviate CO poisoning problems at the anode of polymer electrolyte fuel cells. They contain a more oxidizable element with the ability to activate oxygenated species at lower potentials in order to initiate CO oxidation. The most studied CO-tolerant anode catalysts are Pt-Ru and Pt-Sn alloys [Ross, 1998]. CO poisoning can be largely mitigated by injecting a small air bleed (<2%) just ahead of the PEMFC stack [Gottesfeld, et al., 1988] or within the stack itself [Wilkinson, et al., 1996]. This air bleed removes the CO from the PtRu electrocatalyst sites by gas phase dissociative chemisorption of oxygen on the CO-free Pt catalyst sites, followed by bimolecular surface reaction between Pt-CO and Pt-O to form CO₂. The gas-phase catalytic oxidation reduces the CO coverage on the PtRu electrocatalyst and increases the hydrogen electrooxidation activity. Recently, new anode catalysts containing Mo are

of technical interest for low-temperature fuel cells fed with a reformed fuel and for direct methanol fuel cells (DMFCs). These catalysts are either binary Pt-Mo alloys or ternary alloys such as Pt-Ru-Mo or Pt-Co-Mo or even composite Pt-based catalysts containing Mo oxides [Zhang, *et al.*, 1999].

There is a considerable drive to raise the operating temperature of the PEM fuel cells to above 100°C. This would raise the system efficiency and dramatically improve the CO tolerance of Pt-based electrocatalysts. For example, the CO coverage on Pt drops from in excess of 0.98 at 80°C to ~0.5 at 160°C [Wilkinson, 1997]. At this temperature a Pt-based anode can function in the presence of 1-2% CO rather than with ppm levels of CO, eliminating the need for preferential oxidation reactor. If the temperature can be raised to 160°C, studies in the phosphoric acid fuel cell with 1-2% CO indicate that PtRh and PtNi may offer superior CO tolerance. Indeed, at 200°C pure Pt is the favored electrocatalyst in the PAFC. There are significant research activities to develop membranes capable of proton conduction at 120-200°C [Hoggarth, *et al.*, 2001].

2.3 Electrochemical Reaction in PEM Fuel Cells

2.3.1 Oxygen Reduction Reaction

The oxygen reduction reaction can occur by two different reaction pathways [Kordesch, *et al.*, 1994]: (a) the direct four-electron pathway and (b) the peroxide pathway. In PEMFC, oxygen reduction reaction at cathode proceeds as:

In this case, the Damjanovic mechanism is widely accepted [Antoine, *et al.*, 2001]. Damjanovic *et al.* [1988; 1991] investigated the kinetics and mechanism of the oxygen reduction reaction in acid (H₂SO₄) solution. Two linear E-log i regions are

observed. The kinetics in the low current density region is characterized by a slope of -60 mV/dec ($-RT/F$) and is a result of intermediate coverage of absorbed oxygenated species ($-O$ and $-OH$) derived from water oxidation. The coverage of these species is linearly potential dependent, and can be described by Temkin adsorption. In the high current density region the kinetics are characterized by a Tafel slope of -120 mV/dec ($-2RT/F$) and is a result of oxide free condition which is attributed to the sparse coverage of oxygen containing species under Langmuirian adsorption conditions. The reaction path is summarized as follows: After a fast chemical O_2 -adsorption step which is considered at equilibrium and involving a very low coverage, the first electrochemical step is the protonation of the O_2 molecule, which is the rate-determining step (rds):

Thus the reaction is of first order with respect to O_2 partial pressure in the whole range of potentials. And a second chemical step and a final electrochemical step was proposed [Diard, *et al.*, 1993], i.e. an ECE mechanism in accord with Damjanovic's statement. For this mechanism, the following steps and adsorbed intermediate species O_2H_{ads} and OH_{ads} were considered:

Antoine *et al.* [2001] used rotating ring disk electrode (RRDE) to study oxygen reduction on Pt nanoparticles inside the Nafion and confirmed a direct 4-electron transfer mechanism. Both stationary and EIS techniques were also used to study the

oxygen reduction reaction kinetics on Pt supported on carbon inside Nafion [Antoine, *et al.*, 2001].

A typical polarization curve of a PEM fuel cell shows that the loss in the cell potential occurs due to activation resistance, ohmic losses, and mass-transfer limitations [Mosdale, *et al.*, 1995]. The activation loss is largely determined by the quality, distribution, and the activity of the platinum/carbon catalyst. The ohmic losses are directly related to the proton conductivity of the membrane, the electronic conductivity of the current collectors and the contact resistance between different components. The mass-transfer limitations are caused by the inability of the reactants to keep up with the demands imposed by the electrochemical reaction. It is a widely accepted fact that the cathode in PEMFCs is the performance-limiting component due to the slower kinetics of the oxygen reduction reaction [Voss, *et al.*, 1995] and the mass-transfer limitations caused by the nitrogen barrier layer effect and the liquid water generated by the reaction and electro-osmotic drag, accumulating in the porous catalyst and gas diffusion layers [Nguyen, 1996]. Over the past decade, significant research effort has been focused on fuel cell designs that would alleviate the cathode-flooding problem caused by excessive liquid water, the development of better catalysts, and the catalyst dispersion on the supports for improving the kinetics of the reduction reaction and the development of membranes with higher proton conductivity [Mosdale, *et al.*, 1995].

When methanol is used as a fuel in the anode, a chemical reaction will occur between the crossoverd methanol and oxygen at cathode:

Methanol crossover in Nafion membranes has been studied in order to improve the performance [Ren, *et al.*, 2000]. One way is to develop alternative membranes

with low methanol permeability and to modify the present membranes to reduce the methanol crossover [Arico, *et al.*, 2001; Kreuer, 2001]. The other way is to develop the methanol tolerant cathode catalysts to minimize the effect of the methanol crossover [Shukla, *et al.*, 2003].

2.3.2 Hydrogen Oxidation

The oxidation of hydrogen occurs readily on Pt-based catalysts. The kinetic of this reaction is very fast on Pt catalysts. The oxidation of hydrogen also involves the adsorption of the gas onto the catalyst surface followed by a dissociation of the molecules and electrochemical reaction to hydrogen ions as follows:

Where $\text{Pt}_{(s)}$ is a free surface site and $\text{Pt}-\text{H}_{\text{ads}}$ is an adsorbed H-atom on the Pt active site. The overall reaction of hydrogen oxidation is

Although this reaction is fast on Pt catalysts in a fuel cell, some problems may arise when impure hydrogen is used. Operating a fuel cell with pure hydrogen give the best performance but pure hydrogen is expensive and difficult to transport and store. Alternatives to pure hydrogen are hydrocarbons such as natural gas, propane or alcohols. These substances have to be reformed into hydrogen before use. However, even after gases clean up some contaminants such as carbon monoxide (CO) can still exist in the products. CO, present in the reformed gas in non-negligible concentrations (0.01-2%), acts as a poison to the Pt catalyst. Adsorbed CO not only affects the reactivity of the accessible electrode surface by preventing hydrogen adsorption by

site exclusion, but also lowers the reactivity of the remaining uncovered site through dipole interactions and electron capture [Ciureanu, *et al.*, 1999].

2.3.3 Methanol Oxidation

Methanol is an attractive fuel for fuel cells due to its low price, easy storage, and transportation. There are two ways to use methanol as the fuel for fuel cells. The first is to reform it catalytically into hydrogen-rich reformat gas as a feed for H₂/air fuel cell. The second and more challenging option is to oxidize methanol directly on the anode, i.e., to use it as a feed for the direct methanol fuel cell (DMFC).

The anodic methanol oxidation reaction proceeds as

It is a slow reaction that requires active multiple sites for the adsorption of methanol and the sites that can donate OH species for desorption of the adsorbed methanol residues. Anode catalyst that can be applied in DMFC must be stable in acid media with high electrocatalytic activity for methanol oxidation reaction. Methanol can be rapidly oxidized to carbon dioxide on a clean platinum surface with intermediate species such as CO. The CO_{ad} species are formed in a methanol dehydrogenation step mainly facilitated by Pt sites [Schmidt, *et al.*, 1999]:

However, the platinum catalyst is poisoned by carbon monoxide, and its activity degrades very rapidly. Bimetal catalysts could be the potential catalyst for the methanol oxidation reaction and among many combinations that have been tested, platinum–ruthenium is recognized as the best choice [Wasmus, *et al.*, 1999].

The removal of CO_{ad} proceeds via adsorbed OH on Pt or Ru sites (Eq. (2.12)) formed by dissociative water adsorption (Eq. (2.11)):

Due to the high affinity of Ru towards oxygen-containing species [Ticanelli, *et al.*, 1989], sufficient amounts of OH_{ad} to support reasonable CO oxidation rate are formed at lower potentials (above 0.35V) on Ru sites than on Pt site (above 0.55V). This effect leads to the higher activity for the overall methanol oxidation process on Pt/Ru compared to Pt [Schmidt, *et al.*, 1999].

Different types of PtRu catalysts were investigated with respect to the methanol oxidation: well-defined alloys [Kardash, *et al.*, 2001], Pt polycrystalline surface [Watanabe, *et al.*, 1997] and single crystals [Chrzanowski, *et al.*, 1998] modified by spontaneous Ru deposition, Pt polycrystalline surface modified by Ru electrodeposition [Morimoto, *et al.*, 1998], unsupported dispersed catalysts [Jusys, *et al.*, 2002], dispersed catalysts incorporated in polymer matrix [Hepel, 1998], and dispersed catalysts supported on carbon paper and on high area carbon [Roth, *et al.*, 2002].

2.4 Synthesis of Pt and Pt alloys nanoparticles

It is known that Pt and its alloys are the most effective catalysts for the electrochemical reactions in PEMFCs. However, the high cost of noble metals is one of the obstacles preventing PEMFC from commercialization. To effectively use these metals, they have to be well dispersed to the nanoscale particles with high surface-to-volume ratio. Consequently the surface chemistry of the nanoparticles plays an important role. A variety of methods can be used to form metal nanoparticles, such as sol-gel [Bhattacharya, 2001], chemical vapor deposition, electrodeposition, reflux

[Chen, *et al.*, 2000; Athawale, 2003], radiolytic reduction [Sarkany, 2004; Athawale, 2003], and chemical reduction [Sun, *et al.*, 1999] or photoreduction of metal salts.

Although Pt black and PtM black (M=metal) were synthesized via different methods [Watanabe, *et al.*, 1987], the resulting particle size is relatively large, ranging from 5nm to 10nm. Therefore, the Pt loading employed in PEMFCs was considerably high, resulting in very high cost. To decrease the Pt loading and increase the utilization, the supported catalysts on carbon powder have been prepared via sulfite-complex route [Ravikumar, *et al.*, 1996] or impregnation reduction method [Jia, *et al.*, 2005]. The particle size decreased significantly to 2~5nm, depending on the metal content. Commercially available catalysts are generally supported on the Vulcan XC-72. However, platinum nanoparticles supported on carbon may be not fully utilized due to the electrode structure [Wilson, *et al.*, 1992]. One way to fabricate the catalyst layer was to impregnate PTFE-bonded Pt/C electrode with polymer electrolyte (e.g. Nafion) [Raistrick, 1989]. Nafion impregnation was reported to extend the three phase boundary, thus resulting in the increase of the catalyst utilization. The content and distribution of Nafion played an important role on the electrochemical reaction [Raistrick, 1989; Wilson, *et al.*, 1992; Cha, *et al.*, 1999; Sigaard, 2001]. However, the erratic thickness of catalyst layer and the variations in the impregnation depth of Nafion would result in two unsatisfied areas [Wilson, *et al.*, 1992]. Nafion may not fully impregnate into the catalyst layer or extend into the electrode further than the catalyst layer. Therefore, some catalysts may not be utilized or unnecessary transport barrier may be introduced for the gas diffusion. The other way was to mix Pt/C catalyst directly with polymer electrolyte [Wilson, *et al.*, 1992]. Although better performance can be obtained with optimal Nafion content, it is still difficult for the polymer electrolyte to make contact with all the platinum particles supported on

carbon powder. Nafion micelles has an approximate diameter of 4nm [Shimazu, *et al.*, 1987] and may be excluded from the pores with diameter less than 4nm in carbon support. Therefore, platinum nanoparticles located within carbon pores may be inaccessible to the polymer electrolyte, and therefore they may not be utilized.

Recently, the synthesis and properties of colloidal metal nanoparticles have attracted considerable scientific and commercial attention due to their potential utilization in catalysis, optoelectronic structures and devices, and ultrasensitive chemical sensors. The colloidal metal nanoparticles can be synthesized in the absence or presence of stabilizers. The purpose of the stabilizers is not only to control particle size and prevent agglomeration, but also to make them stable in various solvents, depending on the nature of the stabilizers.

The reduction of transition metal salts and oxides using alkali hydrotriorganoborates in organic media in the absence of stabilizers at -20°C ~ 80°C led to boron-free and amorphous nanopowders of metals and alloys. The particle size is between 1-100nm, depending on the metal used [Bonnemann, *et al.*, 1990]. Wang *et al.* [2000] effectively prepared stable platinum, rhodium, and ruthenium metal nanoclusters with small particle size in organic media by heating the corresponding metal hydroxide colloids in ethylene glycol containing NaOH in the absence of any protective agent. The average diameters of the Pt, Rh, and Ru nanoclusters were in the range of 1 to 2 nm.

Bonnemann *et al.* [1996] prepared organosol of nanometals stabilized by ether (tetrahydrofuran and tetrahydrothiophene) and lipophilic surfactants (tetraalkylammonium halides, i.e., NR_4^+ and trialkylamines, i.e., $\text{N}(\text{R}^1)_2\text{R}^2$) at temperatures between 20 and 60°C. The particles size was in the range of 1 to 10nm. Hydrosol of nanometals was also prepared in the presence of hydrophilic surfactants

(3-(N,N-dimethyldodecylammonio)-propanesulfonate (SB12)) [Bonnemann, *et al.*, 1996]. Cationic, anionic, nonionic and amphiphilic types of surfactants give similar results. The resulting nanometallic materials (particle size 1-10nm) were highly stable in water.

In addition, polymers were also used to prepare nanometal colloids using refluxing method. Ultrafine Pt particles protected by poly(N-vinyl-2-pyrrolidone) (PVP, MW=40000) were prepared by refluxing method [Teranish, *et al.*, 1999], where methanol, ethanol, and 1-propanol were used. Chen *et al.* [2000a; 2000b] prepared the platinum nanoparticles by refluxing a solution of chloroplatinic acid in ethanol/water in the presence of protective polymers, such as poly(N-vinylformamine) (PNVF), poly(N-vinylacetamine) (PNVA), poly(N-vinylisobutyramide) (PNVIBA), poly(N-isopropylacrylamide) (PNIPAAm) and poly(vinylpyrrodine) (PVP). Fig 2.2 shows the molecular structure of the polymers. Different polymers provided different dispersion stability, and the resulting polymer stabilized Pt nanoparticles showed different catalytic activity in hydrogenation.

Fig 2.2 Molecular structure of polymers

Mu *et al.* [2004] also synthesized PVP-Pt nanoparticles. These particles showed very high catalytic activity in hydrogenation and can retain their activity and the size distributions after reactions. This indicated that PVP can not only prevent the agglomeration during the synthesis, but also inhibit the aggregation during the hydrogenation reactions.

As suggested by Duff et al. [1995], reduction of platinum ions to platinum atoms in the presence of ethanol may proceed as equation (2.13):

This reaction can be viewed as a two-step reaction as follows:

In addition to the application of the polymer stabilized or supported Pt and Pt alloys nanoparticles in hydrogenation, they also demonstrated interesting catalytic properties in PEMFCs and DMFCs. Qi et al. [1998] studied polypyrrole (PPy)/polystyrenesulfonate (PSS) as a support for Pt catalyst, which is both electronically and ionically conductive. The deposition of Pt nanoparticles on PPy/PSS particles was accomplished by the reduction of $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ with formaldehyde. The Pt particle size was about 4nm. The preliminary results indicated that PPy/PSS supported Pt nanoparticles were effective for oxygen reduction in PEMFCs, despite their low electronic conductivities.

Nanocomposites of Pt/Ru alloy nanoparticles and the electronically conducting polymer were prepared by adding poly(N-vinyl carbazole) (PVK) or poly(9-(4-vinyl-phenyl) carbazole) (P4VPCz) into PtRu nanoparticle colloidal solution [Choi, et al., 2003]. This colloidal solution was synthesized in anhydrous solvents by reducing platinum and ruthenium ions using LiBH_4 . The nanocomposites showed lower performance for anode in DMFCs than that supported on carbon due to the lower electronic conductivity of the polymers. On the other hand, Pt-Ru nanoparticles stabilized in a conductive polymer matrix were prepared via reflux method using microwave heating [Bensebaa, et al., 2005]. It was shown that the presence of a

relatively large concentration of polymer may have some blocking effect on the catalyst sites.

Wang et al. [2002; 2003] synthesized surfactant stabilized Pt/C and Pt,Ru/C by alcohol reduction. It was found that the existence of surfactant dodecyldimethyl (3-sulfo-propyl) ammonium hydroxide (SB12) and tetraoctylammonium bromide (TOAB) had negligible effect on the activity of Pt in PEMFCs and Pt/Ru in DMFCs. A similar conclusion was also drawn by Bonnemann et al. [1996], who measured the Pt surface accessibility by CO chemisorption and Pt catalytic activity by hydrogenation experiments.

Dispersing Pt and Pt/Ru nanoparticles in Nafion by the impregnation-reduction method also provided interesting results [Fujiwara, et al., 2002; Rajalakshmi, et al., 2004; Zhang, et al., 2005]. Pt and/or Ru ions were first impregnated onto the surface of Nafion membrane, followed by NaBH_4 reduction. This technique was attractive to get better catalyst utilization and facilitated the release of evolving CO_2 in the case of DMFCs. [Fujiwara, et al., 2002]. Zhang et al. [2005] also reported novel Pt-Nafion-carbon black composites synthesized using supercritical deposition. The method consisted of preparation of a Nafion-carbon black composite followed by impregnation of a platinum precursor (PtMe_2COD) into the composite via adsorption from a solution of supercritical carbon dioxide. Subsequently, the impregnated composite is subjected to thermal treatment resulting in a Pt-Nafion-carbon black nanocomposite. The preliminary results demonstrated that the composite displayed promising electroactivity as an electrocatalyst for PEMFCs. Most recently, Sarma et al. [2005] prepared carbon-supported Pt-Ru catalysts by the Nafion-stabilized alcohol reduction for direct methanol fuel cells. It was found that the onset potential of methanol oxidation is lower than that for the standard Pt-Ru/C (E-TEK 40).

2.5 Deposition Techniques

Conventional electrodes are based mainly on PTFE-bonded electrode [Appleby, 1986], Nafion-impregnated PTFE-bonded electrode [Raistrick, *et al.*, 1989; Kim, *et al.*, 1995] and Nafion-bonded electrode [Wilson, *et al.*, 1992; Ren, *et al.*, 1996]. Generally, Pt-based catalyst was mixed with PTFE and/or Nafion to make a paste or ink, which was deposited on backing layers [Appleby, 1986; Raistrick, *et al.*, 1989; Kim, *et al.*, 1995] or directly on the membranes by different methods [Wilson, *et al.*, 1995]. In the decal or transfer process, the catalyst ink is cast onto Teflon blanks for transfer to the membrane by hotpressing [Wilson, *et al.*, 1992]. However, Pt catalyst may not be fully utilized in the conventional electrodes due to the reasons mentioned above.

To improve the catalyst utilization, other deposition techniques have been developed. Srinivasan *et al.* [1988] investigated wet chemical/electrochemical deposition of Pt on the catalyzed electrode ($0.4\text{mg}/\text{cm}^2$ Pt). Chemical deposition of Pt ($0.05\text{mg}/\text{cm}^2$) was carried out by brushing the active layer of the electrodes with an appropriate amount of 1% H_2PtCl_6 solution in 0.05M H_2SO_4 , diluted with an equal volume of methanol, this was then followed by heat treatment of the electrodes for 3 hr at 200°C in air. Electrodeposition of Pt, on the active side of electrodes using the same H_2PtCl_6 (1%)-methanol solution (1:1 vol), was carried out at a constant/pulse current density to deposit $\sim 0.05\text{mg}/\text{cm}^2$ Pt. It was reported 20% increase in the performance as compared to that without depositing this thin layer Pt at the potential of 0.6V.

Vilambi *et al.* [1992] applied an interrupted current to deposit catalysts ($0.05\text{mg}/\text{cm}^2$) on the surface of the Nafion-coated electrode. It indicated no difference in oxygen reduction and hydrogen oxidation performance between the standard

electrode and the electrode of this method. The standard electrode was prepared with a Nafion-impregnated 10%Pt/C ($\sim 0.5\text{mg}/\text{cm}^2$). Choi et al. [1998] investigated the distributing catalysts on the surface of PTFE-coated electrode by using direct current and pulse electrodeposition methods. The pulse electrodeposition method can form Pt deposits of about $15\text{\AA}$ directly on the surface of the electrode and can be operated at a higher current density than the DC electrodeposition. When the DC electrodeposition method was used, the best performance was observed at a deposition current density of $20\text{ mA}/\text{cm}^2$. At higher currents, the performance decreases sharply due to the growth of dendritic crystals and loss of the deposition layer through generation of hydrogen. At a deposition current density of $50\text{ mA}/\text{cm}^2$, the optimum conditions of pulse electrodeposition are 100ms on-time and 300ms off-time, and the performance of the electrode was $320\text{ mA}/\text{cm}^2$ at 0.7 V.

Sputter deposition is widely used for integrated circuit manufacturing and has been investigated for the preparation of effective fuel cell electrodes. Srinivasan et al. [1988] applied a 50nm Pt-sputtered film to the surface of a catalyzed gas diffusion layer and the Pt loading was reduced from $4\text{mg}/\text{cm}^2$ to $0.4\text{mg}/\text{cm}^2$ without reduction in performance. Hirano et al. [1997] deposited platinum on uncatalyzed gas diffusion layers by sputtering technique and observed similar cell performances at Pt loading of $0.10\text{mg}/\text{cm}^2$ as compared to the standard cell at Pt loading of $0.4\text{mg}/\text{cm}^2$. Sputter deposition has also been used to reduce the amount of catalyst required for direct methanol fuel cell anodes. Witham et al. [2000] prepared anode for DMFC using sputtering deposition. And the catalyst activity was one to two orders of magnitude higher than those of conventional ink-based catalysts. It was suggested that DMFC anodes could be manufactured containing less than one-tenth the amounts ($0.03\text{mg}/\text{cm}^2$ Pt) presently used ($2.5\text{--}4\text{ mg Pt}/\text{cm}^2$) without loss in performance.

Cha et al. [1999] used alternative sputtering and deposited a thin (5nm) Pt layer directly onto the surface of Nafion membrane. Instead of single sputtering, multiple sputtering with the application of the ink on the surface after each sputtering was found to increase the utilization of catalyst. Application of carbon/Nafion ink on the bare Nafion membrane prior to the initial sputtering also enhanced the utilization of the loaded platinum. The performance of the electrode with extremely low loadings (0.043 mg/cm^2) made by this method was similar to that of the electrode with high loadings (0.5 mg/cm^2) made by conventional method.

However, sputtering techniques tend to produce column and dense Pt structure which is shown to be detrimental to the electrode performance of PEFC [Huie, et al., 2003]. Roughening the polymer membrane surface as commonly used in the sputtering of Pt catalysts directly on the membrane surface [Huie, et al., 2003; Shimazu et al., 2002] could also potentially pose structural stability problem in long-term stability. Grain growth and dendrite formation is also a common problem faced by the electrodeposition technique.

2.6 Self-assembly and Layer-by-Layer Technique

Self-assembly is a spontaneous process in which, and the driven force is the electrostatic attraction. Self-assembly technique has been extensively used to prepare monolayer on different substrates in the fields of optics, electronic, sensors, catalysis, chemistry, process engineering, and biotechnology [Finklea, 1996]. Fig 2.3 shows the diagram of the self-assembly process. Briefly, the charged substrates or modified substrates were immersed in the oppositely charged polyelectrolyte solution. And then the polyelectrolyte was absorbed spontaneously onto the surface of the substrates due to the electrostatic attraction between the polyelectrolyte and the substrate.

Fig 2.3 Schematic diagram of self-assembly polycation on the negatively charged substrate

Berret et al. [2004] studied systematically the polyelectrolytes and the surfactants of opposite charge. When these materials were mixed in aqueous solution, it forms core-shell microstructure. The core is constituted of densely packed surfactant micelles connected by the polyelectrolyte chains. The outer part of the complex is a corona formed by the neutral soluble chains.

Nuzzo et al. [1983] prepared supported, oriented monolayers of polyfunctional organic molecules with a variety of molecular structures, particularly with a wide range of choice for the functional group located at the ambient interface. This technique employs solution adsorption of disulfides on zerovalent gold [Nuzzo, et al., 1983] or silver [Schweizer, et al., 2004] substrates (useful because of their inertness toward corrosion or oxidation) and involves spontaneous organization of the films, in contrast to the well-known Langmuir-Blodgett deposition.

The self-assembly of nanoparticles into ordered morphologies has also attracted interests as it is expected to create nanostructured material with unique physical and chemical properties [Braun, et al., 1996; Shenton, et al., 1997]. To prepare these novel materials, some techniques have been developed in organizing the nanocrystalline metal, metal oxide or semiconductor into ordered aggregates or superlattices [Motte, et al., 1997; Korgel, et al., 1998; Guo, et al., 1998]. Wang et al. [1999] reported that regular and oriented silver nanocrystal arrays loaded on the

surface of cubic mesoporous silica were obtained by an approach of impregnation followed by thermal treatment. It was considered the nanopores could be filled with Ag^+ containing solution driven by capillary force. With increasing thermal treatment temperature, decomposition occurred and the ultrafine Ag clusters were formed. Yin et al. [2001] combined physical templating and capillary forces to assemble monodispersed spherical colloids (polystyrene beads and silica colloids) into uniform aggregates on flat glass substrates with well-controlled sizes, shapes and structures.

Being stimulated by the simplicity and universality of the assembly procedure, multilayer thin films via layer-by-layer (LBL) are actively studied for a number of electronic and photonic applications. The LBL developed by Decher [1997] is one of the most promising new methods of thin film deposition, which is often used for oppositely charged polymers. Fig 2.4 shows the diagram of LBL process. The substrate may be made from polyelectrolyte or modified by polyelectrolyte, and therefore it is charged.

Fig 2.4 Schematic diagram of the LBL self-assembly of oppositely charged polycation and polyanion on negatively charged substrate

To carry out the LBL process, the substrate is alternately immersed in the oppositely charged polyelectrolyte solution. Strong electrostatic attraction occurs between a charged surface and an oppositely charged molecule in solution. At the

same time, charge reversion occurs so that the sequential assembly of oppositely charged polyelectrolyte is possible. The deposition of the films can be performed in a cyclic manner made possible by overcompensation of surface charge when polyelectrolytes or other species are adsorbed at the solid-liquid interface.

Recently, it has also been successfully applied to thin films of nanoparticles and various inorganic materials [Zotti, *et al.*, 2005]. Importantly, the LBL prevents phase segregation of a nanoparticles/polymer mixture, which often occurs for other methods, and is detrimental for many applications. LBL can also significantly improve the accuracy of thin film deposition and lead to the production of stratified films with alternating layers of different substances of organic or inorganic nature.

The application of self-assembly technique in fuel cell applications is rare. Kim *et al.* [2004c] modified Nafion membrane by self-assembled clay-nanocomposite multilayers to prevent methanol permeability. Substituted ionic polyacetylenes were dissolved in methanol and were used for build-up of polycation layers. The aqueous suspension of exfoliated saponite particles was used for the polyanion build-up. The results showed that only 20 bilayer nanocomposites with a thickness of about 0.1 μm reduced the methanol permeability of the Nafion membrane to a half without deterioration of the in-plane proton conductivity. However, no cell performance was reported.

2.7 Ionic Conductivity of the Membrane

Nafion membrane have been widely used in polymer electrolyte fuel cells due to their high chemical and electrochemical stability, reasonable mechanical strength, extremely low permeability to reactant species, selective and high ionic conductivity, and their ability to provide electronic insulation [Savado, 1998]. Proton

conductivity of the membrane is particularly important since it plays a significant role in controlling the performance of the fuel cell. It is generally accepted that there are distinct regions within the membrane [Eikerling, *et al.*, 1997]. There are a hydrophobic region containing the fluorocarbon backbone and a hydrophilic, ionic region containing the sulfonate sites, the protons and the water of hydration. It is presumed that proton transportation occurs by proton movement between the fixed sulfonate sites.

Many groups have studied the conductivity of Nafion membranes [Silva, *et al.*, 2004a; Sumner, *et al.*, 1998; Zawodzinski, *et al.*, 1991; Slade, *et al.*, 2002]. However, the conductivity data are scattered. This may be due to different cell geometry used, technique employed, different electrolyte and sample preparation methods [Silva, *et al.*, 2004].

Two kinds of cell geometry were reported in the literature regarding the conductivity measurements, that is, in-plane [Sumner, *et al.*, 1998; Zawodzinski, *et al.*, 1991; Kolde, *et al.*, 1995; Gardner, *et al.*, 1998; Kim, *et al.*, 2004c; Yoon, *et al.*, 2002; Tricoli, *et al.*, 1998] and through-plane [Silva, *et al.*, 2004b; Sumner, *et al.*, 1998; Gardner, *et al.*, 1998; Slade, *et al.*, 2002; Verbrugge, *et al.*, 1990; Mohr, *et al.*, 2002; Perez, *et al.*, 1991, Tricoli, *et al.*, 2000; Pourcelly, *et al.*, 1997; Nouel, *et al.*, 1998; Verbrugge, *et al.*, 1992; Haufe, *et al.*, 2001; Halim, *et al.*, 1994]. The in-plane conductivity measurements are known to be relatively insensitive to the contact resistance at the current carrying electrodes [Sumner, *et al.*, 1998], but do not reflect the real conductivity of ionic motion through a membrane in a fuel cell. When the membrane is isotropic, the difference between the in-plane and the through-plane conductivity would be small. However, when the membrane is anisotropic, especially

when the membrane is modified by layer-structure, the difference would be expected to be large.

The in-plane conductivity for a fully hydrated Nafion 117 membrane was reported to be in the range of 0.072 to 0.122 S cm^{-1} [Sumner, *et al.*, 1998; Zawodzinski, *et al.*, 1991; Kolde, *et al.*, 1995; Gardner, *et al.*, 1998; Kim, *et al.*, 2004c; Yoon, *et al.*, 2002; Tricoli, *et al.*, 1998]. Zawodzinski *et al.* [1991] determined the in-plane membrane conductivity using the fixture in Fig 2.5 via impedance measurements. The window structure was employed to allow membrane equilibration in situ. The in-plane conductivity was 0.102 S cm^{-1} for fully hydrated Nafion 117 membranes. Tricoli *et al.* [1998] measured the in-plane conductivity in liquid electrolyte solution ($10^{-3} \text{ M H}_2\text{SO}_4$) via four-probe DC technique using the fixture shown in Fig 2.6. The conductivity was reported to be 0.0759 S cm^{-1} for Nafion 117 membrane.

Fig 2.5 Cell used for determination of the in-plane membrane conductivity: (1) Kel-F block; (2) thumbscrew; (3) open area to allow equilibration; (4) membrane sample; (5) blackened Pt foil; (6) Pt ribbon lead. Reproduced from Zawodzinski *et al.* [1991]

Fig 2.6 Schematic diagram of the experimental setup for the in-plane proton conductivity measurements. C1, C2: Pt mesh electrode; R1, R2: saturated calomel electrodes; B1, B2: Luggin capillary. Reproduced from Tricoli et al. [1998]

The through-plane conductivity was in the range of $0.024\text{--}0.140\text{Scm}^{-1}$ [Silva, et al., 2004; Sumner, et al., 1998; Garner, et al., 1998; Slade, et al., 2002; Verbrugge, et al., 1990; Mohr, et al., 2002; Perez, et al., 1991, Tricoli, et al., 2000; Pourcelly, et al., 1997; Nouel, et al., 1998; Verbrugge, et al., 1992; Haufe, et al., 2001; Halim, et al., 1994]. Silva et al. [2004] carried out the through-plane conductivity in the two-electrode AC impedance mode and the fixture is shown in Fig 2.7. The membrane was hotpressed between two carbon papers in an similar way as the MEA assembly. The conductivity was reported to be $0.048\pm 1\text{ Scm}^{-1}$ for Nafion 117 membranes at 25°C .

Fig 2.7 Schematic illustration of a conductivity cell for Nafion® membranes: (1) graphite current collectors; (2) carbon paper electrodes; (3) membrane; (4) electric connection; (5) beaker filled with deionized water and (6) thermocouple. Reproduced from Silva et al. [2004]

The through-plane conductivity of N117 membrane was also conducted in H_2SO_4 using DC technique (Fig 2.8) [Slade, *et al.*, 2002]. The conductivity was reported to be 0.120Scm^{-1} .

Fig 2.8 Schematic diagram of the four-electrode glass cell used for conductivity measurements on a circular sample (1 cm^2) of membrane, using a steady state linear sweep galvanodynamic technique. Reproduced from Slade *et al.*, [2002]

As mentioned by Slade *et al.* [2002] and Tricoli *et al.* [Tricoli, *et al.*, 2000], the obtained conductivities were affected by an error due to the background electrolyte resistance measurements, which contribute to 60-80% of the cell resistance. Moreover, an influence of absorbed acid on membrane conductivity has been hypothesized [Gardner, *et al.*, 1998]. Gardner *et al.* [1998] reported that the specific conductivity of Nafion 117 is anisotropic and the in-plane conductivity is almost 3.6 times higher than the through-plane conductivity. On the other hand, Nouel *et al.* [1998] reported same value of (0.140Scm^{-1}) the in-plane and through-plane conductivities using the fixture shown in Fig 2.9. This indicates that with similar water content, the in-plane and the through-plane conductivities are supposed to be in the same range, and therefore the Nafion membrane is isotropic.

Fig 2.9 Sketch of the conductivity cell: main body is stainless-steel, two center blocks are Kel-F® with platinum foil used for electrical contact: l is the length between the two platinum foils. Four different conductivity measurements were performed: (1-2) longitudinal top, (3-4) longitudinal bottom, (1-4) transversal 1 and (2-3) transversal 2. Reproduced from Nouel et al. [1998]

In situ conductivity of Nafion 117 membrane in PEMFC was also reported to be about 0.158 Scm^{-1} at 80°C [Slade, et al., 2002]. This value is much lower than ex situ conductivity (0.231 Scm^{-1}) measured in $1\text{M}\text{H}_2\text{SO}_4$ at 80°C [Verbrugge, et al., 1990]. This may be due to the contact resistance although some components resistances have been subtracted.

A few groups also studied the conductivity of Nafion membrane with different thickness [Silva, et al., 2004; Kolde, et al., 1995; Slade, et al., 2002; Nouel, et al., 1998]. Using AC impedance, Kolde et al. [1995] found that the proton conductivity of the membranes immersed in water was 0.100 Scm^{-1} for Nafion 117 ($200\mu\text{m}$) and Nafion 112 ($60\mu\text{m}$). This conductivity is independent of the membranes thickness. This trend was also found in air at 100%RH and 65°C by Nouel et al. [1998]. The conductivities were reported to be 0.140 and 0.144 Scm^{-1} for Nafion 117 ($210\mu\text{m}$) and 112 ($52\mu\text{m}$), respectively. Considering the experimental accuracy, this again reflects

the independence of the conductivity on the membrane thickness. All the above values are reported for the in-plane conductivity. However, so far, the through-plane conductivity was reported to be dependent on the membrane thickness. Silva et al. [2004] measured the through-plane conductivities of Nafion 112, 115 and 117 membranes using an ex situ method. The conductivities were reported to be 0.023, 0.033 and 0.048 S cm⁻¹ for Nafion 112, 115 and 117 membranes, respectively. Slade et al. [2002] found the same trend in ex situ measurements in 1M H₂SO₄ at 25°C and in situ measurements using single cell at 80°C.

2.8 Summary

As reviewed above, significant efforts have been made to improve the performance of PEMFCs and DMFCs. However, the electrocatalytic activities of unsupported and carbon supported Pt-based catalysts are still not satisfactory for oxygen reduction reaction in the absence and in the presence of methanol, and for methanol oxidation reaction. On the other hand, the catalyst utilization is still low. There is an urgent need to develop selective catalysts for different reactions and to improve the catalyst utilization.

Although Pt/Nafion interface has been extensively studied, it is difficult to fabricate the ideal interface by conventional methods, such as painting, sputtering and electrodeposition. Self-assembly can be used to form a monolayer of positively charged Pt nanoparticles on the surface of Nafion membrane due to the electrostatic attraction.

Methanol crossover from anode to cathode through Nafion membrane is still a major barrier for the application of the DMFCs. Although many efforts have been made to reduce the methanol crossover, the modification of membrane causes

significant decrease in the proton conductivity of the polyelectrolyte membrane. The cell performance is therefore reduced. Self-assembly can be used to materialize nanoscale thin film on different substrates, and the thickness of the self-assembled layer can be controlled simply by layer-by-layer technique. The reduction in the methanol crossover and in the proton conductivity of the Nafion membrane could be balanced, thus the optimal cell performance can be obtained.

CHAPTER 3 Experimental Procedures

In this chapter, chemicals, sample preparation, electrochemical set-up and measurements techniques, as well as the synthesis and characterization of Pt nanoparticles were given and described.

3.1 Chemicals

Polymers used in this project include: poly(diallyldimethylammonium chloride) (PDDA, MW = 5000~20000, Aldrich), poly(sodium styrenesulfonate) (PSS, MW=70,000, Aldrich), poly(vinylpyrrolidone) (PVP, MW=40,000, Aldrich), poly(1-(4-(3-carboxy-4-hydroxyphenylazo) benzene sulfonamido)-1,2-ethanediyl, sodium salt) (PAZO, MW=65,000-100,000, Aldrich) Nafion solution (5wt%, DuPont). Fig 3.1 shows the molecular structure of polymers used in this work.

Fig 3.1 Molecular structure of polymers

Catalysts and other chemicals include: 20% Pt/C catalyst (Electrochem.), 40% Pt/C catalyst (Johnson Matthey, UK), Pt/Ru (1:1) black (Johnson Matthey, UK),

carbon powder (Vulcan XC-72, Cabot Corporation, US), carbon paper (Toray TGPH-090, Japan), polytetrafluoroethylene (PTFE) dispersion (Teflon 30, 60% PTFE, Dupont Corporation, US), Nafion membranes (N112-117, 50-175 μ m). H_2PtCl_6 (99.8%) and ethanol (99.8%), sulfuric acid (95~97%), sodium hydroxide (99%), methanol, hydro peroxide (38%) were purchased from Sigma. Deionized water (Millipore Milli-Q, 18.2M Ω at 25°C) was used in the experiments.

3.2 Synthesis of platinum nanoparticle colloidal solutions

Pt nanoparticle colloidal solutions were synthesized by alcohol reduction of platinum ions in 100ml ethanol/water mixture (volume ratio: 4/6) in the presence of polymers, PDDA, PVP, PSS and Nafion. Fig 3.2 shows the schematic diagram of the synthesis process.

Fig 3.2 Schematic diagram of the synthesis process.

2.5ml of H_2PtCl_6 (20mM) solutions and 40ml ethanol were added sequentially into the polymer solutions under intensive stirring. The pH of the solution was adjusted by adding required volume of NaOH. The mixture was then transferred into a three-neck flask and brought to reflux in an oil bath. The color of the solution changed from yellow to dark brown abruptly, indicating the formation of platinum nanoparticles.

3.3 Electrode preparation

3.3.1 Rotating disk electrode (RDE)

RDE technique was used to evaluate the electrocatalytic activity of platinum nanoparticles using Autolab potentiostat (PGSTAT30, Netherlands). 4-40 μ l platinum nanoparticle colloidal solution was dispensed on a glassy carbon electrode (GCE) using a microsyringe. The diameter of the GCE is 3mm. The GCE was polished with a polishing cloth and rinsed with DI water, and then precoated with the mixture of Nafion and carbon powder (XC-72, Cobalt). Nafion content was determined by (Nafion/(Nafion+Carbon)) and was about wt 30wt %. The Pt loading was 5.6~56 μ g/cm² on the GCE.

3.3.2 Gas diffusion electrode and catalyst layer

The wet-proofed carbon paper was prepared by immersing the untreated carbon paper in PTFE dispersion (5 %) for 5min and then dried in air for 30 min. Next, it was sintered in an oven (Carbolite, Eng.) at 350°C for 30min. The PTFE loading was determined by the difference in the weight of the carbon paper before and after the PTFE treatment. The weight percentage of PTFE on the carbon paper was calculated by PTFE/(Carbon paper + PTFE) and the PTFE loading was about 5wt %.

For the preparation of the diffusion layer, carbon powder with PTFE dispersion was mixed and stirred in an ultrasonic bath at room temperature for 30min. Then the suspension was applied to the wet-proof carbon paper. The diffusion layer was dried in air for 30min and sintered in oven at 350°C for 30min. The carbon loading in the diffusion layer was about 2mg/cm². The weight percentage of PTFE in the diffusion layer was determined by PTFE/(Carbon powder+PTFE) and was about 30wt % for the diffusion layer.

The catalyst layer for the anode in DMFCs was prepared by making a homogeneous suspension from the Pt/Ru black (1:1, Johnson Matthey, UK), isopropanol, distilled water and Nafion, which were mixed together and stirred in ultrasonic at ambient temperature for 30min. Pt loading was 0.8mgcm^{-2} and Nafion content was 10wt% for anode. Similarly, the cathode was made with 40% Pt/C and Nafion. Pt loading was 0.8mgcm^{-2} and Nafion content was 30% for cathode. The suspension was then applied onto the diffusion layer. The catalyst layer was dried in air for 20min and sintered in oven at 80°C for another 20min.

3.3.3 Self-assembled Pt/Nafion membrane

Nafion membrane 1135 was treated according to the standard procedure of 30 min in 5wt% H_2O_2 at 80°C , 30 min in Milli-Q water at 80°C , 30 min in 8wt% H_2SO_4 solution at 80°C , and finally 30 min in Milli-Q water at 80°C . The membrane was kept in deionized water before use.

For the preparation of self-assembly monolayer (SAM) of PDDA-Pt nanoparticle colloids on Nafion membrane, the membrane was allowed to float on the surface of or immersed in the Pt nanoparticle colloid solution for 1-48 hrs. The self-assembly of Pt nanoparticles could occur on one or both sides of the membrane. The self-assembled membrane was cleaned with deionized water at 25°C , followed by the re-protonation treatment in 1M H_2SO_4 at 80°C for 30 min and rinsed again with deionized water. Fig 3.3 shows the picture of N1135 membrane before and after the self-assembly process in PDDA-Pt colloid solution. After the self-assembly, the color of Nafion membrane became dark, indicating the successful self-assembly of PDDA-Pt nanoparticles.

Fig 3.3 Nafion 1135 membrane (a) before and (b) after self-assembly process in Pt-PDDA colloid solution and cleaning process

3.3.4 Layer-by-layer self-assembled polyelectrolyte/Nafion membrane

The Layer-by-layer (LBL) self-assembly of PDDA/PSS multi-layer was carried out by alternate dipping of the pretreated Nafion membrane in PDDA (20mM) and PSS (20mM) solutions at room temperature for 5 min. After each dipping, the membrane was rinsed with deionized water to remove the weakly bonded polyelectrolyte molecules. PDDA is self-assembled to the surface of the Nafion membrane through electrostatic interaction between the positively charged PDDA and the negatively charged sulfonic group, SO_3^- , on the Nafion membrane surface. Assembly of a consecutive (negatively charged PSS) layer is possible due to the charge reversal on a surface of the PDDA. The alternative self-assembly of polycation and polyanion was repeated to increase the number of bilayers. The LBL self-assembled membrane was finally cleaned with deionized water, followed by the protonation treatment in 1M H_2SO_4 at 80°C for 30 min and rinsed again with deionized water. The LBL self-assembly of PDDA/PAZO multi-layer on Nafion membrane surface followed the same procedure as that for the LBL self-assembly of PDDA/PSS multi-layers.

3.3.5 Membrane electrode assembly

To study the self-assembled Pt/Nafion membrane interface, the cell was prepared as follow. The membrane with self-assembled Pt nanoparticles on a single side was hotpressed with one piece of carbon paper as gas diffusion layer at 140°C under 4 MPa for 90s. The electrode area was 1 cm². Figure 3.4 shows the schematic diagram of the membrane electrode with the self-assembled PDDA-Pt nanoparticles/Nafion membrane interface.

Fig 3.4 Schematic diagram of (a) the membrane electrode with the self-assembled PDDA-Pt nanoparticles on one side and (b) two sides of Nafion membrane

To evaluate the methanol crossover and the cell performance for DMFC, the membrane-electrode-assembly (MEA) was made by sandwiching the SAM/Nafion/SAM membrane between a Pt/Ru anode and a Pt/C cathode (Fig 3.4b). Pt/Ru black (Johnson Matthey) was mixed homogeneously with 10wt% Nafion and used for the anode. Homogeneous mixture of 40% Pt/C (Johnson Matthey) and 30wt% Nafion was used for the cathode. The loading of Pt was about 0.8 mg cm⁻² for both anode and cathode catalyst layers. The MEA was then hotpressed at 140°C and 4 MPa for 90s. The electrode area was 5 cm².

3.4 Electrochemical Characterization

3.4.1 Rotating disk electrode (RDE) system

Rotating disk electrode system was used to characterize the electrocatalytic activity for the polymer stabilized Pt nanoparticles and Pt/C catalyst. Fig 3.5 shows the schematic of the RDE setup.

Fig 3.5 Schematic diagram for the rotating disk electrode (RDE) system. RE: reference electrode; WE: working electrode; CE: counter electrode.

1M H_2SO_4 was used as the electrolyte and was purged with N_2 or O_2 through gas distributor. Ag/AgCl (0.207V vs standard hydrogen electrode (SHE)) electrode was used as the reference electrode (RE) and placed close to the working electrode (WE) via a luggin capillary. Pt foil was used as the counter electrode (CE). The RDE was rotated at 0~5000rpm. Autolab instrument (PGSTAT 30) was used to carry out the measurements at 25°C.

3.4.2 Half-Cell Testing System

To study oxygen reduction reaction (ORR) on PEMFC cathode, a traditional three-electrode system is used, which is shown in Fig 3.6.

Fig 3.6 Experimental setup for half cell testing. GDE: gas diffusion electrode, WE: working electrode, RE: reference electrode, CE: counter electrode.

This system is composed of two compartments: one for the liquid electrolyte, and the other one for the reactant gas. The working electrode (WE, 1cm^2) was inserted between these two compartment, using gaskets to prevent both liquid electrolyte and reactant gas leaking. Catalyst layer of the membrane electrode was faced to the electrolyte (H_2SO_4 , 1M, 25°C) and the backside (Toray carbon paper) was faced to the gas (oxygen, air or nitrogen). 1M H_2SO_4 was used as the electrolyte. Platinum foil was used as counter electrode (CE). Saturated calomel electrode (SCE) was used as reference electrode (RE) and placed close to the electrode via a Luggin capillary. Platinum mesh and platinum wire were used for current collector and voltage probe, respectively. The flow rate of the gas was controlled using a mass flow controller. Potential of SCE was 0.241V versus SHE at 25°C in 1M H_2SO_4 . In this report, potentials are reported with respect to SHE by adding 0.241V to the measured value. Fresh H_2SO_4 solution was used for every test.

3.4.3 Full Cell Testing System

For a full cell composed of both anode and cathode, two-electrode system was used and shown in Fig 3.8. An MEA (5cm^2) was inserted between the two graphite

plates with a single serpentine flow channel. 2M methanol was fed to the anode at a flow rate of 7.5 ml min^{-1} . Oxygen or nitrogen was supplied at a flow rate of 50 ml min^{-1} to the cathode under humidification at 30°C . The tests were carried out at 30°C with 10psi back pressure on the cathode side. Autolab (PGSTAT 30) was used to conduct the electrochemical measurements.

Fig 3.7 Schematic setup for DMFC measurement

3.4.4 Polarisation

To characterize the electrocatalytic activity of Pt nanoparticles towards ORR, the polarisation curves were measured in O_2 -saturated $1\text{M H}_2\text{SO}_4$ with and without the addition of $0.5\text{M CH}_3\text{OH}$. The potential was scanned from 1.0 to 0.1 V (vs. SHE) at a scan rate of 5 mV s^{-1} . The activity of Pt nanoparticles for the methanol oxidation reaction was measured in N_2 -saturated $1\text{M H}_2\text{SO}_4 + 2\text{M CH}_3\text{OH}$ via dynamic potential scan in the potential range of 0.2 - 1.0V at a scan rate of 5mV s^{-1} . ORR on the self-assembled Pt/Nafion interface was studied by scanning the potential from 1.0 to 0.1V vs SHE at a scan rate of 5mVs^{-1} .

Methanol crossover of the self-assembled N-1135 membrane was measured using an MEA with electrode area of 5 cm^2 at 30°C , similar to that conducted by Ren et al. [2000]. 2 M methanol was fed to the anode at 7.5 ml min^{-1} and humidified nitrogen

was fed to the cathode at 20 ml min^{-1} with 10 psi back pressure. The potential was scanned from 0.1 to 0.9 V at a scan rate of 0.5 mV s^{-1} and the methanol crossovered through the membrane was oxidized at the cathode. The performance of DMFC was evaluated on MEA based on the self-assembled PDDA-Pt nanoparticles/N-1135 membrane. 2M methanol was fed to the anode at a flow rate of 7.5 ml min^{-1} . Oxygen was supplied to the cathode under humidification at 30°C with a flow rate of 50 ml min^{-1} . The tests were carried out at 30°C with 10 psi back pressure on the cathode.

3.4.5 Cyclic Voltammetry

Cyclic voltammetry (CV) has been frequently used to estimate the electrochemically active surface area (ESA) of Pt/C catalyst by adsorption of atomic hydrogen in acidic media [Perez, *et al.*, 1998]. In this test, 1M H_2SO_4 was used as the electrolyte. Before CV measurements were conducted, the electrolyte was purged with nitrogen for 15mins and nitrogen was also applied to the backside of the electrode in the case of membrane electrode. CVs were conducted in the range of 0-1.4V vs SHE in N_2 -saturated 1M H_2SO_4 . The scan rate was 100 mV s^{-1} . Cyclic voltammograms were recorded until a stationary response was obtained.

Fig 3.8 shows a typical cyclic voltammogram obtained for Pt/C electrode in 1 M H_2SO_4 saturated with nitrogen gas at a scan rate of 100mV/s . The coulombic charge for hydrogen desorption (Q_H) was used to calculate the ESA of the electrodes. The value of Q_H (C/cm^2) was calculated as the mean value between the amounts of charge exchanged during the electro-adsorption (Q') and desorption (Q'') of hydrogen on Pt sites. Q'' and Q' corresponded to the anodic peak in the forward scan and cathodic peak in the backward scan respectively, in the potential range of 0.05-0.4V vs SHE. Q' and Q'' can be computed by integrating the area under the current vs potential

curve in a hydrogen desorption region and adsorption region respectively, then subtracting the contribution of double layer charge (shaded area in Fig 3.8).

Fig 3.8 CV (100mV/s) at 25°C on PTFE-bonded Pt/C electrode in the potential range 0-1.4V vs SHE in 1M_HSO₄ saturated with nitrogen, Q' and Q'' represent the amounts of charge exchanged during the electro-adsorption and desorption of hydrogen on Pt sites and the shaded area is the contribution of double layer charge

The electrochemically active surface area (ESA) was calculated by:

$$ESA = \frac{Q_H}{Q_0} (\text{cm}^2/\text{cm}^2) \quad (3.1)$$

where Q_H is the charge for hydrogen desorption (C/cm^2), Q_0 the charge required to oxidize a monolayer of hydrogen on bright Pt (C/cm^2). Q_0 is $210 \times 10^{-6} \text{ C}/\text{cm}^2$ [Perez, *et al.*, 1998].

To characterize the methanol oxidation reaction on Pt nanoparticles, the CV was measured in N₂-saturated 1M H₂SO₄ + 2M CH₃OH in the potential range of 0.2 – 1.2 V at a scan rate of 100 mV s⁻¹.

3.4.6 Electrochemical Impedance Spectroscopy (EIS)

Impedance spectroscopy is a powerful experimental technique to study the complexity of the different processes that take place in fuel cells. The impedance

response of gas diffusion electrodes has been studied in half-cells [Ahn, *et al.*, 1995]. Also, dispersed catalyst materials have been studied with impedance spectroscopy in rotating disc electrodes [Perez, *et al.*, 1998]. Impedance spectroscopy techniques have also been used to study the performance of full cells [Springer, *et al.*, 1996, Paganin, *et al.*, 1998].

EIS technique in general involves the measurement of current through a cell when a sinusoidal voltage of low amplitude is applied. The sine wave is used in impedance measurements because a sinusoidal signal (regardless of its amplitude or frequency) has the same wave and angular frequency for its incident and resultant waves signal. Also for a linear system, the magnitude of the response is directly related to the electrical stimulus for any given frequency. Hence, in the linear system, the applied potential is given by:

$$E(t) = \Delta E \exp(j\omega t) \quad (3.2)$$

The current output of the system is also sinusoidal and has the same angular frequency, ω , but different amplitude and phase with respect to the voltage signal may occur depending on the element in the circuit and can be represent by:

$$I(t) = \Delta I \exp(j\omega t + \phi) \quad (3.3)$$

where ϕ is the phase angle, ΔE is the amplitude of the voltage and ΔI the amplitude of the current signal. For a pure resistor, the phase shift is zero.

Since Ohm's law holds true in the time & frequency domain, the impedance of a circuit consisting of resistor, capacitors and/or inductors is the ratio of the voltage signal divided by the current flowing through the circuit. The impedance of the circuit ($Z(\omega)$) at any frequency can be represented in both polar and Cartesian form and has both magnitude Z and phase angel ϕ .

$$Z(\omega) = \frac{E(t)}{I(t)} = Z \exp(-j\omega) = Z \cos(\phi) - jZ \sin(\phi) = Z_R - Z_I \quad (3.4)$$

Where j is a complex number with a value of $\sqrt{-1}$, Z_R and Z_I are the real and imaginary parts of the impedance. The relationships between various terms are as follows:

$$\phi = \tan^{-1}\left(\frac{Z_I}{Z_R}\right) \quad (3.5)$$

$$Z = \sqrt{Z_R^2 + Z_I^2} \quad (3.6)$$

For a pure resistor (R), capacitor (C) and an inductor (L), the impedance is given by the following relations respectively:

$$Z = R + 0j \quad (3.7)$$

$$Z = 0 - \frac{j}{\omega C} \quad (3.8)$$

$$Z = 0 + j\omega L \quad (3.9)$$

The impedance of a capacitor & an inductor has the same dimensions as the resistor. However, the impedance of a capacitor or an inductor differs from that of a resistor in that it is dependent on the frequency of the alternating current (AC) signal.

In this study, EIS was carried out using a potentiostat-galvanostat AUTOLAB FRA interfaced via USB to a personal computer. The EIS measurements were conducted at various potentials. An alternating sinusoidal signal of 10mV amplitude was superimposed on the DC-potential. The impedance spectra were collected in the frequencies between 100kHz and 5mHz. Fig 3.9 shows an example of the impedance curve for ORR on a PTFE-bonded electrode. The impedance was characterized by two arcs at low and high frequencies. It was fitted by an equivalent circuit as shown in Fig 3.10. Thus the resistance and capacitance for the reaction can be estimated.

Fig 3.9 An example impedance curve for oxygen reduction reaction on PTFE-bonded electrode measured at 0.9V in oxygen. Pt loading and PTFE content of the electrode was 0.4mg/cm² and 10wt%, respectively.

Fig 3.10 Equivalent circuit for fitting impedance in Fig 3.9

3.4.7 Through-plane conductivity measurement

Fig 3.11 shows the schematic of a glass cell used for measuring the membrane conductivity. P1 was fixed in the cell and the current was allowed to flow only through the electrolyte contained in the circular hole in P1. P2 was removable. The membrane was attached onto the surface of P2 to cover the centered hole and they were put slowly in the cell. P1, the membrane and P2 were compressed to make sure the contact between each other was good. Then the external force was released, and the membrane was kept in nature state without compression. The platinum electrodes W1 and W2 were connected to the counter electrode and working electrode of Autolab potentiostat/gavlnostat, respectively. W1 and W2 were used to collect the

current flowing through membrane. The two saturated calomel electrodes (SCEs) C1 and C2 were connected to reference electrode and working sensor electrode of Autolab potentiostat/galvanostat, respectively. C1 and C2 were used to measure the potential drop between the two tips of Luggin capillaries. 1M H_2SO_4 was used as the electrolyte. Positive and negative current were allowed to flow through the membrane for 60s. The potential drop between C1 and C2 were measured in the absence and in the presence of the membrane. Positive and negative current was used to eliminate the potential difference of the two SCEs.

Fig 3.11 Schematic of a four-probe cell for conductivity measurements. W1, W2 Platinum Foil Electrodes; C1, C2: Saturated Calomel Electrodes; M: Nafion Membrane; L: Luggin Capillaries; P1, P2: Perspex plates with a centered circular hole of 1cm^2

Fig 3.12 shows the typical curves obtained for the cell resistance with and without membrane.

Fig 3.12 Typical curves measured for the cell with and without membrane, current: 100mA.

The measured resistance was determined by the following equation (3.10):

$$R = \frac{\Delta E_+ - \Delta E_-}{2I} \quad (3.10)$$

where R is the cell resistance between the tips of the two Luggin capillary, ΔE_+ and ΔE_- are the potential drops when using positive and negative currents, respectively.

Membrane resistance is given by equation (3.11)

$$R_{mem} = R_p - R_a \quad (3.11)$$

R_p and R_a are the cell resistance in the presence and in the absence of membrane, R_m is the membrane resistance. Then the conductivity σ was determined by equation (3.12):

$$\sigma = \frac{l}{\pi r^2 R_{mem}} \quad (3.12)$$

where l is the thickness of the membrane, r is the diameter of the hole in the centre of plates of P1 and P2.

3.5 Physical Characterization

3.5.1 UV-visible Spectroscopy

The principle of UV-visible spectroscopy was based on the property that some materials absorb selectively within the range of ultra-violet and visible regions of the electromagnetic spectrum [Denney, *et al.*, 1987]. Fig 3.13 shows the range of electromagnetic radiation. The wavelength (λ) and the frequency (ν) were related by the equation:

$$\lambda = \frac{c}{\nu} \quad (3.13)$$

where c was the speed of light ($3.0 \times 10^8 \text{ m s}^{-1}$).

The absorbance A at a certain wavelength was defined as:

$$A = \log\left(\frac{I_0}{I}\right) \quad (3.14)$$

where I_0 and I are the transmitted radiation intensities of the reference and sample solutions, respectively. A quartz cell with dimensions of $10 \times 10 \times 40 \text{ mm}$ was used for the measurements.

Fig 3.13 The range of electromagnetic radiation. [Denney, *et al.*, 1987]

UV-visible spectroscopy (HP 8350) was used to monitor the formation of platinum nanoparticles as a function of reflux time. The sample was pipetted as a function of reflux time and then diluted to 10^{-4} M Pt using the mixture of ethanol & water. The mixture of ethanol & water (volume ratio of 4:6) in a quartz cell was used as blank solution. The UV-visible spectroscopy was obtained for sample after calibration with blank solution.

To characterize the build-up of self-assembled monolayer and multi-layers on Nafion membrane, the modified and unmodified Nafion membranes were allowed to dry by flowing nitrogen at room temperature. The quartz cell without membrane was used for the calibration. The dimensions of the membrane were 10×60mm.

3.5.2 Transmission Electronic Microscopy (TEM)/Energy Dispersive Spectroscopy (EDS)

Pt nanoparticles were examined using transmission electronic microscope (TEM, JEOL 2010) under accelerating voltage of 200kV. TEM sample was obtained by immersing a copper grid coated with carbon film in the Pt nanoparticle colloid solution and was allowed to dry at room temperature. Particle size and distribution was obtained by measuring more than 100 particles from the enlarged TEM images.

To observe the distribution of PDDA-Pt self-assembled on the surface of Nafion membrane, TEM sample was prepared as follows: copper grid with carbon film was cast with a thin Nafion film by floating copper grid on the surface of the Nafion solution for 5 min, and then dried at room temperature. As-prepared copper grid was floated on the surface of PDDA-Pt colloid solution, with the Nafion film facing towards the solution, for 1hr. After the self-assembly process, the copper grid was

rinsed intensively with deionized water and dried at room temperature. The compositions were determined using TEM equipped with EDS.

3.5.3 Atomic Force Microscopy (AFM)

A nanoscope IIIA atomic force microscope (Digital Instruments, US) was used to carry out the topographical observation on the specimen surface. The AFM is a three dimensional imaging tool that measures surface structure from the atomic level to millimeter scale. In order to examine the deposition of PDDA/PSS multilayer on the Nafion membrane, the sample was prepared on the glass in a similar way to that on the Nafion membrane. The specimen was cleaned with deionized water and dried before AFM examination. The combination with the tapping mode imaging technique allows high resolution topographic imaging of sample surface. Tapping mode is the second most common mode used in AFM. When operated in air or other gases, the cantilever is oscillated at its resonant frequency (often hundreds of kilohertz) and positioned above the surface so that it only taps the surface for a very small fraction of its oscillation period. When imaging poorly immobilized or soft samples, tapping mode may be a far better choice than contact mode for imaging.

3.5.4 X-ray Diffraction (XRD)

X-ray diffraction (XRD) patterns for Pt nanoparticles were obtained on a diffractometer (Philips PW1710) using Cu K α source operated at 40kV and 30mA. The scan rate was 0.02°. The sample was obtained by depositing Pt nanoparticles on a glass substrate and dried in a vacuum oven at 40°C. From the full width at half height of the (111) peak, the volume-average particle size was calculated using the Scherrer equation [Wang, *et al.*, 2002]:

$$d(\text{\AA}) = \frac{k\lambda}{\beta \cos \theta} \quad (3.15)$$

where k is a coefficient (0.9), λ the wavelength of X-ray used (1.54056 Å), β the full-width half-maximum of respective diffraction peak (rad) and θ the angle at the position of peak maximum (rad). At the same time, lattice constant (a) can be obtained based on the following equation:

$$a = d_a \sqrt{h^2 + k^2 + l^2} \quad (3.16)$$

where d_a is the wavelength of X-ray; h , k , and l are the miller index of the crystal.

3.5.5 X-ray Photoelectron Spectrum (XPS)

XPS measurements were carried out with an ESCA spectrometer (KRATDS Co.). An AlK X-ray source was used and the anode was operated at 15kV and 10mA. The pass energy was fixed at 40eV. Binding energy of Pt_{4f} for Pt nanoparticles was determined after calibration with the binding energy of C_{1s}. XPS was also used to determine the compositions of self-assembled PDDA-Pt nanoparticles on the surface of Nafion.

CHAPTER 4 Electrochemical Characterization of Pt/C Catalysts

In this Chapter, a background study was conducted based on the commercial Pt/C catalyst on a glassy carbon electrode using RDE technique. The effects of Pt loading and the testing conditions were systematically studied for ORR in the absence and presence of methanol and for MOR on the Pt/C catalyst. Basic parameters for the investigation of the ORR and MOR on the polymer stabilized Pt nanoparticles were determined.

4.1 Experimental

RDE technique was used to characterize the electrocatalytic activity of 20% Pt/C catalysts (Electrochem.). To prepare the Pt/C electrode, the glassy carbon electrode was precoated with the ink made of Nafion and carbon powder. The Pt loading varied from 5.6 to 56 μgcm^{-2} . The RDE was rotated at 0~5000rpm. Polarisation and cyclic voltammetry were used to evaluate the electrocatalytic activity for ORR in the absence and presence of methanol, and MOR on Pt/C electrode. For the purpose of comparison, ORR and MOR on the bright Pt RDE were also studied. Autolab was used to carry out all the measurements. The potentials reported were with respect to SHE.

4.2 Results and Discussions

4.2.1 Oxygen Reduction Reaction on Pt/C

Fig 4.1 shows the polarisation curves for ORR on Pt/C in O₂-saturated 1M H₂SO₄ under a scan rate of 5 mVs⁻¹ at 25°C, using RDE with various rotating speeds. Pt loadings were fixed at 56µgcm⁻².

Fig 4.1 Polarisation curves of Pt/C in O₂-saturated 1 M H₂SO₄ under a scan rate of 5 mVs⁻¹ at 25°C using RDE at different rotating speeds. Pt loadings were 56µgcm⁻².

The results showed that, at the potential above 0.85V, the current densities were independent of the rotating speeds. This indicates that the ORR is controlled by activation polarisation. The activation polarisation is determined by electrode materials and active surface area of electrode. At the potential below 0.85V, the current density increased with the increasing rotating speeds. This can be attributed to the contribution of oxygen diffusion. Oxygen diffuses faster at higher rotating speeds, resulting in higher current density. With further decrease of the potential, the limiting current density started to appear. This shows that the ORR on Pt/C in O₂-saturated 1M H₂SO₄ is a diffusion controlled process. The higher the rotating speed, the higher the limiting current density.

Fig 4.2 shows the polarisation curves for ORR on Pt/C electrodes with different Pt loading in O₂-saturated, 1M H₂SO₄ at 25°C. The RDE was rotated at 3000rpm. In comparison, the polarisation curve for ORR on Pt RDE is also shown in the figure. Fig 4.3 shows the current density at 0.7V and the limiting current density as a function of Pt loading. The current density at 0.7V increased significantly from 1.8 to 3.9mAcm⁻² as Pt loading increased from 5.6 to 45μgcm⁻². When Pt loading increased further to 56μgcm⁻², the current density at 0.7V didn't change much. However, the limiting current density was in the range of 4.5~4.9mAcm⁻², and didn't show much dependence on the Pt loading. As expected, the polarisation performance of the Pt/C catalyst is much higher than that of Pt RDE.

Fig 4.2 Polarisation curves of Pt/C and Pt disk electrode in O₂-saturated 1M H₂SO₄ under a scan rate of 5mVs⁻¹ at 25°C using RDE. RDE was rotated at 3000rpm.

It is also worth to note that the onset potential (OSP) for ORR (0.97V) is almost same for Pt RDE and Pt/C with different Pt loading in oxygen saturated 1M H₂SO₄ at various rotating speeds (Fig 4.1 and 4.2). This indicates that Pt/C has similar characteristics for ORR to bare Pt.

Fig 4.3 Current density @ 0.7V and the limiting current density for oxygen reduction reaction as a function of Pt loading

Fig 4.4 shows the CVs for the Pt/C catalyst with different loading and Pt RDE measured in N_2 -saturated, 1M H_2SO_4 at 25°C . The inset shows the enlarged graph in the range of 0~0.35V.

Fig 4.4 Cyclic voltammograms of Pt/C and Pt disk electrode in N_2 -saturated 1M H_2SO_4 under a scan rate of 100 mVs^{-1} at 25°C using RDE under static condition

As shown in Fig 4.4, there were three similar hydrogen desorption peaks for all three electrodes. The difference was only the enclosed area, which can be used to

estimate ESA [Perez, *et al.*, 2002]. The ESAs and the catalyst utilization for the electrodes with different Pt loading were shown in Table 4.1. With the decrease in Pt loading, the ESA decreased significantly, but the catalyst utilization increased from 60 to 86%. On the other hand, the ESA for Pt/C with $5.6\mu\text{g}/\text{cm}^2$ was 4.8 times higher than that for Pt RDE. This is due to the high surface area of the platinum nanoparticles supported on carbon, as compared with the bright Pt.

Table 4.1 ESA for Pt/C electrode with different platinum loading and Pt RDE obtained from CV measurements

Types of electrodes		Pt/C ($\mu\text{g}/\text{cm}^2$)					Pt RDE
		5.6	11	28	45	56	
ESA (cm^2/cm^2)	1M H_2SO_4	6.2	11	25	38	43	1.3
	1M H_2SO_4 + 0.5M CH_3OH	5.0	9.3	18	23	26	0.43
Utilization (%)	1M H_2SO_4	80	77	69	66	60	~
	1M H_2SO_4 + 0.5M CH_3OH	70	65	51	40	36	~

Fig 4.5 shows the polarisation curves for ORR on Pt/C electrode in O_2 -saturated, 1M H_2SO_4 + 0.5M CH_3OH as a function of rotating speed. The platinum loading was $56\mu\text{g}/\text{cm}^2$. An anodic current peak was observed at around 0.71V for all the polarisation curves under various rotating speed. The current was attributed to the methanol oxidation, and was independent of rotating speeds, indicating that the methanol oxidation was kinetically controlled [Jiang, *et al.*, 2000; Wang, *et al.*, 2004].

On the other hand, with the increase of the rotating speed, the cathodic current increased due to faster oxygen diffusion. This was similar to that in the absence of methanol (Fig 4.1). However, the OSP for ORR increased from 0.49 to 0.55V with the increase of the rotating speed. This can be explained as follows: oxygen is more readily diffused to the surface of the Pt electrode with the increased rotating speeds.

Therefore, oxygen concentration can be kept at a somewhat higher level when oxygen is consumed continuously by chemically reacting with methanol as shown in equation (2.5) [Ren, et al., 2000]. Higher concentration of oxygen results in a higher mixed potential, and vice versa [Kulikovsky, 2005]. However, such a low OSP ($\sim 0.5\text{V}$) for ORR is too far away from the reported OCP ($\sim 0.8\text{V}$) for a Pt/C cathode in a DMFC [Liu, et al., 1998; Kreuer, et al., 2001].

Fig 4.5 Polarisation curves for oxygen reduction on Pt/C in O_2 -saturated $1\text{ M H}_2\text{SO}_4 + 0.5\text{M CH}_3\text{OH}$ under a scan rate of 5 mVs^{-1} at 25°C using RDE as a function of rotating speed. Pt loading was $56\mu\text{gcm}^{-2}$

Fig 4.6 shows the comparison of limiting current density for ORR on Pt RDE and Pt/C electrode in O_2 -saturated $1\text{M H}_2\text{SO}_4$ in the presence and absence of methanol. Increasing the rotating speed increased the limiting current density in both cases. At lower rotating speed ($<500\text{rpm}$), the limiting current density was slightly lower for ORR in the presence of methanol than that in the absence. With the increase of the rotating speed, the difference increased and the limiting current density was much lower when the methanol was added. It is concluded that the addition of methanol not only causes mixed potential, thus decreasing OSP by $0.22\sim 0.24\text{V}$, but also degrades the electrocatalytic activity towards ORR on Pt electrode.

Fig 4.6 Plots of limiting current density for oxygen reduction reaction on Pt RDE and Pt/C electrode in oxygen saturated 1M H₂SO₄ (Fig 4.1) and 1M H₂SO₄ + 0.5M CH₃OH (Fig 4.3). The Pt loading was 56 μgcm^{-2} .

It was also found that the limiting current density varied almost linearly with $\omega^{1/2}$, which was observed experimentally [Mo, *et al.*, 2002; Salimi, *et al.*, 2001]. The oxygen diffusion coefficient can be calculated based on the following equations [Salimi, *et al.*, 1999]:

$$\frac{1}{I_{\text{lim}}} = \frac{1}{I_m} + \frac{1}{I_k} \quad (4.1)$$

$$I_m = 0.62nFAD^{2/3}\nu^{-1/6}C_{O_2}\omega^{1/2} \quad (4.2)$$

$$I_k = nFAK\Gamma C_{O_2} \quad (4.3)$$

where n is the number of the electrons transferred, F is the Faraday constant, A the surface area of the electrode, D oxygen diffusion coefficient, ν (0.01cm² s⁻¹) the kinematic viscosity, C_{O_2} (1.25mM) the bulk concentration of oxygen, ω is the angular frequency of rotation.

The results were shown in Table 4.2. The oxygen diffusion coefficient on Pt RDE is comparable with the reported data (1.64 $\times 10^{-5}$ cm²s⁻¹, in 0.5M H₂SO₄) [Salimi, *et al.*, 2001]. The presence of methanol has no significant effect on the oxygen diffusion. However, the oxygen diffusion coefficient is higher for Pt/C electrode than for Pt RDE. It indicates that the porous carbon support could promote the oxygen diffusion.

Table 4.2 Oxygen diffusion coefficient calculated based on Fig 4.6

Electrolyte	1M H ₂ SO ₄		1M H ₂ SO ₄ +0.5M CH ₃ OH	
	Pt/C (56μgcm ⁻²)	Pt RDE	Pt/C (56μgcm ⁻²)	Pt RDE
D_{O_2} (cm ² s ⁻¹)	2.298×10^{-5}	1.725×10^{-5}	2.144×10^{-5}	1.876×10^{-5}

Fig 4.7 shows the polarisation curves for ORR on Pt/C electrode with different loading and Pt RDE measured in 1M H₂SO₄ + 0.5M CH₃OH at 25°C. The RDE was rotated at 3000rpm. Fig 4.8 shows the peak current density for MOR, the current density at 0.6V, the OSP and the limiting current density for ORR as a function of Pt loading. When the Pt loading decreased from 56 to 5.6μgcm⁻², the peak current density for MOR decreased from 25 to 0.2mA/cm², about 22 times lower. This is due to the increase in the active surface area with the increase of Pt loading. At the same time, the peak current density for MOR on Pt RDE was about 0.3mA/cm², 1.5 times higher than that obtained from Pt/C electrode with 5.6μg/cm² platinum.

Surprisingly, the OSP for ORR increased significantly from 0.55V to 0.79V when the Pt loading decreased from 56 to 5.6μg/cm². The OSP for ORR on Pt RDE was 0.75V, which was close to those on Pt/C electrodes with 5.6 and 11μg/cm². The OSP (0.75~0.79V) was significantly higher than that for Pt/C with 56μg/cm² and was close to the reported OCP for a Pt/C cathode in a DMFC [Liu, *et al.*, 1998; Kreuer, *et al.*, 2001]. This OSP was actually the mixed potential caused by the simultaneous oxygen reduction and methanol oxidation reactions on Pt catalyst [Ren, *et al.*, 2000]. The higher the Pt loading, the more the oxygen was consumed, thus resulting a relatively low oxygen concentration on the surface of Pt catalyst. Since the oxygen in liquid electrolyte was very low and the oxygen diffusion coefficient ($\sim 10^{-5}$ cm²s⁻¹) was very small, the oxygen cannot be replenished efficiently even under 3000rpm when it was consumed by direct reacting with methanol. The lower the oxygen concentration, the lower the OSP for ORR.

Fig 4.7 Polarisation curves for oxygen reduction on Pt/C and Pt RDE in O_2 -saturated $1\text{M H}_2\text{SO}_4 + 0.5\text{M CH}_3\text{OH}$ under a scan rate of 5 mVs^{-1} at 25°C using RDE. The RDE was rotated at 3000rpm.

Fig 4.8 Current density @ 0.6V , limiting current density, onset potential for ORR, and peak current density for MOR in N_2 -saturated $1\text{M H}_2\text{SO}_4 + 0.5\text{M CH}_3\text{OH}$ as a function of Pt loading. The RDE was rotated at 3000rpm.

Furthermore, the current density at 0.6V changed from negative to positive when the Pt loading increased from 5.6 to $56\mu\text{gcm}^{-2}$. The negative current was due to ORR, while the positive current was due to MOR. This cannot be explained fully if the low concentration of oxygen on Pt catalyst is neglected. Therefore, to overcome the low

oxygen concentration in liquid electrolyte, it is suggested that relatively low Pt loading ($5.6\sim 11\mu\text{gcm}^{-2}$) be used to characterize the catalytic activity for ORR on Pt/C in the presence of methanol. However, the limiting current density for ORR was in the range of $4.5\sim 5.2\text{mAcm}^{-2}$, only slightly smaller than that in the absence of methanol. In general, the polarisation behaviours for Pt RDE were similar to those for Pt/C with the Pt loading of $5.6\sim 11\mu\text{gcm}^{-2}$.

Fig 4.9 shows the CVs for Pt/C electrode with different Pt loading and Pt RDE in N_2 -saturated $1\text{M H}_2\text{SO}_4 + 0.5\text{M CH}_3\text{OH}$ at 25°C . The inset graph shows an enlarged portion of CVs in the range of $0.5\sim 1.0\text{V}$. In the forward scan, methanol oxidation produced an anodic peak around $0.86\sim 0.90\text{V}$, which was close to 0.89V for Pt/C obtained by Liu et al. [2004]. When the platinum loading was $56\mu\text{g}/\text{cm}^2$, the anodic current in the forward scan at about 0.9V was $32\text{mA}/\text{cm}^2$, which was much higher than $2.8\text{mA}/\text{cm}^2$ at 0.87V for Pt/C with $5.6\mu\text{g}/\text{cm}^2$ platinum and $2.5\text{mA}/\text{cm}^2$ at 0.86V for Pt RDE. From the anodic peaks at $0\sim 0.3\text{V}$, the characteristic peaks of hydrogen desorption, the ESA was calculated and shown in Table 4.1.

Fig 4.9 Cyclic voltammograms of Pt/C and Pt RDE in $1\text{M H}_2\text{SO}_4 + 0.5\text{M CH}_3\text{OH}$ under a scan rate of 100 mVs^{-1} at 25°C

Fig 4.10 shows the ESA and utilization of Pt catalyst based on ESA for Pt/C and Pt RDE in the absence and presence of methanol. Compared with those obtained from CVs in the absence of methanol, these values were much lower. This indicates that the addition of methanol could affect the electrocatalytic activity of Pt/C catalyst for both HOR and ORR due to the poisoning effect of CO produced during methanol oxidation [Goodenough, 1992].

Fig 4.10 ESA for Pt/C electrode with different platinum loading and Pt RDE obtained from CV measurements

4.2.2 Methanol Oxidation Reaction on Pt/C

Fig 4.11 shows the polarisation curves for the methanol oxidation reaction (MOR) on Pt/C electrode in N_2 -saturated 1M H_2SO_4 + 2M CH_3OH at 25°C as a function of the rotating speed. The platinum loading was $5.6\mu\text{g}/\text{cm}^2$.

Under each rotating speed, both cathodic and anodic current were observed. The cathodic current is attributed to the reduction of trace oxygen dissolved in solution, and the anodic current comes from MOR. With the decrease of the rotating speed, the cathodic current decreased significantly, indicating the decrease of oxygen concentration on the surface of electrode. However, the anodic current does not

change much until the rotating speed was decreased to zero. This shows that MOR is kinetically controlled. The difference between anodic currents with and without rotation may be due to the trace of oxygen on the surface of the electrode when the electrode is rotated.

Fig 4.11 Polarisation curves for methanol oxidation on Pt/C electrode in nitrogen saturated 1M H_2SO_4 + 2M CH_3OH at 25°C as a function of rotating speed. The scan rate was 5mv s^{-1} . The platinum loading was $5.6\mu\text{g cm}^{-2}$

The mixed potential also existed in the case of MOR on Pt/C in N_2 -saturated, 1M H_2SO_4 + 2M CH_3OH . As expected, the OSP for MOR on Pt/C decreased significantly from 0.657V to 0.510V with the increase in the rotating speed. This was because that it was unlikely to remove the oxygen completely from the liquid electrolyte by purging N_2 . The higher oxygen concentration on the surface of Pt catalyst under higher rotating speeds resulted in higher mixed potentials [Liu, *et al.*, 1998; Kreuer, *et al.*, 2001]. This made the study the MOR on Pt/C catalyst difficult. Therefore, to minimize the negative effects of the dissolved oxygen, the measurements for methanol oxidation should be conducted under static condition.

Fig 4.12 shows the polarisation curves for MOR on Pt/C electrode with different Pt loading in N_2 -saturated 1M H_2SO_4 + 2M CH_3OH . Fig 4.13 shows the current at

0.7V, the peak current and the OSP for MOR as a function of the Pt loading. When the Pt loading increased from 5.6 to $56\mu\text{g}/\text{cm}^2$, the OSP for MOR decreased significantly from 0.510V to 0.207V. This was due to the simultaneous occurrence of MOR and ORR on Pt catalyst in the presence of the trace oxygen in the electrolyte. The higher the Pt loading, the more oxygen was consumed. Since oxygen cannot be replenished under static condition, and the oxygen concentration would be kept at a very low level. Therefore, the higher the Pt loading, the lower the oxygen concentration on the surface of Pt catalyst, and the lower the OSP for MOR. The OSP (0.207V) for MOR on Pt/C with the Pt loading of $56\mu\text{g}/\text{cm}^2$ was close to the anode potential in a DMFC [Liu, *et al.*, 1998]. At the same time, both the current at 0.7V and the peak current increased significantly with the increase of the Pt loading. This was due to the increase in the active surface area for MOR. Therefore, it is suggested that the relative high Pt loading ($>56\mu\text{g}/\text{cm}^2$) be used to characterize the catalytic activity for MOR in $1\text{M H}_2\text{SO}_4$.

Fig 4.12 Polarisation curves for methanol oxidation on Pt/C electrode with different Pt loading in N_2 -saturated $1\text{M H}_2\text{SO}_4$ at 25°C as a function of methanol concentration. The scan rate was 5mV s^{-1} .

Fig 4.13 Current density at 0.7V, peak current density, and the onset potential for MOR as a function of Pt loading

4.3 Summary

The oxygen reduction reaction on Pt/C catalyst in 1M H₂SO₄ (+ 0.5MCH₃OH) is a diffusion-controlled process. The oxygen diffusion coefficient is 2.1~2.3 and 1.7~1.9cm²s⁻¹ for Pt/C catalyst and Pt RDE, respectively. The presence of methanol has little effect on the oxygen diffusion to the Pt catalyst in 1M H₂SO₄. The methanol oxidation reaction on Pt/C catalyst is a kinetically controlled process.

The parameters used in this study are as follows:

Pt loading (5.6μgcm⁻²) and 3000rpm were used to study ORR in the absence and presence of methanol. The OSP for ORR on Pt/C catalyst in the presence of methanol depends on the dissolved oxygen, the rotating speed, and the Pt loading. This is because that the relative low concentration of oxygen dissolved in liquid electrolyte is readily consumed by the chemical reaction with methanol on the surface of Pt catalyst. The lower the Pt loading, the less amount of oxygen is consumed. The higher the rotating speed, the more amount of oxygen is replenished. In order to overcome the low concentration of dissolved oxygen, the relatively low Pt loading (5.6~11gcm⁻²)

and the relatively high rotating speed (3000rpm) are preferred when measuring the oxygen reduction in the presence of methanol. With the aim of comparison, same conditions are used for oxygen reduction in the absence of methanol.

Pt loading of $56\mu\text{gcm}^{-2}$ with no rotation was used to study the methanol oxidation reaction. Although the liquid electrolyte is saturated with nitrogen, there is still trace of dissolved oxygen. To minimize the adverse effects of dissolved oxygen in the liquid electrolyte on the methanol oxidation behaviours, it is suggested that the relatively high Pt loading ($>56\mu\text{gcm}^{-2}$) and no rotation be used for the testing.

CHAPTER 5 Synthesis and Characterization of PDDA Stabilized Pt Nanoparticles

In this chapter, the positively charged platinum nanoparticles without carbon support were prepared via alcohol reduction method in the presence of polycation, PDDA. The effects of the molar ratio of monomer unit to platinum were studied systematically. The platinum nanoparticles were characterized by TEM, XRD and XPS. The electrocatalytic activity was characterized using ORR with and without methanol, and MOR using RDE technique.

5.1 Experimental

The positively charged PDDA-Pt nanoparticle colloidal solutions were prepared by alcohol reduction of platinum ions in ethanol/water (volume ratio: 4/6, 100ml) in the presence of polycation, PDDA. The molar ratio of PDDA monomer to Pt varied from 1:1 to 15:1. The mixture was then transferred into a three-neck flask and brought to reflux in an oil bath with the reflux temperature of 82°C. The pH of the solution was adjusted to 8.5 by adding NaOH.

The electrocatalytic activity of the PDDA-Pt nanoparticles was characterized by RDE technique using a GCE. The Pt loading was about 5.6 and 56 μgcm^{-2} for ORR and MOR, respectively. In comparison, the electrocatalytic activity of Pt/C (20wt%, E-Tek) was also measured on RDE. To characterize the electrocatalytic activity towards ORR, the polarisation curves were measured in O₂-saturated, 1M H₂SO₄ with and without addition of 0.5M CH₃OH. RDE was rotated at 3000 rpm. The activity of

the PDDA-Pt nanoparticles for the MOR was measured in N_2 -saturated, 1M H_2SO_4 + 2M CH_3OH . The RDE was kept static condition.

5.2 Results and Discussions

5.2.1 Synthesis of the Pt nanoparticles

Fig 5.1 shows the UV-visible spectrum of PDDA, H_2PtCl_6 solutions, and the PDDA- H_2PtCl_6 -ethanol-water system.

Fig 5.1 UV-visible spectrum for PDDA, H_2PtCl_6 and the mixture of PDDA and H_2PtCl_6 solutions

It can be seen that PDDA is almost transparent under UV-visible spectrum. For the H_2PtCl_6 solution, there were two absorbance peaks at around 201nm and 260nm. They are due to the platinum complex of $[PtCl_4]^{2-}$ and $[PtCl_6]^{2-}$, respectively [Rivadullar, *et al.*, 1997; Henglein, *et al.*, 1995; Duff, *et al.*, 1995]. After addition of PDDA, the peak at 201nm did not shift, but the absorbance increase slightly; however, the peak at 260nm shifted to 269nm, with the significant increase in the absorbance. This indicates the strong coordination of N atom from PDDA to Pt^{4+} [Yan, *et al.*, 2001].

The formation of PDDA-Pt nanoparticle colloids via alcoholic reduction was followed by UV-visible spectroscopy. The H_2PtCl_6 and PDDA mixed solution was pale in yellow. After the reaction, the color of the solution changed to dark brown. Figure 5.2 is the spectra during the reduction of Pt ions in ethanol/water (4/6, v/v) with the PDDA/Pt ratio of 5:1 as a function of reflux time at 82°C .

Fig 5.2 UV-visible spectrum of the PDDA- H_2PtCl_6 -alcohol-water system as a function of reflux time, PDDA:Pt=5:1, $[\text{Pt}]=10^{-4}\text{M}$. The inset graph is the absorbance at 500nm vs reflux time.

As shown in Fig 5.2, there is a short induction period before the band at 269 nm decreases. The characteristic absorbance peaks decreased very rapidly and disappeared completely after the induction period of less than 1 min. The peak at 269 nm was no longer visible, suggesting that all PtCl_6^{2-} ions were reduced by ethanol at the refluxing temperature of 82°C . $\text{Pt}(0)$ absorbance peak at 215nm was predicted by calculations[Creighton, *et al.*, 1991] and also observed experimentally [Chen, *et al.*, 2000]. However, this absorbance peak was not observed in this system. Chen *et al.* [2000] reported that the absorbance at 215nm is proportional to that at 500nm. Therefore, the absorbance at 500nm was used as the indication of $\text{Pt}(0)$. The intensity of $\text{Pt}(0)$ absorbance at 500 nm increased very rapidly after the induction period,

indicating that the reduction of PtCl_6^{2-} ions by ethanol is almost instantaneous. The PDDA-Pt nanoparticle colloids synthesized with the PDDA/Pt ratios from 1:1 to 15:1 were stable as indicated by the observation of no precipitates of the colloidal solution stored under the normal laboratory conditions for at least one month.

5.2.2 TEM images of Pt nanoparticles

Figure 5.3 shows TEM images and histogram of the particle size distribution of the PDDA-Pt nanoparticle colloids synthesized in the presence of different PDDA/Pt ratios. In the case of the PDDA/Pt molar ratio of 1:1, the formation of agglomeration is observed (Fig 5.3a), indicating that the concentration of PDDA may not be high enough to prevent the agglomeration of Pt nanoparticle colloids. The particles had a wide size distribution ranging from 1nm to 6nm and the average particle size is 3.64 ± 1.15 nm. As the concentration of PDDA increases, the dispersion of the Pt nanoparticles increases substantially. At the molar ratio of PDDA:Pt = 3:1, there is no agglomeration of Pt nanoparticle colloids, showing uniform and highly dispersed particles (Fig 5.3b). The average particle size is 2.39 ± 0.52 nm, smaller than that obtained with the PDDA/Pt ratio of 1:1. The size distribution was also improved. Further increase in the PDDA/Pt ratio has little effect on the dispersion and particle size of the PDDA-Pt nanoparticle colloids. This indicates that the separation and dispersion of Pt nanoparticles are related to the molar ratio of PDDA and Pt. The specific area (SA) of platinum can be calculated by equation (5.1). Table 5.1 summarizes the particle size and surface area of PDDA-Pt nanoparticles obtained from TEM images.

$$\text{SA} = \frac{6 \times 1000}{21.45 \times d} (\text{m}^2 / \text{g}) \quad (5.1)$$

where 21.45 is the platinum density (g/cm^3) and d is the average catalyst particle size (nm).

Fig 5.3 TEM images and size distribution histograms of PDDA-Pt synthesized at the different molar ratio, (a) 1:1, (b) 3:1, (c) 5:1, (d) 15:1

Table 5.1 Particle size and surface area obtained from TEM images and XRD measurements

Molar ratio	TEM		XRD		CV
	Particle size (nm)	Specific area (m ² /g)	Particle size (nm)	Specific area (m ² /g)	Specific area (m ² /g)
1:1	3.64±1.15	77.0	4.02	69.7	36
3:1	2.39±0.52	117.3	3.16	88.7	88
5:1	2.35±0.48	119.3	2.41	116.3	100
8:1	2.30±0.46	121.9	2.28	123.0	122
15:1	2.29±0.64	122.4	2.17	129.2	112
Pt/C(20wt.%)	2.60±0.54	107.8	2.2	128	43

The well-dispersed PDDA-Pt nanoparticle can be obtained by simply increasing the PDDA/Pt molar ratio during the synthesis. This indicated that PDDA is an effective stabilizer to prevent the agglomeration of Pt nanoparticle. The stabilizing action of nonionic polymer is generally referred to as steric stabilization [Chen, *et al.*, 2000], resulting from hydrophobic and coordination between the polymer and metal nanoparticles [Toshima, *et al.*, 1997]. PDDA is a polycation consisting of N atoms, allyl and methyl as shown in Fig 3.1a. In this case, N atoms from PDDA were considered to coordinate with Pt atoms around the surface of particles, at the same time, the hydrophobic branches stretched towards the liquid phase. From this point, PDDA performed similar steric stabilization to the nonionic polymer [Chen, *et al.*, 2000; Toshima, *et al.*, 1997]. On the other hand, PDDA is an ammonium salt and positively charged. Therefore, PDDA stabilized Pt nanoparticle is also positively charged and will repel one another more or less strongly when they approach [Hunter, 1986]. Therefore, charge stabilization may be another factor for PDDA besides the steric stabilization.

Fig 5.4 shows a high resolution TEM (HRTEM) image of PDDA-Pt with the PDDA/Pt molar ratio of 5:1. The clear crystalline nature of the platinum nanoparticles

was observed. The lattice spacing was $2.3\text{\AA}$, which was indexed to (111) of fcc Pt [Mu, et al., 2004].

Fig 5.4 High resolution TEM image of PDDA-Pt nanoparticles, PDDA:Pt =5:1

5.2.3 Electron Diffraction and XRD patterns of PDDA-Pt nanoparticles

Fig 5.5 shows the electronic diffraction patterns of PDDA-Pt. There are, from inner to outer, four clear rings for both PDDA-Pt and Nafion-Pt nanoparticles, which can be indexed to (111), (200), (220), and (311), respectively. The appearance of diffraction rings indicates that PDDA-Pt nanoparticles show considerable crystallinity and have fcc structure [Murr, et al., 1991].

Fig 5.6 shows XRD patterns of PDDA-Pt nanoparticles synthesized at the different PDDA/Pt molar ratios. The diffraction peaks appear at 2θ of 39.6° , 46.2° , 67.4° , which can be indexed to (111), (200), (220) respectively. This indicates that the as-synthesized PDDA-Pt nanoparticles belong to fcc crystal structure. This is in good agreement with HRTEM image (Fig 5.4) and the electronic diffraction patterns (Fig 5.5).

Fig 5.5 The electron diffraction patterns of PDDA-Pt nanoparticles, PDDA:Pt =5:1

Fig 5.6 XRD patterns of PDDA-Pt synthesized with the different molar ratio of PDDA to Pt, (1) 1:1, (2) 3:1, (3) 5:1, (4) 8:1 and (5) 15:1

At the same time, we can get the lattice constant of $3.925\text{\AA}$ for PDDA-Pt nanoparticles, which was in good agreement with 3.923 for pure platinum. The particle size calculated from the Scherrer equation and the specific area calculated based on XRD measurements are also shown in Table 5.1. The particle size obtained from XRD is in good agreement with that obtained from TEM images.

5.2.4 XPS analysis of Pt nanoparticles

Fig 5.7 shows the Pt 4f spectra of the Pt nanoparticles stabilized by PDDA. The spectrum can be deconvoluted into two components, Pt(0) and Pt(II). The respective Pt4f_{7/2} binding energies were 72.1 and 73.2eV for PDDA-Pt nanoparticles. The relative intensities of these two components were 79.2 and 20.8. We can assign the 4f_{7/2} signal at 72.1eV to Pt(0), which is much higher than that (71.0eV) of Pt foil [Fu, *et al.*, 2001], and the signal at 73.2 is ascribed to Pt(II).

Fig 5.7 X-ray photoelectron spectra of Pt 4f for PDDA-Pt nanoparticles, PDDA:Pt=5:1

The observed increase in Pt 4f binding energy maybe derived from two factors. One is the size-dependent effect of the metal core [Ederhardt, *et al.*, 1990; Cheung, 1984; Wertheim, *et al.*, 1983]; the other one is the ligand effect [Fu, *et al.*, 2001; Chen, *et al.*, 1999]. Ederhardt *et al.* [1990] reported that the Pt 4f binding energy of Pt clusters containing one to six atoms deposited onto a silica substrate increased by 1.3~2.0eV as compared to that of a bulk sample. This phenomenon was interpreted in terms of final state relaxation proposed by Wertheim [1983]. However, Fu *et al.* [2001] reported that the Pt 4f binding energy of Pt nanoparticles prepared by precipitating the “unprotected” Pt nanoparticles (d_{av} =1.3nm) by adding dilute HCl was same as that of

bulk Pt. At the same time, it was found that the strong coordination of ligand to Pt resulted in much higher increase in the Pt 4f binding energy, and the weak coordination resulted in the slight increase in the Pt 4f binding energy. On the other hand, the coordination of polymers containing N atoms was confirmed by the combined use of FTIR and X-ray photoelectron spectroscopy [Chen, *et al.*, 1999]. The large increase in Pt 4f binding energy for PDDA-Pt nanoparticles may result from the strong coordination of N atoms from PDDA to Pt. This agrees with the significant red shift for PDDA-Pt in the UV-visible spectra (Fig 5.1).

5.2.5 Oxygen reduction reaction

Figure 5.8 shows the polarisation curves for ORR on Pt/C and PDDA-Pt nanoparticles in 1M H₂SO₄ saturated with oxygen under a scan rate of 5 mVs⁻¹ at 25°C, using RDE. The RDE was rotated at 3000rpm. The Pt loading was 5.6 µg cm⁻² for both Pt/C and PDDA-Pt nanoparticles synthesized under various PDDA/Pt ratios.

Fig 5.8 Polarisation curves of Pt/C and PDDA-Pt nanoparticle colloids in O₂-saturated 1M H₂SO₄ under a scan rate of 5 mVs⁻¹ at 25°C, using RDE. The RDE was rotated at 3000rpm. The Pt loading was 5.6 µg cm⁻².

As shown in Fig 5.8, the PDDA-Pt nanoparticles synthesized with PDDA:Pt = 1:1 had the lowest electrochemical activity and the limiting current density appeared at $\sim 0.2\text{V}$ (vs SHE). With the increase of molar ratio from 1:1 to 3:1, the electrocatalytic activity increased significantly. The current density at 0.6V was 1.81mAcm^{-2} , ~ 14 times higher than 0.13mAcm^{-2} obtained on the PDDA-Pt nanoparticles synthesized with PDDA:Pt = 1:1. The limiting current density appeared at 0.5V , also much higher than that of PDDA-Pt with molar ratio of 1:1. Further increasing the PDDA/Pt molar ratio, the increase in the performance was not that much.

Figure 5.9 shows the CVs of the Pt/C and PDDA-Pt nanoparticles prepared with various PDDA/Pt molar ratios in N_2 -saturated $1\text{M H}_2\text{SO}_4$ at 25°C on a RDE. The Pt loading was $5.6\text{ }\mu\text{g cm}^{-2}$ for both Pt/C and PDDA-Pt nanoparticle colloids synthesized under various PDDA/Pt ratios. The enlarged hydrogen desorption peaks in the 0.0 to 0.08 V range were shown as inset in the figure. The electrochemically active surface area (ESA) calculated from the CV curves is given in Table 5.2. The ESA estimated from the CV curves is generally smaller than the surface area calculated from the XRD values (Table 5.1). For the PDDA-Pt nanoparticle colloids synthesized with PDDA/Pt ratio of 1:1, the ESA area was $2.02\text{cm}^2\text{cm}^{-2}$, corresponding to the specific area (SA) of $36\text{ m}^2\text{g}^{-1}$, which is smaller than the specific area of $43\text{ m}^2\text{g}^{-1}$ of the commercial Pt/C catalysts. With the increase of the PDDA/Pt ratios, ESA increases. With the PDDA/Pt ratio of 8:1, the ESA is $6.83\text{ cm}^2\text{cm}^{-2}$ (SA: $122\text{ m}^2\text{g}^{-1}$), which is significantly higher than that of the commercial Pt/C catalysts. However, as the PDDA/Pt ratios increased to 15:1, the ESA decreased. This indicates too much PDDA molecules could retard the electrochemical process and reduce the catalyst utilization.

Fig 5.9 Cyclic voltammograms of the Pt/C and PDDA-Pt nanoparticles synthesized with various PDDA/Pt molar ratios in N_2 -saturated 1 M H_2SO_4 at 25°C on a RDE. The enlarged hydrogen desorption peaks in the 0.0 to 0.08 V range were shown as inset. The scan rate was 100 mV s^{-1} .

Table 5.2 ESA for Pt/C and PDDA-Pt with the different molar ratio obtained from CV measurements in 1M H_2SO_4 and 1M $\text{H}_2\text{SO}_4 + 0.5\text{M CH}_3\text{OH}$ saturated with nitrogen. The platinum loading was $5.6 \mu\text{g cm}^{-2}$.

PDDA/Pt Molar Ratio		Pt/C	1:1	3:1	5:1	8:1	15:1
ESA ($\text{cm}^2\text{cm}^{-2}$)	1M H_2SO_4	2.38	2.02	4.90	5.39	6.83	6.26
	1M $\text{H}_2\text{SO}_4 + 0.5\text{M CH}_3\text{OH}$	2.02	1.59	3.49	3.85	4.63	4.00
SA (m^2g^{-1})	1M H_2SO_4	43	36	88	100	122	112
	1M $\text{H}_2\text{SO}_4 + 0.5\text{M CH}_3\text{OH}$	36	28	62	69	82	71

The worst performance for ORR on the PDDA-Pt synthesized with PDDA:Pt = 1:1 is most likely due to the smallest ESA of (Table 5.1) caused by the agglomeration and relatively large particle size (Fig 5.3a and Table 5.1). As shown in Fig 5.3, when the molar ratio of PDDA/Pt increased to 3:1, the Pt nanoparticle colloids agglomerates disappear and the particle size is also reduced. Based on XRD measurements, the specific area of the Pt nanoparticles increased from 70 to $89 \text{ m}^2\text{g}^{-1}$, an increase by 41% as compared to that synthesized with molar ratio of 1:1. However, the ESA increased from 2.02 (SA: $36 \text{ m}^2\text{g}^{-1}$) to $4.90 \text{ cm}^2\text{cm}^{-2}$ (SA: $88 \text{ m}^2\text{g}^{-1}$), about 2.4 times high. This

explains the significant increase in the polarisation performance when the PDDA/Pt molar ratio increased from 1:1 to 3:1. However, further increase in the PDDA/Pt ratio increased the performance marginally. This was consistent with the marginal increase in SA and ESA, resulting from the slight decrease in the size of the Pt nanoparticles (Table 5.1). However, as the PDDA/Pt ratios increased to 15:1, the ESA decreased although the SA increased slightly. The Pt/C catalyst gave a slightly higher performance as compared to that of the PDDA-Pt nanoparticles with the molar ratio higher than 1:1 although the ESA of the latter was much higher. This probably indicates that PDDA stabilizer attached to Pt may have some shielding effect on the electrocatalytic activity of the Pt nanoparticles for the ORR.

5.2.6 Oxygen reduction reaction in the presence of methanol

Fig 5.10 shows the polarisation curves for ORR on Pt/C and PDDA-Pt nanoparticles in O₂-saturated 1M H₂SO₄ + 0.5M CH₃OH under a scan rate of 5 mVs⁻¹ at 25°C, using RDE. The RDE was rotated at 3000rpm. The Pt loading was 5.6µg cm⁻². PDDA-Pt nanoparticles with molar ratio of 1:1 showed the lowest OSP and the worst performance. When the molar ratio increased to 3:1, the OSP increased from 0.75V to 0.83V and the performance also increased significantly. Further increasing the molar ratio, the OSP and the performance for ORR increased slightly. Generally, PDDA-Pt nanoparticles except for PDDA-Pt with the molar ratio of 1:1 showed slightly lower polarisation performance than Pt/C catalyst. However, they showed higher OSP for ORR than Pt/C, indicating that the existence of PDDA would suppress the MOR.

Fig 5.10 Polarisation curves for oxygen reduction on Pt/C and PDDA-Pt nanoparticle colloids in O_2 -saturated 1 M H_2SO_4 + 0.5M CH_3OH under a scan rate of 5 mVs^{-1} at 25°C , using RDE. The RDE was rotated at 3000rpm. The Pt loading was $5.6 \mu\text{g cm}^{-2}$.

Fig 5.11 shows the CVs of Pt/C and PDDA-Pt nanoparticles N_2 -saturated in 1M H_2SO_4 + 0.5M CH_3OH at 25°C on a RDE.

Fig 5.11 Cyclic voltammograms of Pt/C and PDDA-Pt nanoparticle colloids in 1M H_2SO_4 + 0.5M CH_3OH saturated with nitrogen at 25°C on a RDE. The scan rate was 100 mV s^{-1} . The Pt loading was $5.6 \mu\text{g cm}^{-2}$.

At the molar ratio of 1:1, the methanol oxidation peak in the forward scan was even higher than that of Pt/C electrode. With the increase of molar ratio, this current

decreased significantly until it was not observed. In the reverse scan, the similar trend was observed clearly. This indicated that the existence of PDDA did suppress the methanol oxidation on PDDA-Pt nanoparticles. At the same time, the ESA can be calculated according to the hydrogen desorption peak and was shown in Table 5.2. Obviously, the ESA is much smaller in the presence of methanol than in the absence of methanol.

5.2.7 Methanol Oxidation Reaction

The activity of the Pt/C and PDDA-Pt nanoparticle colloids for the MOR was measured by cyclic voltammetry in N₂-saturated, 1M H₂SO₄ + 2M CH₃OH on RDE at 25°C, as shown in Fig 5.12. The Pt loading was 56μgcm⁻². The anodic peak at 0.83 – 0.88V in Fig 5.12a is due to MOR. The as-synthesized PDDA-Pt nanoparticles showed considerable activity for MOR. Although the activity for PDDA-Pt nanoparticles with the molar ratio of 1:1 is comparable with that of Pt/C catalyst, it is interesting to find that the anodic current decreased significantly with the increase of molar ratio. The anodic peak current was 12.7 and 0.4mA/cm² for the PDDA-Pt nanoparticles with the molar ratio of 1:1 and 15:1, respectively.

As shown in Fig 5.12b, the forward oxidation current peak occurs at ~0.91-0.95 V and the backward oxidation current peak at ~0.67 - 0.7 V, which are close to that reported in the literature [Wei, *et al.*, 2004]. The PDDA-Pt nanoparticle colloids synthesized with PDDA/Pt ratio of 1:1 shows the forward anodic peak current (*j_f*) of 27 mAcm⁻² for the MOR at 0.91 V (Fig 5.12b), which is slightly lower than 33 mAcm⁻² for the reaction on the E-TEK Pt/C catalyst. This confirms that as-synthesized PDDA-Pt nanoparticles are highly active for the MOR. However, the rapid reduction in the forward anodic peak current density for the PDDA-Pt

nanoparticle with the increase in the PDDA/Pt ratio is consistent with the polarisation measurements. This indicates that a control of the polycation stabilizers for the PDDA-Pt nanoparticle catalysts is essential to achieve the high stability and high catalytic activity of the PDDA-Pt nanoparticle catalysts.

Fig 5.12 Cyclic voltammograms of PDDA-Pt nanoparticles with different molar ratios in N_2 -saturated $1\text{M H}_2\text{SO}_4 + 2\text{M CH}_3\text{OH}$ at 25°C on a RDE. The platinum loading was $56\mu\text{gcm}^{-2}$. (a) The single scan. The scan rate was 5 mV s^{-1} . (b) The cyclic scan. The scan rate was 100 mV s^{-1} .

Fig 5.13 shows a time vs current density plot for Pt/C and PDDA-Pt nanoparticles synthesized with different PDDA/Pt molar ratios in N_2 -saturated $1\text{M H}_2\text{SO}_4 + 2\text{M CH}_3\text{OH}$. A constant potential of 0.7V was applied for 3600s .

Fig 5.13 Current vs time plot of Pt/C and PDDA-Pt nanoparticles in N_2 -saturated 1M H_2SO_4 + 2M CH_3OH at 25°C on a RDE. The applied potential was 0.7V. The platinum loading was $56\mu gcm^{-2}$.

As shown in Fig 5.13, the current density gradually decayed with time and the initial current densities for each case were smaller than those from cyclic voltammograms at the same potential in Fig 5.12. However, the trend of the initial current densities is same as that in Fig 5.12, i.e. with the increase of PDDA/Pt molar ratio, the current density decreased significantly. Although the initial current density was higher for Pt/C catalyst than for all the PDDA-Pt nanoparticles with different molar ratios, the decay in the current density was faster. Therefore, the current density was lower for Pt/C catalyst than for PDDA-Pt with the molar ratio of 1:1 after 780s. After 1hr, the current density was $0.28mAcm^{-2}$ for Pt/C catalyst, only one third of that for PDDA-Pt with the molar ratio of 1:1. This current density was even lower than those of PDDA-Pt with the molar ratio of 3:1 and 5:1.

The highest anodic current peak was observed for MOR on PDDA-Pt nanoparticle colloids synthesized with PDDA/Pt ratio of 1:1 among the Pt catalysts studied (Fig 5.12). This is very different from the thiol-stabilized Pt nanoparticles assisted by microwave dielectric heating [Liu, *et al.*, 2004]. Without the heat

treatment, the as-synthesized Pt nanoparticles displayed an almost featureless voltammogram with low current density value in 1M H₂SO₄ + 2M CH₃OH electrolyte. The low activity is attributed to the full coverage and passivation by a shell of thiol molecules, which limits the access of the electrolyte to the active site of the Pt nanoparticles [Liu, *et al.*, 2004]. Boennemann *et al.* [2000] synthesized the organoaluminum-stabilized bimetallic colloids with particle size smaller than 2 nm deposited on a commercial support. The stabilizing surfactant shell on the metallic nanoparticles had to be removed before the metal particles could be used for electrocatalysis. Deivaraj *et al.* [2005] also observed that PVP-protected Pt nanoparticles were not catalytically active and thermal activation was required to remove the organic shells. In fact, particle-size enhancement could be a significant side-effect for thermal activation. This indicates that the PDDA polycation attached to Pt nanoparticles would have much less shielding effect on the electrode process in comparison to other neutral polymer stabilizers under the present conditions. However, as the PDDA/Pt ratio increases, the anodic peak current decreases significantly. In the case of PDDA-Pt nanoparticles synthesized with PDDA/Pt ratio of 15:1, the methanol oxidation current peak reduced to 0.4mAcm⁻² (Fig 5.12a). In the CV scanned between 0.2 – 1.2 V, similar dependence of the anodic peak current in the forward scan for MOR on the PDDA-Pt nanoparticle synthesized with different PDDA/Pt ratios was also observed (Fig 5.12b). This indicates that the PDDA stabilizer has a significant shell effect of on MOR.

Interestingly, the existence of PDDA showed similar performance for ORR in the absence of and presence of methanol (Fig 5.8 and 5.10). Although the performance for PDDA-Pt was not as high as that for Pt/C electrode, the OSP for ORR was much higher except PDDA-Pt with the molar ratio of 1:1. Combined with the significant

decrease in activity towards MOR with the increase of molar ratio (Fig 5.12), this indicated that the existence of PDDA would suppress MOR on PDDA-Pt nanoparticles without sacrificing much of the electrocatalytic activity for ORR.

5.3 Summary

PDDA-Pt nanoparticles were synthesized by the alcoholic reduction of the H_2PtCl_6 in ethanol/water system in the presence of charged polymer, PDDA. They showed considerable crystallinity and fcc structure. The coordination of N atoms from PDDA was confirmed by the combined use of UV-visible and X-ray photoelectron spectroscopy.

The morphology, the dispersion and the particle size of the PDDA-Pt nanoparticle colloids are dependent on the PDDA/Pt molar ratio. In the case of PDDA:Pt = 1:1, the PDDA-Pt nanoparticle colloids are characterized by agglomeration with average particle size of ~4 nm. With the increase in the PDDA/Pt molar ratio, highly dispersed Pt nanoparticle colloids are formed with reduced particles size of 2-3 nm.

PDDA-Pt shows the increase in the activity towards ORR in the presence and in the absence of methanol, but the significant decrease in the activity towards MOR with increasing the molar ratio. This indicates that the excess of PDDA would suppress the MOR on Pt nanoparticles. PDDA-Pt nanoparticles may be a potential methanol tolerant cathode catalyst for DMFCs.

CHAPTER 6 Synthesis and Characterization of Polymer Stabilized Pt Nanoparticles

In this chapter, platinum nanoparticles without carbon support were prepared via alcohol reduction method in the presence of negatively charged Nafion. The effects of the Nafion/Pt molar ratio and the temperature were studied systematically. In comparison, different polymer stabilized platinum nanoparticles were also prepared. The Pt nanoparticles were characterized by TEM, XRD, XPS and electrochemical measurements.

6.1 Experimental

Nafion-Pt nanoparticle colloidal solutions were prepared by alcohol reduction of platinum ions in ethanol/water (volume ratio: 4/6, 100ml) in the presence of Nafion. The molar ratio of Nafion to Pt varied from 1:2 to 8:1. The mixture was then transferred into a three-neck flask and brought to reflux in an oil bath at 82°C. The reaction temperature was controlled at 82, 75 and 65°C to study the effect of temperature on the synthesis. Similarly, PSS, PVP stabilized Pt nanoparticles were synthesized at the molar ratio of 4:1, under reflux temperature.

The electrochemical characterization was carried out using RDE similar to PDDA-Pt nanoparticles in Chapter 5.

6.2 Results and Discussions

6.2.1 Synthesis of Nafion-Pt nanoparticles

Fig 6.1 shows the UV-visible spectrum of Nafion, H_2PtCl_6 solutions and their mixture. For pure Nafion solution, there was a plateau from 200 to 245nm with maximum absorption at 235nm. The absorbance at the wavelength of smaller than 200nm may be due to $\text{CF}_2\text{-CF}_2$ group [Orkin, *et al.*, 1997]. Compared with the peaks for PtCl_4^{2-} and PtCl_6^{2-} , the mixture of H_2PtCl_6 and Nafion shows a peak (at 201nm) remained unchanged and the other peak (at 260nm) slightly shifted to lower wavelength. The differences shows the coordination of S or O from Nafion to Pt^{2+} and Pt^{4+} , which may provide the protecting action of Nafion to Pt nanoparticles [Yan, *et al.*, 2001].

Fig 6.1 UV-visible spectrum of Nafion, H_2PtCl_6 and the mixture of H_2PtCl_6 and Nafion, 10^{-4}M Pt^{4+} , Nafion:Pt=2:1

Fig 6.2 shows the UV-visible spectrum as a function of refluxing time during the formation of Nafion-stabilized Pt colloidal with different Nafion/Pt molar ratios. With increasing the refluxing time, the absorbance at both 201nm and 260nm decreased gradually, indicating that the concentration of platinum complex decreased. After an

induction period of 20~30min, these two peaks disappeared completely in one minute, indicating the complete reduction of platinum ions to platinum atoms. At the same time, the color of the solution changed from pale yellow to black suddenly, and the absorbance at 400~500nm increased significantly, indicating the formation of platinum nanoclusters [Chen, *et al.*, 2000].

Fig 6.2 UV-visible spectrum of the Nafion- H_2PtCl_6 -ethanol-water system as a function of reflux time, 10^{-4}M Pt^{4+} , Nafion:Pt=(a) 1:2, (b) 1:1, (c) 4:1, and (d) 8:1.

Fig 6.3 shows the absorbance of Pt^{4+} at 260nm and Pt^0 at 500nm as a function of reflux time during the formation of Nafion-Pt at the different molar ratio of Nafion to Pt. With the increase of reflux time, the absorbance decreased gradually until the

sharp decrease occurred. And then the absorbance began to increase suddenly. At the same time, the absorbance at 500nm was nearly zero under UV-visible spectroscopy before the sharp increase occurred. And then the absorbance at 500nm increased slightly with further increasing reflux time. With the increase of the Nafion/Pt molar ratio, the induction period increased, but the formation of nanoparticles was still fast and finishes in one or two minutes.

Fig 6.3 UV absorbance @ 260nm (Pt^{4+}) and 500nm (Pt^0) as a function of reflux time during the formation of Nafion-Pt at different Nafion/Pt ratios, 10^{-4}M Pt^{4+}

Fig 6.4 shows the UV-visible spectrum, the absorbance of Pt^{4+} at 260nm and Pt^0 at 500nm as a function of reflux time during the formation of Nafion-Pt nanoparticles at different temperatures. Nafion/Pt molar ratio was kept at 2:1. As expected, the temperature had a significant effect on the reduction. At the reflux temperature (82°C , ethanol/water=4/6, v/v), the induction period was only 30min. The formation of Pt nanoparticles was completed in one min. When the temperature decreased to 75°C , the induction period increased to 60min. The formation of nanoparticles was completed in 7mins. With the further decrease of temperature to 65°C , the induction and formation periods increased further to 165min and 35min, respectively.

Fig 6.4 UV-visible spectrum at (a) 82°C, (b) 75°C, (c) 65°C and the absorbance @ 260nm (Pt^{4+}) and 500nm (Pt^0) (d) as a function of reflux time during the formation of Nafion-Pt nanoparticles at different temperatures. Nafion:Pt=2:1, 10^{-4}M Pt^{4+}

Fig 6.5 shows the UV-visible spectrum of PSS, H_2PtCl_6 , the mixture of H_2PtCl_6 and PSS during the formation of PSS-Pt nanoparticles as a function of reflux time. The PSS/Pt molar ratio was 4:1. As shown in Fig 6.5a, PSS showed very strong absorbance at 193nm and 225nm, and a weak absorbance at 260nm, which was same as the characteristic wavelength (260nm) of Pt^{4+} . Absorbance at 225nm was attributed to benzene ring in PSS [Du, et al., 2004]. The characteristic wavelength of Pt^{4+} shifted

from 260 to 261nm after mixing with PSS, and the absorbance increased significantly due to the overlay.

The reduction of Pt ions to Pt atoms was monitored using the absorbance at 261nm (Pt^{4+}) and 500nm (Pt^0) (Fig 6.5b, c). With the increase of reflux time, the absorbance at 261nm decreased gradually until it didn't change after an induction period of 29min. At the same time, the absorbance at 500nm increased significantly, indicating the formation of PSS-Pt nanoparticles [Chen, *et al.*, 2000].

Fig 6.6 shows the UV-visible spectrum of PVP, H_2PtCl_6 , the mixture of H_2PtCl_6 and PVP during the formation of PSS-Pt nanoparticles as a function of reflux time. The PVP/Pt molar ratio was 4:1. As shown in Fig 6.6a, PVP was almost transparent except a strong absorbance at 192nm. The characteristic wavelength for Pt^{4+} shifted from 260nm to 257nm after mixing with PVP, indicating the coordination of N or O from PVP to Pt [Yan, *et al.*, 2004]. With the increase of reflux time, the absorbance at 257nm decreased gradually until it disappeared completely after an induction period of 25min (Fig 6.6b, c). Correspondingly, a broad absorbance appeared at 300~500nm, which was used to monitor the formation of Pt nanoparticles [Chen, *et al.*, 2000] (Fig 6.6a, b).

Fig 6.5 UV-visible spectrum of (a) PSS, H_2PtCl_6 , the mixture of H_2PtCl_6 and PSS, (b) the mixture and (c) the absorbance @ 261nm (Pt^{4+}) and 500nm (Pt^0) during the formation of PSS-Pt nanoparticles as a function of reflux time. 10^{-4}M Pt^{4+} , the PSS/Pt molar ratio was 4:1.

Fig 6.6 UV-visible spectrum of (a) PVP, H_2PtCl_6 , the mixture of H_2PtCl_6 and PVP, (b) the mixture and (c) the absorbance @ 261nm (Pt^{4+}) and 500nm (Pt^0) during the formation of PVP-Pt nanoparticles as a function of reflux time. 10^{-4}M Pt^{4+} . The PVP/Pt molar ratio was 4:1.

6.2.2 TEM images of Nafion-Pt nanoparticles

Fig 6.7 shows the TEM images of Nafion-Pt prepared at the different molar ratios. The Nafion-Pt nanoparticles were characterized by agglomerates and the agglomeration existed despite the increase in the Nafion/Pt molar ratio. However, the particle size decreased from about 4 to 3 nm with the increase of molar ratio.

Fig 6.7 TEM image of Nafion-stabilized platinum nanoparticles with different molar ratio of Nafion to Pt, (a) 1:2, (b) 2:1, (c) 4:1, (d) 8:1

Fig 6.8 shows the TEM images of Nafion-Pt prepared at different temperature. Similarly, the Nafion-Pt nanoparticles were still characterized by the agglomerates, but the particle size increased from about 3 to 4 nm with the decrease of temperature from 82 to 65°C.

Fig 6.8 TEM images of Nafion-Pt synthesized at different reflux temperatures, (a) 65°C, (b) 75°C, and (c) 82°C. Nafion:Pt=2:1

Fig 6.9 shows the TEM images of Pt nanoparticle synthesized in the presence of Nafion, PDDA, PSS and PVP. It was found that the Nafion-Pt nanoparticles were characterized by agglomerates (Fig 6.9a). In the presence of PSS, the dispersion was

improved significantly although the agglomerate was also observed (Fig 6.9d). On the contrary, the PDDA-Pt nanoparticles were well dispersed (Fig 6.9b). The PVP-Pt nanoparticles were also dispersed well although the agglomerates composed of several particles were found (Fig 6.9c). This indicates that different polymers have different stabilization effect on the Pt nanoparticles.

Fig 6.9 TEM images of Pt nanoparticles (a) Nafion-Pt (4:1), (b) PDDA-Pt (3:1), (c) PVP-Pt (4:1), (d) PSS-Pt (4:1)

In the case of Nafion-Pt, increasing the Nafion/Pt molar ratio can reduce the particle size, but can not improve the dispersion. Increasing the reaction temperature also reduced the particle size, but still cannot improve the dispersion. The agglomerates were observed for all the colloids prepared under the investigated conditions. This was different from the PDDA-Pt nanoparticles. The well-dispersed

PDDA-Pt nanoparticles were obtained by increasing the molar ratio of PDDA to Pt. As discussed in the case of PDDA-Pt, the stabilization action of PDDA came from the steric and the charge stabilization. The molecular weight of Nafion was about 1100, which was much smaller than that (5000~20000) of PDDA. Therefore, Nafion may not provide enough steric stabilization. PSS also contained sulfonate function group, but the molecular weight was 70,000, much higher than that of Nafion. The stronger steric stabilization provided by PSS resulted in better dispersion of PSS-Pt nanoparticles although the agglomerates were also observed. On the other hand, Nafion was hydrophilic, also different from hydrophobic PDDA and PVP. The stabilizing action of nonionic polymer was generally referred to as steric stabilization [Chen, *et al.*, 2000], resulting from hydrophobic and coordination between the polymer and metal nanoparticles [Toshima, *et al.*, 1997]. PVP was a neutral polymer, which could provide steric stabilization resulting from hydrophobic hydrocarbon chain and the coordination between N atoms and Pt atoms.

6.2.3 Electron Diffraction and XRD patterns of Pt nanoparticles

Fig 6.10 shows the electronic diffraction patterns of Nafion-Pt. There were, from inner to outer, four clear rings for Nafion-Pt nanoparticles, which were indexed to (111), (200), (220), and (311), respectively. The appearance of diffraction rings indicated that Nafion-Pt nanoparticles also showed considerable crystallinity and had fcc structure [Murr, *et al.*, 1991].

Fig 6.10 The electron diffraction patterns of Nafion-Pt nanoparticles, Nafion:Pt=2:1

Fig 6.11 shows XRD patterns of Nafion-Pt nanoparticles with different Nafion/Pt molar ratio and synthesized at the various temperatures. Similar to PDDA-Pt nanoparticle, the diffraction peaks appeared at 2θ of 39.6° , 46.2° , 67.4° , matching the (111), (200) and (220) characteristics of a platinum fcc structure. From the full width at half height of peak of (111), the particle size was calculated using Scherrer equation [Wang, *et al.*, 2002] and was shown in Table 6.1. At the molar ratio of 1:2, the size of Pt nanoparticles was estimated to be around 4.3nm. These particles were not stable in solution, and precipitated after aging for several days. The size of Pt particles decreased first with increase of the Nafion/Pt molar ratio. And at the molar ratio of 2:1, the smallest particle was obtained. With further increasing the Nafion/Pt molar ratio, the size of particle increased slightly. However, the colloid solutions with the molar ratio higher than 1:1 were quite stable, and no precipitate was observed after aging several months. The size of Nafion-stabilized nanoparticles was much smaller than that of platinum black (5.5nm, E-TEK). The most important was that every

particle was in contact with Nafion. The specific area was calculated according to Eq. (5.1). As shown in Table 6.1, the SA was much higher than that of the commercial Pt black.

Fig 6.11 XRD patterns of Nafion-Pt nanoparticles synthesized (a) with different molar ratio of Nafion to Pt at 82°C, pH=8.5. (1) 1:2, (2) 1:1, (3) 2:1, (4) 4:1, (5) 8:1; and (b) at different temperatures, Nafion:Pt=2:1, pH=8.5. (1) 65°C, (2) 75°C, (3) 82°C.

At the reflux temperature (82°C, ethanol/water=4/6, v/v), the particle size was about 2.7nm. When the temperature decreased to 75°C and 65°C, the particle size increased to 3.2nm and 4.4nm, respectively. Furthermore, the Nafion-Pt colloids prepared at both 75 and 65°C was not stable, and the particles precipitated after aging several days. The specific area calculated was also shown in Table 6.1.

Table 6.1 Particle sizes obtained from XRD and ESA from CV for Nafion-Pt nanoparticles synthesized at various conditions

Synthesis conditions		XRD		CV
		Particle size (nm)	Surface area (m ² /g)	Surface area (m ² /g)
Nafion/Pt Molar ratio	1:2	4.3	65	54
	1:1	2.8	100	37
	2:1	2.7	104	24
	4:1	3.0	93	9.5
	8:1	3.2	87	n.a.
Temperature (°C)	65	4.4	60	n.a.
	75	3.2	87	n.a.
	82	2.7	104	n.a.
Pt black		5.5	29	n.a.

6.2.4 XPS analysis of Pt nanoparticles

Fig 6.12 shows the Pt 4f spectra of the Pt nanoparticles stabilized by Nafion. The spectrum can be deconvoluted into two components, Pt(0) and Pt(II). The respective Pt4f_{7/2} binding energies were 71.4 and 72.5eV for Nafion-Pt nanoparticles. The respective relative intensities were 78.4 and 21.6. The 4f_{7/2} bind energy for Pt(0) was slightly higher than that of Pt foil (71.0eV) [Fu, et al., 2001]. Similar to PDDA-Pt, the small increase in the binding energy for Nafion-Pt nanoparticles indicated the weak coordination of S or O from Nafion to Pt. This was in consistent with the wavelength shift for Nafion-Pt in the UV-visible spectra.

Fig 6.12 X-ray photoelectron spectra of Pt 4f for Nafion-Pt nanoparticles prepared with Nafion/Pt ratio of 2:1

6.2.5 Oxygen reduction reaction on Nafion-Pt

Fig 6.13 shows the polarization curves for ORR on Pt/C and Nafion-Pt nanoparticle colloids in O_2 -saturated 1M H_2SO_4 at a scan rate of 5 mVs^{-1} at 25°C , using RDE. The RDE was rotated at 3000rpm. The Pt loading was $5.6\mu\text{g cm}^{-2}$. At the molar ratio of 1:2, the Nafion-Pt showed lower activity towards ORR than Pt/C. However, with the increase of molar ratio, the electrochemical activity decreased significantly.

Fig 6.14 shows the CVs of Pt/C and Nafion-Pt nanoparticle colloids in 1M H_2SO_4 saturated with nitrogen at 25°C on a RDE. The scan rate was 100mV s^{-1} . In the cyclic voltammograms, the ESA was calculated based on the area under the hydrogen desorption peak and was shown in Table 6.2. At the molar ratio of 1:2, the ESA was estimated to be $3.02\text{cm}^2/\text{cm}^2$, which was much higher than that of Pt/C. However, with the increase of molar ratio, this peak decreased significantly. The ESA was 2.06, 1.35, and $0.53\text{cm}^2/\text{cm}^2$ for Nafion-Pt nanoparticles with the molar ratio of 1:1, 2:1,

and 4:1, respectively. When the molar ratio increased to 8:1, there was no hydrogen desorption peak at all. This indicated that excessive Nafion would retard the diffusion of both hydrogen and oxygen. Therefore, the electrochemical activity decreased significantly with the increase of Nafion/Pt molar ratio.

Fig 6.13 Polarization curves of Pt/C and Nafion-Pt nanoparticles in O_2 -saturated 1M H_2SO_4 under a scan rate of 5 mVs^{-1} at 25°C , using RDE. The RDE was rotated at 3000rpm. The Pt loading was $5.6 \mu\text{g cm}^{-2}$.

Fig 6.14 Cyclic voltammograms of Pt/C and Nafion-Pt nanoparticles in 1M H_2SO_4 saturated with nitrogen at 25°C on a RDE. The scan rate was 100 mV s^{-1} . The Pt loading was $5.6 \mu\text{g cm}^{-2}$.

Table 6.2 ESA for Pt/C and Nafion-Pt with the different molar ratio obtained from CV measurements in 1 M H₂SO₄ and 1 M H₂SO₄ + 0.5M CH₃OH saturated with nitrogen. The platinum loading was 5.6μg cm⁻².

Pt nanoparticles		Pt/C	Nafion/Pt molar ratio				
			1:2	1:1	2:1	4:1	8:1
ESA (cm ² cm ⁻²)	1M H ₂ SO ₄	2.38	3.02	2.06	1.35	0.53	n.a.
	1M H ₂ SO ₄ + 0.5M CH ₃ OH	2.02	1.92	1.66	1.31	0.91	n.a.
SA (m ² g ⁻¹)	1M H ₂ SO ₄	43	54	37	24	9.5	n.a.
	1M H ₂ SO ₄ + 0.5M CH ₃ OH	36	34	30	23	16	n.a.

6.2.6 Oxygen reduction reaction in the presence of methanol

Fig 6.15 shows the polarization curves for ORR on Pt/C and Nafion-Pt in O₂-saturated 1M H₂SO₄ + 0.5M CH₃OH under a scan rate of 5 mVs⁻¹ at 25°C, using RDE. The RDE was rotated at 3000rpm. The Pt loading was 5.6μg cm⁻². Similar to that in the absence of methanol, the electrochemical activity decreased significantly with the increase of the Nafion/Pt molar ratio. However, the respective current densities were much lower in the presence of methanol than those in the absence of methanol.

Fig 6.16 shows the CVs of Pt/C and Nafion-Pt nanoparticle colloids in 1M H₂SO₄ + 0.5M CH₃OH saturated with nitrogen at 25°C on a RDE. The scan rate was 100mV s⁻¹. At the molar ratio of 1:1, the methanol oxidation peak in the forward scan was lower than that for Pt/C. With the increase of molar ratio, this peak decreased significantly until this peak was not observed for Nafion-Pt with the molar ratio higher than 4:1. The peak in the reverse scan showed the similar trend. At the same time, the hydrogen desorption peak also decreased, and the ESA calculated was also shown in Table 6.2. As shown in Table 6.2, the ESA decreased with the increase of the Nafion/Pt molar ratio when measured in 1M H₂SO₄ + 0.5M CH₃OH.

Fig 6.15 Polarization curves of Pt/C and Nafion-Pt nanoparticle colloids in O_2 -saturated $1\text{ M H}_2\text{SO}_4 + 0.5\text{ M CH}_3\text{OH}$ under a scan rate of 5 mVs^{-1} at 25°C , using RDE. The RDE was rotated at 3000 rpm . The Pt loading was $5.6\mu\text{g cm}^{-2}$.

Fig 6.16 Cyclic voltammograms of Pt/C and Nafion-Pt nanoparticle colloids in $1\text{ M H}_2\text{SO}_4 + 0.5\text{ M CH}_3\text{OH}$ saturated with nitrogen at 25°C on a RDE. The scan rate was 100 mV s^{-1} . The Pt loading was $5.6\mu\text{g cm}^{-2}$.

With the increase of the Nafion/Pt molar ratio, the electrochemical activity decreased significantly for ORR in the absence and presence of $0.5\text{ M CH}_3\text{OH}$ as shown in Fig 6.13 and 6.15. At the same time, the ESA decreased significantly until the hydrogen desorption peak could not be detected for the Nafion-Pt with the molar

ratio of 8:1 as shown in Fig 6.14, 6.16 and Table 6.2. This trend was different from that of the specific areas (SA) obtained from XRD measurements. And this was also very different from that for PDDA-Pt nanoparticles. PDDA shows hydrophobic after N atoms coordinated with Pt, and the presence of PDDA did not affect the gas diffusion. However, Nafion showed more hydrophilic although S or O may coordinate with Pt. It is well known that Nafion has been widely used to impregnate the catalyst layer or to mix directly with catalysts to prepare the catalyst ink. However, excessive Nafion would cause additional gas diffusion resistance as reported in half cell and fuel cell testing [Antolini, *et al.*, 1999; Li, *et al.*, 2003; Gode, *et al.*, 2003; Lee, *et al.*, 1998]. Compared with the optimal Nafion content (about 30wt % for Pt/C and 10wt% for Pt black) in the catalyst layer, 80wt% Nafion in the Nafion-Pt with the molar ratio of 1:2 was too high. This inevitably resulted in very high oxygen diffusion resistance. When the molar ratio increased, the gas diffusion resistance also increased significantly. The significant decrease in the activity towards ORR and the ESA indicated that excessive Nafion would retard the diffusion of both hydrogen and oxygen. Therefore, the electrochemical activity decreased significantly.

6.2.7 Methanol oxidation reaction on Nafion-Pt

Fig 6.17 shows the polarization curves for MOR on Nafion-Pt nanoparticles with different molar ratios measured in N₂-saturated 1M H₂SO₄ + 2M CH₃OH at 25°C on a RDE. The RDE was kept static. With the increase of molar ratio, the peak current increased, and the highest current was obtained for the Nafion-Pt with the molar ratio of 1:1. Further increasing the molar ratio resulted in the decrease of the peak current.

Fig 6.17 Cyclic voltammograms of and Nafion-Pt nanoparticles in N_2 -saturated 1M H_2SO_4 + 2M CH_3OH at 25°C on a RDE, (a) single scan at potential range of 0.2 – 1.0 V. The scan rate was 5 $mV s^{-1}$. (b) Cyclic scan between potential range of 0.2 – 1.2 V. The scan rate was 100 $mV s^{-1}$. Pt loading was $56 \mu g cm^{-2}$

In the CVs (Fig 6.17b), there were one anodic peak at around 0.9V in the forwards scan and another anodic peak at around 0.7V in the backward scan. The trend of methanol oxidation peak current in the forward scan with increasing the molar ratio was similar to that in the polarization measurements (Fig 6.17a).

Fig 6.18 shows a time vs current density plot for Pt/C and Nafion-Pt nanoparticles synthesized with different Nafion/Pt molar ratios in N_2 -saturated 1M H_2SO_4 + 2M

CH₃OH. A constant potential of 0.7V was applied for 3600s. The current density gradually decayed with time and the initial current densities for each case were smaller than those from cyclic voltammograms at the same potential in Fig 6.17. However, the trend of the initial current densities was same as that in Fig 6.17, i.e. the current density increased when the Nafion/Pt molar ratio increased from 1:2 to 1:1, and then decreased significantly with further increasing the molar ratio. Compared to Pt/C, the decay in current density was faster at the beginning for all the Nafion-Pt nanoparticles, and much slower afterwards. After 1hr, Pt/C showed much higher current density as compared to that on the Nafion-Pt nanoparticles.

Fig 6.18 Current vs time plot of Pt/C and Nafion-Pt nanoparticles in N₂-saturated 1M H₂SO₄ + 2M CH₃OH at 25°C on a RDE. The applied potential was 0.7V vs SHE. The platinum loading was 56μgcm⁻².

In the case of MOR, Nafion-Pt with the molar ratio of 1:1 showed the best performance (Fig 6.17 and 6.18). The better performance for Nafion-Pt with the molar ratio of 1:1 than that with the molar ratio of 1:2, on the one hand, was due to the reduction of particle size; on the other hand, this indicated that the methanol was more readily diffused through the Nafion around the particles. Methanol diffusion through the Nafion membrane was quite a common issue in DMFC. However, excessive of

Nafion also inhibited the methanol diffusion towards the Pt particles, resulting in the significant decrease in the performance.

6.2.8 Effect of polymer on the electrocatalytic activity

Fig 6.19 shows the polarization curves for ORR on Pt/C and Pt nanoparticles stabilized by different polymers. The measurements were conducted in O₂-saturated 1M H₂SO₄. The RDE was rotated at 3000rpm. The Pt loading was 5.6 μg cm⁻². Among the Pt nanoparticles, PSS-Pt showed better performance at low current densities, but worse performance at high current densities. The current density at 0.7V for the Pt nanoparticles was in the order of Pt/C > PSS-Pt > PDDA-Pt > PVP-Pt > Nafion-Pt.

Fig 6.19 Polarization curves for oxygen reduction reaction on different polymer-Pt nanoparticles in O₂-saturated 1M H₂SO₄. The RDE was rotated at 3000rpm. The scan rate was 5mV s⁻¹. The Pt loading was 5.6 μg cm⁻².

Fig 6.20 shows Tafel curves for ORR on different polymer-Pt nanoparticles. The symbols were the experimental data, and the solid lines were the fitting results for Tafel slopes. Tafel slopes calculated based on Fig 6.20 were shown in Table 6.3.

Fig 6.20 Tafel curves for oxygen reduction reaction on different polymer-Pt nanoparticles in O_2 -saturated 1M H_2SO_4 . The RDE was rotated at 3000rpm. The scan rate was $5mV s^{-1}$. The Pt loading was $5.6 \mu g cm^{-2}$.

Table 6.3 Tafel slopes for oxygen reduction reaction on different polymer-Pt nanoparticles obtained from Fig 6.20

Pt nanoparticles	Nafion-Pt	PDDA-Pt	PVP-Pt	PSS-Pt	Pt/C
Tafel slope (mV/decade)	102	82	132	82	66

As shown in Table 6.3, Tafel slope of ORR on Nafion-Pt was much higher than that of ORR on Pt/C catalyst. The poor performance on Nafion-Pt was most likely due to the severe agglomeration (Fig 6.7c), which led to the smaller active surface area of Pt. On the other hand, excessive Nafion would cause additional oxygen diffusion resistance [Antolini, *et al.*, 1999; Li, *et al.*, 2003; Gode, *et al.*, 2003; Lee, *et al.*, 1998]. PDDA-Pt and PSS-Pt showed similar Tafel slope (82mV/decade) for ORR, but higher than those for ORR on Nafion-Pt and Pt/C. As shown in Fig 6.9, PDDA-Pt and PSS-Pt nanoparticles showed much better dispersion than Nafion-Pt nanoparticles. This corresponded to better performance than that of Nafion-Pt. However, PVP-Pt showed a Tafel slope of 132mV/decade, which was doubled as compared to that of Pt/C. This may be due to the blocking effect of PVP, leading to much worse performance.

Fig 6.21 shows the cyclic voltammograms for Pt/C and Pt nanoparticles stabilized by different polymers measured in N_2 -saturated 1M H_2SO_4 . The RDE was kept under static state. Hydrogen desorption peak was found for all of Pt nanoparticles, but the peak was very small for PVP-Pt nanoparticles. The ESAs obtained from CV were shown in Table 6.4. The ESA was in the order of PDDA-Pt > PSS-Pt > Pt/C > PVP-Pt > Nafion-Pt.

Fig 6.21 Polarization curves for oxygen reduction reaction on different polymer-Pt nanoparticles in N_2 -saturated 1M H_2SO_4 . The RDE was kept under static condition. The scan rate was 100 mV s^{-1} . The Pt loading was $5.6 \mu\text{g cm}^{-2}$.

Table 6.4 ESA for different Pt nanoparticles based on cyclic voltammetry measurements

Pt nanoparticles	Pt/C	Nafion-Pt	PDDA-Pt	PVP-Pt	PSS-Pt
ESA ($\text{cm}^2 \text{cm}^{-2}$)	2.02	0.53	4.02	0.92	2.16

Fig 6.22 shows the polarization curves for ORR on Pt/C and Pt nanoparticles stabilized by different polymers. The measurements were conducted in O_2 -saturated $1 \text{ M } H_2SO_4 + 0.5 \text{ M } CH_3OH$. The RDE was rotated at 3000rpm. The Pt loading was $5.6 \mu\text{g cm}^{-2}$. The performance for the polymer stabilized Pt nanoparticle was in the order of PDDA-Pt > Nafion-Pt $\approx$ PSS-Pt > PVP-Pt. At the same time, a methanol oxidation current peak was clearly found at around 0.8V for Pt/C, but not for the

polymer stabilized Pt nanoparticles. This indicates that polymer has some blocking effect on the methanol oxidation on Pt surface.

Fig 6.22 Polarization curves for oxygen reduction reaction on different polymer-Pt nanoparticles in O_2 -saturated $1M H_2SO_4 + 0.5M CH_3OH$. The RDE was rotated at 3000rpm. The scan rate was $100mV s^{-1}$. The Pt loading was $5.6 \mu g cm^{-2}$.

Fig 6.23 shows the cyclic voltammograms for Pt/C and Pt nanoparticle stabilized by different polymers measured in N_2 -saturated $1MH_2SO_4 + 0.5M CH_3OH$. The RDE was under static condition. As expected, a methanol oxidation peak was observed at about 0.9V for Pt/C. For the polymer stabilized Pt nanoparticles, only PDDA-Pt showed a very small methanol oxidation peak at around 0.8V, and other particles didn't show this peak clearly.

Fig 6.24 shows the polarization curves for MOR on Pt/C and Pt nanoparticles stabilized by different polymers. PSS-Pt showed comparable electrocatalytic activity to Pt/C catalyst. Nafion-Pt and PDDA-Pt showed significant low activity compared with Pt/C catalysis. PVP-Pt showed almost no activity for MOR. This again indicates that different polymers may have different effect on the electrocatalytic activity of Pt nanoparticles for different reactions.

Fig 6.23 Cyclic voltammograms for different polymer-Pt nanoparticles in N_2 -saturated $1M H_2SO_4 + 0.5M CH_3OH$. The RDE was kept under static condition. The scan rate was $100mV s^{-1}$. The Pt loading was $5.6 \mu g cm^{-2}$.

Fig 6.24 Polarization curves for methanol oxidation reaction on different polymer-Pt nanoparticles in O_2 -saturated $1M H_2SO_4 + 2M CH_3OH$. The RDE was kept static. The scan rate was $5mV s^{-1}$. The Pt loading was $56 \mu g cm^{-2}$.

Fig 6.25 shows the cyclic voltammograms for Pt/C and Pt nanoparticles stabilized by different polymers measured in N_2 -saturated $1M H_2SO_4 + 2M CH_3OH$. The RDE was kept under static condition. The Pt loading was $56 \mu g cm^{-2}$. As shown in the figure, all the particles showed two anodic peaks. One was at about 0.9V in the forward scan,

and the other one was at about 0.7V in the backward scan. However, the peak current was very different for these Pt nanoparticles. PSS-Pt showed comparable peak current in the forward scan to Pt/C catalysts. PDDA-Pt and Nafion-Pt showed similar peak current, but much lower than those of PSS-Pt and Pt/C. PVP-Pt showed the lowest peak current, which was 10 times lower than that of Pt/C.

Fig 6.25 Cyclic voltammograms for Pt/C and Pt nanoparticles stabilized by different polymers measured in N_2 -saturated $1\text{M H}_2\text{SO}_4 + 2\text{M CH}_3\text{OH}$. The RDE was kept under static condition. The scan rate was 100mVs^{-1} . The Pt loading was $56\mu\text{gcm}^{-2}$.

Fig 6.26 shows the current density vs time plot for Pt/C and Pt nanoparticles synthesized in the presence of different polymers in N_2 -saturated $1\text{M H}_2\text{SO}_4 + 2\text{M CH}_3\text{OH}$. A constant potential of 0.7V was applied for 3600s. The trend of the initial current for Pt nanoparticles was generally consistent with that in polarization curves (Fig 6.23) and cyclic voltammograms (Fig 6.24). It was found that the current density degraded rapidly initially for all these Pt nanoparticles. Then the current density degraded gradually until a relative stable state was reached. However, it was relatively fast for Pt/C catalyst, and was quite slow for Pt nanoparticles protected by polymers. Comparatively, PSS-Pt showed the most stable performance. Nafion-Pt showed the worst performance. PDDA-Pt and PVP-Pt showed the comparable performance.

Fig 6.26 Current vs time plot of Pt/C and Nafion-Pt nanoparticles in N_2 -saturated 1M H_2SO_4 + 2M CH_3OH at 25°C on a RDE. The applied potential was 0.7V vs SHE. The platinum loading was $56\mu gcm^{-2}$.

As shown in Fig 6.19~6.26, polymer has a significant effect on the electrocatalytic activity of Pt nanoparticles. Fig 6.27 shows the comparison of the current densities for ORR in the absence and presence of methanol and MOR on different polymer stabilized Pt nanoparticles.

Fig 6.27 The current densities for ORR at 0.6V (1) in the absence and (2) in the presence of methanol and (3) MOR at 0.7V and (4) MOR at 0.7V after 1hrs on different polymer stabilized Pt nanoparticles

Among the polymer-stabilized Pt nanoparticles, PDDA-Pt and PSS-Pt show higher catalytic activity for ORR in the absence of methanol. However, it was very different for ORR in the presence of methanol. PDDA-Pt showed much higher current density than that for PSS-Pt. On the contrary, current density for MOR was much higher for PSS-Pt than that on PDDA-Pt. Although the current density decayed with the time, the current density for MOR on PSS-Pt was 3 times higher than that of PDDA-Pt. This indicates that PDDA-Pt is not very active for MOR, resulting in relatively high activity for ORR in the presence of methanol. As discussed in Chapter 5, PDDA-Pt may be a potential methanol resistant cathode catalyst for DMFCs. In the case of PSS-Pt, it was very active for both ORR and MOR, thus leading to very poor performance for ORR in the presence of methanol. This was due to the chemical reaction between methanol and oxygen occurred directly on Pt nanoparticles [Drillet, *et al.*, 2002; Jiang, *et al.*, 2000]. In contrast to the extensive literatures on the studies of electronically conjugated conducting polymers (e.g., polyaniline, polypyrrole, polythiophene, and their substitutes) on various electrode substrates, there was little information on the Pt-electrolytes interaction and the effect of the polyelectrolyte stabilizers on the electrocatalytic activity and selectivity of Pt nanoparticles [Lyons, *et al.*, 1994; Yang, *et al.*, 2006]. Polyelectrolytes in the present study were not electronic conductors. However, the ionic functional groups in the polyelectrolytes may not be completely neutral to the electrochemically activity and selectivity of the Pt nanoparticles. As shown by Modrow *et al.* [2003], even a small change in the protection ligand shell can lead to varying electronic properties of the metal core as seen with N(alkyl)4Cl-stabilized Co nanoparticles. The high electrocatalytic activities of PDDA-Pt and PSS-Pt imply that the NH_4^+ end groups in PDDA and SO_3^- end groups in PSS would facilitate the reaction species transfer for both MOR and ORR.

This appears to be supported by the low electrocatalytic activity of Pt nanoparticles stabilized by PVP without the end groups NH_4^+ or SO_3^- in the polymeric chain structure. Deivaraj et al. [2005] also studied the PVP-protected Pt nanoparticles, which was not catalytically active. However, no details were reported. This indicates that PVP has a significant shielding effect on the catalytic activity of Pt nanoparticles for ORR and MOR. The relatively low catalytic activity of Nafion-Pt was mainly due to the severe agglomeration and the diffusion resistance caused by excess Nafion.

Different polymer-stabilized Pt nanoparticles showed different catalytic activity for different reactions, indicating that the polymers may attach different selectivity to Pt nanoparticles. However, the polymer may cover part of the active surface of Pt nanoparticles, thus showing not as good performance as that Pt/C catalyst. On the other hand, the existence of polymer can reduce the poison effect and improve the stability of activity for MOR on polymer-stabilized Pt nanoparticles. It is necessary to further investigate the polymer effects on the catalytic activity of Pt nanoparticles and the interesting results would be expected.

6.3 Summary

Polymer stabilized Pt nanoparticles were synthesized by the alcoholic reduction of the H_2PtCl_6 in ethanol/water system in the presence of Nafion. They showed considerable crystallinity and fcc structure. The weak coordination of S or O atoms from Nafion to Pt was confirmed by the combined use of UV-visible and X-ray photoelectron spectroscopy. Different from PDDA-Pt nanoparticles, the agglomerates were observed for all the Nafion-Pt nanoparticles synthesized under the conditions investigated. This indicates that Nafion cannot prevent agglomeration of platinum nanoparticles.

Generally, Nafion-Pt showed the decrease in the activity towards both ORR and MOR with increasing the molar ratio. This was due to the additional diffusion resistance caused by the excess of Nafion.

For the purpose of comparison, PSS and PVP stabilized Pt nanoparticles were synthesized. PVP and PSS can give better dispersion of Pt nanoparticles. The electrochemical characterization showed that different polymer-stabilized Pt nanoparticles had different catalytic activity. PDDA-Pt nanoparticles showed higher activity for ORR with and without addition of methanol, but lower activity for MOR. This indicates that PDDA-Pt nanoparticles may be a potential methanol resistant catalyst. PSS-Pt nanoparticles showed high catalytic activity for ORR without addition of methanol and for MOR, but low activity for ORR with addition of methanol. PVP-Pt nanoparticles gave the lowest catalytic activity for both ORR and MOR. This indicates that neutral polymers such as PVP have significant blocking effect on the electrocatalytic activity of Pt nanoparticles as compared to that of polyelectrolytes. The results also demonstrate that different polymers may exhibit different selectivity of electrocatalytic activity of Pt nanoparticles for electrode reactions in low temperature fuel cells.

CHAPTER 7 Self-Assembled PDDA-Pt/Nafion Interface

In this chapter, the self-assembled monolayer (SAM) of PDDA-Pt nanoparticles was prepared on the surface of Nafion membrane. The distribution of PDDA-Pt nanoparticles and the electrochemical behaviors of the SAM of PDDA-Pt/Nafion interface were characterized.

7.1 Experimental

For the preparation of self-assembled membrane electrodes, the membrane was allowed to float on the surface of PDDA-Pt colloid solution or immersed in the solution for 24 h for the self-assembly process. The membrane was rinsed with deionized water. As-prepared membrane was hotpressed with one or two pieces of carbon paper with gas diffusion layer on it at 140°C and 4MPa, for 90s.

The distribution of PDDA-Pt self-assembled on the surface of Nafion membrane was characterized by TEM. The composition was obtained using EDS. The electrochemical characterization of self-assembled membrane electrodes was conducted in a half-cell fixture (Fig 3.3) using Autolab potentiostat. Polarization curves were obtained in 1M H₂SO₄ at 25°C by scanning the potential from open circuit potential to 0.1V vs SHE. Cyclic voltammetry was carried out in 1M H₂SO₄ purged with nitrogen. Impedance responses were obtained under dc bias with signal amplitude of 10mV in the frequency range of 100kHz to 0.01Hz. All the potentials were reported vs SHE. To measure the cell performance of MEAs made with PDDA-

Pt nanoparticles self-assembled membranes, the potential was scanned from open circuit voltage to 0.1 V.

7.2 Results and Discussion

7.2.1 TEM images of self-assembled nanoparticles

The self-assembly of the positively charged PDDA-Pt nanoparticles on Nafion was examined by TEM using copper grid with carbon film cast with a thin Nafion film (Fig 7.1). In the case of PDDA-Pt nanoparticles prepared with PDDA:Pt = 1:1, the distribution of the self-assembled PDDA-Pt nanoparticles was not uniform and was characterized by agglomerates (Fig 7.1a). This was due to the original PDDA-Pt nanoparticle agglomerates in the colloidal solution (Fig 5.3a). In the case of PDDA-Pt nanoparticle colloids prepared with the PDDA:Pt = 5:1, the distribution of the self-assembled Pt nanoparticles on Nafion film was uniform most likely due to the well-dispersed PDDA-Pt nanoparticle colloidal solution (Fig 7.1b). Based on the TEM image (Fig 7.1b), it was estimated that there were about 3×10^{12} platinum nanoparticles per square centimeter. The loading was estimated to be $\sim 1.13 \mu\text{gcm}^{-2}$ based on the average diameter from XRD measurements (Table 5.1) and this corresponded to $\sim 33\%$ coverage on the Nafion surface. As the PDDA/Pt ratio increased to 15:1, the density of the self-assembly of the PDDA-Pt nanoparticles onto the Nafion surface decreased significantly (Fig 7.1c). The density of the self-assembled PDDA-Pt nanoparticles was $\sim 7.8 \times 10^{11} \text{ cm}^{-2}$. This corresponded to a Pt loading of $\sim 0.19 \mu\text{gcm}^{-2}$ and 6% coverage of Pt nanoparticles on the Nafion membrane surface. This indicates that the self-assembly of the PDDA-Pt nanoparticle colloids only covers part of the Nafion membrane surface and this may be due to the

competing adsorption between the PDDA-Pt nanoparticles and free PDDAs in the colloidal solution.

Fig 7.1 TEM images of the self-assembled PDDA-Pt nanoparticle colloids on the thin Nafion film cast on the copper grid. The PDDA-Pt nanoparticle colloids were synthesized with (a) PDDA:Pt = 1:1, (b) PDDA:Pt = 5:1 and (c) PDDA:Pt = 15:1.

7.2.2 EDS analysis of self-assembled nanoparticles

Fig 7.2 shows the EDS spectrum for PDDA-Pt nanoparticles self-assembled on Nafion thin film. The strong signals were observed for C, F, S, Pt and Cu. F and S were from Nafion cast on the copper grid. C was from Nafion and PDDA. Cu was

from copper grid. The atomic compositions and the atomic ratio of S/Pt were shown in Table 7.1. As shown in Table 7.1, with the increase of PDDA/Pt molar ratio, Pt content decreased significantly, and the atomic ratio of S/Pt increased. This indicates that the molar ratio affects the density of PDDA-Pt nanoparticles self-assembled on the Nafion thin film.

Fig 7.2 EDS spectrum for PDDA-Pt nanoparticles self-assembled on Nafion thin film. PDDA:Pt =5:1

Table 7.1 Atomic compositions and atomic ratio of S/Pt for PDDA-Pt nanoparticles self-assembled on copper grid precoated with Nafion

PDDA/Pt molar ratio in colloids	C	F	S	Cu	Pt	S/Pt
1:1	54.82	33.45	0.61	10.02	1.11	0.55
3:1	69.74	19.03	2.15	8.72	0.36	5.97
5:1	56.97	35.01	1.07	6.86	0.09	11.9
8:1	59.77	33.58	1.44	5.15	0.06	24.0
15:1	57.16	33.95	1.74	7.12	0.03	58.0

7.2.3 PDDA-Pt/Nafion interface

Figure 7.3 shows cyclic voltammograms of the membrane electrodes prepared by the self-assembly of PDDA-Pt nanoparticles in 1M H₂SO₄ saturated with N₂ at 25°C.

The scanning rate was 100mV s^{-1} . The hydrogen desorption peak around $0\sim 0.4\text{ V}$ was not observed for all the membrane electrodes studied. This hydrogen desorption peak was generally used to estimate the electrochemical surface area of the platinum catalyst [Poizo, *et al.*, 2002]. The disappearance of the hydrogen desorption peak for the self-assembled PDDA-Pt nanoparticles electrodes may be due to the very low platinum loading. However, it was observed that hydrogen evolution current decreased with the increase of molar ratio of PDDA to Pt and highest hydrogen evolution current was observed for the self-assembled electrode with PDDA:Pt = 1:1. As shown in Fig 5.3a, the morphology of the PDDA-Pt nanoparticles prepared in the PDDA to Pt ratio of 1:1 was characterized by the agglomeration.

Fig 7.3 Cyclic voltammograms of the membrane electrodes prepared by the self-assembly of PDDA-Pt nanoparticles with various PDDA to Pt ratios in $1\text{M H}_2\text{SO}_4$ saturated with N_2 at 25°C . The scanning rate was 100mV s^{-1} .

Figure 7.4 shows the polarization behavior of self-assembled PDDA-Pt nanoparticles membrane electrodes prepared in the presence of different molar ratios of PDDA to Pt. The polarization curves were measured in $1\text{M H}_2\text{SO}_4$ saturated with O_2 at 25°C under scanning rate of 5mVs^{-1} . It was found that the best performance was

obtained for the membrane electrode self-assembled in the PDDA-Pt colloid solution with the molar ratio PDDA /Pt 1:1. At 0.4V, the polarization current was 3.8 mAcm^{-2} . When the PDDA to Pt molar ratio increased to 3:1, the current density decreased to 1 mAcm^{-2} , a reduction in the current density by 74% as compared to the self-assembled electrode with PDDA:Pt = 1:1. However, with the further increase in the PDDA to Pt ratio, the decrease in the polarization performance is very small.

Fig 7.4 Polarization curves of self-assembled PDDA-Pt nanoparticles membrane electrodes prepared in the presence of different molar ratios of PDDA to Pt. The curves were measured in 1M H_2SO_4 saturated with O_2 at 25°C under scanning rate of 5 mVs^{-1} .

Figure 7.5 shows the impedance curves for the O_2 reduction on the self-assembled PDDA-Pt nanoparticles membrane electrodes prepared with different molar ratios of PDDA to Pt. The curves were measured in 1M H_2SO_4 saturated with O_2 at 0.3V. The impedance responses for ORR in H_2SO_4 were characterized by an almost perfect semicircle and thus were fitted using a simple R(RC) circuit inset in Fig 7.5. The fitting results were shown in Table 7.2.

Fig 7.5 Impedance behavior for the O_2 reduction on the self-assembled PDDA-Pt nanoparticles membrane electrodes prepared with different molar ratios of PDDA to Pt. The curves were measured in 1M H_2SO_4 saturated with O_2 at 0.3V (i.e., under dc bias of 0.6 V). Symbols are the measured results and lines are the fitted results. Numbers are frequencies in Hz. The inset graph is the equivalent circuit for the fitting.

Table 7.2 Fitting results of EIS in Fig 7.5

PDDA/Pt Molar Ratio in colloids	1:1	3:1	5:1	8:1	15:1
R_p (Ωcm^2)	69.9	109.5	128.5	135.3	135.2
C (F/ cm^2)	0.0183	0.0147	0.0140	0.0142	0.0135

The results showed that the electrode polarization resistance (R_p) increased significantly with the increase of the PDDA/Pt molar ratio from 1:1 to 3:1. With the molar ratio higher than 3:1, the change in R_p was relatively small. This was consistent with that of the polarization results. In general, the capacitance (C) decreased with the increase of the PDDA/Pt molar ratio. It is known that C is an indication of the electrochemically active surface area of Pt. The increase in R_p was mainly due to the decrease in the Pt loading, which was also confirmed by TEM images.

Fig 7.6 is the impedance of the membrane electrode self-assembled in the PDDA-Pt colloid solution with PDDA:Pt=1:1, measured under different dc bias. The

impedance arc decreased significantly with the increase of cathodic dc bias. This suggests that oxygen reduction reaction on the self-assembled membrane electrode could be controlled by the charge transfer process.

Fig 7.6 Impedance curves of the membrane electrode self-assembled in the PDDA-Pt colloid solution with PDDA:Pt=1:1, measured under different dc bias.

The self-assembled Pt nanoparticles electrode/membrane interface showed significant electrocatalytic activity for the ORR in polymer electrolyte fuel cells and the electrocatalytic activity of the self-assembled electrode/Nafion membrane depended strongly on the morphology of the PDDA-Pt nanoparticles assembled. This was in turn related to the PDDA to Pt ratio during the alcoholic reduction of the PtCl_6^{2-} ions. As shown in this study, the self-assembled electrode/membrane with PDDA to Pt molar ratio of 1:1 showed the lowest electrode polarization resistance and high polarization performance. On the other hand, the PDDA-Pt nanoparticles prepared with the molar ratio of 1:1 showed the distinct agglomeration of nanoparticles while with the increase of the molar ratios, the agglomeration decreased significantly (Fig 5.3). This indicates that appropriate agglomeration of PDDA-Pt nanoparticles can be beneficial for the self-assembled electrode/Nafion membrane

interface. In the case of PDDA-Pt nanoparticle prepared with molar ratio of 1:1, the self-assembly would be taking place between the PDDA-Pt nanoparticle agglomerates and the sulfonic acid group, SO_3^- , on the Nafion membrane while in the case of well-dispersed PDDA-Pt nanoparticles the interaction would be between well-dispersed individual PDDA-Pt nanoparticles and the SO_3^- sites at the membrane surface.

Fig 7.7 Schematic diagram of the self-assembly process of (a) the PDDA-Pt nanoparticles and (b) the PDDA-Pt nanoparticle agglomerates to the Nafion surface.

Fig 7.7 shows schematically the self-assembly process of the PDDA-Pt nanoparticle and nanoparticle agglomerates. As the sulfonic acid groups on the Nafion surface was limited, appropriate agglomeration could increase the loading and coverage of the Pt nanoparticles on the Nafion membrane surface. This explained the high performance and activity of the self-assembled Nafion membrane interface for the agglomerated PDDA-Pt nanopartilces. With the increase of the molar ratio, well-dispersed and distributed PDDA-Pt nanoparticles were observed. This demonstrates that dispersion of PDDA-Pt nanoparticles can be controlled by the PDDA to Pt molar ratio.

7.2.4 Cell performance of self-assembled MEA

Fig 7.8 shows the cell performance of self-assembled PDDA-Pt/N1135/PDDA-Pt MEA. The MEAs were made with PDDA-Pt nanoparticle colloidal solutions with the molar ratio of 1:1 and 5:1. The measurements were conducted under H_2/O_2 at 30°C .

Fig 7.8 Cell performance of MEA self-assembled by PDDA-Pt nanoparticles with different PDDA/Pt molar ratio. The Cell was fed with H₂/O₂ and operated at 30°C.

As shown in Fig 7.8, there was substantial reduction in the current density at the early stage of polarization. The rapid reduction in the cell performance is consistent with that of the ORR on the self-assembled Pt- PDDA electrode (Fig 7.4). This showed that the rapid reduction in the cell performance was most likely due to the limiting step of the ORR on the cathode side. Similar to the half-cell testing, MEA made with the PDDA-Pt nanoparticle agglomerates gave much higher performance than that with the well-dispersed PDDA-Pt nanoparticles. The maximum power outputs were 5.4 and 2.1 mWcm⁻² for the MEA made with the PDDA-Pt nanoparticle agglomerates and the well-dispersed PDDA-Pt nanoparticles, respectively. Based on the Pt loading (1.1μgcm⁻²) estimated from Fig 7.1b, the power output of the self-assembled MEA was 955W per g_{Pt}. O'Hayre et al. [2002] prepared a MEA with Pt loading of 40 μg cm⁻² using sputtering deposition technique and the power density achieved was 33 mW cm⁻² under H₂/O₂. This gave the power output of 825 W per g_{Pt}, which was slightly lower than the performance of our self-assembled MEA.

7.3 Summary

Positively charged PDDA-Pt nanoparticles can be self-assembled onto the surface of Nafion membrane to form electrocatalytic active membrane interface. The activity of the self-assembled PDDA-Pt nanoparticle electrode/Nafion membrane interface depended on the morphology and agglomeration of the PDDA-Pt nanoparticles, which in turn were related to the molar ratio of PDDA to Pt during the reduction of the PtCl_6^{2-} ions in the ethanol/water solution. The highest activity of the self-assembled membrane interface was obtained on agglomerated PDDA-Pt nanoparticles which was prepared with PDDA to Pt molar ratio of 1:1. Increase of the molar ratio increased the dispersion and distribution of the PDDA-Pt nanoparticles, but decreased the electrochemical activity of the self-assembled interface. This showed that appropriate agglomeration of the PDDA-Pt nanoparticles would be beneficial to the self-assembled electrode/Nafion membrane interface. However, the well-dispersed PDDA-Pt nanoparticles would give a uniform self-assembled monolayer on the membrane surface.

MEA with Pt loading of $1.1\mu\text{g cm}^{-2}$ achieved a power output of 2.1 mW cm^{-2} under H_2/O_2 at room temperatures. The comparable performance of the self-assembled MEA as to that prepared by sputtering [O'Hayre, *et al.*, 2002] despite the preliminary nature of the present study demonstrated the feasibility of the self-assembly technology in the development of polymer electrolyte fuel cell.

The self-assembly monolayer (SAM) structure of the Pt nanoparticles on the membrane surface would be close to the ideal tripe phase structure at the Pt catalyst and Nafion membrane interface. Such ideal electrode/electrolyte interfacial structure without the complications associated with gas diffusion and proton transportation in

conventional multi-layered MEA structure provides a potentially powerful tool in the fundamental study of the electrochemical and catalytic processes in PEFC.

CHAPTER 8 Self-assembly Monolayer of PDDA-Pt Nanoparticles for Direct Methanol Fuel Cells

In this chapter, the self-assembly monolayer by the PDDA-Pt/Nafion membrane was used to reduce the methanol crossover through the Nafion membrane. The cell performance for DMFCs was presented based on the self-assembled Nafion membrane.

8.1 Experimental details

For the preparation of self-assembly monolayer of PDDA-Pt nanoparticle colloids on Nafion membrane, the membrane was immersed in the PDDA-Pt nanoparticle colloid solution. Compositions of the self-assembled PDDA-Pt nanoparticles on the surface of Nafion were examined using XPS (ESCA spectrometer).

To evaluate the methanol crossover and the cell performance, the membrane-electrode-assembly (MEA) was made by sandwiching the SAM/Nafion/SAM membrane between a Pt/Ru anode and a Pt/C cathode. The overall cell resistance was also measured by electrochemical impedance technique (Autolab PGSTAT 30) at 30°C.

8.2 Results and Discussions

8.2.1 XPS analysis of PDDA-Pt nanoparticles self-assembled Nafion membrane

Fig 8.1 shows the survey scan of the XPS for PDDA-Pt nanoparticles self-assembled Nafion membrane. In addition to the very strong signals of F_{1s}, O_{1s}, C_{1s} and Pt_{4f}, the signals of N_{1s} and S_{2p} were also observed. The inset graph shows the XPS of N_{1s}. The elements of F and S are from Nafion membrane. Pt and N were from the self-assembled PDDA-Pt. These observations indicate that the PDDA-Pt nanoparticles are indeed self-assembled onto the surface of Nafion membrane. It is known that the drive for the self-assembly process is the electrostatic attraction between the positively charged PDDA-Pt and the negatively charged SO₃⁻ on the Nafion membrane surface. Once the sites of SO₃⁻ were occupied by PDDA-Pt nanoparticles, no more particles were allowed to be self-assembled. As shown in Fig 7.1, the self-assembled layer was a monolayer. The atomic compositions obtained from XPS analysis were shown in Table 8.1. Increasing the molar ratio of PDDA/Pt resulted in the decrease in the atomic content of Pt and the increase in the S/Pt atomic ratio. Since the atomic content of S was fixed in the Nafion membrane, the increase in the atomic ratio of S/Pt indicated the decrease in the amounts of self-assembled Pt particles on the surface of Nafion membrane. At the same time, the atomic ratio of N/Pt increased with increasing the nominal PDDA/Pt molar ratio. At the molar ratio of 1:1, the atomic ratio of N/Pt was 1.48, even higher than the nominal molar ratio of PDDA/Pt. When the molar ratio increased up to 15:1, the atomic ratio of N/Pt increased 8.95, but still smaller than the nominal values. From the observations on TEM images in Fig 7.1, the free PDDA can also be self-assembled on the surface of Nafion membrane. This

indicates that there is competitive self-assembly between the free PDDA and the coordinated PDDA.

Fig 8.1 A typical XPS spectrum for PDDA-Pt nanoparticles self-assembled Nafion membrane

Table 8.1 Atomic compositions for PDDA-Pt nanoparticles with various molar ratios self-assembled Nafion membrane

PDDA/Pt Molar ratio	C	F	O	S	N	Pt	S/Pt	N/Pt
1:1	39.02	45.23	11.08	1.5	1.89	1.28	1.17	1.48
3:1	45.57	38.55	12.36	1.52	1.32	0.69	2.20	1.91
5:1	37.3	48.13	10.03	1.26	2.33	0.55	2.29	4.24
8:1	50.99	34.61	11.44	1.25	1.47	0.25	5.00	5.88
15:1	43.67	42.31	10.68	1.25	1.88	0.21	5.95	8.95

8.2.2 Methanol crossover current measurement

Figure 8.2 is the methanol crossover current curves in a membrane electrode assembly (MEA) with the self-assembled PDDA-Pt nanoparticles/N-1135 membrane as a function of self-assembly time. The molar ratio of PDDA/Pt was 5:1. The measurement was carried out at 30°C. In comparison, the methanol crossover current curve with an unmodified N-1135 membrane was also shown in the figure. The

limiting current of the methanol crossover with unmodified N-1135 membranes was 109 mA cm^{-2} . After assembling for only 0.5hr, the limiting current of the methanol crossover decreased to 96 mA cm^{-2} . This indicates that the self-assembly process is very fast and the self-assembled PDDA-Pt reduces the methanol crossover. When the assembling time increased up to 24hr, the limiting current decreased again to 93 mA cm^{-2} . The limiting current didn't change much with the further increase in the assembly time.

Fig 8.2 Methanol crossover current curves in a membrane-electrode-assembly (MEA) with the self-assembly monolayer of PDDA-Pt nanoparticles on N-1135 membrane as a function of self-assembly time. The measurements were carried out at 30°C.

Figure 8.3 is the methanol crossover current curves in a MEA with the self-assembled PDDA-Pt nanoparticles/N-1135 membrane at 30 °C as a function of PDDA/Pt molar ratio. The assembly time was 24hr. After the modification with self-assembly monolayer of PDDA-Pt nanoparticles synthesized with various PDDA/Pt ratios, the limiting current was in the range of 88 to 95 mA cm^{-2} . This indicates the reduction of methanol crossover of the Nafion membrane by 12 to 19% on the self-assembly monolayer modified N-1135 membrane. The well-dispersed PDDA-Pt nanoparticle colloids synthesized with PDDA/Pt ratio higher than 1:1 showed in

general higher blocking effect than that of the agglomerated PDDA-Pt nanoparticle colloids synthesized with PDDA:Pt = 1:1. The reduction in the methanol crossover current demonstrates the potential of the efficient blocking of the methanol crossover by the self-assembly of the positively charged PDDA-Pt nanoparticles.

Fig 8.3 Methanol crossover current curves in a membrane-electrode-assembly (MEA) with the self-assembly monolayer of PDDA-Pt nanoparticles on N-1135 membrane at 30°C as a function of PDDA/Pt molar ratio.

8.2.3 Cell performance

The blocking of the methanol by the self-assembly of PDDA-Pt nanoparticle colloids was also supported by the increase in the open circuit potential (OCP) of the DMFC. Fig 8.4 shows the polarization curves and the power output DMFC using the pure N1135 membrane the modified N1135 membranes. The OCP was measured at 30°C with 2M CH₃OH on the anode side and oxygen with 10 psi back pressure on the cathode side. For the cell prepared from original N-1135, the OCP was 0.540 V at 30°C. For the cell with the modified membranes, the increase in the OCP was in the range of 5~34mV. Although the increase was very small, the power output increased significantly. The maximum power output was 36~40mW, an increase of 24~38%.

When the assembly time increased up to 24hr, the maximum power output increased up to 39mW. The open circuit potential, the limiting methanol crossover current and the maximum power density of the DMFC based on the un-modified and modified N-1135 membrane were summarized in Table 8.2.

Fig 8.4 Polarization curves and power output of DMFC using pure N-1135 membrane and self-assembly monolayer of PDDA-Pt nanoparticles on N-1135 membrane measured at 30°C.

Table 8.2 Open circuit potential, methanol crossover limiting current and maximum power density of DMFC prepared by un-modified N-1135 and N-1135 modified by the self-assembly monolayer of PDDA-Pt nanoparticles at 30°C.

Assembly time (hr)	0	0.5	2	24
Open circuit potential / V	0.540	0.545	0.567	0.574
Limiting CH ₃ OH crossover current / mAcm ⁻²	109	96	97	93
Maximum power density / mWcm ⁻²	29	36	37	39

Fig 8.5 shows the polarization curves and power output of DMFC using the modified N1135 membrane as a function of the PDDA/Pt molar ratio. The assembly time was 24hr. The measurement was carried out at 30°C. For the cell with modified N-1135 membrane, the increase in the OCP was in the range of 10 to 39 mV with highest OCP (0.579 V) observed for cell with the N-1135 membrane modified by the self-assembly of PDDA-Pt nanoparticles synthesized with PDDA:Pt = 3:1.

Nevertheless, the increase in the OCP was small. This may be due to the fact that the coverage by the self-assembled PDDA-Pt nanoparticle colloids on the Nafion membrane is low (33%).

Fig 8.5 Polarization curves and power output of DMFC using pure N-1135 membrane and self-assembly monolayer of PDDA-Pt nanoparticles on N-1135 membrane measured at 30°C.

However, the enhancement in the performance of the DMFC based on the self-assembly monolayer of PDDA-Pt nanoparticle colloids was encouraging. The DMFC based on the modified N-1135 membrane clearly showed higher cell performance as compared to the cell prepared with the original N-1135 membrane. The best performance was obtained on the N-1135 modified by the self-assembly of PDDA-Pt nanoparticle colloids synthesized with PDDA/Pt ratio of 3:1. The maximum power output of the best cell with the self-assembled PDDA-Pt nanoparticles/N-1135 membrane was 39 mWcm^{-2} , which was 34% higher than 29 mWcm^{-2} of the cell with the unmodified N-1135 membrane. The resistance of the cell with the N-1135 membrane modified by the self-assembly of PDDA-Pt nanoparticles was $\sim 0.218 \Omega\text{cm}^2$, which was also close to $\sim 0.206 \Omega\text{cm}^2$ for the cell with the N-1135 membrane without modification. The improvement in the cell performance agreed well with the

enhanced methanol crossover resistance of the self-assembled PDDA-Pt nanoparticles/N-1135 membrane, as shown in Fig 8.3. The open circuit potential, the limiting methanol crossover current and the maximum power density of the DMFC based on the un-modified and modified N-1135 membrane were summarized in Table 8.3.

Table 8.3 Open circuit potential, methanol crossover limiting current and maximum power density of DMFC prepared by un-modified N-1135 and N-1135 modified by the self-assembly monolayer of PDDA-Pt nanoparticles at 30°C.

Membrane	N-1135	Modified N-1135				
PDDA:Pt ratio	n.a.	1:1	3:1	5:1	8:1	15:1
Open circuit potential / V	0.545	0.550	0.579	0.574	0.570	0.573
Limiting methanol crossover current / mAcm ⁻²	109	95	88	93	92	87
Maximum power density / mWcm ⁻²	29	36	39	39	38	37

Preparation of metallic nanoparticles via alcoholic reduction in the presence of surfactant or polymer stabilizers is well known in the areas of electrocatalysis and catalysis [Liu, *et al.*, 2004; Boennemann, *et al.*, 2000; Wei, *et al.*, 2004; Wang, *et al.*, 2002; Adlim, *et al.*, 2004]. Unlike the nanoparticles stabilized by neutral polymers such as poly(vinylpyrrolidone) (PVP) and chitosan, the metallic nanoparticles stabilized by the ionic polymer had unique advantages of the self-assembly capability. In the case of PDDA-Pt nanoparticles, the positively charged PDDA-Pt nanoparticle colloids can be self-assembled to the negatively charged sulfonic acid group, SO₃⁻, on the surface of the Nafion membrane. As the self-assembly process in this case was most likely governed by the electrostatic interaction, the surface charge density of the substrate and orientation and morphology of the charged nanoparticles were crucial for the formation of self-assembly monolayer (SAM). As the sulfonic acid groups (i.e.,

the charge density) on the Nafion surface was primarily determined by the molecular weight of the Nafion membrane, the monolayer construction would be mainly controlled by the dispersion and size of the PDDA-Pt nanoparticle colloids. As PDDA was a strong polycation [Kim, *et al.*, 2004d], the self-assembly of PDDA-Pt nanoparticle colloids would be a competitive process with the self-assembly of free PDDA molecules in the colloidal solution. With the self-assembly of positively-charged PDDA-Pt nanoparticles and PDDA molecules, the charge inversion could take place on the Nafion surface. Hence further adsorption or self-assembly of PDDA-Pt and PDDA molecules could be inhibited. This appeared to be supported by the TEM observation of the distribution of the PDDA-Pt nanoparticles self-assembled on Nafion film cast Cu grid (Fig 7.1). Figure 8.6 shows schematically the self-assembly process of the PDDA-Pt nanoparticle colloids and PDDA molecules.

The competitive self-assembly of PDDA-Pt and PDDA could be one of the reasons of the low coverage of PDDA-Pt nanoparticles on Nafion membrane (6 - 33%). However, the similar methanol crossover current and cell performance of DMFC based on the SAM modified Nafion membrane with PDDA-Pt nanoparticle colloids synthesized with various PDDA/Pt ratios indicate that self-assembled PDDA molecules could also be effective in the inhibiting of the methanol crossover. The maximum power output of the best cell with the self-assembled PDDA-Pt nanoparticles/N-1135 membrane was 39 mWcm^{-2} , which was 34% higher than 29 mWcm^{-2} of the cell with the unmodified N-1135 membrane even though the loading of the self-assembled Pt nanoparticles was very low ($\sim 1.13 \text{ } \mu\text{gcm}^{-2}$). Most important, the self-assembled PDDA-Pt nanoparticle colloids had little adverse effect on the proton conductivity of the Nafion membrane, a significant advantage as compared to the hybrid or composite modification approaches [Jia, *et al.*, 2000; Miyake, *et al.*,

2001; Yang, *et al.*, 2001; Tricoli, *et al.*, 1998; Pu, *et al.*, 1995; Kim, *et al.*, 2004a; Kim, *et al.*, 2004b; Shao, *et al.*, 2002]. Nevertheless, significant amount of work is still needed to optimize the self-assembly process of the PDDA-Pt nanoparticle colloids and to understand the effect of the self-assembly of PDDA-Pt nanoparticles on the proton conductivity and catalytic activity for the methanol oxidation reaction.

Fig 8.6 Schematic diagram of the self-assembly process between the Nafion membrane and the PDDA-Pt nanoparticle colloidal solution.

8.3 Summary

It was found that the positively charged PDDA-Pt nanoparticles are self-assembled to the sulfonic acid group, SO_3^- , on the Nafion membrane surface by electrostatic interaction. With the increase of PDDA/Pt molar ratio in the PDDA-Pt nanoparticle colloids, the amount of Pt nanoparticles self-assembled on the Nafion membrane decreased due to the competitive self-assembly of free PDDA.

The electrochemical functionality of the self-assembled PDDA-Pt nanoparticle colloids on Nafion membrane was investigated for the blocking of methanol crossover in DMFC. The present study showed that self-assembled PDDA-Pt nanoparticles significantly reduced the methanol crossover and enhanced the power output of direct

methanol fuel cells by as much as 34% as compared to the DMFC based on unmodified Nafion membrane. The self-assembled PDDA-Pt nanoparticle colloids on Nafion membrane show great potential in the development of high performance DMFC.

CHAPTER 9 Layer-by-Layer Self-Assembly of Polyelectrolyte for DMFCs

In chapter 8, the self-assembled monolayer (SAM) of PDDA-Pt nanoparticles is shown to reduce the methanol crossover through the Nafion membrane. However, the distribution of PDDA-Pt nanoparticles depends on the dispersion PDDA-Pt nanoparticles and the PDDA/Pt molar ratio in colloidal solution. The competitive self-assembly of PDDA-Pt and the free PDDA could be one of the reasons of the low coverage (6-33%) of PDDA-Pt nanoparticles on Nafion membrane. The similar methanol crossover current and cell performance of DMFC based on the SAM modified Nafion membrane with PDDA-Pt nanoparticle colloids synthesized with various PDDA/Pt ratios indicate that self-assembled PDDA molecules could also be effective in the inhibiting of the methanol crossover.

In this chapter, layer-by-layer self-assembly of multilayered PDDA/PSS onto the Nafion membrane was investigated for the methanol crossover and cell performance in comparison with the unmodified Nafion membrane.

9.1 Experimental

The self-assembly of PDDA/PSS multi-layer was carried out by immersing the pretreated Nafion membrane alternatively in the PDDA (20mM) solution and the PSS (20mM) solution at room temperature for 5min. As a comparison, PDDA/PAZO multi-layer on Nafion membrane was also prepared.

The build-up of multi-layer on Nafion membrane was monitored using UV-visible spectroscopy (HP 8350) as a function of the number of bilayer. The cross-

plane conductivity of Nafion membrane before and after LBL self-assembly was measured using an in-house built 4-probe DC technique. The measurement was carried out in 1M H₂SO₄ solution at 25°C. To evaluate the methanol crossover and the cell performance, the membrane-electrode-assembly (MEA) was made by sandwiching the self-assembled Nafion membrane between a Pt/Ru anode and a Pt/C cathode. The methanol crossover current and the cell performance were measured using Autolab (PG30STAT) instruments.

9.2 Results and discussions

Fig 9.1 shows the UV-visible spectra of the LbL self-assembled N1135 membrane as a function of the number of PDDA/PSS and PDDA/PAZO bilayers. For PDDA/PSS multilayers, although the absorbance peak at 225 nm was not shown clearly, the absorbance increased with the increase of the number of PDDA/PSS bilayers (Fig. 9.1a). Absorbance at 225 nm is most likely related to the characteristic wavelength of 228 nm for the sodium styrenesulfonate mers [Zapotoczny, *et al.*, 2005]. Since PDDA was almost transparent under UV-visible spectrum, the increase in absorbance was attributed to the adsorption of PSS on previous PDDA layer. The inset graph shows the absorbance at 225 nm as a function of the number of the PDDA/PSS bilayers, which increased linearly with the number of LbL self-assembled PDDA/PSS bilayers. The linear relationship indicates that in every dipping cycle same amount of polymer is deposited and the multilayer is formed in a regular manner. The linear dependence of the absorbance on the number of bilayers was also observed on the LbL self-assembly of PDDA/PAZO bilayers on Nafion (Fig. 9.1b). The absorption peaks at 269 and 355 nm in the LbL self-assembled films are characteristics of the PAZO polyelectrolyte.

Fig 9.1 UV-visible spectra of the Nafion 1135 membrane as a function of LBL self-assembled (a) PDDA/PSS and (b) PDDA/PAZO bilayers.

Fig 9.2 shows the AFM images of glass substrates before and after self-assembly of 4 PDDA/PSS bilayers. The glass substrate was very smooth before the self-assembly. After self-assembling in PDDA solutions, it cannot be observed any obvious change. This indicated that the initial adsorption of PDDA to the surface of Nafion membrane was not significant. However, the roughness increased significantly after self-assembling 4-bilayer of PDDA/PSS. This indicated that PDDA and PSS were self-assembled to the surface of glass substrate successfully.

Fig 9.2 AFM images of (a) glass substrate, (b) monolayer of PDPA and (c) 4 PDPA/PSS bilayers on glass substrate.

To evaluate the effect of PDPA/PSS and PDPA/PAZO multilayers on the proton conductivity of N-1135 membranes, the conductivity was measured at 25°C. The results were given in Table 9.1.

Table 9.1 The proton conductivity, limiting methanol crossover current, and maximum power density of Nafion 1135 membrane as a function of number of PDDA/PSS bilayer

Number of PDDA/PSS bilayers	0	1	2	4	8	5 bilayer PDDA/PAZO
Conductivity (S.cm)	0.124	0.113	0.109	0.107	0.106	0.071
OCP (V)	0.540	0.558	0.552	0.560	0.554	0.560
Limiting methanol crossover current (mA/cm ²)	98	92	90	78	69	76
Maximum power density (mW/cm ²)	26	30	36	37	33	29

The conductivity of an unmodified N-1135 membrane was 0.124 Scm⁻¹. With the increase in the number of self-assembled PDDA/PSS bilayers, the conductivity of the membrane decreased. However, the decrease in the proton conductivity was small. After self-assembly of 8 PDDA/PSS bilayers, the proton conductivity was 0.106Scm⁻¹, a decrease of 15% compared with that of the pristine Nafion membrane. On the other hand, with the self-assembly of 5 PDDA/PAZO bilayers, the conductivity decreased to 0.071 Scm⁻¹, a reduction in conductivity by 43%. The reduction in the proton conductivity of Nafion membrane modified with PDDA/PAZO bilayers was significantly higher than that with PDDA/PSS bilayers. Since PAZO was a comb-like polymer, its layer thickness would be greater than that of PSS which contains smaller monomeric blocks [Johal, *et al.*, 2003]. The much smaller decrease in the conductivity in the case of self-assembled PDDA/PSS bilayers could also be resulted from the fact that the PSS contains sulfonic acid group, which may serve as a proton conductor. The LbL self-assembly of oppositely charged polyelectrolyte bilayers had some detrimental effect on the conductivity of the membrane. However, the detrimental effect was dependent on the nature of the polyelectrolyte bilayers and can

be reduced to a minimum by using proper combination of polycation and polyanion as shown in the case of PDDA/PSS.

Fig. 9.3 shows the limiting current curves for the oxidation of methanol crosscovered from anode to cathode through N-1135 membranes as a function of self-assembled PDDA/PSS and PDDA/PAZO multilayers. The methanol oxidation current was measured at 30°C. For the purpose of simplicity, only the limiting current data for the methanol crossover on N-1135 membrane with 5 PDDA/PAZO bilayers was shown in the figure.

Fig 9.3 Polarisation curves for methanol crossovered through the membrane as a function of PDDA/PSS bilayer measured at 30°C

With one self-assembled PDDA/PSS bilayer, the limiting methanol crossover current density was 92 mAcm^{-2} , a decrease of 6% in comparison to 98 mAcm^{-2} measured on the unmodified N-1135 membrane. This indicates that the LbL self-assembly of PDDA/PSS bilayer reduces the methanol crossover. When the number of PDDA/PSS bilayers increased to 4, the limiting methanol crossover current density decreased further to 78 mAcm^{-2} , which was similar to 76 mAcm^{-2} observed on N-1135 membrane with 5 PDDA/PAZO bilayers. With the 8 PDDA/PSS bilayers, the

crossover current was 69mAcm^{-2} , a decrease in the methanol permeability by 30% compared with the unmodified N-1135 membrane. The methanol crossover decreased with the increase of the LbL self-assembled oppositely charged polyelectrolytes.

The cell performance of DMFC prepared with the unmodified N-1135 membrane and the N-1135 membranes modified with PDDA/PSS and PDDA/PAZO bilayers at 30°C is shown in Fig 9.4. The open circuit potential (OCP) was 0.545V for the cell with the unmodified N1135 membrane. With the increase of the number of PDDA/PSS bilayer, the OCP increased slightly to 0.56 V most likely due to the reduction of methanol crossover. The best performance was observed for the DMFC using N-1135 membrane with 4 self-assembled PDDA/PSS bilayers, achieving a power density of 37mWcm^{-2} . This was an increase of 42% in power output as compared to the cell using the unmodified N1135 membrane (26mWcm^{-2}).

However, with further increasing the number of PDDA/PSS bilayers to 8, the maximum power density decreased to 30mWcm^{-2} . The reason could be due to the fact that increasing the number of PDDA/PSS bilayer also decreased the proton conductivity (see Table 1), thus increasing the overall cell resistance. This could result in the decrease in the overall cell performance. Therefore, there was a dedicate balance between the reduction in the methanol crossover and decrease in proton conductivity for the self-assembled multilayer thin film. The relatively small increase in the power density of the cell with Nafion membrane modified with 5 PDDA/PAZO bilayer (29mWcm^{-2} , an increase of 12% in comparison to the cell with unmodified Nafion membrane) was most likely due to the significant reduction of the proton conductivity of the modified Nafion membrane (see Table 9.1).

Fig 9.4 Polarisation curves and power output of DMFC using N-1135 membrane as a function of self-assembled PDDA/PSS layer measured at 30°C

It is known that Nafion has a dual structure with hydrophobic region interspersed with an ion-rich hydrophilic domain and methanol diffuses primarily through the hydrophilic water-rich domains [Verbrugge, 1989; Divisek, *et al.*, 1998]. Thus blocking the water-rich domains which were primarily associated with $-\text{SO}_3^-$ cluster on the Nafion membrane surface would be effective to inhibit the methanol crossover. Due to the existence of the negatively charged sulfonic acid group, SO_3^- , on the surface of the Nafion membrane, self-assembly of positively charged polycation occurs as the result of the electrostatic interaction. PDDA was a strong polycation and thus, with the self-assembly of positively-charged PDDA monolayer, the charge inversion would take place on the Nafion surface [Kim, *et al.*, 2002]. The dipping of the self-assembled PDDA/Nafion in a negatively charged polyanion such as PSS or PAZO will lead to the self-assembly of a polyanion monolayer. Fig 9.5 shows

schematically the structure of the LbL self-assembled polycation and polyanion multilayers on a Nafion membrane, inhibiting the methanol crossover.

Fig 9.5 Schematic diagram of the structure of the LbL self-assembly of oppositely charged polycation and polyanion on Nafion electrolyte membrane, showing the blocking of the methanol crossover.

The LbL self-assembly of oppositely charged polyelectrolytes on Nafion membrane showed significant effect on the reduction in methanol crossover and on the enhancement of the performance of DMFC (Fig 9.2 and 9.3). In the case of a DMFC using Nafion membrane self-assembled with 4 PDDA/PSS bilayers the power density was increased by 42% in comparison to the cell with the unmodified Nafion membrane, a significant enhancement in the performance of DMFCs. Most importantly, the LbL self-assembly approach appeared to have much smaller detrimental effect on the proton conductivity, chemical and thermal stability of the Nafion membrane, a significant advantage as compared to other modification approaches [Jia, *et al.*, 2000; Yang, *et al.*, 2001; Yoon, *et al.*, 2002]. LbL self-assembly of composite polyelectrolyte multilayer thin films offers a potentially very effective technique to minimize the methanol crossover problem in DMFCs. Nevertheless, significant amount of work is still needed to optimize the LbL self-assembly process of the oppositely charged polyelectrolyte and to understand the

effect of interaction between the polycation and polyanion on the proton conductivity and methanol crossover process.

9.3 Summary

Multilayer of PDDA/PSS was self-assembled alternatively from dilute PDDA and PSS solutions onto the Nafion membrane via layer-by-layer technique. This multilayer reduced the methanol crossover effectively with only slight decrease of proton conductivity. The open circuit potential increased from 0.54 to 0.56V for the cell with N1135 membrane modified by 4 PDDA/PSS bilayers. And the maximum power density increased to 37mW/cm^2 , by 28% compared with that of the unmodified N1135 membrane. When the number of PDDA/PSS bilayer increased to 8, the maximum power density decreased slightly to 33mW/cm^2 although the methanol crossover was reduced more effectively. This indicated that there was a compromise between the reduction in methanol crossover and the decrease in proton conductivity. However, the LBL technique is a simple and flexible method by which we can control the number of bilayers in order to obtain the optimal cell performance.

CHAPTER 10 Measurement of Through-Plane Ionic Conductivity of Polymer Electrolyte Membrane

In this chapter, a modified method to improve the accuracy for measuring the through-plane conductivities of Nafion membrane with different thickness was reported. The conductivities of Nafion membrane were found to be independent of the membrane thickness.

10.1 Experimental

Nafion membranes (N112, 1135, 115, 117) were treated according to the standard procedure and stored in deionized water before use. The measurement was conducted at 25°C using the fixture in Fig 3.12.

10.2 Results and Discussion

10.2.1 Determination of current used

Fig 10.1 shows the potential curves for the cell without the membrane as a function of current. When the current was 1mA, the potentials were positive for both positive and negative currents. This was due to the potential difference (1-5mV) between the two SCE references. When the current increased to 10mA~1000mA, the sign of the potential was same as that of the current. This indicated the potential difference between the two SCE electrodes was so small that the sign of the potential recorded didn't change with that of the current any more. However, it can be seen that

the potential was quite stable for the current of 10mA and 100mA, but not for the current of 1mA and 1000mA.

Fig 10.1 Potential curves for the cell without the membrane as a function of current, (a) 1mA, (b) 10mA, (c) 100mA and (d) 1000mA. The measurement was conducted at 25°C.

Table 10.1 shows the cell (without membrane) resistance obtained from Fig 10.1. There was no much difference among the cell resistances when using the current of 1mA~100mA. When the current was 1000mA, the resistance was lower than those obtained using lower current. It was also worthwhile to note that the standard deviation (SD) was different when using different current. The SDs obtained using the current of 10mA~100mA were lower compared with that obtained using the current of 1mA and 1000mA. The higher SD when using the current of 1mA may be due to

the potential drift of SCEs. Although the potential drift of SCEs was very small, it may result in higher SD when the current employed was very small. The lower resistance and higher SD when using the current of 1000mA may be due to the electrode polarisation. When using the current of 10mA and 100mA, the SD was significantly low. It indicates that we can get reasonable and stable resistance when we use the current of 10~100mA. In this chapter, the current of 100mA was used for all the measurements.

Table 10.1 Cell (without membrane) resistance obtained using different current

Current (mA)	1	10	100	1000
Resistance(Ω)	0.804 $\pm$ 0.0083	0.798 $\pm$ 0.0002	0.795 $\pm$ 0.0004	0.730 $\pm$ 0.0102

10.2.2 Measurement of membrane conductivity

Table 10.2 shows the nominal membrane thickness and hydrated membrane thickness of Nafion membranes. It was found that the thickness of membrane N112 was slightly smaller than the nominal thickness, while all the rest membranes increased in the thickness by 12-18%. This is different from those reported by others. Slade et al. [2002] and Silva et al. [2004] reported that all the membranes increased in the thickness after full hydration. However, Nouel et al. [1998] reported the thickness of 52 μ m for N112 membrane. The reason remains unclear. However, this indicates that it is of importance to calculate the conductivity based on the hydrated membrane thickness.

Table 10.2 Nominal thickness and fully hydrate membrane thickness of Nafion membranes

Nafion membrane	N112	N1135	N115	N117
Nominal thickness (μ m)	51	89	127	183
Hydrated membrane thickness (μ m)	50.3	100	150	210

Fig 10.2 shows the membrane area resistance against the hydrated membrane thickness. Obviously, the membrane area resistance increased with the increase of the membrane thickness. The increase was almost linear as expected by ohmic law.

Fig 10.2 Membrane area resistance as a function of hydrated membrane thickness measured in 1M H_2SO_4 at 25°C, the inserted are the equation and R-squared value obtained by linear simulation

The insets in Fig 10.2 are the equation and R-squared value obtained by linear simulation. The R-squared value of 0.9999 indicated that the simulation was reasonable. If we extrapolated the plot to the membrane thickness of 0, the area resistance was $0.0012\Omega\text{cm}^2$ rather than zero as expected. However, this value was very small, and may be due to some errors involved in the measurements.

Fig 10.3 shows the conductivity of Nafion membrane with error bar vs the hydrated membrane thickness. All the data were in the range of $0.120 \pm 0.005 \text{ Scm}^{-1}$. Considering the experiment accuracy, this showed that the conductivity was independent of the membrane thickness. The same trend was also found by Kolde et al. [1995] and Nouel et al. [1998]. Kolde et al. [1995] reported the in-plane conductivities obtained by ac impedance were 0.100Scm^{-1} for both Nafion 117

(200 μm) and Nafion 112 (60 μm). Nouel et al. [1998] reported in-plane conductivities for Nafion 117 (210 μm) and Nafion 112 (52 μm) were 0.140 ± 0.005 and 0.144 ± 0.005 Scm^{-1} in air at 100% relative humidity and at 65°C. These data were almost same if the experiment error was taken into account. Fig 10.3 also shows the comparison of the conductivities of Nafion 1135 in H^+ and Na^+ form. Nafion 1135 in H^+ form and Na^+ form showed similar conductivity as expected because we measured ionic conductivity. This again showed the reproducibility of the conductivity measurements.

Fig 10.3 Membrane conductivity as a function of hydrated membrane thickness measured in 1M H_2SO_4 at 25°C

However, the through-plane conductivities were reported so far to be dependent on the membrane thickness [Silva, et al., 2004; Slade, et al., 2002; Buchi, et al., 2001; Dimitrova, et al., 2002]. Buchi et al. [2001] investigated the conductivity of Nafion 117, 115, 112 and multiple membranes composed of Nafion 117, 115 and 112 at 60°C. The conductivity decreased from 0.095Scm^{-1} for the thinnest membrane (Nafion 112) to 0.111Scm^{-1} for the thickest membrane (Nafion 117). Buchi et al. assumed that the variation of the resistance with thickness could be due to a not completely isotropic conductivity across the membrane thickness. That is, the boundary layer at the

interface with the electrode could have a slightly different composition or orientation resulting in a lower conductivity than that of the bulk membrane. However, they did not exclude the contribution of cell resistance and the effect of pressure applied to the cell.

Dimitrova et al. [2002] obtained similar values of the specific area resistance for Nafion 112, 115, 117 at 15°C, but observed the linear increase of the resistance with the membrane thickness at 90°C. They suggested that the membrane has a layered structure. The specific superficial structure may differ from that of the bulk material so that it determines the proton migration behaviours of the membrane. Silva et al. [2004] reported same results at 25 and 65°C using a quite similar designed cell. They ruled out the transient dry effects as an explanation for this dependence because the measurements were performed in cells fully immersed in water. However, they observed an obvious decrease in λ ($\lambda = n\text{H}_2\text{O}/\text{SO}_3\text{H}$). Silva et al. [2004] again suggest that the increase of conductivity with the increase of the thickness may be ascribed to the difference in the structure probably due to the production process.

Slade et al. [2002] also used DC four-probe technique to measure the through-plane conductivity ex situ in H_2SO_4 at 25°C and adopted current interrupt technique to determine the through-plane conductivity in situ in PEMFC operated at 80°C. They ruled out that the decrease in conductivity with decreasing membrane thickness could be due to the uneven water distribution or inhomogeneous distribution of sulfonate acid group. The unexpected decrease in the conductivity for thin membranes was attributed to their production process, where temperature and pressure must have a pronounced effect on the surface structure of the materials. The thinner membrane may have been produced with a higher roller pressure, resulting in different surface

structure from bulk materials. However, it was recently reported also by Silva et al. [2005] that the in-plane conductivity decreased with the increase of thickness of the membrane using two-electrode AC impedance method and a commercially available conductivity cell (BekkTeck). The decrease of conductivity with increasing the thickness was attributed to the layered-structure of the membrane. It was suggested [Silva, et al., 2005] that the surface conductivity of Nafion membrane was strongly anisotropic with a lower value in the through-plane direction than in the in-plane direction, which was also lower and higher than the membrane bulk conductivity.

So far, three hypotheses have been suggested to explain the increase of conductivity with increasing the membrane thickness: (1) differences in the water uptake [Silva, et al., 2004], (1) structural changes due to the production process [Silva, et al., 2004; Slade, et al., 2002] and (3) layered structure of the membranes [Buchi, et al., 2001; Dimitrova, et al., 2002; Silva, et al., 2005]. However, all of these have not been confirmed. Even if Nafion membrane has layered structure, the resistance contribution from the superficial layer may be very small as compared with the resistance of the bulk membrane. Therefore, the through-plane conductivity is still independent of the membrane thickness.

In the literature references cited here, the contact resistance and/or some inevitable errors were not considered carefully. However, since the membrane thickness (50-210 μm) is so small that the resistance (0.05~0.17 Ωcm^2) is very small, any errors, contact resistance and resistance of components may result in much inaccuracy of measurements. If we extrapolate the specific resistance of Nafion membrane at 90°C obtained by Buchi et al. [2001] to the thickness of 0, the specific resistance is about 0.05 Ωcm^2 . This value is 50 times higher than that obtained at 25°C in this study and is nearly same as the specific resistance of Nafion 112 obtained in

the present work. The magnitude of this value may inevitably cause much inaccuracy of measurements.

10.3 Summary

A simple, accurate DC four-probe technique was developed to measure the through-plane conductivity of ionic exchange membrane. The conductivity of Nafion membrane was found to be independent of the membrane thickness.

CHAPTER 11 Conclusions and Recommendations

11.1 Conclusions

Based on the results in this thesis, the following conclusions can be drawn:

1. MOR on the Pt/C catalyst is a kinetically controlled process. Although the liquid electrolyte is saturated with nitrogen, there is still trace of dissolved oxygen. To minimize the interference of the dissolved oxygen in the liquid electrolyte on the behaviours of MOR, it is suggested that the relatively high Pt loading ($\geq 56 \mu\text{gcm}^{-2}$) be used to evaluate the Pt-based catalyst for the methanol oxidation reaction. However, the relatively low Pt loading ($5.6\text{--}11 \mu\text{gcm}^{-2}$) is preferred for ORR in the presence of methanol. This is because that relatively low concentration of dissolved oxygen would be readily consumed by chemical reaction with methanol on the surface of Pt.
2. Polymer-stabilized Pt nanoparticles were synthesized by the alcoholic reduction of the H_2PtCl_6 in ethanol/water system in the presence of positively charged polymer PDDA, negatively charged polymer Nafion and PSS, and neutral polymer PVP. They showed considerable crystallinity and fcc structure. The morphology, dispersion and particle size of Pt nanoparticle were dependent on the polymer structure, and the polymer monomer/Pt molar ratio. PDDA-Pt nanoparticles showed high catalytic activity for ORR, but relatively low activity for MOR. PDDA-Pt nanoparticles may be potential methanol tolerant cathode catalysts for

DMFC. PSS-Pt nanoparticles were very active for ORR and MOR, therefore very low activity for oxygen reduction reaction in the presence of methanol. However, PVP-Pt showed very low catalytic activity for all reactions investigated. This indicated that PVP had a significant shielding effect on Pt activity. The relatively low activity for Nafion-Pt may be due the agglomeration and the additional diffusion resistance caused by the excessive Nafion.

3. Positively charged PDDA-Pt nanoparticles can be self-assembled onto the surface of Nafion membrane to form electrocatalytic active membrane interface. The electrocatalytic activity of the self-assembled PDDA-Pt nanoparticle electrode/Nafion membrane interface depends on the morphology and agglomeration of the PDDA-Pt nanoparticles, which in turn are related to the molar ratio of PDDA to Pt during the reduction of the PtCl_6^{2-} ions in the ethanol/water solution. The highest activity of the self-assembled membrane interface was obtained on agglomerated PDDA-Pt nanoparticles which was prepared with PDDA/Pt molar ratio of 1:1. An increase in the molar ratio increased the dispersion and distribution of the PDDA-Pt nanoparticles, but decreased the electrocatalytic activity of the self-assembled interface. With an increase of PDDA/Pt molar ratio in the PDDA-Pt nanoparticle colloids, the amount of Pt nanoparticles self-assembled on the Nafion membrane decreased due to the competitive self-assembly of free PDDA. This showed that appropriate agglomeration of the PDDA-Pt nanoparticles would be beneficial to the self-assembled electrode/Nafion membrane interface.

4. The self-assembly of PDDA-Pt nanoparticles on Nafion membrane was investigated for the blocking of methanol crossover in DMFC. The present study showed that self-assembly of PDDA-Pt nanoparticles on the surface of Nafion membrane significantly reduced the methanol crossover and enhanced the power output of DMFCs by as much as 34% as compared to the DMFC based on unmodified Nafion membrane. Not only can the self-assembled PDDA-Pt nanoparticles reduce the methanol crossover effectively, but also can the self-assembled PDDA reduce the methanol crossover to some degree. The self-assembled PDDA-Pt nanoparticles on Nafion membrane showed great potential in the development of high performance DMFCs.
5. Multilayered PDDA/PSS was self-assembled alternatively from dilute PDDA and PSS solutions onto the Nafion membrane via layer-by-layer technique. The multilayers also reduced the methanol crossover effectively with only slight decrease in the proton conductivity. The maximum power density was 37mW/cm^2 , increased by 28% as compared with that of the unmodified N1135 membrane. When the number of PDDA/PSS bilayer increased to 8, the maximum power density decreased slightly to 33mW/cm^2 . This indicates that there is a compromise between the reduction in methanol crossover and the decrease in proton conductivity. However, the LBL technique is a simple and flexible method by which we can control the number of bilayers in order to obtain the optimal cell performance.

6. A simple, accurate DC four-probe technique was developed for measuring the through-plane conductivity of ionic exchange membrane. The conductivity of Nafion membrane is independent of the membrane thickness.

11.2 Major achievements

- Developed a new concept, and demonstrated the possibility of the selective catalysts for DMFCs based on polyelectrolytes

DMFCs have attracted many interests due to their ability to use liquid fuel instead of gaseous hydrogen. However, methanol was readily crossovered from anode to cathode through the polymer electrolyte. The crossovered methanol chemically reacted with oxygen on the surface of platinum catalysts, thus resulting in the mixed cathode potential ($\sim 0.2\text{V}$ lower than that without methanol) and degrading the cathode performance. One way to solve this problem is to develop methanol tolerant cathode catalyst. Platinum alloys were investigated widely with the aims of developing their methanol tolerance. In this work, a new concept was proposed: if the platinum particles were stabilized by the ionic polymers, which has little effect on oxygen diffusion, but can block the methanol diffusion towards the platinum surface. According to this concept, we synthesized platinum nanoparticles in the presence of various ionic polymers. PDDA-Pt nanoparticles showed considerable activity towards ORR and tolerance to MOR. PSS-Pt nanoparticles showed high catalytic activity for both ORR and MOR, and much higher stability for MOR than a commercial Pt/C catalyst. However, PVP-Pt nanoparticles showed very low activity for all the reactions investigated here.

- Developed a LBL self-assembly technique to modify the Nafion membrane to reduce its methanol crossover

Since Nafion membrane was negatively charged due to the SO_3^- on the surface, positively charged polymers and polymer stabilized nanoparticles can be self-assembled onto the surface of Nafion membrane due to the electrostatic interaction. PDDA is a positively charged polymer. Therefore, PDDA-Pt should be positively charged. The results have shown for the first time that the self-assembled monolayer of PDDA-Pt on the surface of Nafion membrane reduces the methanol crossover and enhances the cell performance. Multilayer was also achieved via alternative self-assembly of oppositely charged polymers. Multilayer of PDDA/PSS on the surface of Nafion membrane has been proved to reduce the methanol crossover. Reduction of the methanol crossover depends on the thickness of multilayer and this can be conveniently controlled via LBL technique.

- Developed a method to improve the measurement of the through-plane conductivity of polymer electrolyte

Proton conductivity is an important factor for the polymer electrolyte membrane in controlling the cell performance. Many methods have been developed to measure both the in-plane and the through-plane conductivity. However, the data were very scattered due to the differences in cell design, technique employed, electrolyte used, and sample preparation methods. At the same time, in-plane conductivity was reported to be independent of the membrane thickness, but the through-plane conductivity was dependent. Although some hypotheses were

proposed, they were not confirmed. In this work, we developed a method to measure the ex situ through-plane conductivity in 1M H₂SO₄. The results show that the through-plane conductivity is independent of the membrane thickness. In this cell design, the contact resistance is minimized, and the measurement error is quite small.

11.3 Recommendations

1. PDDA/Pt molar ratio affects not only the dispersion and the size of PDDA-Pt nanoparticles during the synthesis, but also their distribution on the surface of Nafion membrane after self-assembly. The agglomeration affects the activity of the nanoparticles significantly. Increasing the molar ratio can improve the dispersion and also reduce the particle size. However, excessively high molar ratio is not good for the self-assembly of PDDA-Pt nanoparticles on the Nafion membrane. The free PDDA will also occupy the SO₃⁻ sites on the surface of Nafion membrane, and this will affect the assembly of PDDA coordinated with platinum nanoparticles. Therefore the self-assembled platinum nanoparticles decrease, leading to the decreased activity of PDDA-Pt/Nafion membrane interface. On the other hand, the self-assembled PDDA-Pt nanoparticle is more effective to reduce the methanol crossover than that of PDDA. Thus, the decrease in the coverage of PDDA-Pt nanoparticles may reduce the effectiveness for the reduction of the methanol crossover. Therefore, it is necessary to study the method to remove the free PDDA from the PDDA-Pt nanoparticle colloids.
2. LBL self-assembly of PDDA/PSS has been proved to reduce the methanol

crossover effectively, but it also decreases the proton conductivity. Therefore, it is necessary to optimize the proton conductivity and methanol impermeability with optimum combination of opposite charged polyelectrolytes. The stability of the self-assembled monolayer of PDDA-Pt and multilayer of PDDA/PSS also needs to be investigated.

List of Publications

Journal Paper

- 1) San Ping Jiang, Zengcai Liu, Zhi Qun Tian, 2006, Layer-by-Layer Self-assembly of Composite Polyelectrolyte/Nafion membrane for Direct Methanol Fuel Cells, *Advanced Materials* 18, 1068-1072
- 2) Zengcai Liu, San Ping Jiang, 2005, Synthesis of PDDA-Pt nanoparticles for the self-assembly of electrode/Nafion membrane interface of polymer electrolyte fuel cells, *Journal of Power Sources* 159, 55-58
- 3) Zengcai Liu, Zhi Qun Tian and San Ping Jiang, 2006, Synthesis and characterization of Nafion-stabilized Pt nanoparticles for polymer electrolyte fuel cells, *Electrochimica Acta*, 52 1213-1230
- 4) San Ping Jiang, Zengcai Liu, Mu Pan, Hao Lin Tang, 2006, Synthesis and characterization of PDDA-stabilized Pt nanoparticles for direct methanol fuel cells, *Electrochimica Acta* 51, 5721-5730
- 5) San Ping Jiang, Lin Li, Zengcai Liu, Mu Pan, Hao Lin Tang, 2005, Self-assembly of PDDA-Pt nanoparticle/Nafion membranes for direct methanol fuel cells, *Electrochemical and Solid-State Letters* 8, A574-A576
- 6) Zhi Qun Tian, San Ping Jiang, Zengcai Liu, Lin Li, 2007, Polyelectrolyte-stabilized Pt nanoparticles as new electrocatalysts for low temperature fuel cells, *Electrochemistry Communications*, 9, 1613-1618
- 7) Mu Pan, Hao Lin Tang, San Ping Jiang, Zengcai Liu, 2005, Self-assembled membrane electrode-assembly of polymer electrolyte fuel cells, *Electrochemical Communications* 7,119-124
- 8) Mu Pan, Hao Lin Tang, San Ping Jiang, Zengcai Liu, 2005, Fabrication and Performance of Polymer Electrolyte Fuel Cells by Self-Assembly of Pt Nanoparticles, *Journal of the Electrochemical Society* 152, A1081-A1088

Conference Paper:

- 9) Zengcai Liu, San Ping Jiang, 2005, Synthesis and Characterization of Platinum nanoparticles Protected by PDDA for Polymer Electrolyte Fuel Cells, ***World Hydrogen Technologies convention 2005***, 3-5 October 2005, Singapore
- 10) Zengcai Liu, San Ping Jiang, 2004, Effect of Nafion Impregnation on Cathode Behaviors in Proton Exchange Membrane Fuel Cells, ***The 3rd International Conference on Materials Processing for Properties and Performance (MP3)***, 24 - 26 November 2004, Singapore,

Reference:

- Antoine O., Bultel Y., Durand R. (2001), Oxygen Reduction Reaction Kinetics and Mechanism on Platinum Nanoparticles Inside Nafion[®], J. Electroanal. Chem. **499**, 85–94
- Adlim M., Bakar M.A., Liew K.Y., Ismail J. (2004), Synthesis of Chitosan-stabilized Platinum and Palladium Nanoparticles and Their Hydrogenation Activity, J. Molecular Catalysis A **212** 141.
- Adjemian K.T., Lee S.J., Srinivasan S., Eenziger J., Bocarsly A.B. (2002), Silicon Oxide Nafion Composite Membranes for Proton-Exchange Membrane Fuel Cell Operation at 80–140°C, J. Electrochem. Soc. **149**, A256-261
- Antolini E., Giorgi L., Pozio A., Passalacqua E. (1999), Influence of Nafion Loading in the Catalyst Layer of Gas-diffusion Electrodes for PEFC, J. Power Sources **77**, 136-142
- Appleby A. J. and Yeager E.B. (1986), Energy (oxford) **11**, 137
- Arico A.S., Antonucci P.L., Modica E., Baglio V., Kim H., Antonucci V. (2002), Effect of Pt-Ru Alloy Composition on High-Temperature Methanol Electro-Oxidation, Electrochim. Acta **47**, 3723.
- Arico A.S., Antonucci V., Alderucci V., Modica E. and Giordano N. (1993), J. Appl. Electrochem. **23**, 1107
- Arico A.S., Srinivasan S., Antonucci V. (2001), DMFCs: From Fundamental Aspects to Technology Development, Fuel Cells **1**, 133
- Athawale A.A., Bhagwat S.V., Katre P.P., Chandwadkar A.J., Karandikar P. (2003), Aniline as a Stabilizer for Metal Nanoparticles, Materials Letters **57**, 3889-3894
- Bensebaa F., Farah A.A., Wang D., Bock C., Du X. Kung J., Page Y.L. (2005), Microwave Synthesis of Polymer-Embedded Pt-Ru Catalyst for Direct Methanol Fuel Cell, J. Phys. Chem. B **109**, 15339-15344
- Bhattacharya a., Chakraborti P.C., Mukharjee S., Mitra M.K., Das G.C. (2001), Sci. Technol. Adv. Mater. **2**, 449
- Berret J.F., Vigolo B., Eng R., Hervé P., Grillo I., and Yang L. (2004), Electrostatic Self-Assembly of Oppositely Charged Copolymers and Surfactants: A Light, Neutron, and X-ray Scattering Study, Macromolecules **37**, 4922
- Besmann T.M., Klett J.W., Henry Jr J.J., Lara-Curzio E. (2000), Carbon/Carbon Composite Bipolar Plate for Proton Exchange Membrane Fuel Cells, J. Electrochem. Soc. **147**, 4083
- Bessel C.A., Laubernd K., Rodriguez N.M., Baker R.T. (2001), J. Phys. Chem. B **105**, 1115
- Bonnemann H, Brijoux W., Joussen Th. (1990), Angew.Chem. Int. Ed. Engl. **29**, 273
- Bonnemann H, Brijoux W. (1991), Angew.Chem. Int. Ed. Engl. **30**, 1312–14

Reference

- Bonnemann H., Braun G., Brijoux W., Brinkmann R., Tilling A., Seevogel K., Siepen K. (1996), Nanoscale Colloidal Metals and Alloys Stabilized by Solvents and Surfactants: Preparation and Use as Catalyst Precursors, *J. Organomet. Chem.* **520**, 143
- Bönnemann H., Brinkmann R., Britz P., Endruschat U., Mörtel R., Paulus U. A., Feldmeyer G. J., Schmidt T. J., Gasteiger H. A. and Behm R. J. (2000), Nanoscopic Pt-Bimetal Colloids As Precursors For PEM Fuel Cell Catalysts, *J. New Mater. Electrochem. Syst.* **3**, 199–206
- Braun P.U., Osenar P., Stupp S. (1996), Semiconducting superlattices templated by molecular assemblies, *Nature* **380**, 325
- Bron M., Bogdanoff P., Fiechter S., Dorbandt I., Hilgendorff M. (2001), Influence of Selenium on the Catalytic Properties of Ruthenium-Based Cluster Catalysts for Oxygen Reduction, *J. Electroanal. Chem.* **500**, 510-517
- Buchi F.N., Scherer G.G. (2001), Investigation of the Transversal Water Profile in Nafion Membranes in Polymer Electrolyte Fuel Cells, *J. Electrochem. Soc.*, **148**, A183-188
- Busick D.N., Wilson M.S. 1998, *Fuel Cell Seminar*, Palm Springs, Abstract 1186
- Cha S.Y. and Lee W.M. (1999), Performance of Proton Exchange Membrane Fuel Cell Electrodes Prepared by Direct Deposition of Ultrathin Platinum on the Membrane Surface, *J. Electrochem. Soc.* **146**, 4055-4060
- Chen C.-W., Serizawa T., and Akashi M. (1999), Preparation of Platinum Colloids on Polystyrene Nanospheres and Their Catalytic Properties in Hydrogenation, *Chem. Mater.* **11**, 1381
- Chen C.-W., Akashi M. (1997), “Synthesis, Characterization, and Catalytic Properties of Colloidal Platinum Nanoparticles Protected by Poly(N-isopropylacrylamide)”, *Langmuir* **13**, 6465-6472
- Chen C.-W., Takezako T., Yamamoto K., Serizawa T., Akashi M. (2000), “Poly(N-vinylisobutyramide)-Stabilized Platinum Nanoparticles: Synthesis and Temperature-Responsive Behavior in Aqueous Solution”, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **169**, 107-116
- Cheung T.T.P. (1984), X-ray photoemission of small platinum and palladium clusters, *Surf. Sci.* **140**, 151
- Choi K.H., Kim H.S., Lee T.H. (1998), Electrode Fabrication for Proton Exchange Membrane Fuel Cells by Pulse Electrodeposition, *J. Power Sources* **75**, 230-235
- Choi J-H, Park K-W, Lee H-K, Kim Y-M, Lee J-S, Sung Y-E (2003), Nano-composite of PtRu alloy Electrocatalyst and Electronically Conducting Polymer for Use as the Anode in a Direct Methanol Fuel Cell, *Electrochim. Acta* **48**, 2781-2789
- Chrzanowski W., Kim H., Wieckowski A. (1998), Enhancement in methanol oxidation by spontaneously deposited ruthenium on low-index platinum electrodes, *Catal. Lett.* **50**, 69.
- Ciureanu M. and Wang H. (1999), Electrochemical Impedance Study of Electrode-Membrane Assemblies in PEM Fuel Cells: I. Electro-oxidation of H₂ and H₂/CO Mixtures on Pt-Based Gas-Diffusion Electrodes, *J. Electrochemical Soc.*, **146**(11), 4031-4040

Reference

- Damjanovic A., Brusic V. (1967), Electrode Kinetics of Oxygen Reduction on Oxide-free Platinum Electrodes, Electrochim. Acta **12**, 615
- Damjanovic, A., (1991), On the Kinetics and Mechanism of Oxygen Reduction at Oxide Film-Covered Pt Electrodes in Acid Solutions, J. Electrochem. Soc. **138**, 2315-2320
- Damjanovic, A., and Hudson, P. G., (1988), On the Kinetics and Mechanism of Oxygen Reduction at Oxide Film-Covered Pt Electrodes, J. Electrochem. Soc. **135**, 2269-2273
- Decher G. (1997), Fuzzy Nanoassemblies: Toward Layered Polymeric Multicomposites, Science **277**, 1232
- Deivarj T.C., Lee J.Y., (2005), Preparation of Carbon-supported PtRu Nanoparticles for Direct Methanol Fuel Cell Applications- a Comparative Study, J. Power Sources **142**, 43-49
- Denney R.C., Sinclair R., Editor Mowthorpe D. (1987), Visible and Ultraviolet Spectroscopy, ISBN 0-471-91379-0, London, 7
- Diard J.P., Le Gorrec B., Montella C., Montero-Ocampo C. (1993), Calculation, Simulation and Interpretation of Electrochemical Impedance Diagrams: Part IV. Second-Order Electrochemical Impedances, J. Electroanal. Chem. **352**, 1
- Dimitrova P., Friedrich K.A., Vogt B., Stimming U. (2002), J. Electroanal. Chem. **532**, 75- 83
- Doyle M., Choi S., Proulx G. (2000), High-Temperature Proton Conducting Membranes Based on Perfluorinated Ionomer Membrane-Ionic Liquid Composites, J. Electrochem. Soc. **147**, 34-37
- Drillet J.-F., Ee A., Friedemann J., Kotz R., Schnyder B., Schmidt V.M. (2002), Oxygen Reduction at Pt and Pt₇₀Ni₃₀ in H₂SO₄/CH₃OH Solution, Electrochim. Acta **47**, 1983-1988
- Du Z., Hao J., Li H. (2004), Nucleation and growth of CaCO₃ crystals on PDAC/PSS self-assembled multilayers, Chemical Journal on Internet **6**, 59
- Duff G.D., Edwards P.D., Johnson B.F.G. (1995), Formation of a Polymer-Protected Platinum Sol: A New Understanding of the Parameters Controlling Morphology, J. Phys. Chem. **99**, 15934-15944
- Ederhardt W., Fayet P., Cox D.M., Fu Z., Kaldor A., Sherwood R., and Sondericker D. (1990), Photoemission from mass-selected monodispersed Pt clusters, Phys. Rev. Lett. **64**, 780
- Eikerling M., Kornyshev A.A., and Stimming U. (1997), Electrophysical Properties of Polymer Electrolyte Membranes: A Random Network Model, J. Phys. Chem. B **101**, 10807
- Ferreira M., Cheung J.H., Rubner M.F. (1994), Molecular self-assembly of conjugated polyions: a new process for fabricating multilayer thin film heterostructures, Thin Solid Films **244**, 806
- Fournier J., Faubert G., Tilquin J.Y., Cote R., Guay D. and Dodelet J.P. (1997), High-Performance, Low Pt Content Catalysts for the Electroreduction of Oxygen in Polymer-Electrolyte Fuel Cells, J. Electrochem. Soc., **44**, 145
- Fu X., Wang Y., Wu N., Gui L., and Tang Y. (2001), Surface Modification of Small Platinum Nanoclusters with Alkylamine and Alkylthiol: An XPS Study on the Influence of Organic

Reference

- Ligands on the Pt 4f Binding Energies of Small Platinum Nanoclusters, J. Colloid Interface Sci. **243**, 326-330
- Fujiwara N., Yasuda K., Ioroi T., Siroma Z., Miyazaki Y. (2002), Preparation of Platinum-Ruthenium onto Solid Polymer Electrolyte Membrane and the Application to a DMFC Anode, Electrochim. Acta **47**, 4079-4084
- Gardenas-Trivino G., Klabunde K., Brock D.E. (1987), Living colloidal palladium in nonaqueous solvents. Formation, stability, and film-forming properties. Clustering of metal atoms in organic media. 14, Langumier **3**, 986
- Gardner C.L., Anantaraman A.V. (1998), Studies on ion-exchange membranes. II. Measurement of the anisotropic conductance of Nafion®, J. Electroanal. Chem. **449**, 209
- Gode P., Jaouen F., Lindbergh G., Lundblad A., Sundholm G. (2003), Influence of the Composition on the Structure and Electrochemical Characteristics of the PEFC cathode, Electrochemical Characteristics of the PEFC cathode, Electrochim. Acta **48**, 4174-418
- Goodenough J.B., Hamnett A., Kennedy B.J., Weeks S.A. (1987), XPS investigation of platinized carbon electrodes for the direct methanol air fuel cell, Electrochim. Acta **32**, 1233.
- Manohara R., Goodenough J.B. (1992), Methanol oxidation in acid on ordered NiTi, J. Mater. Chem. **2**, 875
- Gottesfeld S. and Pafford J. (1988), A New Approach to the Problem of Carbon Monoxide Poisoning in Fuel Cells Operating at Low Temperatures, J. Electrochem. Soc. **135**(10), 2651
- Gottesfeld S. and Zawodzinski T. A. (1997), Adv. Electrochem. Sci. Eng. **5**, 195
- Guo S., Popovitz-Biro R., Arad T., Hodes G., Leiserowitz L., Lahav M. (1998), Superlattices of Semiconductor Quantum-Size Lead Sulfide Particles Prepared by Topotactic Gas-Solid Reaction, Adv. Mater. **10**, 657
- Halim K.M., Buchi F.N., Haas O., Stamm M., Scherer G.G. (1994), Characterization of perfluorosulfonic acid membranes by conductivity measurements and small-angle x-ray scattering, Electrochim. Acta **39**, 1303
- Hara M., Mallouk T.E. (2000), Photocatalytic water oxidation by Nafion-stabilized iridium oxide colloids, Chem. Commun. **12**, 1903-1904
- Haufe S., Stimming U. (2001), Proton conducting membranes based on electrolyte filled microporous matrices, J. Membr. Sci. **185**, 95
- Haug A.T. , White R.E., Weidner J.W., Huang W., Shi S., Stoner T., Rana N. (2002), Increasing Proton Exchange Membrane Fuel Cell Catalyst Effectiveness Through Sputter Deposition, J. Electrochem. Soc. **149**, A280.
- Henglein A., Ershov B.G., Malow M. (1995), "Absorption Spectrum and Some Chemical Reactions of Colloidal Platinum in Aqueous Solution", J. Phys. Chem. **99**, 14129.
- Hepel M. (1998), The Electrocatalytic Oxidation of Methanol at Finely Dispersed Platinum Nanoparticles in Polypyrrole Films, J. Electrochem. Soc. **145**, 124

Reference

- Hirano S., Kim J. and Srinivasan S. (1997), High Performance Proton Exchange Membrane Fuel Cells with Sputter-deposited Pt Layer electrodes, Electrochim. Acta **42**, 1587-1593
- Hodgson D.R., May B., Adcock P.L., Davies D.P. (2001), New Lightweight Bipolar Plate System for Polymer Electrolyte Membrane Fuel Cells, J. Power Sources **96**, 233
- Hoggarth M. and Glipa X. (2001), High Temperature Membranes for Solid Polymer Fuel Cells”, ETSU Ref: ETSU F/02/00189/REF (DTI/Pub URN 01/893), Johnson Metthey Technology Centre
- Hunter R.J (1986), Foundations of Colloid Science, **Vol 1**, Oxford University Press
- Jia N., Lefebvre M.c., Halfyard J., Qi Z., Pickup P.G. (2000), Modification of Nafion Proton Exchange Membranes to Reduce Methanol Crossover in PEM Fuel Cells, Electrochem. Solid-State Lett. **3**, 529
- Jia R-L., and Wang C-Y (2005), Preparation of Platinum supported on Carbon Blacks with Different Surface Chemical Characteristics, Third International Conference on Fuel Cell Science, Engineering and Technology, Proceedings of Fuel Cell 2005, May 23-25, Ypsilanti, Michigan
- Jiang R., Chu D. (2000), Remarkably Active Catalysts for the Electroreduction of O₂ to h₂O for Use in an Acidic Electrolyte Containing Concentrated Methanol, J. Electrochem. Soc. **147**, 4605-4609
- Johal M.S., Casson J.L., Chiarelli P.A., Liu D.-G., Shaw J.A, Robinson J.M., Wang H.-L. (2003), Langmuir **19**, 8876-8881
- Jusys Z., Kaiser J., Behm R.J. (2002), Composition And Activity Of High Surface Area Pt/Ru Catalysts towards Adsorbed CO and Methanol Electrooxidation: A DEMS Study, Electrochim. Acta **47**, 3693
- Kardash D., Korzeniewski C., Markovic N. (2001), Effects of Thermal Activation on the Oxidation Pathways of Methanol at Bulk Pt–Ru Alloy Electrodes, J. Electroanal. Chem. **500**, 518
- Kerres J.A. (2001), Development of Ionomer Membranes for Fuel Cells, J. Membrane Sci. **185**, 3
- Kim D.W., Choi H.-S., Lee C., Blumstein A., Kang Y. (2004a), Investigation on methanol permeability of Nafion modified by self-assembled clay-nanocomposite multilayers, Electrochim. Acta **50**, 659
- Kim H., Popov B.N. (2004b), Development of Novel Method for Preparation of PEMFC Electrodes, Electrochem. Solid-State Lett. **7**, A71
- Kim H.J. , Kim H.J., Shul Y.G., Han H.S. (2004c), Nafion–Nafion/polyvinylidene fluoride–Nafion laminated polymer membrane for direct methanol fuel cells, J. Power Sources **135**, 66
- Kim J., Lee S.M. and Srinivasan S. (1995), Modeling of Proton Exchange Membrane Fuel Cell Performance with an Empirical Equation, J. Electrochem. Soc. **142**, 2670
- Kim Y.J., Choi W.C., Woo S.I., Hong W.H. (2004d), Evaluation of a palladinized Nafion™ for direct methanol fuel cell application, Electrochim. Acta **49**, 3227

Reference

- Kolde J.K., B. Bahar (1995), Proceedings of the Fourth Grove Fuel Cell Symposium, September 19-22, 1995, London, England.
- Kordesch K, Simader G.(1994), Fuel Cells and Their Applications. Weinheim: VCH, 1994.
- Korgel B.A., Fitzmaurice D. (1998), Self-Assembly of Silver Nanocrystals into Two-Dimensional Nanowire Arrays, Adv. Mater. **10**, 661
- Kreuer K.D. (2001), On the development of proton conducting polymer membranes for hydrogen and methanol fuel cells, J. Membrane Sci. **185**, 29
- Kumar G.S., Raja M., and Parthasarathy S. (1995), High Performance Electrodes with Very Low Platinum Loading for Polymer Electrolyte Fuel Cells, Electrochim. Acta **40**, 285
- Kullkovsky A. (2005), On the Nature of Mixed Potential in a DMFC, J. Electrochem. Soc. **152**, A1121-1127
- Le Rhan V., Alonso-Vante N. (2000), Tailoring of Nanodivided Electrocatalyst Materials Based on Transition Metal, J. New Mater. Electrochem. Syst. **3**, 331-336
- Lee C., Scotti M., Ulman A., White H., Rafailovich M., and Sokolov J. (1999), One-Phase Synthesis of Thiol-Functionalized Platinum Nanoparticles, Langmuir **15**, 4314
- Lee S.J., Mukerjee S., McBreen J., Rho Y.W., Kho Y.T., Lee T.H. (1998), Effects of Nafion Impregnation on Performances of PEMFC Electrodes, Electrochim. Acta **43**, 3693-3701
- Li G., Pickup P.G. (2003), Ionic Conductivity of PEMFC Electrodes-Effect of Nafion Loading, J. Electrochem. Soc. **150**, C745-C752
- Liu L., Pu C., Viswanathan R., Fan Q., Liu R., Smotkin E.S. (1998), Carbon Supported and Unsupported Pt-Ru Anodes for Liquid Feed Direct Methanol Fuel Cells, Electrochim Acta **43**, 3657-3663
- Liu Y.C., Qin X.P., Huang Y.W., Zhu W.T., Wu G.S. (2002), J. Appl. Electrochem. **32**, 1279
- Liu Z. , Ling X.Y., Su X., Lee J.Y. (2004), Carbon Supported Pt and PtRu Nanoparticles as Catalysts for a Direct Methanol Fuel Cells, J. Phys. Chem. B **108**, 8234.
- Lvov Y., Ariga K., Ichinose I., Kunitake T. (1995), Assembly of Multicomponent Protein Films by Means of Electrostatic Layer-by-Layer Adsorption, J. Am. Chem. Soc. **117**, 6117
- Lyons, M.E.G., (1994), Electroactive Polymer Electrochemistry, Plenum Press, New York
- Maceda J.P. (1999), "Funding Fuel Cells", Presentation at Conference on Commercializing Advanced Vehicle Propulsion Systems 99, Vancouver, BC, March 22-24, 1999. Intertech, Inc., Portland, ME
- Mahlendorf K.F., Peincke V., Heinzl A. (1995), Development of Electrode/Membrane Units for the Reversible Solid Polymer Fuel Cell (RSPFC), Electrochim. Acta **40**, 315
- Maillard F., Martin M., Gloaguen F., Leger J-M. (2002), Oxygen Electroreduction on Carbon-Supported Platinum Catalysts. Particle-Size Effect on the Tolerance to Methanol Competition, Electrochim. Acta **47**, 3431-40

Reference

- Makkus R. C., Janssen A. H. H., de Bruijn F. A., and Mallant R. K. A. M. (2000), Use of Stainless Steel for Cost Competitive Bipolar Plates in the SPFC, J. Power Sources **86**, 274
- Malhotra S., Datta R. (1997), Membrane-Supported Nonvolatile Aodic Electrolytes Allow Higher Temperature Operation of Proton-Exchange Membrane Fuel Cells, J. Electrochem. Soc. **144**, L23-26
- Manohara R., Goodenough J.B. (1992), Methanol oxidation in acid on ordered NiTi, J. Mater. Chem. **2**, 875
- Maoka T. (1988), Electrochemical Reduction of Oxygen on Small Platinum Particles Supported on Carbon in Concentrated Phosphoric Acid-II Effects of Teflon Content in the Catalyst Layer and Baking Temperature of the Electrode, Electrochim. Acta **33**, 379
- Middelmann E. (2002), Improved PEM Fuel Cell Electrodes by Controlled Self-assembly, Fuel Cells Bull. November (2002) 9
- Miyake N., Wainright J.S., Savinell R.F. (2001), Evaluation of a Sol-Gel Derived Nafion/Silica Hybrid Membrane for Polymer Electrolyte Membrane Fuel Cell Applications: II. Methanol Uptake and Methanol Permeability, J. Electrochem. Soc. **148**, A905
- Modrow, H., Bucher, S., Hormes, J., Brinkmann, R., Bonnemann, H., (2003), Model for Chainlength-Dependent Core-Surfactant Interaction in N(Alkyl)₄Cl-Stabilized Colloidal Metal Particles Obtained from X-ray Absorption Spectroscopy, J. Phys. Chem. B **107**, 3684
- Mohr R., Kudela V., Schauer J., Richau K. (2002), Comparison of Different Cells for Resistance Determination of Freely Standing Polymer Membranes Developed for Direct Methanol Fuel Cell (DMFC) Applications, Desalination **147**, 191
- Morimoto Y., Yeager E.B. (1998), Comparison of Methanol Oxidations on Pt, Pt/Ru and Pt/Sn Electrodes, J. Electroanal. Chem. **444**, 95
- Mosdale R. and Srinivasan S. (1995), Analysis of Performance and of Water and Thermal Management in Proton Exchange Membrane Fuel Cells, Electrochim. Acta **40**, 413
- Motte L., Billoudet F., Jacaze E., Douin J., Pileni M.P. (1997), Self-Organization into 2D and 3D Superlattices of Nanosized Particles Differing by Their Size, J. Phys. Chem. B **101**, 138
- Mu X.-D., Evans D.G., Kou Y. (2004), A General method for Preparation of PVP-stabilized Noble Metal Nanoparticles in Room Temperature Ionic Liquids, Catalysis Letters **97**, 151-154
- Murr L.E. (1991), Electron and Ion Microscopy and Microanalysis: Principles and Applications (Optical Engineering, **v.29**), ISBN 0-8247-8556-8, Marcell Dekker, Inc. 1991:381
- Nguyen T.V. (1996), A Gas Distributor for Proton-Exchange-Membrane Fuel Cells, J. Electrochem. Soc. **143**, L103
- Niu L. , Li Q., Wei F., Wu S., Liu P., Cao X. (2005), Electrocatalytic Behavior of Pt-Modified Polyaniline Electrode for Methanol Oxidation: Effect of Pt Deposition Modes, J. Electroanal. Chem. **578**, 331.

Reference

- Nouel K.M., Fedkiw P.S. (1998), Nafion[®]-based Composite Polymer Electrolyte Membranes, Electrochim. Acta **43**, 2381
- Nuzzo R.G., Allara D.L. (1983), Adsorption of Bifunctional Organic Disulfides on Gold Surfaces, J. Am. Chem. Soc. **105**, 4481
- O'Hayre R., Lee S.-J., Cha S.-W., Prinz F.B. (2002), A Sharp Peak in the Performance of Sputtered Platinum Fuel Cells at Ultra-low Platinum Loading, J. Power Sources **109**, 483.
- Ochida M., et al. (1995), New Preparation Method for Polymer-Electrolyte Fuel Cells, J. Electrochem. Soc. **142**, 463
- Orkin V.L., Huie R.E. (1997), Kurylo M.J., Rate Constants for the Reactions of OH with HFC-245cb (CH₃CF₂CF₃) and Some Fluoroalkenes (CH₂CHCF₃, CH₂CFCF₃, CF₂CFCF₃, and CF₂CF₂), J. Phys. Chem. A **101**, 9118-9124
- Paganin V.A., Oliveira C.L.F., Ticianelli E.A., Springer T.E. and Gonzalez E.R. (1998), Modelistic Interpretation of the Impedance Response of a Polymer Electrolyte Fuel Cell, Electrochim. Acta **43**, 3761
- Paulus U.A., Endruschat U., Eeldmeyer G.J., Schmid T.J., Bonnemann H., Behm R.J. (2003), New PtRu Alloy Colloids as Precursors for Fuel Cell Catalysts. J. Catal. **195**, 383
- Perez J., Gonzalez E.R., Ticianelli A. (1998), Oxygen Electrocatalysis on Thin Porous Coating Rotating Platinum Electrodes, Electrochim. Acta **44**, 1329-1339
- Perez J.R., Lopez-Atalaya M., Codina G., Vazquez J.L., Aldaz A. (1991), Bull. Electrochem. **7**, 559
- Petrow H.G., Allen R.J. (1976), U.S. Patent, No. 3992331
- Poizo A., De Francesco M., Cemmi A., Cardellini F., Giorgi L. (2002), Comparison of High Surface Pt/C Catalysts by Cyclic Voltammetry, J. Power Sources **105**, 12
- Pourcelly G., Oikonomon A., Gavach C., Hurwitz H.D. (1997), Influence of the water content on the kinetics of counter-ion transport in perfluorosulphonic membranes, J. Electroanal. Chem. **287**, 43
- Prabhuram J., Zhao T.S., Liang Z.X., Yang H., Wong C.W. (2005), Pd and Pd-Cu alloy of Methanol Crossover in Direct Methanol Fuel Cells, J. Electrochem. Soc. **152**, A1390-1397
- Prabhuram J., Wang X., Hui C.L., Hsing I-M. (2003), Synthesis and Characterization of Surfactant-Stabilized Pt/C Nanocatalysts for Fuel Cell Applications, J. Phys. Chem. B **107**, 11057-11064
- Pu C., Huang W., Ley K.L., Smotkin E.S. (1995), A Methanol Impermeable Proton Conducting Composite Electrolyte System, J. Electrochem. Soc. **142**, L119
- Qi Z., Pickup P.G., (1998) Novel Supported Catalysts: Platinum and Platinum Oxide Nanoparticles Dispersed on Polypyrrole/Polystyrenesulfonate Particles, Chem. Commun. **10**, 15-16
- Qi Z., Kaufman A. (2002), Open Circuit Voltage and Methanol Crossover in DMFCs, Journal of Power Sources **110**, 177-185

Reference

- Raistrick I.D. (1989), Electrode Assembly for Use in a Solid Polymer Electrolyte Fuel Cell, US Patent, 4876115
- Ravikumar M.K., Shukla A.K. (1996), Effect of Methanol Crossover in a Liquid-Feed Polymer Electrolyte Direct Methanol Fuel Cell, J. Electrochem. Soc. **143**, 2601
- Ren X., M.S. Wilson and Gottesfeld S. (1996), High Performance Direct Methanol Polymer Electrolyte Fuel Cells, J. Electrochem. Soc. **143**, L12
- Ren X., Springer T. E., and Gottesfeld S. (2000), Water and Methanol Uptakes in Nafion Membranes and Membrane Effects on Direct Methanol Cell Performance, J. Electrochem. Soc. **147**, 92
- Rajalakshmi N., Ryu H., Dhathathreyan K.S. (2004), Platinum Catalysed Membranes for Proton Exchange Membrane Fuel Cells-Higher Performance, Chem. Eng. J. **102**, 241-247
- Rivadullar J.F., Vergara M.C., Blanco M.C., López-Quintela M.A., Rivas J. (1997), "Optical Properties of Platinum Particles Synthesized in Microemulsions" J. Phys. Chem. B **101**, 8997
- Ross P. N. (1998), Jr. in Electrocatalysis, Lipkowski J. and Ross P. N., Editors, Chap. 2, p. 43, Wiley-VCH, New York
- Roth C., Marty N., Hahn F., Leger J.-M., Lamy C., Fuess H. (2002), Characterization of Differently Synthesized Pt-Ru Fuel Cell Catalysts by Cyclic Voltammetry, FTIR Spectroscopy, and in Single Cells, J. Electrochem. Soc. **149**, E433
- Sara L.S., Lin T.O., Tsai Y.-W, Chen J.H., Hwang B.J. (2005), Carbon-supported Pt–Ru catalysts prepared by the Nafion stabilized alcohol-reduction method for application in direct methanol fuel cells, J. Power Sources **139**, 44-54
- Sasikumar G., Ihm J.W., Ryu H. (2004), Dependence of optimum Nafion content in catalyst layer on platinum loading, J. Power Sources **132**, 11
- Savadogo (1998), J. New Mater. Electrochem. Sys. **1**, 47
- Schmidt T.J., Gasteiger H.A., Behm R.J. (1999), Methanol Oxidation on a Colloidal PtRu-alloy Fuel-cell Catalyst, Electrochem. Commun. **1**, 1-4
- Schimid G., Emde S., Maihack V., Meyer-Zaika W., Peschel St. (1996), Synthesis and Catalytic Properties of Large Ligand Stabilized Palladium Clusters, J. Molecular Catalysts A: Chemical **107**, 95-104
- Sebastian P.J, Rodriguez F.J., Solorza O., Rivera R. (1999), J. New Mater. Electrochem. Soc. **145**, 115-119
- Shao Z.-G., Wang X., Hsing I.-M. (2002), Composite Nafion/polyvinyl Alcohol Membranes for the Direct Methanol Fuel Cell, J. Membrane Sci. **210**, 147
- Shenton W., Pum D., Sleytr U.B., Mann S. (1997), Synthesis of Cadmium Sulphide Superlattices Using Self-Assembled Bacterial S-Layers, Nature **389**, 585
- Shimaze E., Kawaguchi T., Tada K. (2002), Preparation of binary metal electrocatalysts by self-assembly of precursor ionic species on gold and reduction of nitrate ions, J. Electroanal. Chem. **529**, 20

Reference

- Shukla A.K. and Raman R.K. (2003), Methanol-Resistant Oxygen-Reduction Catalysts for Direct Methanol Fuel Cells, Annu. Rev. Mater. Res. **33**, 155-68
- Sigaard M., Odgaard M., Skou E.M. (2001), An Improved Method for the Determination of the Electrochemical Active Area of Porous Composite Platinum Electrodes, Solid State Ionics **145**, 31
- Silva R.F., De Francesco M., Poizo A. (2004), Tangential and normal conductivities of Nafion[®] membranes used in polymer electrolyte fuel cells, J. Power Sources **134**, 18-26
- Silva R.F., Passerini S., Pozio A. (2005), Solution-cast Nafion[®]/montmorillonite composite membrane with low methanol permeability, Electrochim. Acta **50**, 2639-2645
- Slade S., Campbell S.A., Ralph T.R., Walsh F.C. (2002), Ionic Conductivity of an Extruded Nafion 1100 EW Series of Membranes, J. Electrochem. Soc. **149** (12), A1556
- Springer T.E., Zawodzinski T.A., Wilson M.S. and Gottesfeld S. (1996), Characterization of Polymer Electrolyte Fuel Cells Using AC Impedance Spectroscopy, J. Electrochem. Soc. **143**, 587
- Srinivasan S., Ticianelli E.A., Derouin C.R. and Redondo A. (1988), Advances in solid polymer electrolyte fuel cell technology with low platinum loading electrodes, J. Power Sources **22**, 359
- Sumner J.J., Creager S.E., Ma J.J., Desmarteau D.D. (1998), Proton Conductivity in Nafion[®]117 and in a Novel Bis[(perfluoroalkyl)sulfonyl]imide Ionomer Membrane, J. Electrochem. Soc. **145** (1), 107
- Sun Y.-P., Rollins H.W., Guduru R. (1999), Preparations of Nickel, Cobalt, and Iron Nanoparticles through the Rapid Expansion of Supercritical Fluid Solutions (RESS) and Chemical Reduction, Chem. Mater. **11**, 7
- Taylor E.J., Anderson E.B., and Vilambi N.R.K. (1992), Preparation of High-Platinum-Utilization Gas Diffusion Electrodes for Proton-Exchange-Membrane Fuel Cells, J. Electrochem. Soc. **139**, L45
- Teranishi T., Hosoe M., Tanaka T., Miyake M. (1999), Size Control of Monodispersed Pt Nanoparticles and Their 2D Organization by Electrophoretic Deposition, J. Phys. Chem. B **103**, 3818.
- Thompson S.D., Jordan L.R., Forsyth M. (2001), Platinum Electrodeposition for Polymer Electrolyte Membrane Fuel Cells, Electrochim. Acta **46**, 1657.
- Ticianelli E.A., Derouin C.R. and Srinivasan S. (1988), Localization of Platinum In Low Catalyst Loading Electrodes to Attain High Power Densities in SPE Fuel Cells, J. Electroanal. Chem. **251**, 275
- Ticianelli E., Beery J.G., Paffett M.T., Gottesfeld S. (1989), An Electrochemical, Ellipsometric, and Surface Science Investigation of the PtRu Bulk Alloy Surface, J. Electroanal. Chem. **258**, 61-77
- Toshima N., Nakata K., Kitoh H. (1997), "Giant platinum clusters with organic ligands: preparation and catalysis", Inorg. Chim. Acta **265**, 149

Reference

- Toshima N., Shiraishi Y., Teranishi T., Miryake M., Tominagam T., Watanabe H., Brijoux W., Bonnemann H., Schmid, G. (2001), Various ligand-stabilized metal nanoclusters as homogeneous and heterogeneous catalysts in the liquid phase, Appl. Organometal. Chem. **15**, 178
- Tributsch H., Bron M., Hilgendorff M., Schulenburg H., Dorbandt I. (2001), Methanol-Resistant Cathodic Oxygen Reduction Catalysts for Methanol Fuel Cells, J. Appl. Electrochem. **31**, 739–48
- Tricoli V. (1998), Proton and Methanol Transport in Poly(perfluorosulfonate) Membranes Containing Cs⁺ and H⁺ Cations, J. Electrochem. Soc. **145**, 3798-3800
- Tricoli, Carretta N., Bartolozzi M. (2000), A Comparative Investigation of Proton and Methanol Transport in Fluorinated Ionomeric Membranes, J. Electrochem. Soc. **147** (4) 1286
- Uchida H., Mizuno Y., and Watanabe M. (2000), Suppression of Methanol Crossover in Pt-Dispersed Polymer Electrolyte Membrane for Direct Methanol Fuel Cells, Chem. Lett. **29**, 1268
- Uchida M., Fukuoka Y., Sugawara Y., Ohara H., Ohta A. (1998), Improved Preparation Process of Very-Low-Platinum-Loading Electrodes for Polymer Electrolyte Fuel Cells, J. Electrochem. Soc. **145**, 3708
- Ulman A. (1996), Formation and Structure of Self-Assembled Monolayers, Chem. Rev. **96**, 1533
- Verbrugge M., Hill R. (1990), Analysis of Promising Perfluorosulfonic Acid Membranes for Fuel-Cell Electrolytes, J. Electrochem. Soc. **137**, 3770
- Vielstich W., Paganin V.A., Lima F.H.B., Ticianelli E.A. (2001), Nonelectrochemical Pathway of Methanol Oxidation at a Platinum-Catalyzed Oxygen Gas Diffusion Electrodes, J. Electrochem. Soc. **148**, A502-A505
- Vilambi N.R.K. (1992), Anderson E.B., Taylor E.J., US patent 5,084,144
- Voss H.H., Wilkinson D.P., Pickup P.O., Johnson M.C., Basura V. (1995), Anode Water Removal: A Water Management and Diagnostic Technique for Solid Polymer Fuel Cells, Electrochim. Acta **40**, 321-328
- Wakizoe M., Velez O.A., Srinivasan S. (1995), Analysis of proton exchange membrane fuel cell performance with alternate membranes, Electrochim. Acta **40**, 335
- Wang L-Z., Shi J-L., Zhang W-H., Ruan M-L., Yu J., Yan D-S. (1999), Self-organization of Ordered Silver Nanocrystal Arrays on Cubic Mesoporous Silica Surfaces, Chem. Mater. **11**, 3015-3017
- Wang C., Waje M., Wang X., Tang J.M., Haddon R.C., Yan Y.S. (2004), Proton Exchange Membrane Fuel Cells with Carbon Nanotube Based Electrodes, Nano. Lett. **4**, 345
- Wang X., Hsing I-M. (2002), Sufactant Stabilized Pt and Pt Alloy Electrocatalysts for Polymer Electrolyte Fuel Cells, Electrochim. Acta **47**, 2981-2987
- Wang Y., Ken J.-W, Deng K., Gui L.-L., Tang Y.-Q (2000), Chem. Commun. **12**, 1622

Reference

- Wasmus S., Kuver A. (1999), Methanol Oxidation and Direct Methanol Fuel Cells: A Selective Review, J. Electroanal. Chem. **461**, 14
- Watanabe M., Genjima Y., Turumi K. (1997), Direct Methanol Oxidation on Platinum Electrodes with Ruthenium Adatoms in Hot Phosphoric Acid, J. Electrochem. Soc. **144**, 423.
- Watanabe M., Uchida M., Motoo S. (1987), Preparation of Highly Dispersed Pt + Ru Alloy Clusters and the Activity for the Elecicrooxidation of Methanol, J. Electroanal. Chem. **229**, 395-406
- Wei Z.D. , S.H. Chan (2004), Electrochemical deposition of PtRu on an uncatalyzed carbon electrode for methanol electrooxidation , J. Electroanal. Chem. **569**, 23
- Wertheim G.K., Diczno S.B., and Young S.E. (1983), Unit Charge on Supported Gold Clusters in Photoemission Final State, Phys. Rev. Lett. **51**, 2310
- Wilkinson D.P. and Thompsett D. (1997), in “Proc. of the Second Int. Symp. on New materials for Fuel Cell and modern Battery Systems”, eds. Savadogo O. and Roberge P.R., Les Edition de l'Ecole polytechnique de montreal, Canada, p266
- Wilkinson D.P., Voss H.H., Dudley J., Lamont G.J. and Basura V. (1996), U.S. Patent 5,482,680
- Wilson M.S., Gottesfeld S. (1992), High Performance Catalyzed Membranes of Ultra-Low Platinum Loadings for Polymer Electrolyte Fuel Cells, J. Electrochem. Soc. **139**, L28.
- Wilson M.S., Gottesfeld S. (1992), Thin-Film Catalyst Layer for Polymer Electrolyte Fuel Cell Electrodes, J. Applied Electrochem. **22**, 1-7
- Witham, C.K. chun W., Valdez T.I. and Narayanan S.R. (2000), Performance of Direct Methanol Fuel Cells with Sputter-Deposited Anode Catalyst Layers, Electrochem. Solid-state Lett. **3**, 497
- Yan, X. Liu H., Liew K.Y. (2001), “Size Control of Polmer-stabilized Ruthenium Nanoparticles by Polyol Reduction”, J. Mater. Chem. **11**, 3387-3391
- Yang C., Srinivasan S., Arico A. S., Creti P., Baglio V., and Autonuucci V. (2001), Composite Nafion/Zirconium Phosphate Membranes for Direct Methanol Fuel Cell Operation at High Temperature, Electrochem. Solid-State Lett. **4**, A31
- Yang, N., Zoski, C.G., (2006), Polymer Films on Electrodes: Investigation of Ion Transport at Poly(3,4-ethylenedioxythiophene) Films by Scanning Electrochemical Microscopy, Langmuir **22**, 10338
- Yin Y., Lu L., Gates B., Xia Y., Template-Assisted Self-assembly: A Pratical Route to Complex Aggregates of Monodispersed Colloids with Well-Defined Sizes, Shapes, and Structures, J. Am. Chem. Soc., 123(2001)8718-8729
- Yoon S.R., Hwang G.H., Cho W.I., Oh I.-H., Hong S.-A., Ha H.Y. (2002), Modification of Polymer Electrolyte Membranes for Dmfcs Using Pd Films Formed by Sputtering, J. Power Sources **106**, 215-223

Reference

- Zapotoczny S., Golonka M., Nowakowska M. (2005), Novel Photoactive Polymeric Multilayer Films Formed via Electrostatic Self-Assembly, Macromol. Rapid Commun. **26**, 1049
- Zawodzinski T.A. , Neeman M., Sillerud L.O., Gottesfeld S. (1991), Determination of Water Diffusion Coefficients in Perfluorosulfonate Ionomeric Membranes, J. Phys. Chem. **95**, 6040
- Zhang H., Wang Y., Fachini E. R., and Cabrera C. R. (1999), Electrochemically Codeposited Platinum/Molybdenum Oxide Electrode for Catalytic Oxidation of Methanol in Acid Solution, Electrochem. Solid-State Lett. **2**, 437
- Zhang Y., Erkey C. (2005), Preparation of Platinum-Nafion-Carbon Black Nanocomposites via a Supercritical Fluid Route as Electrocatalysts for Proton Exchange Membrane Fuel Cells, Ind. Eng. Chem. Res. **44**, 5312-5317
- Zotti G., Zecchin S., Vercelli B., Berlin A., Grimoldi S., Bertoncello R., Milanese (2005), Self-assembled Monolayers and Electrostatically Self-assembled Multilayers of Polyalkylviologens on Sulfonate-modified Gold and Indium-tin-oxide Electrodes, J. Electroanal. Chem. **580**, 330-339