Non-platinum based electrocatalysts for alkaline direct ethanol fuel cell

Nguyen, Truong Son

2012

Nguyen, T. S. (2012). Non-platinum based electrocatalysts for alkaline direct ethanol fuel cell. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/48684>

<https://doi.org/10.32657/10356/48684>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**NON-PLATINUM BASED
ELECTROCATALYSTS FOR ALKALINE
DIRECT ETHANOL FUEL CELL**

NGUYEN TRUONG SON

NGUYEN TRUONG SON

SCHOOL OF CHEMICAL AND BIOMEDICAL ENGINEERING

2012

2012

**NON-PLATINUM BASED
ELECTROCATALYSTS FOR ALKALINE
DIRECT ETHANOL FUEL CELL**

NGUYEN TRUONG SON

SCHOOL OF CHEMICAL AND BIOMEDICAL
ENGINEERING

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

2012

ACKNOWLEDGEMENTS

I would like to express my deepest gratitude and appreciation to my supervisors, Assoc. Prof. Wang Xin and Prof. Chan Siew Hwa for their support, encouragement and guidance throughout the project.

I am very grateful to Nanyang Technological University and AUN/SEED-Net for giving me the PhD scholarship.

I am so thankful to Dr. Nguyen Tien Hoa, Dr. Wang Shuangyin, Dr. Noel Kristian, Dr. Yu Yaolun and other lab members for their useful advice and help with materials characterization.

I would like to appreciate the Technical Executives, Ms. Mah Sook Yee, Ms. Lee Shuhui Valerie and Mr. Muhammad Ruzaini Bin Ghazali with the help in purchasing lab items.

I would also like to thank my parents for bringing me up and supporting me at every step of my life. Finally, I would like to thank my wife for her love and support during these years.

ABSTRACT

It is well-known that conventional fossil fuel is not going to last more than a few hundred years in the face of increasing energy demand in the developed and developing countries. Moreover, the gas emission from the combustion of fossil fuels by heat engines has been polluting the living environment and causing green-house effect. Therefore, it is urgent to find new technologies for energy conversion and power generation. Recently, direct ethanol fuel cells (DEFCs) have attracted more and more attention as clean and high efficient energy conversion devices. However, the expensive cost of Pt in the fuel cell electrocatalysts limits the commercialization of DEFCs. Pd, which is cheaper than Pt, has been found to be more active for ethanol electrooxidation in alkaline media than Pt. On the other hand, the corrosion of carbon-based catalyst supports in polymer electrolyte membrane fuel cells (PEMFCs) has been known as one of the main factors limiting the lifetime of the fuel cells. As a result, the research work in this thesis is focused on the designing of effective non-platinum based electrocatalysts for alkaline DEFCs (ADEFCs) by modifying Pd with promoters to reduce the cost of fuel cells and thus, improve their commercialization. Moreover, corrosion-resistance of titania-based materials is also studied in this work to explore their capability to replace carbon black in the role of catalyst support for ADEFCs.

Firstly, alloyed PdAg nanoparticles supported on carbon black were successfully synthesized by a co-reduction method. The alloyed catalysts showed their dominant ethanol oxidation reaction (EOR) activity compared with those of Pd/C and Pt/C in alkaline solutions. Among various PdAg/C catalysts with different Ag/Pd ratios, the highest EOR performance and poisoning-tolerance were observed for 10%Pd-10%Ag/C. The excellent EOR behavior of the alloyed catalysts derived from the improvement of hydroxyl

adsorption onto the catalyst surface due to the d-band center up-shift. Secondly, Tb, a rare-earth element, was used to modify Pd/C. Different Tb-promoted Pd/C catalysts were prepared and tested for EOR in alkaline condition. The catalysts displayed good activity for EOR with the most prominent performance obtained for 10%Pd-2%Tb/C. Thirdly, mesoporous titania was hydrothermally synthesized and used as an alternative support for Pd towards EOR in basic solutions. The mesoporous TiO₂-supported Pd catalyst showed better activity for EOR than Pd/C and Pd/commercial TiO₂ due to the mesoporosity and high hydroxyl content of mesoporous TiO₂. Durability tests confirmed that Pd/mesoporous TiO₂ has higher stability than the catalysts supported on carbon black and commercial TiO₂. Besides the mesoporous TiO₂, sub-stoichiometric Ti_nO_{2n-1} was prepared from commercial TiO₂ by H₂ reduction. Higher EOR activity and durability were observed for Pd/Ti_nO_{2n-1} in comparison with Pd/C and Pd/commercial TiO₂. Finally, Nb-doping was used to improve the electrical conductivity of TiO₂. Nb-doped TiO₂ showed an increase of electronic conductivity with the increase of Nb-doping level. Electrochemical characterization results determined that PdAg/Nb-doped TiO₂ catalysts possess outstanding catalytic activity for EOR, which is attributed to the interaction between the supports and PdAg nanoparticles. The PdAg/Nb-doped TiO₂ catalysts also displayed excellent durability with the best performance obtained for PdAg/Nb_{0.20}Ti_{0.80}O₂ and PdAg/Nb_{0.30}Ti_{0.70}O₂. PdAg/Nb_{0.30}Ti_{0.70}O₂ was found to have better electrocatalytic activity for EOR and higher durability in alkaline condition than PdAg/Ti_nO_{2n-1} and PdAg/mesoporous TiO₂.

Keywords: *alkaline direct ethanol fuel cell, palladium, silver, terbium, titanium dioxide, Nb-doped titania*

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	i
ABSTRACT.....	ii
TABLE OF CONTENTS	iv
LIST OF FIGURES	ix
LIST OF TABLES	xiv
LIST OF PUBLICATIONS.....	xv
NOMENCLATURE.....	xvi
1 Chapter 1 INTRODUCTION AND SCOPE OF THE THESIS	1
1.1 Introduction	1
1.2 Scope of the thesis	3
2 Chapter 2 LITERATURE REVIEW	7
2.1 Overview of direct ethanol fuel cells (DEFCs)	7
2.2 Working principles of ADEFCs.....	8
2.3 Thermodynamic data for ADEFC.....	8
2.4 Mechanism of ethanol oxidation in alkaline media.....	10
2.5 Pd-based anodic electrocatalysts for ADEFC.....	11
2.6 TiO_2 , $\text{Ti}_n\text{O}_{2n-1}$ and Nb-doped titania as catalyst supports	13

3	Chapter 3 ENHANCEMENT EFFECT OF Ag FOR Pd/C TOWARDS THE ETHANOL ELECTRO-OXIDATION IN ALKALINE MEDIA	16
3.1	Introduction	16
3.2	Experimental and characterization methods	17
3.2.1	Catalyst synthesis	17
3.2.2	Physical characterization	18
3.2.3	Electrochemical characterization	18
3.3	Results and discussion	20
3.3.1	Physical characterization	20
3.3.2	Electrochemical tests	24
3.4	Summary	38
4	Chapter 4 Tb PROMOTED Pd/C CATALYSTS FOR THE ELECTROOXIDATION OF ETHANOL IN ALKALINE MEDIA	39
4.1	Introduction	39
4.2	Experimental and characterization procedures	40
4.2.1	Materials	40
4.2.2	Synthesis of catalysts	41
4.2.3	Characterization	41
4.3	Results and discussion	42

4.4	Summary.....	53
5	Chapter 5 DURABILITY AND ETHANOL OXIDATION PERFORMANCE OF MESOPOROUS TiO ₂ -SUPPORTED Pd IN ADEFC.....	55
5.1	Introduction	55
5.2	Experimental and characterization methods.....	56
5.2.1	Materials and chemicals	56
5.2.2	Synthesis of mesoporous TiO ₂ and catalysts.....	56
5.2.3	Characterization	57
5.2.3.1	Physical characterization.....	57
5.2.3.2	Electrochemical characterization	58
5.3	Results and discussion	59
5.4	Summary.....	71
6	Chapter 6 PERFORMANCE OF SUB-STOICHIOMETRIC TITANIUM OXIDE AS CATALYST SUPPORT FOR Pd IN ADEFC	73
6.1	Introduction	73
6.2	Experimental and characterization methods.....	74
6.2.1	Materials.....	74
6.2.2	Synthesis of catalysts	74
6.2.3	Sample preparation for conductivity measurement.....	75

6.2.4	Characterization	75
6.2.5	Durability tests	76
6.3	Results and discussion	76
6.4	Summary	89
7	Chapter 7 EXPLORATION OF Nb-DOPED TiO ₂ AS CATALYST SUPPORT IN ADEFC	90
7.1	Introduction	90
7.2	Experimental and characterization methods	92
7.2.1	Preparation of Nb-doped TiO ₂ with 2, 5, 10, 20 and 30% Nb	92
7.2.2	Preparation of PdAg electrocatalysts	93
7.2.3	Sample preparation for conductivity measurement	94
7.2.4	Physical and electrochemical characterization	94
7.2.5	Durability tests	95
7.3	Results and discussion	96
7.3.1	Nb-doped TiO ₂	96
7.3.1.1	Nb _{0.10} Ti _{0.90} O ₂	96
7.3.1.2	Nb _x Ti _{1-x} O ₂	101
7.3.2	PdAg/Nb-doped TiO ₂	107

7.3.3	PdAg supported on different materials.....	119
7.4	Summary.....	122
8	Chapter 8 CONCLUSIONS AND RECOMMENDATIONS	124
8.1	Conclusions	124
8.2	Recommendations	126
	REFERENCES	128

LIST OF FIGURES

Figure 2-1 Working principle of ADEFC.....	8
Figure 2-2 Structures of (a) anatase and (b) rutile phases of TiO_2	15
Figure 3-1 XRD patterns of (a) 10%Pd/C, (b) 10%Ag/C, (c) 10%Pd-10%Ag/C and (d) 10%Pt/C.....	20
Figure 3-2 TEM images of (a) 10%Pt/C, (b) 10%Pd/C, (c) 10%Ag/C, (d) 10%Pd-10%Ag/C and (e) EDX pattern of 10%Pd-10%Ag/C.....	23
Figure 3-3 CV plots of 10%Ag/C in (a) 1M KOH and (b) 1M KOH + 1M $\text{C}_2\text{H}_5\text{OH}$ with a scan rate of 50 mV/s.....	24
Figure 3-4 LSVs for ethanol oxidation on (a) 10%Pt/C, 10%Pd/C and 10%Pd-10%Ag/C and (b) 10%Pd-5%Ag/C, 10%Pd-10%Ag/C, 10%Pd-15%Ag/C, 10%Pd-20%Ag/C and 10%Pd-25%Ag/C in 1M KOH+1M $\text{C}_2\text{H}_5\text{OH}$ with 50 mV/s scan rate	25
Figure 3-5 CO stripping voltammograms for (a) 10%Ag/C, (b) 10%Pd/C, (c) 10%Pd-5%Ag/C, (d) 10%Pd-10%Ag/C, (e) 10%Pd-15%Ag/C, (f) 10%Pd-20%Ag/C and (g) 10%Pd-25%Ag/C in 1M KOH solution, scan rate: 50 mV/s.....	27
Figure 3-6 CA curves for (a) 10%Pt/C, 10%Pd/C and 10%Pd-10%Ag/C and (b) 10%Pd-5%Ag/C, 10%Pd-10%Ag/C, 10%Pd-15%Ag/C, 10%Pd-20%Ag/C and 10%Pd-25%Ag/C in 1M KOH + 1M $\text{C}_2\text{H}_5\text{OH}$ solution at -0.25 V (vs. Hg/HgO)	31
Figure 3-7 Blank CVs of (a) Pd/C and (b) Pd-Ag/C in different KOH solutions, scan rate: 50 mV/s.....	33
Figure 3-8 LSV tests in 1M KOH+1M $\text{C}_2\text{H}_5\text{OH}$ solutions at different temperatures for (a) 10%Pd/C, (b) 10%Pd-5%Ag/C, (c) 10%Pd-10%Ag/C, (d) 10%Pd-15%Ag/C, (e) 10%Pd-20%Ag/C and (f) 10%Pd-25%Ag/C, scan rate: 50 mV/s.....	35

Figure 3-9 Arrhenius plots for (a) 10%Pd/C, (b) 10%Pd-5%Ag/C, (c) 10%Pd-10%Ag/C, (d) 10%Pd-15%Ag/C, (e) 10%Pd-20%Ag/C and (f) 10%Pd-25%Ag/C at -0.1 V	36
Figure 4-1 XRD spectra of (1) 10%Tb/C, (2) 10%Pd/C, (3) 10%Pd-0.5%Tb/C, (4) 10%Pd-1%Tb/C, (5) 10%Pd-2%Tb/C, (6) 10%Pd-5%Tb/C and (7) 10%Pd-10%Tb/C	42
Figure 4-2 TEM images of (a) 10%Tb/C, (b) 10%Pd/C, (c) 10%Pd-0.5%Tb/C, (d) 10%Pd-1%Tb/C, (e) 10%Pd-2%Tb/C, (f) 10%Pd-5%Tb/C and (g) 10%Pd-10%Tb/C	43
Figure 4-3 CVs for 10%Tb/C in 1M KOH and 1M KOH + 1M C ₂ H ₅ OH solutions, scan rate: 50 mV/s	45
Figure 4-4 LSVs for 10%Pd/C, 10%Pd-0.5%Tb/C, 10%Pd-1%Tb/C, 10%Pd-2%Tb/C, 10%Pd-5%Tb/C and 10%Pd-10%Tb/C in 1M KOH + 1M C ₂ H ₅ OH solution, scan rate: 50 mV/s	45
Figure 4-5 CVs for 10%Pd-10%Tb/C in different KOH solutions, scan rate: 50 mV/s	48
Figure 4-6 CVs for 10%Pd/C, 10%Pd-0.5%Tb/C, 10%Pd-1%Tb/C, 10%Pd-2%Tb/C, 10%Pd-5%Tb/C and 10%Pd-10%Tb/C in 1M KOH solution, scan rate: 50 mV/s	48
Figure 4-7 CA plots for (a) 10%Pd/C, (b) 10%Pd-0.5%Tb/C, (c) 10%Pd-1%Tb/C, (d) 10%Pd-2%Tb/C, (e) 10%Pd-5%Tb/C and (f) 10%Pd-10%Tb/C in 1M KOH + 1M C ₂ H ₅ OH solution at -0.25 V	51
Figure 4-8 Arrhenius plots for (a) 10%Pd/C, (b) 10%Pd-0.5%Tb/C, (c) 10%Pd-1%Tb/C, (d) 10%Pd-2%Tb/C, (e) 10%Pd-5%Tb/C and (f) 10%Pd-10%Tb/C in 1M KOH + 1M C ₂ H ₅ OH solutions at -0.1 V	52
Figure 5-1 WAXRD profiles of the supports and catalysts	60
Figure 5-2 SAXRD spectrum of mesoporous TiO ₂	60

Figure 5-3 N ₂ adsorption/desorption isotherms of (a) carbon black, (b) commercial TiO ₂ and (c) as-synthesized and calcined mesoporous TiO ₂	62
Figure 5-4 BJH pore size distribution curves of (a) as-synthesized mesoporous TiO ₂ , (b) calcined mesoporous TiO ₂ , (c) commercial TiO ₂ and (d) carbon black	63
Figure 5-5 Corrosion current-time curves of the catalysts at (a) 0.3 V and (b) 0.7 V	65
Figure 5-6 Normalized Pd ECSAs of the catalysts in fixed-potential test in 1M KOH solution	66
Figure 5-7 CVs of (a) 10%Pd/C, (b) 10%Pd/commercial TiO ₂ and (c) 10%Pd/mesoporous TiO ₂ after 20 and 1000 cycles in multi-scan test in 1M KOH solution, scan rate of 50 mV/s.....	67
Figure 5-8 Normalized Pd ECSAs of the catalysts in multi-scan test in 1M KOH solution	68
Figure 5-9 FTIR spectra of commercial TiO ₂ and mesoporous TiO ₂	69
Figure 5-10 LSV results of the catalysts in 1M C ₂ H ₅ OH + 1M KOH solution.....	71
Figure 5-11 CA results (at -0.25 V) of the catalysts in 1M C ₂ H ₅ OH + 1M KOH solution	71
Figure 6-1 XRD profiles of commercial TiO ₂ , Ti _n O _{2n-1} and standard XRD spectra of anatase TiO ₂ and different Magnéli phase titanium oxides	78
Figure 6-2 XRD profiles of the supports and catalysts.....	79
Figure 6-3 Nitrogen adsorption isotherms of (a) carbon black, (b) commercial TiO ₂ and (c) Ti _n O _{2n-1}	82
Figure 6-4 Corrosion curves of the catalysts in fixed potential tests at (a) 0.3 and (b) 0.7 V ..	84
Figure 6-5 Normalized Pd ECSAs of the catalysts after fixed potential tests	85

Figure 6-6 Normalized Pd ECSAs of the catalysts after multi-scan tests.....	85
Figure 6-7 LSV plots of the catalysts in 1M C ₂ H ₅ OH + 1M KOH solution with a scan rate of 50 mV s ⁻¹	88
Figure 6-8 CA results of the catalysts at – 0.25 V (vs Hg/HgO) in 1M C ₂ H ₅ OH + 1M KOH solution.....	89
Figure 7-1 XRD patterns of (a) commercial TiO ₂ , (b) as-synthesized Nb _{0.10} Ti _{0.90} O ₂ , (c) calcined Nb _{0.10} Ti _{0.90} O ₂ and different Nb _{0.10} Ti _{0.90} O ₂ samples activated at (d) 400°C, (e) 700°C and (f) 900°C.....	96
Figure 7-2 Nitrogen adsorption/desorption isotherms of (a) commercial TiO ₂ , (b) as-synthesized, (c) calcined Nb _{0.10} Ti _{0.90} O ₂ and Nb _{0.10} Ti _{0.90} O ₂ activated at (d) 400 °C, (e) 700 °C and (f) 900 °C.....	99
Figure 7-3 XRD patterns of Nb _x Ti _{1-x} O ₂ activated at 700 °C with x=0.02 (a), 0.05 (b), 0.10 (c), 0.20 (d) and 0.30 (e).....	101
Figure 7-4 Electrical conductivity of Nb _x Ti _{1-x} O ₂ with different Nb contents.....	104
Figure 7-5 Nitrogen adsorption/desorption isotherms of Nb _x Ti _{1-x} O ₂ activated at 700°C with x=0.02 (a), 0.05 (b), 0.10 (c), 0.20 (d) and 0.30 (e).....	106
Figure 7-6 XRD profiles of PdAg/C (a), PdAg/commercial TiO ₂ (b), PdAg/Nb _x Ti _{1-x} O ₂ with x=0.02 (c), 0.05 (d), 0.10 (e), 0.20 (f) and 0.30 (g)	107
Figure 7-7 (a) CVs and (b) forward scans of CV of PdAg/C, PdAg/commercial TiO ₂ , PdAg/Nb _x Ti _{1-x} O ₂ with x=0.02, 0.05, 0.10, 0.20 and 0.30 in 1M KOH + 1M C ₂ H ₅ OH solution, scan rate of 50 mV s ⁻¹	108
Figure 7-8 CA results of PdAg/C, PdAg/commercial TiO ₂ , PdAg/Nb _x Ti _{1-x} O ₂ with x=0.02, 0.05, 0.10, 0.20 and 0.30 at – 0.25 V (vs Hg/HgO) in 1M C ₂ H ₅ OH + 1M KOH solution	111

Figure 7-9 CO stripping curves of PdAg/C, PdAg/commercial TiO ₂ , PdAg/Nb _x Ti _{1-x} O ₂ with x=0.02, 0.05, 0.10, 0.20 and 0.30 in 1M KOH solution, scan rate of 50 mV s ⁻¹	112
Figure 7-10 Blank CVs of PdAg/C, PdAg/commercial TiO ₂ , PdAg/Nb _x Ti _{1-x} O ₂ with x=0.02, 0.05, 0.10, 0.20 and 0.30 in 1M KOH solution, scan rate of 50 mV s ⁻¹	113
Figure 7-11 Corrosion curves of PdAg/C, PdAg/commercial TiO ₂ , PdAg/Nb _x Ti _{1-x} O ₂ with x=0.02, 0.05, 0.10, 0.20 and 0.30 in 1M KOH solution at (a) 0.3 V and (b) 0.7 V, 1h	115
Figure 7-12 Normalized Pd ECSAs of PdAg/C, PdAg/commercial TiO ₂ , PdAg/Nb _x Ti _{1-x} O ₂ with x=0.02, 0.05, 0.10, 0.20 and 0.30 after (a) fixed-potential and (b) multi-scan tests.....	116
Figure 7-13 TEM images of PdAg/C: (a) before and (b) after 2000 scans; of PdAg/commercial TiO ₂ : (c) before and (d) after 2000 scans; and of PdAg/Nb _{0.30} Ti _{0.70} O ₂ : (e) before and (f) after 2000 scans	118
Figure 7-14 Forward scans of CVs of PdAg/mesoporous TiO ₂ , PdAg/Ti _n O _{2n-1} and PdAg/Nb _{0.30} Ti _{0.70} O ₂ in 1M KOH + 1M C ₂ H ₅ OH solution, scan rate of 50 mV s ⁻¹	119
Figure 7-15 Corrosion curves of PdAg/mesoporous TiO ₂ , PdAg/Ti _n O _{2n-1} and PdAg/Nb _{0.30} Ti _{0.70} O ₂ in 1M KOH solution at 0.7 V, 1h.....	120
Figure 7-16 Normalized Pd ECSAs of PdAg/mesoporous TiO ₂ , PdAg/Ti _n O _{2n-1} and PdAg/Nb _{0.30} Ti _{0.70} O ₂ after (a) fixed-potential test at 0.7 V and (b) multi-scan test	121

LIST OF TABLES

Table 3-1 Mean particle sizes and lattice parameters of catalysts.....	21
Table 3-2 OH ⁻ adsorption peak potential values for Pd/C and Pd-Ag/C in blank solutions with different concentrations of KOH	34
Table 4-1 The peak potentials of the ethanol oxidation on the catalysts	46
Table 4-2 The adsorption peak area of the hydroxyl group on the catalysts	49
Table 4-3 Activation energy of the ethanol electrooxidation on the catalysts at -0.1 V	51
Table 5-1 N ₂ adsorption/desorption test results	61
Table 5-2 FTIR data of commercial TiO ₂ and mesoporous TiO ₂	69
Table 6-1 Measured properties of different supports	81
Table 6-2 Unit cell parameters of palladium, anatase titanium oxide and some Magnéli phase titanium oxides.....	86
Table 7-1 Properties of commercial TiO ₂ and Nb _{0.10} Ti _{0.90} O ₂ materials	97
Table 7-2 Properties of Nb _x Ti _{1-x} O ₂ materials compared with commercial TiO ₂	103
Table 7-3 Normalized Pd ECSAs of the catalysts after fixed -potential and multi-scan tests.	114

LIST OF PUBLICATIONS

1. **Nguyen, S. T.**; Law, H. M.; Nguyen, H. T.; Kristian, N.; Wang, S.; Chan, S. H.; Wang, X., Enhancement effect of Ag for Pd/C towards the ethanol electro-oxidation in alkaline media. *Applied Catalysis B: Environmental* **2009**, *91* (1-2), 507-515.
2. **Nguyen, S. T.**; Ling Tan, D. S.; Lee, J.-M.; Chan, S. H.; Wang, J. Y.; Wang, X., Tb promoted Pd/C catalysts for the electrooxidation of ethanol in alkaline media. *Int. J. Hydrogen Energy* **2011**, *36* (16), 9645-9652.
3. **Nguyen, S. T.**; Yang, Y.; Wang, X., Ethanol electro-oxidation activity of Nb-doped-TiO₂ supported PdAg catalysts in alkaline media. *Applied Catalysis B: Environmental* **2012**, *113–114* (0), 261-270.
4. **Nguyen, S. T.**; Lee, J.-M.; Yang, Y.; Wang, X., Excellent Durability of Substoichiometric Titanium Oxide As a Catalyst Support for Pd in Alkaline Direct Ethanol Fuel Cells. *Industrial & Engineering Chemistry Research* **2012**, *accepted*, DOI: 10.1021/ie202696z.
5. Wang, Y.; **Nguyen, S. T.**; Wang, C.; Wang, X., Ethanol electrooxidation on Pt/C catalysts promoted with praseodymium oxide nanorods. *Dalton Transactions* **2009**, (37), 7606-7609.
6. Wang, Y.; **Nguyen, S. T.**; Liu, X.; Wang, X., Novel palladium-lead (Pd-Pb/C) bimetallic catalysts for electrooxidation of ethanol in alkaline media. *Journal of Power Sources* **2010**, *195* (9), 2619-2622.

NOMENCLATURE

ADAFC	: alkaline direct alcohol fuel cell
ADEFC	: alkaline direct ethanol fuel cell
CA	: chronoamperometry
CV	: cyclic voltammetry
DAFC	: direct alcohol fuel cell
DEFC	: direct ethanol fuel cell
DMFC	: direct methanol fuel cell
ECSA	: electrochemically active surface area
EDX	: energy-dispersive X-ray spectroscopy
EOR	: ethanol oxidation reaction
FCC	: face-centered cubic
FTIR	: Fourier transform infrared spectroscopy
GCE	: glassy carbon electrode
LSV	: linear sweep voltammetry
ORR	: oxygen reduction reaction
PEMFC	: polymer electrolyte membrane fuel cell

TEM : transmission electron microscopy

XRD : x-ray diffraction

Chapter 1 INTRODUCTION AND SCOPE OF THE THESIS

1.1 Introduction

Progress in human society and especially, the industrial development, have been increasing energy consumption and power requirements. Up to date, most of the energy needs have been supplied by combustion of fossil fuels. Heat engines, such as car engines, combust fossil fuels and thus, result in air pollution, affecting the health of people living in urban areas. These engines also emit carbon dioxide, the main reason of green-house effect and global warming. Moreover, fossil fuel resources are limited and not reproducible. Therefore, the demand for new technologies for energy conversion and power generation is more and more urgent. New technologies must be more efficient than the conventional heat engines, and compatible with renewable energy sources and carriers for sustainable development and energy security [1].

Recently, fuel cell has been found as the most promising and potential energy conversion technology. The fuel cell efficiency is much higher than the efficiency of internal combustion engines. Therefore, they are attractive for automobile applications. Moreover, their efficiency is higher than the efficiency of conventional power plants, so they may be used for decentralized power generation. Nowadays, the market for portable electronic devices is expanding more and more largely. At the moment, rechargeable battery systems are the main power supplies for portable devices. However, it is necessary to increase the specific energy of the power supplies due to the fact that the rechargeable battery systems are not suitable for new generations of portable electronic equipment with

higher power demand. Therefore, fuel cell systems have been recognized as promising potential candidates to complement or substitute batteries for mobile and portable devices. For environmental aspect, fuel cells generate little emission. For example, fuel cells operating on hydrogen generate zero emissions; the only exhaust is air and water. This advantage is attractive not only for transportation but also for indoor applications, as well as submarines. With fuel cells using liquid fuels such as alcohols, some emissions are generated, including carbon dioxide. In general, these emissions are lower than those of conventional energy conversion technologies. Fuels for fuel cells can be produced from local sources, such as by electrolysis of water or by fermentation of renewable agricultural products. This is favorable to national energy security issue. Besides, fuel cells possess simple structures consisting of layers of repetitive components. Because of this, they have the potential to be mass produced at a cost comparable to that of existing energy conversion technologies or even lower. With simple structures, fuel cells can be made in any size from a few watts to megawatt scale plant with equal efficiency. Fuel cells are electrochemical devices and have no moving components except for peripheral compressors and motors. As a result, their operations are very quiet. This makes them attractive to a variety of applications, such as military applications [1-3].

In different types of fuel cells, direct alcohol fuel cells (DAFCs) have attracted much attention from scientists due to their high efficiency, high energy density and low or zero emissions. Among them, most of research works have been focused on direct methanol fuel cells (DMFCs) [4-5]. However, methanol is widely known as a toxic and harmful chemical [6-9]. In contrast, ethanol has no toxicity compared to methanol and can be

produced in large quantity from fermentation process [7, 10]. Moreover, ethanol possesses a higher theoretical energy density (8.01 kWh kg^{-1}) than methanol (6.09 kWh kg^{-1}) and is easy to store and handle [10-12]. Therefore, the attention on direct ethanol fuel cell (DEFC) has been more and more increasing [12].

Pt has been widely used as the main component for electrocatalysts of DAFC. However, Pt supply is limited and its price is high [13-16]. These facts are barriers for the commercialization of DAFC. To overcome the drawbacks, it is necessary to find effective replacements for Pt to cut down the high cost of DAFC to improve its commercialization probability.

Besides the expensive cost of Pt, the oxidation of catalyst supports significantly affects the practical applications of fuel cells. Carbon-based materials are commonly used as supports for catalysts for polymer electrolyte membrane fuel cells (PEMFCs). These materials are strongly corroded during the fuel cell operation and thus, reduce the lifetime of fuel cell [17-20]. Therefore, exploring more durable materials to replace carbon-based materials is essential for the development of PEMFCs.

1.2 Scope of the thesis

Recently, Pd has been found to possess good electrocatalytic activity towards ethanol oxidation in basic solutions. Pd amount in the earth is at least fifty times more than that of Pt. Furthermore, corrosion is less important and kinetics of alcohol oxidation process is significantly improved in alkaline media [21-24]. On the other hand, titania-based materials

have been found to be stable in corrosive conditions [25-31]. Therefore, the research in this thesis is focused on the development of Pd-based electrocatalysts for the oxidation of ethanol in basic media and the exploration of new TiO₂-based catalyst supports for alkaline direct ethanol fuel cell (ADEFC).

The specific objectives of the thesis are described below:

- i) Synthesis and characterization of PdAg/C catalysts for ethanol electrooxidation in alkaline media.
- ii) Synthesis and investigation of PdTb/C catalysts towards ethanol oxidation in basic solutions.
- iii) Exploration of mesoporous TiO₂ as a support for Pd nanoparticles for ethanol oxidation.
- iv) Preparation of Ti_nO_{2n-1} and investigation of its behavior as catalyst support for Pd towards ethanol oxidation.
- v) Synthesis of Nb-doped titania with different Nb contents, characterization of these materials and investigation of durability and ethanol oxidation activity of PdAg/Nb-doped titania in alkaline condition.

The thesis consists of eight chapters as follows:

- Chapter 1 presents the motivation and the objectives of the thesis.
- An overview of DEFC is provided in Chapter 2. A review of Pd-based anodic

electrocatalysts for ADEFC and TiO_2 -based catalyst supports for PEMFC is also presented in the chapter.

- Chapter 3 describes the preparation of PdAg/C by a co-reduction method with NaBH_4 and the examination of their electrocatalytic activity for ethanol oxidation in 1M KOH + 1M ethanol solution. It was found that PdAg/C catalysts exhibited excellent activity, enhanced CO tolerance and better stability than Pt/C and Pd/C. The improvement resulted from the d-band center up-shift of Pd.
- In Chapter 4, Tb was combined with Pd to form a new catalyst for ethanol oxidation in alkaline solution. The highest performance was observed for 10%Pd-2%Tb/C in terms of the highest activity, stability and lowest activation energy for ethanol oxidation. The enhancement may be attributed to the promotion effect of Tb on OH^- adsorption.
- Chapter 5 presents the work on the investigation of mesoporous TiO_2 as catalyst support for Pd towards ethanol oxidation. The mesoporous TiO_2 -supported Pd catalyst showed higher stability than Pd/C and Pd/commercial TiO_2 in holding-potential and multi-scan tests. The peak current density of ethanol oxidation on Pd/mesoporous TiO_2 is 2.6 and 4.4 times those of Pd/commercial TiO_2 and Pd/C, respectively, indicating the better activity of the catalyst.
- In Chapter 6, non-stoichiometric titania $\text{Ti}_n\text{O}_{2n-1}$ was synthesized from commercial TiO_2 by H_2 reduction at high temperature. Pd supported on $\text{Ti}_n\text{O}_{2n-1}$ showed significant improvement in durability and activity for ethanol oxidation.
- The low conductivity of TiO_2 can be enhanced by doping it with a donor-type

element. This was carried out in Chapter 7. Nb-doped TiO_2 was synthesized and tested as support for PdAg for the oxidation of ethanol in alkaline solution. Conductivity of the material was seen to increase with an increase of Nb-doping level. PdAg/Nb-doped titania displayed better ethanol oxidation activity than PdAg/C and PdAg/commercial TiO_2 , possibly due to an interaction between the alloy particles and the support. A higher durability was also observed for PdAg/Nb-doped titania. PdAg/ $\text{Nb}_{0.30}\text{Ti}_{0.70}\text{O}_2$ was found to possess better electrocatalytic activity for EOR and higher durability in alkaline condition than PdAg/ $\text{Ti}_n\text{O}_{2n-1}$ and PdAg/mesoporous TiO_2 .

- Finally, conclusions of the research and suggestions for future work are given in Chapter 8.

Chapter 2 LITERATURE REVIEW

2.1 Overview of direct ethanol fuel cells (DEFCs)

Over several years, there has been extensive research on direct methanol fuel cells (DMFCs) for portable power applications at low to moderate temperatures. However, there are a number of problems associated with the use of methanol as a fuel for portable power supplies. As stated in Chapter 1, methanol is highly toxic and could lead to long-term environmental problems because methanol is so miscible in water. These limitations have led researchers to investigate other fuels. Ethanol is an attractive alternative to methanol as a fuel for fuel cells. Ethanol is a renewable fuel and can be produced from farm products and biomass. Ethanol and its intermediate oxidation products have been shown to be less toxic than other alcohols [4-12, 32].

Direct ethanol fuel cells (DEFCs) are electrochemical devices that directly convert the chemical energy stored in ethanol into electricity. There are two types of DEFC based on the electrolyte used: acidic DEFC and alkaline DEFC. Much attention has been focused on acidic DEFCs [33]. However, due to the strongly corrosive property of acidic media, Pt-based catalysts have been used for acidic DEFCs. As Pt is rare and expensive, this limits the wide commercialization of acidic DEFCs. Alkaline media have been known to be less corrosive than acidic ones. Therefore, non-Pt catalysts can be employed in alkaline media. These advantages have attracted increasing attention to alkaline DEFCs (ADEFCs) [21, 33].

2.2 Working principles of ADEFCs

Generally, ADEFCs contain three main components: the anode, the cathode, and the polymer electrolyte membrane that separates the anode solution from the cathode solution. This polymer electrolyte membrane is a hydroxyl transport membrane.

Figure 2-1 Working principle of ADEFC

The ethanol aqueous solution is added to the anode compartment. With the aid of the electrocatalysts, ethanol reacts with hydroxyl ions to produce carbon dioxide, water and release electrons. The electrons then flow through an external circuit, and then arrive at the cathode. At the cathode, air or pure oxygen reacts with water and electrons transported from the anode to produce hydroxyl ions. OH^- ions are transported to the anode through the polymer electrolyte as shown in Fig. 2-1 [34-35].

2.3 Thermodynamic data for ADEFC

The ethanol electrooxidation occurs at the anode:

corresponding to an anode potential $E^\circ_1 = -2.374\text{ V}$ versus SHE, as calculated from standard energy of formation ΔG°_f of reactant (i):

$$-\Delta G^\circ_1 = 2\Delta G^\circ_{\text{CO}_2} + 9\Delta G^\circ_{\text{H}_2\text{O}} - \Delta G^\circ_{\text{C}_2\text{H}_5\text{OH}} = -2 \times 394.4 - 9 \times 237.1 + 174.8 = -2747.9$$

kJ/mol

$$\text{Anode potential: } E^\circ_1 = -\Delta G^\circ_1 / (12F) = -2747.9 \times 1000 / (12 \times 96485) = -2.374\text{ V}$$

The electroreduction of oxygen occurs at the cathode:

corresponding to the cathode potential: $E^\circ_2 = -\Delta G^\circ_2 / (4F) = -2 \times 237.1 \times 1000 / (4 \times 96485) = -1.229\text{ V}$ versus SHE.

The total combustion reaction:

$$\text{with } -\Delta G^\circ \text{ (kJ/mol)} = 3\Delta G^\circ_2 - \Delta G^\circ_1 = 3 \times 2 \times 237.1 - 2747.9 = -1325.3$$

The equilibrium standard cell potential (open-circuit potential):

$$E^\circ_{\text{eq}} = -\Delta G^\circ / (nF) = 1325.3 \times 1000 / (12 \times 96485)$$

$$= E^\circ_2 - E^\circ_1 = -1.229 + 2.374 = 1.145\text{ V}$$

This value is comparable to that of DMFCs (1.213 V) [32, 36-37].

2.4 Mechanism of ethanol oxidation in alkaline media

In Tripkovic et al.'s work [38], a mechanism was proposed for the ethanol electrooxidation on Pt:

Recently, a mechanism of the ethanol oxidation process on Pd/C in alkaline media has been proposed by Liang et al. [33]:

2.5 Pd-based anodic electrocatalysts for ADEFC

Shen's group [6, 22] investigated the ethanol oxidation activity of Pd-based catalysts and observed that Pt had less catalytic activity than Pd in alkaline media. They modified the catalysts with several oxides, i.e., CeO_2 , NiO , Co_3O_4 and Mn_3O_4 and the oxide-promoted catalysts displayed better activities than a commercial E-TEK PtRu/C catalyst. Among them, Pd-NiO (6:1 by weight)/C showed the highest performance. The onset potential for the ethanol oxidation reaction (EOR) on Pd-NiO/C is shifted negatively by 300 mV compared with that of Pt/C. The authors proposed that OH_{ad} species could easier form on the surface of oxide at lower potential and helped to transform CO-like poisoning species on Pd to CO_2 or other products, releasing the active sites on Pd for further electrochemical reaction [21-22, 39]. Recently, Chu et al. [40] have synthesized carbon nanotube – supported Pd- In_2O_3 and tested its activity for EOR. It was shown that the catalytic activity of Pd for EOR was promoted by the addition of In_2O_3 nanoparticles into the catalyst. The catalyst with a mass ratio of Pd to In_2O_3 of 10:3 showed the highest activity.

The combination of Pd with other metals has been used to create new catalysts for ethanol oxidation. Carbon-supported Pd_4Au - and $\text{Pd}_{2.5}\text{Sn}$ -alloyed nanoparticles were prepared and used for EOR in high pH media [41]. It was found that the Pd alloy nanocatalysts showed higher current density and long term stability than commercial Pt/C. The alloy catalysts also showed significantly higher current densities in comparison to Pd/C. The Pd-based alloy catalysts showed a higher tolerance to surface poisoning compared with Pt/C. $\text{Pd}_4\text{Au}/\text{C}$ displayed the best catalytic activity among the catalysts. Bagchi's group [42-43] investigated the electroactivity of binary PdRu catalyst on Ni

support for EOR in ADEFCs. The catalyst was seen to improve the current density and reduce the anodic overvoltage compared to pure Pt, Pd and Ni. Its electrocatalytic capability is similar to that of Pt-Ru supported on Ni.

❖ **Fundamentals for designing of DEFC electrocatalysts:**

- ✓ Bifunctional mechanism (promoted mechanism) was proposed to explain the promotion effect of Ru or Sn for Pt/C towards the ethanol oxidation in acidic media [6, 35, 44-48]. According to the promoted mechanism, Pt active sites are the place where the adsorption and decomposition of ethanol and its intermediate reaction products happen, while the dissociative adsorption of water to form OH⁻ species takes place on Ru (Sn) sites. These species will help to remove CO-like intermediates out of the catalyst surface. Xu et al. [22] observed that the addition of oxide (CeO₂, NiO) to Pt/C and Pd/C could significantly promote catalytic activity for EOR in alkaline media. It was suggested that the promotion is derived from the easier formation of OH_{ad} species on the surface of oxide. The OH_{ad} species formed at lower potential can convert CO-like poisoning species on Pt and Pd into CO₂ or other products, which can be dissolved in water, releasing the active sites on Pt and Pd.
- ✓ According to d-band center theory proposed by Nørskov and co-workers [49-58], the trend of reactivity will follow the trend in d-band center values. When metals with small lattice constants are overlaid or alloyed on metals with larger lattice constants, the d-band center shifts up and vice versa, which subsequently affects the reaction rate. If the d-band center is shifted up, the

adsorption ability of the adsorbate onto the metals will be stronger and this may help to improve the electro-oxidation of ethanol on the surface of the metals. An application of d-band center theory was shown in Lima et al.'s work [56]. Pt monolayers were deposited on different metal surfaces as electrocatalysts for oxygen reduction reaction (ORR) in alkaline media. The lattice mismatch between Pt and the host metals induced either compressive or expansive strain in the Pt monolayers. The Pt monolayer was compressed on Ir(111), Ru(0001) and Rh(111), whereas it was stretched on Au(111), compared to Pt(111) surface [59]. As a result, Pt/Au(111) binds oxygen much more strongly than Pt(111) while Pt/Ru(0001), Pt/Rh(111) and Pt/Ir(111) bind oxygen considerably less strongly than Pt(111) [56]. This causes Pt/Ru(0001), Pt/Rh(111) and Pt/Ir(111) to be less active in ORR than Pt because breaking the O-O bond is more difficult on these surfaces than on Pt(111). On the other hand, the Pt/Au(111) surface, which binds oxygen most strongly, will facilitate the O-O bond breaking but will slow down the O and OH hydrogenation. This slowing down will increase the coverage of these species on the catalyst surface and impede the adsorption of the main reactant, O₂ [51, 56, 59-60]. Pd/Pt(111) with d-band center lying in the middle and therefore forming a moderate bond with the adsorbates has the best activity for ORR.

2.6 TiO₂, Ti_nO_{2n-1} and Nb-doped titania as catalyst supports

Carbon-based materials have been extensively used as electrocatalyst supports for PEMFCs. However, as mentioned previously, they are oxidized during fuel cell working

process and start-up/shut-down cycles [25-27, 61-64]:

The corrosion of the carbon-based supports leads to changes of their surface properties, which results in a loss of active surface area of the electrocatalysts. Therefore, it is necessary to find other materials that are more stable.

TiO₂ has been widely used in several applications, such as photocatalysis, photovoltaics and water splitting. TiO₂ is cheap, non-toxic and abundant. Two common polymorphs of titania are anatase and rutile. These structures are formed from chains of TiO₆ octahedra in which a Ti⁴⁺ is surrounded by six O²⁻ [25-26, 65-67]. Anatase phase is made from zigzag chains of TiO₆ by sharing an edge while rutile phase is formed by linear chains of TiO₆ by sharing a pair of opposite edges (Fig. 2-2) [67-68]. An anatase unit cell is composed of four chemical TiO₂ units whereas a rutile unit cell contains two units [68]. TiO₂ has been found to possess good corrosive resistance in acidic and oxidative conditions [25-26, 30, 65, 69].

Recently, titania-based materials have been investigated as catalyst supports for PEMFC. For instance, Huang et al. [70] studied Pt/TiO₂ as a cathodic electrocatalyst. It showed similar ORR activity to that of Pt/C. However, after 2500 scans between 0.6 and 1.4 V in an accelerated durability test, Pt/C lost 96 % of its ORR activity while Pt/TiO₂ only lost 48 %. In Ioroi et al.'s research [31] with a membrane electrode assembly (MEA), Pt/Ti₄O₇ showed higher stability than Pt/C in a high-potential holding test for 1 h. Furthermore,

Chhina et al. [63] compared the stability of Pt/10Nb-TiO₂ with that of Pt/C in a PEMFC. It was found that the performance of Pt/10Nb-TiO₂ slightly reduced after holding the MEA for 20 h at 1.4 V. In contrast, the performance of Pt/C significantly decreased after the test. The Pt surface area of Pt/10Nb-TiO₂ was nearly maintained after the durability test but that of Pt/C sharply decreased due to the oxidation of carbon.

Figure 2-2 Structures of (a) anatase and (b) rutile phases of TiO₂

Chapter 3 ENHANCEMENT EFFECT OF Ag FOR Pd/C TOWARDS THE ETHANOL ELECTRO-OXIDATION IN ALKALINE MEDIA

(The content in this chapter has been published in Applied Catalysis B, 2009, 91, 507-515)

3.1 Introduction

As stated in Chapters 1 and 2, “most of research on DAFC has been done in acidic media with Pt-based electrocatalysts for the electro-oxidation of alcohols. This largely contributes to the high cost of fuel cells [14-15, 71-72]. In alkaline media, corrosion is less important and kinetics of alcohol oxidation process is significantly improved [21, 23]. Therefore, Pt-free catalysts may be used in ADAFC. This advantage will increase the commercialization probability of DAFC.

Pd has been found as a good catalyst for the oxidation of ethanol in alkaline solutions and its abundance is at least fifty times more than that of Pt on earth [22, 24]. However, the activity of Pd for ethanol oxidation in alkaline media needs to be enhanced. There have been some efforts to improve the performance of Pd, such as Shen et al., Zhu et al. or Singh et al.’s works, by combining Pd with other metals, metal oxides or metal carbides and some enhancements have been achieved [21, 39, 73-75]. In this chapter, it is aimed to tune the reactivity of Pd by modifying it with cheaper metals, based on d-band theory. According to d-band theory of Nørskov and co-workers (section 2.5) [49-57], the trend of reactivity will follow the trend in d-band center values of overlayer and impurity atoms. When metals with small lattice constants are overlaid or alloyed on metals with larger lattice constants, the d-band center shifts up and vice versa, which subsequently affects the

reaction rate. If the d-band center is shifted up, the adsorption ability of the adsorbate onto the metals will be stronger and this may help to improve the electro-oxidation of ethanol (EOR) on the surface of the metals.

Ag is a metal which is much cheaper and more abundant than Pt. According to Hammer's calculation [50], d-band centre of Pd with a lattice value of 3.89 Å will be shifted up when combining with Ag (a=4.09 Å) [76]. Therefore, Ag was chosen to be alloyed with Pd in this research. Here, we report for the first time the enhanced activity of Pd-Ag/C for the ethanol oxidation in alkaline media compared with Ag/C, Pt/C and Pd/C.

3.2 Experimental and characterization methods

Chemicals used in this work were deionized water, sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) (Sigma-Aldrich), $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich), $\text{Pd}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (Sigma-Aldrich), AgNO_3 (Sigma-Aldrich), NaBH_4 (Sigma-Aldrich), $\text{C}_2\text{H}_5\text{OH}$ (Fluka), Nafion solution (5% in isopropanol and water), and carbon black (Vulcan XC-72, Gashub). All the chemicals were used as received without further purifications.

3.2.1 Catalyst synthesis

To synthesize electrocatalysts, 100 ml aqueous solution of $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ and various metal precursors were prepared. Then appropriate amount of 0.01M NaBH_4 (freshly prepared) was added slowly into the solution. The mixture was stirred for 2 h. After that, carbon black was added into the mixture and stirred overnight at room temperature. Then the suspension was filtered and washed several times with suitable amount of hot deionized water to

completely remove all excess reducing agents. The remaining solid was dried in a vacuum oven for 24 h at ambient temperature. The final catalysts were 10%Pt/C, 10%Pd/C, 10%Ag/C, 10%Pd-10%Ag/C, 10%Pd-5%Ag/C, 10%Pd-15%Ag/C, 10%Pd-20%Ag/C and 10%Pd-25%Ag/C. All percentages reported here are based on weight.

3.2.2 Physical characterization

Structure and morphology of the catalysts were investigated using X-ray diffraction (XRD, D8 Bruker AXS X-ray diffractometer, Cu K α radiation, 40 kV, 20 mA, 2 θ range of 20° to 90°, scan rate 0.025°/s) and transmission electron microscopy (TEM, JEOL 3010, 200 kV). Elemental analyses were performed using energy dispersive X-ray spectroscopy (EDX, LEO 1530VP, Germany).

3.2.3 Electrochemical characterization

To prepare samples for electrochemical analyses, 3.3 mg of each catalyst was dispersed in 1 ml of ethanol by sonication for 2 h. Then 10 μ l of this suspension was dropped onto a glassy carbon electrode (GCE, 4mm in diameter) and dried at room temperature. 5 μ l of 0.5 % Nafion in ethanol was added onto GCE to fix the catalyst. Electrochemical tests were performed on an Autolab PGSTAT302 potentiostat (Eco Chemie, Netherlands) with a three-electrode cell using a Pt wire and Hg/HgO electrode (0.1 V vs. NHE) [77] as the counter and reference electrode, respectively. Blank voltammograms were done in 1M KOH solution (blank solutions) and other tests were done in 1M KOH+1M C₂H₅OH solution. N₂ was used for solution deaeration.

In order to compare the activities of different catalysts, the current obtained from electrochemical tests were normalized by using electrochemically active surface area (ECSA). For 10%Pt/C, ECSA value was obtained by integrating the charges on hydrogen adsorption-desorption regions by cyclic voltammetry and using a charge of $210 \mu\text{C}/\text{cm}^2$ for smooth Pt surface [78]. For Pd-based catalysts, ECSA values were calculated from the PdO reduction charge, assuming a value of $405 \mu\text{C}/\text{cm}^2$ for the reduction of PdO monolayer due to the fact that Pd on carbon exhibits a poor definition of the hydrogen region and hydrogen can penetrate into the structure of Pd-based alloys [79-80].

3.3 Results and discussion

3.3.1 Physical characterization

Figure 3-1 XRD patterns of (a) 10%Pd/C, (b) 10%Ag/C, (c) 10%Pd-10%Ag/C and (d) 10%Pt/C

XRD patterns of 10%Pd/C, 10%Ag/C, 10%Pd-10%Ag/C and 10%Pt/C are shown in Fig.3-1. Typical peaks of face-centered cubic (FCC) structure including (111), (200), (220) and (311) lattices are marked on all the patterns. A peak of carbon black is observed in the range of $20\text{--}30^\circ$ of the diffraction spectra [81-82]. Peak position of Pd-Ag/C is between those of Pd/C and Ag/C, which suggests that an alloy of Pd and Ag was formed. Scherrer's equation was used to estimate the average size of the metal nanoparticles from (220) peaks:

$$d = \frac{k\lambda}{\beta \cos \theta}$$

where k : a coefficient (0.9)

λ : the wavelength of X-ray (1.54056 Å)

β : the half-peak width for (220) peak (rad)

θ : the angle at the (220) peak position (rad)

Table 3-1 Mean particle sizes and lattice parameters of catalysts

Catalyst	Lattice parameter, a (nm)	Average particle size, d (nm)
10%Pt/C	0.391	3.8
10%Pd/C	0.393	2.6
10%Ag/C	0.408	15.7
10%Pd-10%Ag/C	0.402	3.7

The average particle sizes of 10%Pt/C, 10%Pd/C, 10%Ag/C and 10%Pd-10%Ag/C are 3.8, 2.6, 15.7 and 3.7 nm, respectively (Table 3-1). The morphology and EDX spectra of these catalysts are shown in Fig.3-2. In the case of 10%Pd-10%Ag/C, a nano-structured

network was formed. The sizes of metal particles observed by TEM images are larger than those estimated by XRD data. This phenomenon was also observed by Liu et al. and Antolini et al. [83-84]. There are some possible explanations for this particle size inconsistency. The first reason is that the size calculated from XRD data is the size of single crystal particles while the TEM pictures show images of nanoparticle clusters formed from the agglomeration of single crystal particles as a result of intermolecular forces in the synthesis process [85-87]. Another reason is that the XRD peak broadening is due not only to the crystallite size but also to the non-homogeneity of the alloy [84]. Lattice constants of 10%Pt/C, 10%Pd/C and 10%Ag/C (Table 3-1) calculated from d-spacing data of (220) lattices are in good agreement with the values reported ($a_{Pt}=0.392$ nm; $a_{Pd}=0.389$ nm; $a_{Ag}=0.409$ nm) [76]. Lattice parameter value of 10%Pd-10%Ag/C which is larger than that of 10%Pd/C but smaller than that of 10%Ag/C confirmed again that a Pd-Ag alloy has been successfully formed. EDX profile of 10%Pd-10%Ag/C shows that the catalyst is composed of Pd and Ag, except for the Cu signal from the sample holder and some Na left from the reducing agent used for the synthesis of the catalyst.

(a)

(b)

(c)

(d)

(e)

Figure 3-2 TEM images of (a) 10%Pt/C, (b) 10%Pd/C, (c) 10%Ag/C, (d) 10%Pd-10%Ag/C and (e) EDX pattern of 10%Pd-10%Ag/C

3.3.2 Electrochemical tests

To investigate the activity of 10%Ag/C catalyst for ethanol oxidation in alkaline media, cyclic voltammetry (CV) tests were done in 1M KOH solution (blank solution) and 1M KOH+1M C₂H₅OH solution (Fig. 3-3). The CV plots of 10%Ag/C in both 1M KOH and 1M KOH + 1M C₂H₅OH solutions show a pair of anodic and cathodic peaks in the range from 0.2 to 0.3 V due to the formation of silver oxide and silver oxide reduction, respectively [88-90]. There is another small reduction peak at -0.2 to -0.1 V, which belongs to the reduction of trace oxygen left in the solutions [90]. No EOR peaks are observed for Ag/C implying that it is not active for ethanol oxidation process in alkaline media.

Figure 3-3 CV plots of 10%Ag/C in (a) 1M KOH and (b) 1M KOH + 1M C₂H₅OH with a scan rate of 50 mV/s

Figure 3-4 LSVs for ethanol oxidation on (a) 10%Pt/C, 10%Pd/C and 10%Pd-10%Ag/C and (b) 10%Pd-5%Ag/C, 10%Pd-10%Ag/C, 10%Pd-15%Ag/C, 10%Pd-20%Ag/C and 10%Pd-25%Ag/C in 1M KOH+1M C₂H₅OH with 50 mV/s scan rate

The electrocatalytic activities of 10%Pt/C, 10%Pd/C and 10%Pd-10%Ag/C for EOR

were characterized by linear sweep voltammetry (LSV) technique. The results normalized by electrochemically active surface area (ECSA) are shown in Fig.3-4a. Pd/C shows a similar onset potential to that of Pt/C with a little higher peak intensity. It is evident from Fig.3-4a that Ag can promote oxidation behavior of Pd/C for EOR in alkaline environment. The oxidation onset potential on 10%Pd-10%Ag/C catalyst (ca. -0.70 V) is shifted approximately 200 mV more negative than that on 10%Pd/C (ca. -0.50 V). In addition, the peak current for 10%Pd-10%Ag/C is about 3.5 times higher than that for 10%Pd/C. This enhancement is similar to what was obtained in He et al. and Chen et al.'s works with the combinations between Pd and Au, Sn or Ru [39, 91-92]. This fact can be explained based on the d-band centre theory [50] and the mechanism recently proposed by Liang et al. [33], which will be mentioned in more details in the latter section. The lattice constant of Pd is smaller than that of Ag. Therefore, the addition of Ag to Pd causes a tensile strain in the structure of surface Pd and shifts up the d-band centre of Pd [50, 53]. This can improve the adsorption of OH⁻ onto the surface of the catalyst and thus, improve the elimination of ethoxi intermediates from the catalyst surface and help to enhance the EOR process.

To examine the effect of Ag composition onto the EOR activity of Pd/C, LSV tests were performed on Pd-Ag/C catalysts with different compositions of Ag (Fig. 3-4b). The results show that 10%Pd-10%Ag/C has the highest activity toward ethanol oxidation in terms of onset potential and peak current while 10%Pd-5%Ag/C has the lowest one. The EOR activity of Pd-Ag/C decreases on increasing Ag composition from 10 to 25 %. This is maybe due to the excessive adsorption of hydroxyl ions onto the catalyst causing a competition in adsorption between hydroxyl and ethanol species.

Figure 3-5 CO stripping voltammograms for (a) 10%Ag/C, (b) 10%Pd/C, (c) 10%Pd-5%Ag/C, (d) 10%Pd-10%Ag/C, (e) 10%Pd-15%Ag/C, (f) 10%Pd-20%Ag/C and (g) 10%Pd-25%Ag/C in 1M KOH solution, scan rate: 50 mV/s

Figure 3-5 (Continued)

It is well-known that CO is a common poisoning intermediate to electrocatalysts in alcohol oxidation processes. Therefore, CO stripping tests were performed for the catalysts 10%Ag/C, 10%Pd/C, 10%Pd-5%Ag/C, 10%Pd-10%Ag/C, 10%Pd-15%Ag/C, 10%Pd-20%Ag/C and 10%Pd-25%Ag/C to compare their activities for CO oxidation. Fig. 3-5a

displays CO stripping results for 10%Ag/C. There is no difference between CO stripping and after CO stripping curves, which indicates Ag/C has no activity for CO oxidation in alkaline media. Fig. 3-5b and 3-5d show that the onset potential of CO oxidation on 10%Pd-10%Ag/C (ca. -0.35 V) was more negative than that on 10%Pd/C (ca. -0.20 V). This means that the addition of Ag has facilitated the removal of CO from the surface of Pd-Ag/C. These results are in line with the higher activity of Pd-Ag/C for the oxidation of ethanol. In addition, there exist two peaks for CO stripping on 10%Pd-10%Ag/C. Similar results are obtained for Pd-Ag/C with other ratios, as shown in Fig. 3-5c, e-g. The possible cause for this could be that some Pd has not been alloyed with Ag, which leads to the presence of two different types of sites for CO adsorption, i.e., Pd alone and Pd-Ag alloy. Comparing Fig. 3-5a and b with Fig. 3-5c-g, it is interesting to observe that there is no appearance of silver oxide reduction peak (ca. 0.25 V) except for palladium oxide reduction peak (ca. -0.2 V). This confirms that the upper layer of the alloy is rich of palladium.

Recently, a mechanism of the EOR process on Pd/C in alkaline media has been proposed by Liang et al. (section 2.4) [33]. In the mechanism, the rate-determining step is proposed to be step (4) (Eq. 2.11), in which the adsorbed ethoxi intermediate is removed by adsorbed hydroxyl ions to form acetate as the main product and release free active catalytic sites. As shown in Fig. 3-5, CVs of Pd/C and Pd-Ag/C catalysts in N₂-saturated solutions (dashed lines) show a peak around -0.25 V in forward scan, which is assigned to OH⁻ adsorption [33, 93]. The OH⁻ adsorption peak potentials are -0.247 V, -0.261 V, -0.272 V, -0.279 V, -0.287 V and -0.291 V for 10%Pd/C, 10%Pd-5%Ag/C, 10%Pd-10%Ag/C, 10%Pd-15%Ag/C, 10%Pd-20%Ag/C and 10%Pd-25%Ag/C, respectively. This phenomenon

indicates that OH^- ions are more easily adsorbed onto Pd-Ag/C than Pd/C. According to reaction (4) (Eq. 2.11), this helps to remove more intermediates and release more active sites on the surface of the catalyst. The tendency becomes more apparent with the increase of Ag component in the catalyst and can also be explained by d-band centre theory. When more Ag is added into the structure of Pd, more upshift of d-band center is achieved. As a result, more OH^- is adsorbed onto the catalyst surface and thus, more active sites are released via reaction (4). However, excess adsorption of OH^- also causes a competition with the adsorption of ethanol. This could be the possible reason for the activity decrease on the catalysts when the Ag composition increases from 10% to 25%. Ag was reported to adsorb OH^- at rather low potentials (-0.9 to -0.4 V vs Hg/HgO) [88, 94-95] and this feature may also contribute to the more negative values of the OH^- adsorption potential of Pd-Ag/C catalysts. However, the surface layer of the alloy is rich of Pd and therefore, the affinity of Ag for OH^- just plays a small role in the ethanol oxidation improvement.

To evaluate both the steady-state activity towards EOR and the poisoning of the catalysts, chronoamperometric (CA) measurements were carried out at -0.25 V for 1000 s in the solution of 1M KOH + 1M $\text{C}_2\text{H}_5\text{OH}$. In all the three CA curves displayed in Fig. 3-6a, the current drops sharply during the first few minutes and then becomes relatively stable. Firstly, the active sites are free from adsorbed ethanol; after that, the adsorption of new ethanol molecules would depend on the liberation of the active sites by the oxidation of ethanol or intermediates, such as ethoxi or CO-like species, formed during the first few minutes, which poisons the active surface. It can be seen that at the beginning, the current for 10%Pt/C is the highest but then decreases much faster than that for other catalysts and

becomes the lowest one. This phenomenon is due to the fact that Pt is more easily poisoned by CO-containing intermediates [12, 38, 96]. In the stable stage, the current produced by 10%Pd-10%Ag/C is the highest, indicating the better CO-tolerance feature of this catalyst.

Figure 3-6 CA curves for (a) 10%Pt/C, 10%Pd/C and 10%Pd-10%Ag/C and (b) 10%Pd-5%Ag/C, 10%Pd-10%Ag/C, 10%Pd-15%Ag/C, 10%Pd-20%Ag/C and 10%Pd-25%Ag/C in 1M KOH + 1M C₂H₅OH solution at -0.25 V (vs. Hg/HgO)

Fig. 3-6b shows CA curves for Pd-Ag/C catalysts with different compositions of Ag. The results indicate that 10%Pd-10%Ag/C is the best poisoning-tolerance catalyst and 10%Pd-5%Ag/C is the worst one, among all the catalysts investigated. Current values of Pd-Ag/C catalysts decrease when Ag content increases from 10 to 25 %. This trend, consistent with the LSV result, may be explained by the same argument, i.e., the adsorption competition between ethanol and hydroxyl with excess Ag. In consequence, less poisoning species are removed to free active sites and the catalysts become less stable.

For better understanding the adsorption of hydroxyl ions onto Pd/C and Pd-Ag/C catalysts, blank CV tests were performed for Pd/C and Pd-Ag/C in solutions with different concentrations of KOH (Fig. 3-7). At low OH^- concentration (0.1 M), no clear peaks for hydroxyl adsorption can be observed for both of the catalysts. When the OH^- concentration is increased from 0.5 to 6 M, clear hydroxyl adsorption peaks appear. Fig. 3-7 and table 3-2 display the adsorption peak potential values for the two catalysts. The results show a negative shift in hydroxyl adsorption peak potentials on both of the catalysts when the OH^- concentration goes up. The possible reason for this trend is the adsorption of hydroxyl ion onto the active sites of the catalysts is more favorable when there are more hydroxyl ions in the solution. Another observation is that the OH^- adsorption peak potential for Pd-Ag/C is always more negative than that for Pd/C at the same OH^- concentration value. This fact again confirms the alloyed catalyst facilitates the adsorption of OH^- .

Figure 3-7 Blank CVs of (a) Pd/C and (b) Pd-Ag/C in different KOH solutions, scan rate: 50 mV/s

Table 3-2 OH⁻ adsorption peak potential values for Pd/C and Pd-Ag/C in blank solutions with different concentrations of KOH

KOH concentration (M)	0.1	0.5	1.0	2.0	4.0	6.0
OH adsorption peak potential (V) for Pd/C	no peak	-0.235	-0.249	-0.278	-0.301	-0.318
OH adsorption peak potential (V) for Pd-Ag/C	no peak	-0.292	-0.301	-0.317	-0.317	-0.324

Beside the promotion effect of Ag, another possible reason for the high activity of Pd-Ag/C is the special morphology of this catalyst. The TEM picture in Fig. 3-2d shows a network structure of Pd-Ag/C. It means the Pd-Ag nanoparticles are interconnected. The interconnected network possesses more boundary defects (such as steps and kinks) than individual particles. Therefore, it has more active catalytic sites for OH⁻ adsorption and ethanol oxidation [97].

Figure 3-8 LSV tests in 1M KOH+1M C₂H₅OH solutions at different temperatures for (a) 10%Pd/C, (b) 10%Pd-5%Ag/C, (c) 10%Pd-10%Ag/C, (d) 10%Pd-15%Ag/C, (e) 10%Pd-20%Ag/C and (f) 10%Pd-25%Ag/C, scan rate: 50 mV/s

Figure 3-9 Arrhenius plots for (a) 10%Pd/C, (b) 10%Pd-5%Ag/C, (c) 10%Pd-10%Ag/C, (d) 10%Pd-15%Ag/C, (e) 10%Pd-20%Ag/C and (f) 10%Pd-25%Ag/C at -0.1 V

To exclude the effect of other factors, such as the catalyst surface area, on the resulting current, LSV tests in 1M KOH+1M C₂H₅OH solution was performed at different temperatures for 10%Pd/C, 10%Pd-5%Ag/C, 10%Pd-10%Ag/C, 10%Pd-15%Ag/C, 10%Pd-20%Ag/C and 10%Pd-25%Ag/C (Fig. 3-8). From the abstracted data, Fig. 3-9 is plotted and the activation energy values were calculated based on Arrhenius equation [98] as below:

$$\ln I = \ln A - E_a/(RT)$$

where I: current at a specific potential

R: gas constant, 8.314 J/(mol.K)

T: temperature in K

E_a: activation energy at a specific potential (kJ/mol)

At the same potential of -0.1V, the lowest value of 27.6 kJ/mol for the ethanol oxidation on 10%Pd-10%Ag/C is obtained as against the highest value of 31.1 kJ/mol on 10%Pd/C. The activation energy values for 10%Pd-5%Ag/C, 10%Pd-15%Ag/C, 10%Pd-20%Ag/C and 10%Pd-25%Ag/C are 30.2, 28.2, 28.8 and 29.5 kJ/mol, respectively. The lower E_a means a higher intrinsic activity for the Pd-Ag/C, as the effect of catalyst surface area has been excluded. This result is consistent with the above observations.

3.4 Summary

In this chapter, the high activity of Pd-Ag/C catalysts towards EOR in alkaline media in comparison with Ag/C, Pt/C and Pd/C was reported. The catalyst was synthesized with NaBH_4 as a reducing agent and sodium citrate as a stabilizer. XRD results showed the formation of alloy structure for the Pd-Ag/C. Electrochemical measurements indicated that it possessed a better intrinsic activity towards EOR than Pt/C and Pd/C and the best performance was observed for 10%Pd-10%Ag/C. This makes Pd-Ag/C a promising anodic catalyst for ADEFC.”

Besides the combination of Pd with Ag, another strategy was employed to improve its activity for ethanol electrooxidation in alkaline media by the use of a rare-earth metal, as reported in the following chapter.

Chapter 4 Tb PROMOTED Pd/C CATALYSTS FOR THE ELECTROOXIDATION OF ETHANOL IN ALKALINE MEDIA

(The content in this chapter has been accepted by International Journal of Hydrogen Energy, 2011, 36, 9645-9652)

4.1 Introduction

“Rare-earth metals combined with Pt or Pd have shown improved activity towards alcohol electrooxidation in both acidic and alkaline media. The promotion effect of rare-earth metals has been commonly explained based on the bi-functional mechanism, in which water molecules are dissociated on the rare-earth compounds at low potential and oxygen-containing species formed from this process will react with poisoning intermediates to release active sites for the alcohol oxidation [22, 99-101]. Several works have displayed the enhancement effect of ceria for Pt in alcohol electrooxidation in acidic condition [101-105]. Ceria promoted Pt and Pd were also found to give better performance for methanol and ethanol electrooxidation reaction than Pt and Pd in basic solutions [21-22, 61, 100, 106-108]. Besides cerium, other rare-earth elements have been used to modify Pt/C and shown strong promotion effects for the oxidation of ethanol and methanol. Wang et al. [109] tested the activity of Pt-Pr₆O₁₁/C catalysts towards ethanol electrooxidation in 1M KOH + 1M C₂H₅OH solution. The praseodymium oxide promoted Pt/C catalysts showed more negative onset potentials and larger peak current densities for ethanol oxidation than Pt/C. In Neto et al.’s research [110-111], several Pt-rare earth/C catalysts of La, Ce, Pr, Nd, Sm, Tb, Dy, Ho, Er, Tm, and Lu were synthesized and applied for the oxidation of methanol and

ethanol in 0.5 M H₂SO₄ solution. It was found that most of the composite catalysts showed superior performance for methanol and ethanol oxidation reaction compared with that of Pt/C [110-111]. Among them, PtTb/C and PtEr/C had the highest activity for methanol oxidation while PtTb/C and PtLu/C were the best for ethanol oxidation in the acidic solutions. From these works [110-111], it is obvious that Tb has an enhancement effect for the electrooxidation of ethanol and methanol in acidic condition. However, up to the knowledge of the authors, Tb has not been investigated for its possible promotive role towards the oxidation of ethanol in alkaline media with Pd/C. In this chapter, to explore the effect of Tb on the activity of Pd for the electrooxidation of ethanol, several Pd-Tb/C catalysts with different Pd/Tb ratios were synthesized and characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), cyclic voltammetry (CV), linear sweep voltammetry (LSV) and chronoamperometry (CA) techniques. Possible mechanism for the activity enhancement was also discussed.

4.2 Experimental and characterization procedures

4.2.1 Materials

Materials used in this work include deionized (DI) water, sodium citrate (Na₃C₆H₅O₇·2H₂O, Sigma–Aldrich), terbium nitrate (Tb(NO₃)₃·5H₂O) (Sigma–Aldrich), palladium nitrate (Pd(NO₃)₂·xH₂O, Sigma–Aldrich), sodium borohydride (NaBH₄, Sigma–Aldrich), ethanol (C₂H₅OH, Fluka), Nafion solution (5% in isopropanol and water, Gashub), and carbon black (Vulcan XC-72, Gashub). All the chemicals were used as received without further purifications.

4.2.2 Synthesis of catalysts

10%Pd/C, 10%Pd-0.5%Tb/C, 10%Pd-1%Tb/C, 10%Pd-2%Tb/C, 10%Pd-5%Tb/C and 10%Pd-10%Tb/C catalysts were synthesized by the following procedure: 41-115 mg of $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ was dissolved in 100 ml of DI water. 0-27 mg of $\text{Pd}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ and 0-34 mg of $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ were added into the solution and stirred for 10 min. After that, 0.01M NaBH_4 solution was dropped slowly into the solution and the mixture was stirred for 2 h. 100 mg of carbon black was then added into the mixture and the stirring was kept continuously overnight. In the next step, the solution was filtered and washed with DI water and the remaining solid was dried at room temperature.

4.2.3 Characterization

X-ray diffraction (XRD) was conducted on the samples with a D8 Bruker AXS X-ray diffractometer (Cu $\text{K}\alpha$ radiation, 40 kV, 20 mA, 2θ range of $20-90^\circ$, scan rate $0.025^\circ/\text{s}$). To observe the morphology of the catalysts, transmission electron microscopy (TEM) was carried out on a JEOL 3010 instrument with an accelerating voltage of 200kV.

Electrochemical tests were performed on an Autolab PGSTAT302 potentiostat (Eco Chemie) with a three-electrode cell using a Pt wire and a Hg/HgO electrode (1M KOH) as the counter and reference electrode, respectively [21, 33]. To prepare the working electrode, 3.3 mg of each catalyst was mixed with 1 ml of ethanol by a sonicator. From this suspension, 10 μl was dropped onto a glassy carbon electrode. To fix the catalyst to the electrode, 5 μl of 0.5% Nafion solution was added onto the electrode. N_2 gas was bubbled into the test solutions for deaeration. All current values in electrochemical results were

normalized by the Pd active surface area determined by the PdO reduction peak of the blank CV in 1M KOH solution, with the assumption that a value of 405 mC/cm^2 is needed for the reduction of PdO monolayer [79, 112].

4.3 Results and discussion

Figure 4-1 XRD spectra of (1) 10%Tb/C, (2) 10%Pd/C, (3) 10%Pd-0.5%Tb/C, (4) 10%Pd-1%Tb/C, (5) 10%Pd-2%Tb/C, (6) 10%Pd-5%Tb/C and (7) 10%Pd-10%Tb/C

(a)

(b)

(c)

(d)

(e)

(f)

(g)

Figure 4-2 TEM images of (a) 10%Tb/C, (b) 10%Pd/C, (c) 10%Pd-0.5%Tb/C, (d) 10%Pd-1%Tb/C, (e) 10%Pd-2%Tb/C, (f) 10%Pd-5%Tb/C and (g) 10%Pd-10%Tb/C

Fig. 4-1 shows the XRD spectra of the catalysts. The XRD pattern of 10%Tb/C displays three peaks at ca. 25°, 44° and 79°. These peaks are believed to be carbon black associated [113]. No peaks of terbium compounds are observed for 10%Tb/C, which implies that the terbium compounds have amorphous form. According to the literature, platinum-group metals and rare-earth metals have very different reduction potentials [111, 114]. Therefore, with NaBH₄ as the reducing agent, it is possible that borate or hydroxide compounds of Tb have been formed instead of Tb metal. The XRD pattern of 10%Pd/C catalyst shows typical peaks of face-centered cubic (FCC) structure of Pd at ca. 39°, 45°, 67° and 80°, which are assigned to (111), (200), (220) and (311) planes, respectively [112, 115]. The peak positions of Pd-Tb/C catalyst are the same as those of Pd/C, indicating that no alloys were formed between Pd and Tb. A peak at ca. 25° observed in all Pd/C and Pd-Tb/C XRD patterns is believed to belong to the carbon black [81-82]. XRD results of 10%Pd-0.5%Tb/C, 10%Pd-1%Tb/C and 10%Pd-10%Tb/C show a peak of the sample holder at ca. 22°. Similar to the Tb/C case, no peaks of Tb compounds are present in the Pd-Tb/C XRD spectra, indicating that they are in amorphous form. TEM images in Fig. 4-2 reveal a well dispersion of nanoparticles on carbon black with average particle sizes of 3.6, 4.8, 4.7, 5.1, 4.2, 4.8 and 5.2 nm for 10%Tb/C, 10%Pd/C, 10%Pd-0.5%Tb/C, 10%Pd-1%Tb/C, 10%Pd-2%Tb/C, 10%Pd-5%Tb/C and 10%Pd-10%Tb/C, respectively.

Fig. 4-3 presents CV results for 10%Tb/C in 1M KOH and 1M KOH + 1M C₂H₅OH solutions. The tests in both solutions show similar results with no ethanol oxidation peaks, indicating that Tb has no activity for EOR in alkaline condition. A small reduction peak around -0.15 V is believed to be due to the reduction of trace oxygen left in the solution

[90].

Figure 4-3 CVs for 10%Tb/C in 1M KOH and 1M KOH + 1M C₂H₅OH solutions, scan rate: 50 mV/s

Figure 4-4 LSVs for 10%Pd/C, 10%Pd-0.5%Tb/C, 10%Pd-1%Tb/C, 10%Pd-2%Tb/C, 10%Pd-5%Tb/C and 10%Pd-10%Tb/C in 1M KOH + 1M C₂H₅OH solution, scan rate: 50 mV/s

To investigate the performance of Pd/C and Pd-Tb/C catalysts for the electrooxidation of ethanol in alkaline media, LSV tests were carried out in 1M KOH + 1M C₂H₅OH solutions (Fig. 4-4). An onset potential of ca. -0.63 V was observed for the oxidation of ethanol on the Pd-Tb/C catalysts, which is 130 mV more negative than that on Pd/C (ca. -0.50 V). This negative shift of the onset potential is much larger than those reported for Pd-CeO₂/C (50 mV), Pd-NiO/C (70 mV), Pd-Co₃O₄/C (40 mV), Pd-Mn₃O₄/C (10 mV) and Pd-CoNiO_x/C (80 mV) when comparing with the onset potential of the EOR on Pd/C in other studies [22, 39, 116]. Furthermore, peak current values of the bimetallic catalysts are higher than that of Pd/C. The maximum peak current density is obtained at 10%Pd-2%Tb/C, which is about five-fold higher than that of Pd/C. These facts indicate a better activity of the catalysts for the EOR in basic condition compared to that of Pd/C. However, further increase in the composition of Tb leads to a reduction of peak current density. These phenomena are certainly related to the nature of Tb compounds. From the small variation in the peak potential values of PdTb/C catalysts compared with that of Pd/C (Table 4-1), it can be seen that the addition of Tb to Pd/C has little effect on the peak potential of the ethanol oxidation process and thus, has little effect on the surface passivation of the catalysts.

Table 4-1 The peak potentials of the ethanol oxidation on the catalysts

Catalyst	10%Pd/C	10%Pd- 0.5%Tb/C	10%Pd- 1%Tb/C	10%Pd- 2%Tb/C	10%Pd- 5%Tb/C	10%Pd- 10%Tb/C
Peak potential, V	-0.12 ~ -0.09	-0.14 ~ -0.13	-0.11	-0.13	-0.09	-0.11

In the mechanism of the EOR process on Pd in alkaline media proposed by Liang *et al.*

(section 2.4) [33], the rate-determining step in the process is step 4, in which adsorbed ethoxi intermediates ($(\text{CH}_3\text{CO})_{\text{ads}}$) on the surface of Pd are removed by adsorbed hydroxyl groups. From the mechanism, it is obvious that the adsorption of OH^- onto the catalyst plays a key role in the EOR. In acidic media, due to the lack of OH^- in the solution, most of hydroxyl ions for the removal of poisoning intermediates are supplied by the favorable dissociation of water on rare-earth compounds (lower potential) or Pd [22, 99-101, 111, 117]. In contrast, the amount of hydroxyl ion in alkaline solutions is abundant. Therefore, in alkaline condition, both OH^- concentration and rare-earth compounds could potentially enhance the adsorption of hydroxyl groups. To identify which one is more important, the influences of these two factors were examined.

To verify the effect of OH^- concentration, CV tests were performed in various solutions with different KOH concentrations. Fig. 4-5 shows blank CV results for 10%Pd-10%Tb/C in 1M, 2M, 4M and 6M KOH solutions. It can be observed that the onset potential and peak area of OH^- adsorption barely change, indicating the negligible influence of OH^- concentration on the adsorption of hydroxyl group for KOH concentration of 1M and above.

Figure 4-5 CVs for 10%Pd-10%Tb/C in different KOH solutions, scan rate: 50 mV/s

Figure 4-6 CVs for 10%Pd/C, 10%Pd-0.5%Tb/C, 10%Pd-1%Tb/C, 10%Pd-2%Tb/C, 10%Pd-5%Tb/C and 10%Pd-10%Tb/C in 1M KOH solution, scan rate: 50 mV/s

Table 4-2 The adsorption peak area of the hydroxyl group on the catalysts

Catalyst	10%Pd/C	10%Pd- 0.5%Tb/C	10%Pd- 1%Tb/C	10%Pd- 2%Tb/C	10%Pd- 5%Tb/C	10%Pd- 10%Tb/C
OH adsorption peak area (mA.V.cm ⁻²)	4.97 x 10 ⁻³	4.75 x 10 ⁻³	0.019	0.014	0.010	9.31 x 10 ⁻³

The adsorption of hydroxyl groups on the catalysts with various Tb ratios was studied using blank CV tests in 1M KOH solution (Fig. 4-6). Table 4-2 summarizes the calculated adsorption area of hydroxyl group. All the Pd-Tb/C catalysts show a peak around -0.30 ~ -0.25 V in the forward scan and a peak around -0.20 V in the backward scan. The first peak is associated with the adsorption of OH⁻ onto the catalyst [33] while the second peak is associated with the reduction of PdO [79]. As shown in Fig. 4-6 and Table 4-2, most of the OH⁻ adsorption peak areas of the composite catalysts are much larger than that of Pd/C. Noting that the CV results have been normalized by the Pd active surface area, these data imply that the addition of Tb into Pd/C promotes the adsorption of OH⁻ onto the catalysts and its influence is more significant compared to hydroxide concentration. The OH⁻ adsorption peak area increases with the addition of Tb, reaches maximum values at Tb composition of 1-2 % and then decreases when Tb content increases to 10%. The largest amounts of adsorbed hydroxyls facilitated a quick removal of poisoning species from the catalyst surface in order to release active sites for the EOR process as shown in the mechanism above, which explains why 10%Pd/C with 1-2%Tb having the highest activity for EOR compared with other Pd-Tb combinations in the alkaline media. It is interesting

that with the further increase in the content of Tb, the amount of adsorbed oxygen-containing species reduces and results in the decrease of the ethanol oxidation activity of the catalyst. This indicates that the optimal content of Tb for improving the ethanol oxidation activity of 10%Pd/C in 1M KOH + 1M C₂H₅OH solution is 1-2 %. It is possible that the increase of Tb content might also help to improve the adsorption of ethanol onto the catalysts. This will cause a competition in adsorption between OH⁻ and ethanol. As a result, the OH⁻ adsorption peak area is reduced when Tb content increases from 1 to 10 %. In the EOR mechanism, the process depends on the adsorption of ethanol and hydroxyl onto the catalysts. Therefore, the highest EOR activity is reached when adsorbed ethanol and OH⁻ amounts reach the optimum level at the Tb content of 2 %. Thus, the best performance was observed for the PdTb/C catalyst with 2 % of Tb.

The chronoamperometric curves measured at a constant potential of -0.25 V for the electrocatalysts in 1M KOH + 1M C₂H₅OH solution are presented in Fig. 4-7. At the fixed potential, ethanol was oxidized continuously and the poisoning intermediates like (CH₃CO)_{ad} would accumulate onto the catalyst surface, resulting in the decay in current density for all the catalysts. After 1000 s, the Pd-Tb/C catalysts still show higher current densities compared to Pd/C, indicating better poisoning-tolerance and higher activity of the composite catalysts. As mentioned above, this can be explained by a bifunctional mechanism in which the Tb compounds promote the removal of CH₃CO species by improving the adsorption of OH⁻. The highest current value observed for 10%Pd-2%Tb/C has again confirmed the excellent behavior of this catalyst.

Figure 4-7 CA plots for (a) 10%Pd/C, (b) 10%Pd-0.5%Tb/C, (c) 10%Pd-1%Tb/C, (d) 10%Pd-2%Tb/C, (e) 10%Pd-5%Tb/C and (f) 10%Pd-10%Tb/C in 1M KOH + 1M C₂H₅OH solution at -0.25 V

Table 4-3 Activation energy of the ethanol electrooxidation on the catalysts at -0.1 V

Catalyst	10%Pd/C	10%Pd-0.5%Tb/C	10%Pd-1%Tb/C	10%Pd-2%Tb/C	10%Pd-5%Tb/C	10%Pd-10%Tb/C
Activation energy (kJ/mol)	31.1	25.2	19.2	18.7	20.1	21.3

Figure 4-8 Arrhenius plots for (a) 10%Pd/C, (b) 10%Pd-0.5%Tb/C, (c) 10%Pd-1%Tb/C, (d) 10%Pd-2%Tb/C, (e) 10%Pd-5%Tb/C and (f) 10%Pd-10%Tb/C in 1M KOH + 1M C₂H₅OH solutions at -0.1 V

LSV tests were carried out for the electrocatalysts in 1M KOH + 1M C₂H₅OH solution at various temperatures to evaluate apparent activation energies for the ethanol oxidation in alkaline media. From the LSV results at -0.1 V and Arrhenius equation [98], Arrhenius plots were built and displayed in Fig. 4-8. From the slopes of the Arrhenius plots, activation energy values were calculated and shown in Table 4-3. A maximum activation energy value of 31.1 kJ/mol was obtained for 10%Pd/C while a minimum value of 18.7 kJ/mol was found for 10%Pd-2%Tb/C, which again confirms the excellent performance of this catalyst for EOR in alkaline condition. 10%Pd-0.5%Tb/C, 10%Pd-1%Tb/C, 10%Pd-5%Tb/C and 10%Pd-10%Tb/C have lower E_a values than that of 10%Pd/C but higher than that of 10%Pd-2%Tb/C. These values are consistent with the previous results.”

All the results above indicate that among several PdTb//C catalysts, 10%Pd-2%Tb/C has the highest EOR activity in tested solutions. Compared with 10%Pd-10%Ag/C in Chapter 3, 10%Pd-2%Tb/C showed a less negative onset potential (ca. -0.63 V) and lower peak current density (3.33 mA cm⁻²) for EOR than those of 10%Pd-10%Ag/C (ca. -0.70 V, 3.56 mA cm⁻²). From these results, it seems that 10%Pd-10%Ag/C is slightly more active for EOR than 10%Pd-2%Tb/C.

4.4 Summary

“Various Pd-Tb/C catalysts were synthesized and compared with Pd/C. XRD results verified that no alloys were formed between Pd and Tb in the composite catalysts. Different CV and LSV tests were performed for the catalysts and showed that Pd-Tb/C catalysts had higher activity for EOR in the alkaline media. It was found that 10%Pd-2%Tb/C exhibited

the highest performance for EOR. By carrying out LSV tests at various temperatures, activation energy values were determined for the catalysts and the lowest one was observed for 10%Pd-2%Tb/C, which confirmed its outstanding behavior for the oxidation of ethanol in alkaline media.” 10%Pd-2%Tb/C is somewhat less active for EOR than 10%Pd-10%Ag/C.

Chapters 3 and 4 show that the combination of Pd with Ag or Tb considerably improves the EOR activity of Pd in basic environment. Apart from catalysts, catalyst supports have a big role in the performance and lifetime of PEMFCs. Carbon-based materials have been commonly used as catalyst supports for fuel cells. However, they suffer severe corrosion during fuel cell performance. Therefore, the investigation of alternative materials as replacement for carbon-based supports was performed in this thesis, as presented in Chapters 5, 6 and 7.

Chapter 5 DURABILITY AND ETHANOL OXIDATION PERFORMANCE OF MESOPOROUS TiO₂-SUPPORTED Pd IN ADEFEC

5.1 Introduction

Up to date, the commercialization of PEMFC and ADEFEC still faces many challenges. One of the biggest problems is the degradation of the catalyst supports during fuel cell performance [19-20, 112]. Carbon materials, especially carbon black, have been widely used as supports for the catalysts in PEMFC due to their high surface area and good conductivity. However, the oxidation of carbon supports causes the detachment of the catalyst particles as well as their agglomeration. This results in the decrease of PEMFC performance. Therefore, it is essential to find durable supports for PEMFC. Carbon nanotube (CNT) was considered as a good alternative for carbon black due to its high conductivity and better durability than carbon black [20]. However, its expensive price has a negative effect on the commercialization probability of PEMFC [118]. TiO₂, which is cheap and has been widely used as a catalyst for photocatalysis, has high stability in acidic and alkaline media [25]. It was found that TiO₂ had promotion effect on activity of Pt/C for ORR in acidic media [119]. The combination of TiO₂ with Pt and CNT showed a better oxidation activity for ethanol in 1M HClO₄ solution compared with Pt/CNT and E-TEK Pt/C [120]. Apart from the poor corrosion resistance property, carbon black contains mostly micropores, which is rather small for the access of fuels to the metal catalyst particles in the pores [121]. To overcome this disadvantage, a support with larger pores is needed.

Recently, mesoporous TiO_2 has been used as a cathodic support for Pt in PEMFC. Experimental results showed that Pt/mesoporous TiO_2 had better ORR performance and greater stability than carbon-supported Pt in acidic PEMFC [29, 121]. These achievements show that mesoporous TiO_2 is a good alternative for carbon black in PEMFC. So far, however, there have been few studies about the behavior of mesoporous TiO_2 as a support for electrocatalysts in ADEFC. Hence, the aim of our research in this chapter is to synthesize and investigate the performance of mesoporous TiO_2 as a catalyst support for Pd towards ethanol oxidation as well as its durability in alkaline media.

5.2 Experimental and characterization methods

5.2.1 Materials and chemicals

Ethylene glycol (EG), $\text{Pd}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, KOH, KBr, Pluronic P123, concentrated H_2SO_4 , acetylacetone, titanium isopropoxide were purchased from Sigma-Aldrich. Commercial anatase TiO_2 was purchased from Alfa Aesar. Vulcan XC-72 carbon black was bought from Gashub.

5.2.2 Synthesis of mesoporous TiO_2 and catalysts

Mesoporous TiO_2 was synthesized by the following procedure. 4.073 g of Pluronic P123 was dissolved completely in 100 mL of deionized (DI) water at 40 °C. Then 1.5 g of concentrated H_2SO_4 was added into the solution. This first mixture was stirred at 40 °C. The second solution was formed from acetylacetone and titanium isopropoxide: 4.15 g of acetylacetone was added into 11.79 g of titanium isopropoxide and stirred for 10 min. This solution then was added dropwise into the first solution and the mixture was stirred for 30

min. A yellow powder was formed after a while. The mixture was aged at 55 °C for 12 h without stirring. Then it was transferred into a Teflon autoclave and aged at 90 °C for 24 h. The solid product was separated by filtration and washed several times by DI water. After drying at 65 °C for overnight, the solid powder was calcined at 500 °C for 4 h with a rate of 1 °C/min in flowing air [122-123].

The catalysts were prepared by a polyol method: 100 mg of a support (carbon black, commercial TiO₂, mesoporous TiO₂) was dispersed in 40 ml of ethylene glycol (EG)-DI water (1/1, v/v) solution. Another solution was formed by mixing 25.5 mg of Pd(NO₃)₂.xH₂O with 10 ml of DI water. Then the second solution was dropped slowly into the first one and the mixture was stirred for 15 min. 50 ml of 1M KOH in EG-water (1/1, v/v) was added into the mixture and the solution was stirred and refluxed at 140 °C for 3 h. After reflux, the mixture was filtered and the solid was washed several times with DI water. The catalyst was dried at 65 °C for overnight [124].

5.2.3 Characterization

5.2.3.1 Physical characterization

Wide-angle X-ray diffraction (WAXRD) was performed with a 2θ range of 20–90°, a scan rate of 0.025°/s on a D8 Bruker AXS X-ray diffractometer (Cu Kα radiation, 40 kV, 20 mA.). Small-angle XRD (SAXRD) was performed with a 2θ range of 0.5–5°.

N₂ adsorption/desorption tests on degassed samples were measured at -196 °C with an Autosorb 6B (Quanta Chrome). Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods were used to calculate the specific surface area and pore size of the

samples.

Hydroxyl group content on the surface of the catalyst supports were determined by Fourier Transform Infrared Spectroscopy (FTIR) with a Spectrum One FTIR Spectrometer. Before FTIR measurement, the supports were dried at 110 °C for overnight to remove adsorbed water. To prepare test samples, 2 mg of each support powder was mixed with KBr powder and pressed to form a transparent pellet of 12 mm in diameter with 5 wt% support content.

5.2.3.2 Electrochemical characterization

Electrochemical studies of the samples were carried out with a three-electrode cell and a Pt wire and a Hg/HgO electrode as the counter and reference electrode, respectively. An Autolab PGSTAT302 potentiostat was used for the investigation. To prepare the working electrode, 3.3 mg of each catalyst was mixed with 1 ml of ethanol. 10 µl of this slurry was dropped onto a glassy carbon electrode (GCE). Then 5 µl of 0.5 % Nafion solution was used to bind the catalyst with the GCE. N₂ gas was purged into the test solutions for air removal. The electrochemically active surface area (ECSA) of the catalysts was determined by the PdO reduction peak of the blank cyclic voltammetry (CV) test in 1M KOH solution with the assumption that a value of 405 mC/cm² is needed for the reduction of PdO monolayer [112].

To investigate the durability of the catalysts, two methods were used with a PAR VMP2 Multichannel Potentiostat (Princeton Applied Research).

- *Durability test at fixed potentials:* In this test, the working electrode was kept at 0.3 and 0.7 V for 1 h in N₂ purged 1M KOH solution. Then the ECSA value of the catalyst was determined by CV technique.
- *Durability test with multiple CV scans:* To evaluate the durability of the catalysts, several CV scans were carried out for each catalyst in N₂ purged 1M KOH solution with a potential range of -0.8 ÷ 0.3 V and a scan rate of 50 mV/s.

5.3 Results and discussion

WAXRD results of the supports and the catalysts are shown in Fig. 5-1. The commercial TiO₂ displays typical diffraction peaks of anatase polymorph reported in the literature [122, 125]. A similar WAXRD spectrum is found for the calcined TiO₂ indicating that an anatase structure was successfully prepared. SAXRD profile of the calcined TiO₂ (Fig. 5-2) shows two peaks at 0.65 and 0.76°, which implies that the material has a certain ordered mesoporous structure [126-128]. A FCC structure is observed for Pd/C (Fig. 5-1) with typical peaks of (111), (200), (220) and (311) lattices at 40, 46.4, 68 and 82°, respectively [112]. In the WAXRD profiles of Pd/commercial TiO₂ and Pd/mesoporous TiO₂, a small peak is found at 40° in addition to other peaks of anatase TiO₂. This peak belongs to (111) lattice of Pd indicating the presence of Pd particles on the supports. Other peaks of Pd are lapped by stronger peaks of TiO₂ supports.

Figure 5-1 WAXRD profiles of the supports and catalysts

Figure 5-2 SAXRD spectrum of mesoporous TiO_2

Table 5-1 N₂ adsorption/desorption test results

	BET surface area, m ² g ⁻¹	BJH mean pore size, Å
Carbon black	255	23.4
Commercial TiO ₂	266	11.2
As-synthesized mesoporous TiO ₂	261.9	36.5
Calcined mesoporous TiO ₂	117.6	46.9

To investigate the porous structure of the substrates, N₂ adsorption/desorption tests were performed at – 196 °C. Fig. 5-3a and b show poor porosity of carbon black and commercial TiO₂. The adsorption/desorption isotherms of as-synthesized and calcined mesoporous TiO₂ present type IV curves with H2 hysteresis loops (Fig. 5-3c). These characteristics are typical for materials with ordered ink-bottle-shaped mesopores [123, 126, 129]. As shown in Fig. 5-4 and Table 5-1, BJH mean pore sizes of 23.4, 11.2, 36.5 and 46.9 Å are obtained for carbon black, commercial TiO₂, as-synthesized mesoporous TiO₂ and calcined mesoporous TiO₂, respectively. The pore size distribution of as-synthesized mesoporous TiO₂ shows two peaks at ca. 10 and 37 Å (Fig. 5-4a). This indicates that the material contains micropores in addition to mesopores. The same phenomenon is found for calcined mesoporous TiO₂ (Fig. 5-4b). It can be seen that the BJH mean pore size of commercial TiO₂ increases after calcination, resulting in a reduction in BET surface area. The pore size increase is possibly due to the removal of the surfactant template inside the pores as well as the growth of crystallite size at high temperature [122]. Figures 5-4c and d display the non-uniformity of the pore size of commercial TiO₂ and carbon black, respectively.

Figure 5-3 N_2 adsorption/desorption isotherms of (a) carbon black, (b) commercial TiO_2 and (c) as-synthesized and calcined mesoporous TiO_2

Figure 5-4 BJH pore size distribution curves of (a) as-synthesized mesoporous TiO_2 , (b) calcined mesoporous TiO_2 , (c) commercial TiO_2 and (d) carbon black

The durability of the electrocatalysts is essential for the real applications of ADEFC. The oxidation of the supports is the main reason for the detachment and aggregation of the catalyst particles, which reduce the performance of ADEFC. Therefore, fixed-potential tests were performed for all catalysts in 1M KOH solution. Fig. 5-5 and -6 show the results of this durability test. At 0.3 V, Pd/mesoporous TiO₂ exhibits the lowest corrosion current compared with those of Pd/C and Pd/commercial TiO₂. As displayed in Fig. 5-5, it is obvious that higher test potential has a strong impact on the corrosion behavior of the catalysts. For Pd/mesoporous TiO₂, its corrosion current at 0.7 V is ca. 10 times that at 0.3 V. Similar phenomena were obtained for Pd/C and Pd/commercial TiO₂. A clearer difference in stability of the catalysts is shown at 0.7 V (Fig. 5-5b). After 1h holding test at 0.7 V, the corrosion current of Pd/C is 0.054 mA/cm², which is ca. 2 and 8 times higher than those of Pd/commercial TiO₂ (0.028 mA/cm²) and Pd/mesoporous TiO₂ (0.007 mA/cm²), respectively. After each fixed potential test, the Pd ECSAs of the catalysts were determined by CV and are displayed in Fig. 5-6 after being normalized by the initial Pd ECSA. It is found that Pd/C has the highest ECSA loss (17 % at 0.3 V and 35 % at 0.7 V) while Pd/mesoporous TiO₂ has the lowest one (4 % at 0.3 V and 7 % at 0.7 V). These results indicate the greater corrosion resistance of mesoporous TiO₂ in comparison with commercial TiO₂ and carbon black in alkaline solution.

Figure 5-5 Corrosion current-time curves of the catalysts at (a) 0.3 V and (b) 0.7 V

Figure 5-6 Normalized Pd ECSAs of the catalysts in fixed-potential test in 1M KOH solution

For better understanding the durability of the catalysts and supports in ADEFC, multiple-scan investigations were performed in N₂-purged 1M KOH solution. The CV profiles of the catalysts after 20 and 1000 scans are presented in Fig. 5-7. A depression of the PdO reduction peak (at -0.2 V) is observed for all the catalysts after 1000 scans. However, Pd/mesoporous TiO₂ shows the smallest depression compared with Pd/C and Pd/commercial TiO₂. This observation is confirmed in Fig. 5-8. After 1000 cycles, a Pd ECSA loss of 58 % is seen for Pd/C while 51 and 32 % loss are found for Pd/commercial TiO₂ and Pd/mesoporous TiO₂, respectively. The results again confirm the effect of the supports on the durability of the electrocatalysts. It is possible that the structure of mesoporous TiO₂ with large uniform pore size helps to improve the dispersion of Pd

nanoparticles on the support as well as prevent the detachment and agglomeration of the metal particles, which helps to enhance the durability of the catalysts.

Figure 5-7 CVs of (a) 10%Pd/C, (b) 10%Pd/commercial TiO₂ and (c) 10%Pd/mesoporous TiO₂ after 20 and 1000 cycles in multi-scan test in 1M KOH solution, scan rate of 50 mV/s

Figure 5-8 Normalized Pd ECSAs of the catalysts in multi-scan test in 1M KOH solution

The surface of the commercial TiO₂ and mesoporous TiO₂ were investigated by FTIR to determine the presence and content of hydroxyl groups. As shown in Fig. 5-9, FTIR spectra of the two materials show a broad peak at 3700-2500 cm⁻¹ which is assigned to the O-H stretching mode and a small peak at 1622 cm⁻¹ is due to the bending vibration mode of H-O-H bonding. The area of the O-H stretching peak represents the surface hydroxyl content of the supports [130-131]. Therefore, the area of this peak was calculated and normalized by BET surface area of each TiO₂ support, as displayed in Table 5-2. The normalized O-H stretching peak area of mesoporous TiO₂ is 59.1, which is ca. 4 fold that of commercial TiO₂ (14.5) indicating that the hydroxyl content on the surface of mesoporous TiO₂ support is much more abundant than that of commercial TiO₂. This might help to improve the removal of ethoxy intermediate in the ethanol electrooxidation process and thus, enhance the ethanol oxidation activity of Pd [33], as proposed by Liang et al.

Figure 5-9 FTIR spectra of commercial TiO₂ and mesoporous TiO₂

Table 5-2 FTIR data of commercial TiO₂ and mesoporous TiO₂

Support	OH stretching peak area from FTIR	OH stretching peak area normalized by BET surface area
Commercial TiO ₂	3867	14.5
Mesoporous TiO ₂	6950	59.1

To investigate the performance of the catalysts for EOR in alkaline media, LSV tests were carried out in 1M C₂H₅OH + 1M KOH solution. Fig. 5-10 shows the EOR behavior of 10%Pd/C, 10%Pd/commercial TiO₂ and 10%Pd/mesoporous TiO₂ in alkaline solution. It can be seen that Pd/mesoporous TiO₂ exhibits an extraordinary activity for the oxidation of ethanol compared with Pd/C and Pd/commercial TiO₂. The peak current density observed for Pd/mesoporous TiO₂ is 4.71 mA/cm², which is 2.6 and 4.4 times those of

Pd/commercial TiO₂ (1.85 mA/cm²) and Pd/C (1.06 mA/cm²), respectively. This means that Pd/mesoporous TiO₂ is more favorable for the EOR in alkaline media than the other two catalysts. The better ethanol oxidation performance of Pd on the mesoporous TiO₂ support again indicates the important role of supporting materials. There are some possible reasons for the high activity of Pd/mesoporous TiO₂ for the oxidation of ethanol in alkaline media. Firstly, as stated previously, the mesoporous structure of TiO₂ may enhance the dispersion of Pd nanoparticles on the support and thus, improve the ethanol oxidation activity of the catalyst [121]. Secondly, the fuel can easily access the Pd particles in the large pores of the mesoporous TiO₂ and hence, the kinetics of the fuel oxidation reaction is improved. Thirdly, as reported above, the surface of the mesoporous TiO₂ possesses high hydroxyl content and this helps to eliminate the poisoning intermediates on the catalyst surface and free active sites for the EOR process [33].

Fig. 5-11 presents the CA curves of the ethanol oxidation on Pd/C, Pd/mesoporous TiO₂ and Pd/commercial TiO₂ in 1M C₂H₅OH + 1M KOH solution at a potential of – 0.25 V. All the catalysts show a rapid decay before steady currents are obtained due to the accumulation of poisoning intermediates on the catalyst surfaces. In the steady-state region, Pd/mesoporous TiO₂ exhibits a current density of 0.55 mA/cm² after 1000 s while Pd/commercial TiO₂ and Pd/C show current densities of 0.04 and 0.15 mA/cm², respectively. The highest current value of Pd/mesoporous TiO₂ indicates its better poison-tolerance capability compared with the other two catalysts. Possessing high activity and good stability for ethanol oxidation, Pd/mesoporous TiO₂ is a promising electrocatalyst for practical applications in ADEFC.

Figure 5-10 LSV results of the catalysts in 1M C₂H₅OH + 1M KOH solution

Figure 5-11 CA results (at -0.25 V) of the catalysts in 1M C₂H₅OH + 1M KOH solution

5.4 Summary

In this chapter, a mesoporous anatase TiO₂ was successfully prepared, used as an

electrocatalyst support and compared with a commercial anatase TiO_2 and carbon black in alkaline media. The TiO_2 exhibited typical characteristics of a mesoporous structure via N_2 adsorption/desorption test. Pd/mesoporous TiO_2 presented the highest durability in fixed-potential and multi-scan tests in 1M KOH solution while Pd/C showed the worst durability behavior. Pd/mesoporous TiO_2 was found to have better activity and higher poison-tolerance for EOR compared with Pd/commercial TiO_2 and Pd/C. It is believed that the mesoporous structure of TiO_2 plays an important role in the excellent performance of Pd/mesoporous TiO_2 .

Chapter 6 PERFORMANCE OF SUB-STOICHIOMETRIC TITANIUM OXIDE AS CATALYST SUPPORT FOR Pd IN ADEFC

6.1 Introduction

Apart from TiO_2 , Magnéli-phase titanium oxides $\text{Ti}_n\text{O}_{2n-1}$ ($4 \leq n \leq 9$) with good electrical conductivity and high oxidation-resistivity have been explored as electrode materials and catalyst supports in electrochemical systems. A commercial product of $\text{Ti}_n\text{O}_{2n-1}$, known as “Ebonex”, has been found to be electrochemically stable in acidic and basic solutions [62, 132-135]. PtCo/Ebonex showed better catalytic efficiency for oxygen evolution than Pt/Ebonex and unsupported PtCo. The electronic interaction between the metals and the support was assumed to play a big role in the activity enhancement [136]. Vracar et al. investigated the activity of Ebonex-supported Pt towards oxygen reduction reaction (ORR) in 0.5 M HClO_4 solution. A significant improvement in the kinetics of ORR on the Pt/Ebonex was observed, compared with that on polycrystalline Pt [137]. Ti_4O_7 - a member of sub-stoichiometric titanium oxides possessing a high electrical conductivity [133-135, 138] has been recently examined as an effective support for electrocatalysts in PEMFCs [18, 31]. Ioroi et al. found that Ti_4O_7 -supported Pt catalysts had similar catalytic activities for ORR and hydrogen oxidation, but higher stability in comparison with those of carbon-supported Pt catalysts in acidic condition. As mentioned above, ADEFC is a promising type of PEMFCs. However, there have been no studies about using $\text{Ti}_n\text{O}_{2n-1}$ as catalyst supports for ADEFC. Therefore, in the content of this chapter, we carried out an investigation for the utilization of $\text{Ti}_n\text{O}_{2n-1}$ as a support for palladium for EOR and compared this material with

the convenient support, Vulcan XC-72 carbon black, and the commercial TiO_2 in alkaline media.

6.2 Experimental and characterization methods

6.2.1 Materials

Commercial anatase TiO_2 was purchased from Alfa Aesar. Carbon black Vulcan XC-72 was bought from Gashub (Singapore). Ethylene glycol (EG), $\text{Pd}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ and KOH were purchased from Sigma-Aldrich. All the chemicals were used without further purification.

6.2.2 Synthesis of catalysts

Briefly, $\text{Ti}_n\text{O}_{2n-1}$ was synthesized by heating the commercial anatase TiO_2 with a hydrogen flow at 1050 °C for 6 h [18, 139]. The catalysts were prepared by a polyol reducing method: 100 mg of a support (carbon black, commercial TiO_2 , $\text{Ti}_n\text{O}_{2n-1}$) was added into 40 ml of ethylene glycol (EG)-deionized (DI) water (1/1, v/v) solution and dispersed by sonication and stirring. 25.5 mg of $\text{Pd}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ was mixed with 10 ml of DI water by sonication and stirring. Then the second solution was added dropwise into the first one and the mixture was stirred for 15 min. 50 ml of 1M KOH in EG-water (1/1, v/v) was added into the mixture and the solution was stirred and refluxed at 140 °C for 3 h. After reflux, the mixture was filtered or centrifuged and the solid was washed several times with DI water. Finally, it was dried at 65 °C for overnight.

6.2.3 Sample preparation for conductivity measurement

Solid powder was dried at 105 °C for overnight and then was pressed into pellets (diameter of 6.1 mm) using a Carver hydraulic press (model 4128) with a pressure of 457 MPa. All the pellets were dried again at 105 °C for overnight before conductivity measurement.

6.2.4 Characterization

X-ray diffraction (XRD) measurement was carried out with a D8 Bruker AXS X-ray diffractometer (Cu K α radiation, 40 kV, 20 mA, 2 θ range of 20–90°, scan rate 0.025°/s).

Electrical conductivity measurement was carried out at room temperature by a two - Pt probe DC technique with an Autolab PGSTAT302 potentiostat (Eco Chemie). To eliminate the effect of contact resistance between the samples and the probes, the conductivity of each material was calculated from the measurement of samples with different thickness. The electrical resistance of the samples was determined from the slopes of linear voltage vs. current curves.

N₂ adsorption/desorption isotherms were measured at -196 °C with an Autosorb 6B (Quanta Chrome). Prior to the measurement, the samples were degassed at 250°C for overnight. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method. Pore size was calculated by the Barrett–Joyner–Halenda (BJH) method.

Electrochemical investigation was performed with the Autolab PGSTAT302 potentiostat using a three-electrode cell with a Pt wire and a Hg/HgO electrode as the counter and

reference electrode, respectively. To prepare the working electrode for electrochemical tests, 3.3 mg of each catalyst was mixed with 1 ml of ethanol. From this mixture, 10 μ l was dropped onto a glassy carbon electrode (GCE) and the GCE was dried in air. The catalyst layer was fixed to the electrode by 5 μ l of 0.5% Nafion solution. N₂ gas was bubbled into the test solutions for air removal. All current values in electrochemical results were normalized by the electrochemical active surface area (ECSA) of the catalysts determined by the PdO reduction peak of the blank cyclic voltammetry (CV) test in 1M KOH solution with the assumption that a value of 405 mC/cm² is needed for the reduction of PdO monolayer [112].

6.2.5 Durability tests

Durability tests were carried out with a PAR VMP2 Multichannel Potentiostat (Princeton Applied Research) using two different methods. (1) Potentiostatic measurement: The catalysts were kept at 0.3 and 0.7 V in N₂ purged 1M KOH solution for 1h. After each test, the electrochemical active surface area (ECSA) values of the catalysts were determined by CV technique. (2) Multiple CV sweeps: In this test, 500 and 1000 CV scans in N₂ purged 1M KOH solution were performed for each catalyst with a potential range of -0.8 V÷ 0.3 V and a scan rate of 50 mV s⁻¹.

6.3 Results and discussion

Fig. 6-1 shows XRD patterns of the commercial TiO₂ and the partially reduced product of the commercial TiO₂ at 1050°C, as well as standard XRD spectra of anatase TiO₂ and different Magnéli phase titanium oxides. The XRD profile of the commercial TiO₂ displays

typical peaks of anatase structure as reported in the literature [122, 140] and displayed in the standard XRD spectrum of anatase TiO_2 . These peaks are absent in the XRD spectrum of $\text{Ti}_n\text{O}_{2n-1}$, indicating that the anatase structure of TiO_2 was completely converted into the structure of $\text{Ti}_n\text{O}_{2n-1}$ which is validated by its black-blue color appearance, in contrast to the white color of the commercial TiO_2 . A weight loss of ca. 7% was also observed for $\text{Ti}_n\text{O}_{2n-1}$ compared to TiO_2 . These phenomena are consistent with what was obtained in previous studies [18, 31, 133-134, 141]. Compared with the standard XRD patterns of sub-stoichiometric titanium oxides, the product mainly consists of Ti_9O_{17} , Ti_8O_{15} , Ti_7O_{13} and Ti_6O_{11} . These compounds were formed from the reaction of TiO_2 and H_2 at high temperature: $n\text{TiO}_2 + \text{H}_2 \rightarrow \text{Ti}_n\text{O}_{2n-1} + \text{H}_2\text{O}$ [135]. Fig. 6-2 presents XRD results of 10%Pd/commercial TiO_2 , 10%Pd/ $\text{Ti}_n\text{O}_{2n-1}$ and 10%Pd/C in comparison with those of commercial TiO_2 and $\text{Ti}_n\text{O}_{2n-1}$. The XRD profile of 10%Pd/C displays typical peaks of FCC structure of Pd, including (111), (200), (220) and (311) lattices [112]. The XRD spectra of 10%Pd/commercial TiO_2 and 10%Pd/ $\text{Ti}_n\text{O}_{2n-1}$ show two small peaks at 40° and 46° , which belongs to (111) and (200) lattice of Pd structure, respectively. This indicates the presence of Pd nanoparticles on the commercial anatase TiO_2 and $\text{Ti}_n\text{O}_{2n-1}$ support. Other FCC peaks of Pd are overlapped by the peaks of TiO_2 and $\text{Ti}_n\text{O}_{2n-1}$.

Figure 6-1 XRD profiles of commercial TiO_2 , $\text{Ti}_n\text{O}_{2n-1}$ and standard XRD spectra of anatase TiO_2 and different Magnéli phase titanium oxides

Figure 6-2 XRD profiles of the supports and catalysts

The support materials were compressed into small pellets and the electrical conductivity was measured by a DC method. The results shown in Table 6-1 indicate that $\text{Ti}_n\text{O}_{2n-1}$ has a higher conductivity than commercial TiO_2 , but lower than that of carbon black. The measured conductivities of carbon black and commercial TiO_2 are 6.9 and $4.9 \times 10^{-8} \text{ S.cm}^{-1}$, respectively, which are consistent with those in the literature (4.0 , 5.4 , 7.4 S.cm^{-1} for carbon black and 10^{-13} , $10^{-6} \text{ S.cm}^{-1}$ for TiO_2) [142-147]. However, the conductivity value measured for $\text{Ti}_n\text{O}_{2n-1}$ ($1.7 \times 10^{-7} \text{ S.cm}^{-1}$) is different from those of Ti_4O_7 , Ti_5O_9 , Ti_6O_{11} and Ti_8O_{15}

reported in the literature (1035, 1995 S.cm⁻¹ for Ti₄O₇, 631 S.cm⁻¹ for Ti₅O₉, 63 S.cm⁻¹ for Ti₆O₁₁ and 25 S.cm⁻¹ for Ti₈O₁₅; no conductivity reports for Ti₇O₁₃ and Ti₉O₁₇ in the literature) [135, 138, 147-148]. The experiments were repeated several times and double checked by AC impedance measurement to ensure the validity of the obtained conductivity values. As analyzed above, the XRD pattern of Ti_nO_{2n-1} confirmed that the sub-stoichiometric titanium oxide is a mixture of Ti₉O₁₇, Ti₈O₁₅, Ti₇O₁₃ and Ti₆O₁₁. The difference of the measured conductivity of the material from those in the literature may be due to the conductivity dependence of the pellets on their intraparticle/interparticle porosity. As examined below, the sub-stoichiometric titanium oxides synthesized all show porous structure, while the reported values are based on nonporous single crystal. Besides, with different compression pressures, the pellets will have different interparticle porosities, which may result in the variation in measured conductivities [145, 149]. The low electrical conductivity may also be attributed to the mixed polycrystalline phase of the titanium oxides.

To investigate the intraparticle porosity of the supports, nitrogen adsorption/desorption tests were performed and the results are displayed in Table 6-1 and Fig. 6-3. The mean pore size of Ti_nO_{2n-1} (41.5 Å) is larger than that of commercial TiO₂ (11.2 Å) due to the broadening effect of the partial reduction with H₂ at high temperature. As a result, the BET surface area of Ti_nO_{2n-1} is smaller than that of TiO₂. The BET surface area values are 255, 266 and 135 m²/g for carbon black, TiO₂ and Ti_nO_{2n-1}, respectively.

Table 6-1 Measured properties of different supports

Support	Conductivity, S.cm ⁻¹		BET	BJH pore
	Literature value	Measured value	surface area (m ² /g)	diameter (Å)
Carbon black	4.0, 5.4, 7.4	6.9	255	23.4
TiO ₂	10 ⁻¹³ , 10 ⁻⁶	4.9x10 ⁻⁸	266	11.2
Ti _n O _{2n-1}	1035, 1995 (Ti ₄ O ₇) 631 (Ti ₅ O ₉) 63 (Ti ₆ O ₁₁) 25 (Ti ₈ O ₁₅)	1.7x10 ⁻⁷	135	41.5

Figure 6-3 Nitrogen adsorption isotherms of (a) carbon black, (b) commercial TiO_2 and (c)

$\text{Ti}_n\text{O}_{2n-1}$

Two strategies were used to investigate the durability of Pd/C, Pd/commercial TiO₂ and Pd/Ti_nO_{2n-1} in this work. In the first one, fixed potential values of 0.3 and 0.7 V were applied to the working electrode for 1h in 1M KOH solution to measure the corrosion currents and CVs were recorded before and after the tests to determine Pd ECSAs of the catalysts. The chronoamperometric curves in Fig. 6-4a show that Pd/Ti_nO_{2n-1} has a smaller corrosion current than that of Pd/commercial TiO₂ and Pd/C at 0.3 V. Corrosion current values of 1.15, 2.44, 2.86 $\mu\text{A}/\text{cm}^2$ were observed for Pd/Ti_nO_{2n-1}, Pd/commercial TiO₂ and Pd/C after 1h, respectively. This trend was also found in Fig. 6-4b. At 0.7 V, Pd/Ti_nO_{2n-1} shows a corrosion current of 0.013 mA/cm^2 at 1h, which is only 25 % and 42 % of those obtained for Pd/C (0.052 mA/cm^2) and Pd/commercial TiO₂ (0.031 mA/cm^2), respectively. With much higher values of corrosion current at 0.7 V, it is clear that the higher holding potential has a stronger effect on the degradation of the catalysts. Pd ECSAs of the catalysts normalized with initial ECSA values are plotted versus the holding potentials in Fig. 6-5. The Pd ECSA losses again confirm the above trend. Pd/Ti_nO_{2n-1} lost 5 and 7 % of its Pd ECSA at 0.3 and 0.7 V, respectively while Pd/C lost 18 and 35 % of its Pd ECSA value. Pd/commercial TiO₂ shows a better result than Pd/C but worse than Pd/Ti_nO_{2n-1} with a Pd ECSA loss of 13 and 22 % in the two fixed potential tests. In the second durability test strategy, multiple CV cycles were performed on the working electrode with a potential range of -0.8 to 0.3 V. As shown in Fig. 6-6, Pd/Ti_nO_{2n-1} exhibits a slower degradation rate of Pd ECSA than Pd/commercial TiO₂ and Pd/C. After 1000 cycles, only a loss of 39 % of Pd ECSA was found for Pd/Ti_nO_{2n-1} while 58 % and 51 % of Pd ECSA were lost for Pd/C and Pd/commercial TiO₂, respectively.

Figure 6-4 Corrosion curves of the catalysts in fixed potential tests at (a) 0.3 and (b) 0.7 V

Figure 6-5 Normalized Pd ECSAs of the catalysts after fixed potential tests

Figure 6-6 Normalized Pd ECSAs of the catalysts after multi-scan tests

As reported above, all the results of the two durability test methods showed that $\text{Ti}_n\text{O}_{2n-1}$ possesses a better stability compared to commercial TiO_2 and carbon black in alkaline media. This is in agreement with the results by Ioroi's group for acidic media [18, 31]. In that work, it was found that carbon black was oxidized beyond 0.9 V (vs RHE) while Ti_4O_7 still showed a stable state up to 1.8 V (vs RHE) in a single cell test.

Table 6-2 Unit cell parameters of palladium, anatase titanium oxide and some Magnéli phase titanium oxides

Phase	a (nm)	b (nm)	c (nm)	Structure
Anatase TiO_2	0.374		0.951	Tetragonal
Ti_6O_{11}	0.555	0.713	3.223	Triclinic
Ti_7O_{13}	0.554	0.713	3.815	Triclinic
Ti_8O_{15}	0.553	0.713	4.406	Triclinic
Ti_9O_{17}	0.552	0.714	5.003	Triclinic
Palladium	0.389			Face-centered cubic

Electrocatalytic activity of the catalysts for EOR in ADEFC was investigated in 1M KOH + 1M $\text{C}_2\text{H}_5\text{OH}$ solutions. Linear sweep voltammograms of the catalysts for EOR are displayed in Fig. 6-7. Pd/C and Pd/ TiO_2 shows an onset potential for EOR at ca. -0.50 V while a more negative value of - 0.55 V is seen for Pd/ $\text{Ti}_n\text{O}_{2n-1}$. Furthermore, the highest peak current of 2.10 mA/cm^2 is observed for Pd/ $\text{Ti}_n\text{O}_{2n-1}$ while 1.05 and 1.85 mA/cm^2 is found for Pd/C and Pd/ TiO_2 , respectively. These data imply that Pd/ $\text{Ti}_n\text{O}_{2n-1}$ has the greatest

activity for EOR among the three catalysts. With similar onset potential and higher peak current density, Pd/commercial TiO_2 shows a better oxidation activity for ethanol in alkaline media compared to the convenient Pd/C catalyst. The excellent activity of Pd/ $\text{Ti}_n\text{O}_{2n-1}$ for EOR possibly results from an electronic interaction between the support and the metal nanoparticles [133, 150]. According to Hammer and Nørskov's d-band center theory, the lattice constant of small metal particles on an oxide support suffers a compression or expansion due to an interaction with the lattice of the support, which causes a change in the d-band center of the metal and results in its adsorption capability change [50, 55, 151]. As shown in Table 6-2, Pd has a lattice constant of 0.389 nm while unit-cell parameters of Ti_6O_{11} , Ti_7O_{13} , Ti_8O_{15} and Ti_9O_{17} are larger [112, 152]. The lattice constant mismatch between Pd and $\text{Ti}_n\text{O}_{2n-1}$ causes a tensile strain in the structure of Pd particles and shifts up the d-band center of Pd. This improves the adsorption of OH^- onto the catalyst surface and helps to remove ethoxy species out of active sites of the catalyst [33, 50, 112]. As a consequence, the kinetics of the EOR is enhanced. Moreover, as shown in Table 6-1, the mean pore size of $\text{Ti}_n\text{O}_{2n-1}$ is larger than those of carbon black and commercial TiO_2 . This will help to prevent the agglomeration of Pd nanoparticles and therefore, improve the EOR process. In the case of Pd/ TiO_2 , the anatase TiO_2 has lattice constants of 0.374 and 0.951 nm [65, 153], which are smaller than those of Ti_6O_{11} , Ti_7O_{13} , Ti_8O_{15} and Ti_9O_{17} (Table 6-2). As a result, the d-band center of Pd is less shifted up and thus, TiO_2 is less effective than $\text{Ti}_n\text{O}_{2n-1}$ in improving the ethanol oxidation activity of Pd. In the other hand, $\text{Ti}_n\text{O}_{2n-1}$ and TiO_2 are hypo-d-electron oxides while Pd is a hyper-d-electron metal [137, 154-161]. According to Brewer's theory, the stronger the hypo-hyper-d-interelectronic

bonding between the support and the metal, the weaker the adsorptive bonding of poisoning intermediates (ethoxy CH_3CO), and consequently, the higher the electrocatalytic activity for ethanol oxidation [137, 154-161].

Figure 6-7 LSV plots of the catalysts in 1M $\text{C}_2\text{H}_5\text{OH}$ + 1M KOH solution with a scan rate of 50 mV s^{-1}

The stability of the catalysts for EOR was investigated by using CA technique at an anodic potential of -0.25 V in the 1M KOH + 1M $\text{C}_2\text{H}_5\text{OH}$ solution (Fig. 6-8). At initial stage, current densities of all the catalysts degrade rapidly due to the adsorption of poisoning intermediates. Then, a slow decay was observed after 100 s. At the second stage, the highest current was found for $\text{Pd/Ti}_n\text{O}_{2n-1}$ while the lowest one was observed for $\text{Pd/commercial TiO}_2$. These results suggest that among the three electrocatalysts, $\text{Pd/Ti}_n\text{O}_{2n-1}$ has the best tolerance to the poisoning species.

Figure 6-8 CA results of the catalysts at -0.25 V (vs Hg/HgO) in $1\text{M C}_2\text{H}_5\text{OH} + 1\text{M KOH}$ solution

6.4 Summary

The application of $\text{Ti}_n\text{O}_{2n-1}$ and commercial TiO_2 as catalyst supports for Pd in ADEFC was investigated in this chapter. $\text{Ti}_n\text{O}_{2n-1}$ showed a higher electronic conductivity than that of TiO_2 but lower than that of carbon black. From fixed potential and multiple scan tests, excellent durability was found for $\text{Ti}_n\text{O}_{2n-1}$ compared with carbon black and commercial TiO_2 in alkaline media. Among the three catalysts, $\text{Pd/Ti}_n\text{O}_{2n-1}$ displayed the highest activity and stability for the electrooxidation of ethanol. The study showed that $\text{Ti}_n\text{O}_{2n-1}$ is an effective support for the catalysts in ADEFC.

Chapter 7 EXPLORATION OF Nb-DOPED TiO₂ AS CATALYST SUPPORT IN ADEFC

(The content in this chapter has been accepted for publication in Applied Catalysis B: Environmental, 2011, 10.1016/j.apcatb.2011.11.046)

7.1 Introduction

As stated in previous chapters, there have been several efforts in searching for oxidation-resistant non-carbon catalyst supports. Generally, a good fuel cell catalyst support should possess a high surface area, a good electrical conductivity and high stability. Among various materials, TiO₂ has attracted researchers' attention due to its high corrosion-resistance in fuel cell working environment and mesoporous TiO₂ has been shown as a good support for Pd towards EOR in alkaline condition in Chapter 5. Although TiO₂ showed impressive effects on the stability and activity of the fuel cell catalysts, the low electrical conductivity of TiO₂ at temperatures below 200°C inhibits its application in PEMFCs. Therefore, it is essential to improve the electronic conductivity of titania for its practical use as a promising replacement of carbon black in PEMFCs.

There are two approaches to enhance the electrical conductivity of titania. The first way is to convert TiO₂ into sub-stoichiometric titania Ti_nO_{2n-1}, as presented in Chapter 6. However, during the fuel cell operation, sub-stoichiometric titania can be oxidized and converted to the stoichiometric one, which is nonconductive [62-63]. This problem is solved in the second approach. In this approach, the electronic conductivity of TiO₂ is

improved by doping the material with a donor-type element [147]. This method creates no anion vacancy in the structure and thus, the material is more stable to thermal and electrochemical oxidation [26, 62-63]. Nb has been observed as a good donor-dopant for titania. In Park et al.'s study, Pt/NbTiO₂ showed a higher ORR current compared with Pt/C in 0.5 M H₂SO₄. The excellent activity of Pt/NbTiO₂ was believed to derive from the well dispersion of Pt particles on the support and an interaction between the metal catalyst and the support [146]. Chhina et al. found that rutile Nb_{0.1}Ti_{0.9}O₂ was more conductive than anatase Nb_{0.1}Ti_{0.9}O₂ while W doped-TiO₂ was much less conductive than rutile Nb_{0.1}Ti_{0.9}O₂. Pt/Nb_{0.1}Ti_{0.9}O₂ and Pt/C were examined their activity and durability as cathode catalysts in half-cell and full-cell tests. Pt/C showed a bit better ORR performance than Pt/Nb_{0.1}Ti_{0.9}O₂ before the stability test. However, the catalytic activity of Pt/C was considerably reduced after the fixed-potential test while Pt/ Nb_{0.1}Ti_{0.9}O₂ nearly remained its activity after the test [26, 63]. Rutile Nb-doped TiO₂ was also investigated as cathode catalyst support for PEMFC in Huang et al.'s work. At first, Nb_{0.25}Ti_{0.75}O₂ supported Pt catalyst presented similar ORR activity to that of a ETEK Pt/C. However, after an accelerated durability test by cycling between 0.6 and 1.4 V, Pt/ Nb_{0.25}Ti_{0.75}O₂ showed 10-time higher ORR activity compared to Pt/C. A full-cell test indicated that Pt/C had no activity after 1000 cycles while Pt/ Nb_{0.25}Ti_{0.75}O₂ only lost a small voltage (0.11 V at 0.6 Acm⁻²) after 3000 cycles [30]. In Elezovic et al.'s research, Pt/anatase Nb_{0.005}Ti_{0.995}O₂ was synthesized and investigated its ORR activity in acidic solutions with or without the appearance of methanol. The catalyst showed a more positive onset potential for ORR compared with that of Pt/C. Tafel plots displayed the higher ORR activity of

Pt/Nb_{0.005}Ti_{0.995}O₂ than that of Pt/C through a considerable improvement of current density at constant potentials. Pt/Nb_{0.005}Ti_{0.995}O₂ showed better methanol tolerance than Pt/C [66]. An anatase Nb_{0.1}Ti_{0.9}O₂ was synthesized and used as a support for PtRu alloy for oxidation of methanol. It was found that the mass activity (A/g_{Pt}) of PtRu/Nb_{0.1}Ti_{0.9}O₂ was 6% higher than that of PtRu/C in a cyclic voltammetric study in a 0.5 M H₂SO₄ + 1.0 M methanol solution. A DMFC test showed that PtRu/Nb_{0.1}Ti_{0.9}O₂ possessed 46% higher mass current density compared to PtRu/C at 0.40 V [162].

ADEFC has been attracting more and more scientists' attention due to the high specific energy, low toxicity and easiness of mass production of ethanol from agricultural products as well as the ability of using non-platinum metals as electrocatalysts in alkaline environments [6, 61, 163-164]. However, there have been rare studies on the use and durability of Nb-doped TiO₂ as a catalyst support for ADEFCs. In Chapter 3, PdAg alloy was found to be highly effective for the electrooxidation of ethanol in basic condition [112]. Therefore, in this chapter, we synthesized PdAg supported on Nb-doped TiO₂ with different Nb contents and investigated the effect of various Nb/Ti ratios to the conductivity, durability and catalytic activity of the catalysts for the ethanol oxidation in alkaline media. A comparison of PdAg catalysts supported on various materials was also carried out in the work.

7.2 Experimental and characterization methods

7.2.1 Preparation of Nb-doped TiO₂ with 2, 5, 10, 20 and 30% Nb

The materials were synthesized by a hydrothermal method: 4.073 g of Pluronic P123

(Aldrich) was dissolved completely in 100 mL of deionized (DI) water at 40 °C. Then 1.5 g of concentrated H₂SO₄ was added into the solution. This mixture was stirred at 40 °C. The second solution was formed from acetylacetone, niobium ethoxide and titanium isopropoxide (Aldrich): acetylacetone was added into a mixture of niobium ethoxide and titanium isopropoxide and stirred for 10 min. This solution then was added dropwise into the first solution and the mixture was stirred at 40 °C for 30 min. A yellow powder was formed after a while. The mixture was aged at 55 °C for 12 h without stirring. Then it was transferred into a Teflon autoclave and aged at 90 °C for 24 h. The solid product was separated by filtration and washed several times by DI water. After drying at 65 °C for overnight, the solid powder was calcined at 500 °C for 4 h with a rate of 1 °C min⁻¹ in flowing air to remove the template. Then the material was annealed at high temperature for 2 h under hydrogen flow to activate Nb donor dopant in TiO₂ [26, 30, 63, 146].

7.2.2 Preparation of PdAg electrocatalysts

The preparation procedure of the catalysts was modified from the literature [124, 165]. In a typical preparation, 100 mg of a support (carbon black, commercial TiO₂, Nb_xTi_{1-x}O₂, mesoporous TiO₂, Ti_nO_{2n-1}) was dispersed in 50 ml of 0.1 M NaOH in ethylene glycol (EG). Then 27 mg of Pd(NO₃)₂·xH₂O and 20 mg of AgNO₃ were added and mixed with the solution. The mixture was refluxed at 180 °C for 3 h. After reflux, the mixture was filtered or centrifuged and the solid was washed several times with DI water. Finally, it was dried at 65 °C for overnight.

7.2.3 Sample preparation for conductivity measurement

Pellets (diameter of 6.1 mm) were made from dry powder using a Carver hydraulic press (model 4128) with a pressure of 457 MPa. All the pellets were dried at 105 °C for overnight before conductivity measurement.

7.2.4 Physical and electrochemical characterization

Structure of the samples was investigated by X-ray diffraction (XRD) with a D8 Bruker AXS X-ray diffractometer (Cu K α radiation, 40 kV, 20 mA, 2θ ranges of 20–90°, scan rate 0.025°s⁻¹).

Transmission electron microscopy (TEM, JEOL 2010) at an acceleration voltage of 200 keV was used to examine the morphology of the samples.

Electrical conductivity measurement was performed at room temperature by a two - Pt probe DC technique with an Autolab PGSTAT302 potentiostat (Eco Chemie). The electrical resistance of the samples was determined from the slopes of linear voltage vs. current curves.

N₂ adsorption/desorption isotherms were measured at -196 °C with an Autosorb 6B (Quanta Chrome). Prior to the measurement, the samples were degassed at 250°C for overnight. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method.

Electrochemical investigation was performed with the Autolab PGSTAT302 potentiostat

using a three-electrode cell with a Pt wire and a Hg/HgO (1M KOH) electrode as the counter and reference electrode, respectively. To prepare the working electrode for electrochemical tests, 3.3 mg of each catalyst was mixed with 1 ml of ethanol. From this mixture, 10 μ l was dropped onto a glassy carbon electrode (GCE) and the GCE was dried in air. The catalyst layer was fixed to the electrode by 5 μ l of 0.5% Nafion solution. N₂ gas was purged into the test solutions for deaeration. All current values in electrochemical results were normalized by the electrochemical active surface area (ECSA) of the catalysts determined by the PdO reduction peak of the blank cyclic voltammetry (CV) test in 1M KOH solution with the assumption that a value of 405 mC/cm² is needed for the reduction of PdO monolayer.

7.2.5 Durability tests

Durability tests were carried out with a PAR VMP2 Multichannel Potentiostat (Princeton Applied Research) using two different methods. (1) Potentiostatic measurement: The catalysts were kept at 0.3 and 0.7 V in N₂ purged 1M KOH solution for 1h. After each test, the electrochemical active surface area (ECSA) values of the catalysts were determined by CV technique. (2) Multiple CV scans: In this test, multiple CV scans in N₂ purged 1M KOH solution were performed for each catalyst with a potential range of -0.8 V÷ 0.3 V and a scan rate of 50 mV s⁻¹.

7.3 Results and discussion

7.3.1 Nb-doped TiO₂

7.3.1.1 Nb_{0.10}Ti_{0.90}O₂

Figure 7-1 XRD patterns of (a) commercial TiO₂, (b) as-synthesized Nb_{0.10}Ti_{0.90}O₂, (c) calcined Nb_{0.10}Ti_{0.90}O₂ and different Nb_{0.10}Ti_{0.90}O₂ samples activated at (d) 400°C, (e) 700°C and (f) 900°C

Structure of commercial TiO₂, as-synthesized, calcined Nb_{0.10}Ti_{0.90}O₂ and Nb_{0.10}Ti_{0.90}O₂ activated at different temperatures was investigated by XRD (Fig. 7-1). The commercial TiO₂ and the as-synthesized Nb_{0.10}Ti_{0.90}O₂ display typical peaks of anatase phase while the one activated at 900 °C has a clear structure of pure rutile. After the template removal by calcination at 500 °C and the activation at 400 °C, the material still preserve its anatase structure. However, as shown in Fig. 7-1e, strong peaks of rutile phase appear after the

activation at 700 °C while the peaks of anatase phase show a large decrease in intensity. It means that the structure of Nb_{0.10}Ti_{0.90}O₂ activated at 700 °C is a mixture of rutile and anatase. This is consistent with previous studies [26, 30, 64].

Table 7-1 Properties of commercial TiO₂ and Nb_{0.10}Ti_{0.90}O₂ materials

Material		Crystallite size (nm)		BET surface area (m ² g ⁻¹)	Conductivity (S cm ⁻¹)
		Anatase	Rutile		
Commercial TiO ₂		17.1		266	4.9x10 ⁻⁸
Nb _{0.10} Ti _{0.90} O ₂	As-synthesized	11.9		211	n/a
	Calcined at 500 °C	13.0		182	2.3 x 10 ⁻⁷
	Activated at 400 °C	12.1		142	1.9 x 10 ⁻⁶
	Activated at 700 °C	24.4	36.3	30	7.9 x 10 ⁻⁵
	Activated at 900 °C		59.7	20	0.001

Koninck et al. and Fluentes et al. found the appearance of TiNb₂O₇ in the structure of Nb_{0.10}Ti_{0.90}O₂ annealed at 1050 and 1000 °C [28, 64]. In our work, neither TiNb₂O₇ nor niobium oxides were observed in the XRD patterns of Nb_{0.10}Ti_{0.90}O₂ samples, implying that Nb was well-incorporated into the lattice of TiO₂. It was found that TiO₂ would form sub-stoichiometric titania Ti_nO_{2n-1} when reduced at high temperature. However, no Ti_nO_{2n-1}

compounds were found in the XRD spectra of $\text{Nb}_{0.10}\text{Ti}_{0.90}\text{O}_2$ samples reduced at 700 and 900 °C, indicating that the addition of Nb into TiO_2 inhibits the formation of $\text{Ti}_n\text{O}_{2n-1}$ [26]. Crystallite sizes of the materials were calculated from the XRD patterns using Scherrer equation [26, 64] based on (101) peak at $2\theta=25.3^\circ$ for anatase and (110) peak at $2\theta=27.5^\circ$ for rutile phases and presented in Table 7-1. The crystallite sizes of the as-synthesized, calcined $\text{Nb}_{0.10}\text{Ti}_{0.90}\text{O}_2$ and $\text{Nb}_{0.10}\text{Ti}_{0.90}\text{O}_2$ activated at 400 °C are similar, implying that the calcination at 500 °C and the activation at 400 °C have little effect on the grain size. However, the crystallite size of the material sharply increases after the activation at 700 °C (from 12.1 to 24.4 nm for anatase) and 900°C (from 39.3 to 59.7 nm for rutile). This phenomenon was also observed in other works [26, 64]. The increase of crystallite size is attributed to the thermally promoted grain growth [64, 166].

The electrical conductivity of commercial TiO_2 and $\text{Nb}_{0.10}\text{Ti}_{0.90}\text{O}_2$ materials was measured at room temperature and presented in Table 7-1. The measured conductivity of the commercial TiO_2 is $4.9 \times 10^{-8} \text{ S cm}^{-1}$, which is in high agreement with values (10^{-13} , $10^{-6} \text{ S cm}^{-1}$) in the literature [146-147]. The calcined $\text{Nb}_{0.10}\text{Ti}_{0.90}\text{O}_2$ has a conductivity of $2.3 \times 10^{-7} \text{ S cm}^{-1}$, which is nearly five-fold that of the commercial TiO_2 , indicating the donor effect of Nb. The reduction of calcined $\text{Nb}_{0.10}\text{Ti}_{0.90}\text{O}_2$ at 400, 700 and 900 °C greatly improved the electronic conductivity of the material, as indicated by their measured conductivity (1.9×10^{-6} , 7.9×10^{-5} and 0.001 S cm^{-1} , respectively).

Figure 7-2 Nitrogen adsorption/desorption isotherms of (a) commercial TiO_2 , (b) as-synthesized, (c) calcined $\text{Nb}_{0.10}\text{Ti}_{0.90}\text{O}_2$ and $\text{Nb}_{0.10}\text{Ti}_{0.90}\text{O}_2$ activated at (d) 400 °C, (e) 700 °C and (f) 900 °C

To examine the porosity of the materials, N₂ adsorption/desorption isotherms were measured at -196 °C and the results are shown in Fig. 7-2 and Table 7-1. The commercial TiO₂ shows a N₂ adsorption/desorption isotherm with a narrow hysteresis loop due to its poor porosity. Fig. 7-2b shows a typical type-IV isotherm with a large H2 hysteresis loop caused by mesopores with interconnecting channels in the structure of the as-synthesized Nb_{0.10}Ti_{0.90}O₂ [129, 167]. As shown in Fig. 7-2c and d, the material maintained its mesoporosity after the calcination at 500 °C and activation at 400 °C with unchanged isotherm shape although its BET surface area slightly decreased from 211 to 182 and 142 m² g⁻¹, respectively. After the activation at 700 °C, the isotherm of the solid shows a narrower H1 hysteresis loop with nearly vertical and parallel adsorption and desorption branches, which is attributed to mesopores without interconnecting channels [129]. The reduction at 700 °C caused a collapse of the interconnecting channels, resulting in a sharp decrease of BET area from 182 to 30 m² g⁻¹. The solid reduced at 900 °C displays a nitrogen adsorption/desorption isotherm with no typical characteristics of mesopores, indicating that the ordered mesoporous structure was destroyed. As a result, the BET area was reduced to 20 m² g⁻¹. Considering the values of electrical conductivity and porosity of the materials, the Nb-doped TiO₂ activated at 700 °C was chosen for further study due to the potential benefit of its high conductivity and mesoporous structure for the application as electrocatalyst support in ADEFC.

7.3.1.2 $Nb_xTi_{1-x}O_2$

Figure 7-3 XRD patterns of $Nb_xTi_{1-x}O_2$ activated at 700 °C with $x=0.02$ (a), 0.05 (b), 0.10 (c), 0.20 (d) and 0.30 (e)

As shown above, the addition of Nb into TiO_2 structure significantly enhanced the conductivity of TiO_2 . Therefore, we synthesized various Nb-doped TiO_2 with different Nb contents (2, 5, 10, 20 and 30 %) and investigated the effect of Nb-doping level to their properties. All the $Nb_xTi_{1-x}O_2$ materials were calcined at 500 °C in air flow and then

activated at 700°C in H₂ flow. XRD patterns of the Nb-doped TiO₂ solids are displayed in Fig. 7-3 with reference spectra of anatase and rutile TiO₂ (JCPDS 21-1272 and 65-0191, respectively). A mixture of rutile and anatase phases is observed for all the Nb_xTi_{1-x}O₂ materials. It can be found that the diffraction peaks of Nb_xTi_{1-x}O₂ are shifted to lower angles when Nb-doping level increases. This phenomenon indicates an increase in unit-cell parameters of the material due to the replacement of Ti⁴⁺ (r_{Ti4+}=60.5 pm) by larger ion Nb⁵⁺ (r_{Nb5+}=64 pm) [26, 168-171]. Table 7-2 shows the lattice constants of Nb-doped TiO₂ obtained by fitting XRD patterns of Nb_xTi_{1-x}O₂ with anatase and rutile structures using PowderCell 2.4 software developed by Kraus and Nolze [169, 172]. The values of lattice constants again confirm the fact that unit cells of titania expanded their volume after the addition of Nb. The highest expansion is observed for Nb_xTi_{1-x}O₂ with 30 % of Nb. Crystallite sizes of the materials were calculated using Scherrer equation and displayed in Table 7-2. The results show a decreasing trend in the crystallite size of both anatase and rutile phases when increasing Nb content from 2 to 30 %. It is believed that the presence of Nb in titania structure inhibits the growth of crystallites [64, 173].

The electronic conductivity of Nb_xTi_{1-x}O₂ was measured and shown in Table 7-2 and Fig. 7-4. The addition of Nb to TiO₂ lattice structure dramatically improved the conductivity of the material from 4.9x10⁻⁸ S cm⁻¹ of anatase TiO₂ to 8.9x10⁻⁷, 9.6x10⁻⁷, 7.9x10⁻⁵, 0.0012 and 0.0014 S cm⁻¹ of Nb-doped TiO₂ with Nb contents of 2, 5, 10, 20 and 30 %, respectively. TiO₂ has large band gaps (3.2 eV of anatase and 3.0 eV of rutile), which result in its low electrical conductivity [30, 146, 173]. Nb atom has five outer-shell electrons. When it substitutes Ti sites in TiO₂ lattice, only four electrons are used for bonding. The

extra electron is in donor state which is 0.02-0.03 eV below the conduction band minimum and therefore, is easy to be donated into the conduction band to increase the charge carrier concentration [30, 170, 174]. As a result, Nb doping enhances the electronic conductivity of the material:

Table 7-2 Properties of $\text{Nb}_x\text{Ti}_{1-x}\text{O}_2$ materials compared with commercial TiO_2

Material	Lattice constant (nm)		Crystallite size (nm)		BET surface area ($\text{m}^2 \text{g}^{-1}$)	Conductivity (S cm^{-1})
	Anatase	Rutile	Anatase	Rutile		
Commercial TiO_2	a=b=0.37853 c=0.95070		17.1		266	4.9×10^{-8}
$\text{Nb}_{0.02}\text{Ti}_{0.98}\text{O}_2$	a=b=0.37864 c=0.95190	a=b=0.45979 c=0.29611	33.0	45.7	22	8.9×10^{-7}
$\text{Nb}_{0.05}\text{Ti}_{0.95}\text{O}_2$	a=b=0.37909 c=0.95246	a=b=0.46033 c=0.29637	28.0	39.9	31	9.6×10^{-7}
$\text{Nb}_{0.10}\text{Ti}_{0.90}\text{O}_2$	a=b=0.38170 c=0.95263	a=b=0.46380 c=0.29804	24.4	36.3	30	7.9×10^{-5}
$\text{Nb}_{0.20}\text{Ti}_{0.80}\text{O}_2$	a=b=0.38261 c=0.95501	a=b=0.46504 c=0.29847	23.0	30.5	36	0.0012
$\text{Nb}_{0.30}\text{Ti}_{0.70}\text{O}_2$	a=b=0.38326 c=0.95774	a=b=0.46607 c=0.29937	21.7	25.6	46	0.0014

Figure 7-4 Electrical conductivity of $\text{Nb}_x\text{Ti}_{1-x}\text{O}_2$ with different Nb contents

However, it can be seen that the conductivity of Nb-doped TiO_2 with 30 % of Nb (0.0014 S cm^{-1}) is only a bit higher than that of the one with 20% of Nb (0.0012 S cm^{-1}). This phenomenon is consistent with the literature [168]. This fact can be explained by several possible ways. Firstly, when Nb is doped into TiO_2 lattice, the Fermi energy will move towards the conduction band. Consequently, the formation energy of Ti vacancy will decrease. At some points, this formation energy is so low that Ti vacancies will form spontaneously (Eq. 7.2) and weaken the donor effect (Eq. 7.1) [168, 175-176].

Moreover, the substitution of Nb for Ti can also create oxygen interstitials – another type of electron killer, which reduce the electronic conductivity of Nb-doped TiO₂. Besides, the incorporation of Nb into the titania structure causes a lattice deformation, which leads to a decrease in electron mobility [168, 174-176].

The porosity of the Nb_xTi_{1-x}O₂ materials was examined by N₂ adsorption/desorption at -196 °C and the results are displayed in Fig. 7-5 and Table 7-2. Adsorption/desorption isotherms of all the solids have the same shape as that of Nb_{0.10}Ti_{0.90}O₂ indicating that all of them possess mesoporous structures with no interconnecting channels. It can be observed that BET area of the Nb_xTi_{1-x}O₂ solids increases with the raise of Nb-doping level.

The lowest area of 22 m² g⁻¹ was found for Nb_{0.02}Ti_{0.98}O₂ while the maximum value of 36 m² g⁻¹ was seen with Nb_{0.30}Ti_{0.70}O₂. The same phenomenon was also observed in Koninck et al.'s study [64]. As stated previously, the Nb doping prevents the grain growth, and thus, increases the BET specific surface area of Nb_xTi_{1-x}O₂.

Figure 7-5 Nitrogen adsorption/desorption isotherms of $\text{Nb}_x\text{Ti}_{1-x}\text{O}_2$ activated at 700°C with $x=0.02$ (a), 0.05 (b), 0.10 (c), 0.20 (d) and 0.30 (e)

7.3.2 PdAg/Nb-doped TiO₂

Figure 7-6 XRD profiles of PdAg/C (a), PdAg/commercial TiO₂ (b), PdAg/Nb_xTi_{1-x}O₂ with x=0.02 (c), 0.05 (d), 0.10 (e), 0.20 (f) and 0.30 (g)

Fig. 7-6 shows XRD profiles of PdAg alloy supported on carbon black, commercial TiO₂ and various Nb_xTi_{1-x}O₂. PdAg/C displays typical (111), (200), (220) and (311) peaks of face-centered cubic (FCC) structure of PdAg alloy at 38.8, 44.6, 65.5 and 78.8°. In XRD patterns of PdAg/commercial TiO₂ and PdAg/ Nb_xTi_{1-x}O₂, the peaks of PdAg alloy are overlapped by strong diffraction peaks of the supports.

Figure 7-7 (a) CVs and (b) forward scans of CV of PdAg/C, PdAg/commercial TiO_2 , PdAg/ $\text{Nb}_x\text{Ti}_{1-x}\text{O}_2$ with $x=0.02, 0.05, 0.10, 0.20$ and 0.30 in $1\text{M KOH} + 1\text{M C}_2\text{H}_5\text{OH}$ solution, scan rate of 50 mV s^{-1}

The electrocatalytic activity for EOR of the catalysts was examined in an aqueous solution of 1M C₂H₅OH and 1M KOH by CV technique and the results are shown in Fig. 7-7. The forward scan of CV is associated with the oxidation of ethanol while the reverse scan is attributed to the removal of incompletely oxidized carbonaceous species [105, 177-178]. It can be seen that peak current densities of the forward scans of all the PdAg catalysts have higher values than those of the backward scans. This fact indicates the high activity of PdAg alloy towards EOR in alkaline condition. PdAg supported on commercial TiO₂ and Nb_xTi_{1-x}O₂ show a 75 mV more negative onset potential for ethanol oxidation compared to that of PdAg/C. This proves the enhancement effect of TiO₂ and Nb_xTi_{1-x}O₂ to the catalytic property of the catalyst. On the other hand, PdAg/Nb_xTi_{1-x}O₂ catalysts have higher peak current density than that of PdAg/TiO₂ with the best behavior observed for PdAg/Nb_{0.20}Ti_{0.80}O₂ and PdAg/Nb_{0.30}Ti_{0.70}O₂.

As proposed by Hammer and Nørskov, the electronic structure of small metal particles supported on substrates is altered by the interaction between the substrates and the nanoparticles due to lattice constant mismatch, which results in a change in their adsorption and catalytic activity [50, 66, 133]. From the XRD data of (200) peak, a lattice constant value of 0.403 nm was found for the PdAg alloy supported on carbon black. This value is smaller than those of Nb_xTi_{1-x}O₂ presented in Table 7-2. Therefore, an expansion of the unit-cell of the alloy is created when the alloy nanoparticle is deposited on the Nb-doped TiO₂ support. As a result, d-band center of the alloy moves up and the adsorption of OH⁻ on the catalyst surface is improved [50, 53].

According to Liang et al. [33], the adsorbed OH^- plays an important role in the removal of CH_3CO to release active sites for further ethanol electrooxidation process. Hence, the improvement of OH^- adsorption leads to a faster ethanol oxidation. Furthermore, the good conductivity and possible high stability of $\text{Nb}_x\text{Ti}_{1-x}\text{O}_2$ might significantly contribute to the excellent EOR activity of the catalysts.

The activity and stability of PdAg/C, PdAg/commercial TiO_2 and PdAg/ $\text{Nb}_x\text{Ti}_{1-x}\text{O}_2$ for EOR were also examined by CA tests. Fig. 7-8 shows CA curves of the catalysts in 1M KOH + 1M $\text{C}_2\text{H}_5\text{OH}$ solution for 3600 s at -0.25 V. The current densities are gradually decayed with time due to the accumulation of poisoning intermediates of the EOR process. After 3600 s, the current densities of PdAg/ $\text{Nb}_x\text{Ti}_{1-x}\text{O}_2$ remain higher than those of PdAg/ TiO_2 and PdAg/C with the highest values observed for PdAg/ $\text{Nb}_{0.20}\text{Ti}_{0.80}\text{O}_2$ and PdAg/ $\text{Nb}_{0.30}\text{Ti}_{0.70}\text{O}_2$, indicating that the addition of Nb to TiO_2 facilitates the removal of the adsorbed ethoxi intermediates and helps the catalysts be more resistant to poisoning.

Figure 7-8 CA results of PdAg/C, PdAg/commercial TiO₂, PdAg/Nb_xTi_{1-x}O₂ with x=0.02, 0.05, 0.10, 0.20 and 0.30 at –0.25 V (vs Hg/HgO) in 1M C₂H₅OH + 1M KOH solution

CO-like species are known as the main poisoning intermediates during alcohol electrooxidation. Therefore, for better understanding the poisoning tolerance of the PdAg supported on Nb-doped TiO₂ catalysts in alkaline media, CO stripping test was performed in 1M KOH solution. Fig.7-9 presents CO stripping curves of the catalysts. All the CO stripping profiles of the PdAg catalysts display two broad peaks due to two different types of Pd sites, which is consistent with what was found in our previous work [112]. It can be seen that onset potential values of the CO oxidation on PdAg/Nb_xTi_{1-x}O₂ are more negative than those of PdAg/C and PdAg/TiO₂ with the most negative ones observed for PdAg/Nb_{0.20}Ti_{0.80}O₂ and PdAg/Nb_{0.30}Ti_{0.70}O₂. These results again confirm the good poisoning-tolerance of the PdAg supported on Nb_xTi_{1-x}O₂.

Figure 7-9 CO stripping curves of PdAg/C, PdAg/commercial TiO₂, PdAg/Nb_xTi_{1-x}O₂ with x=0.02, 0.05, 0.10, 0.20 and 0.30 in 1M KOH solution, scan rate of 50 mV s⁻¹

Fig. 7-10 shows blank CVs of the catalysts in 1M KOH solution. A broad peak at ca. -0.300 V in forward scans is assigned to the adsorption of OH⁻ on the catalysts while the peak at ca. -0.230 V in reverse scans belongs to the reduction of palladium oxide. The hydroxyl adsorption peak potentials are -0.270, -0.273, -0.279, -0.298, -0.310, -0.326 and -0.332 V for PdAg supported on carbon black, commercial TiO₂, Nb-doped TiO₂ with 2, 5, 10, 20 and 30 % of Nb, respectively. It can be seen that the more Nb is added, the more negative the peak potential of OH⁻ adsorption is. The easier adsorption of OH⁻ facilitates the oxidation of CO-like species and thus, releases fresh active sites for the adsorption of

ethanol molecules for further ethanol oxidation activities.

Figure 7-10 Blank CVs of PdAg/C, PdAg/commercial TiO₂, PdAg/Nb_xTi_{1-x}O₂ with x=0.02, 0.05, 0.10, 0.20 and 0.30 in 1M KOH solution, scan rate of 50 mV s⁻¹

The stability of the catalyst is very important for the practical applications of fuel cells. Therefore, durability tests were carried out by two methods in our study. In the first method, the catalysts were kept at 0.3 and 0.7 V for 1 h and CV was done before and after each test to verify the Pd ECSA change of the catalysts. Fig. 7-11 shows corrosion current densities of the PdAg catalysts at 0.3 (Fig. 7-11a) and 0.7 V (Fig. 7-11b). At both of the potentials, the lowest corrosion currents are found for PdAg supported on Nb-doped TiO₂ with Nb content of 20 and 30 % while the highest ones are observed for PdAg supported on

carbon black and commercial TiO_2 . The corrosion current values of the catalysts at 0.7 V are approximately 20-time higher than those at 0.3 V, indicating the considerable effect of the potential to the corrosion of catalysts. Pd ECSAs of the catalysts after the tests normalized by the initial ones are plotted against the tested potentials in Fig. 7-12a and shown in Table 7-3. It is found that PdAg/C and PdAg/commercial TiO_2 lost 25 and 19 % of their ECSA, respectively, while PdAg/ $\text{Nb}_x\text{Ti}_{1-x}\text{O}_2$ only lost 13, 10, 5, 2.7 and 2 % of their ECSA, corresponding to Nb percentages of 2, 5, 10, 20 and 30 %, respectively, after the durability test at 0.7 V. The results confirm the weak stability of carbon black and strong corrosion-resistance of Nb-doped TiO_2 materials in the alkaline condition.

Table 7-3 Normalized Pd ECSAs of the catalysts after fixed -potential and multi-scan tests

Catalyst	PdAg/C	PdAg/ commercial TiO_2	PdAg/ $\text{Nb}_{0.02}\text{Ti}_{0.98}\text{O}_2$	PdAg/ $\text{Nb}_{0.05}\text{Ti}_{0.95}\text{O}_2$	PdAg/ $\text{Nb}_{0.10}\text{Ti}_{0.90}\text{O}_2$	PdAg/ $\text{Nb}_{0.20}\text{Ti}_{0.80}\text{O}_2$	PdAg/ $\text{Nb}_{0.30}\text{Ti}_{0.70}\text{O}_2$
After test at 0.3V	0.92	0.95	0.97	0.975	0.98	0.99	0.99
After test at 0.7V	0.75	0.81	0.87	0.90	0.95	0.973	0.98
After 1000 scans	0.81	0.85	0.88	0.89	0.93	0.95	0.96
After 2000 scans	0.71	0.76	0.80	0.82	0.86	0.91	0.91

Figure 7-11 Corrosion curves of PdAg/C, PdAg/commercial TiO_2 , PdAg/ $\text{Nb}_x\text{Ti}_{1-x}\text{O}_2$ with $x=0.02, 0.05, 0.10, 0.20$ and 0.30 in 1M KOH solution at (a) 0.3 V and (b) 0.7 V, 1h

Figure 7-12 Normalized Pd ECSAs of PdAg/C, PdAg/commercial TiO₂, PdAg/Nb_xTi_{1-x}O₂ with x=0.02, 0.05, 0.10, 0.20 and 0.30 after (a) fixed-potential and (b) multi-scan tests

In the second way for investigating the durability of the catalysts, several CV scans were performed and Pd ECSA of each catalyst was recorded after the test to evaluate their oxidation resistance. As presented in Fig. 7-12b and Table 7-3, PdAg/C lost 19 % and 29 % of its Pd ECSA after 1000 and 2000 scans, respectively. Meanwhile, losses of 15 and 24 % of Pd ECSA were found for PdAg/commercial TiO₂. The PdAg supported on Nb_xTi_{1-x}O₂ shows less corrosion with a decreasing trend in Pd ECSA loss when increasing Nb content in Nb-doped TiO₂. PdAg/ Nb_{0.02}Ti_{0.98}O₂ lost 12 and 20 % of Pd ECSA after 1000 and 2000 scans, respectively, while ECSAs of PdAg/Nb_{0.20}Ti_{0.80}O₂ and PdAg/Nb_{0.30}Ti_{0.70}O₂ decreased 5 and 4 % after 1000 scans, respectively, and 9 % after 2000 scans. As stated above, the corrosion of the supports causes the detachment of the alloy particles from the supports as well as their agglomeration and the decrease of the charge transfer between the catalyst particles and the conductive support, which results in the ECSA and activity loss. The smaller Pd ECSA loss of PdAg/Nb_xTi_{1-x}O₂ compared with those of PdAg/C and PdAg/TiO₂ during the corrosion tests proves that Nb-doped TiO₂ supports are electrochemically more stable than carbon black and commercial TiO₂. Fig.7-13 exhibits TEM images of PdAg nanoparticles supported on carbon black, commercial TiO₂ and Nb_{0.30}Ti_{0.70}O₂ before and after 2000 scans. Fig. 7-13a, b, c and d reveal the fact that PdAg particles on carbon black and commercial TiO₂ highly aggregate to form larger particles after the durability test, which result in a large reduction in their ECSA. In contrast, a slight agglomeration of PdAg particles is seen for PdAg/Nb_{0.30}Ti_{0.70}O₂, explaining why the catalyst still maintains most of its ECSA after the test.

Figure 7-13 TEM images of PdAg/C: (a) before and (b) after 2000 scans; of PdAg/commercial TiO₂: (c) before and (d) after 2000 scans; and of PdAg/Nb_{0.30}Ti_{0.70}O₂: (e) before and (f) after 2000 scans

7.3.3 PdAg supported on different materials

As shown in section 7.3.2, PdAg supported on $\text{Nb}_{0.30}\text{Ti}_{0.70}\text{O}_2$ has excellent activity and stability for ethanol electrooxidation in alkaline solutions. In Chapters 5 and 6, mesoporous TiO_2 and sub-stoichiometric $\text{Ti}_n\text{O}_{2n-1}$ showed impressive effects on the EOR activity and durability of Pd. To compare these two materials with $\text{Nb}_{0.30}\text{Ti}_{0.70}\text{O}_2$, PdAg/mesoporous TiO_2 and PdAg/ $\text{Ti}_n\text{O}_{2n-1}$ were synthesized using the same method as that of PdAg/ $\text{Nb}_{0.30}\text{Ti}_{0.70}\text{O}_2$. These two catalysts were tested their activity for EOR in 1M KOH + 1M $\text{C}_2\text{H}_5\text{OH}$ solution by CV technique and compared with PdAg/ $\text{Nb}_{0.30}\text{Ti}_{0.70}\text{O}_2$.

Figure 7-14 Forward scans of CVs of PdAg/mesoporous TiO_2 , PdAg/ $\text{Ti}_n\text{O}_{2n-1}$ and PdAg/ $\text{Nb}_{0.30}\text{Ti}_{0.70}\text{O}_2$ in 1M KOH + 1M $\text{C}_2\text{H}_5\text{OH}$ solution, scan rate of 50 mV s^{-1}

Fig. 7-14 shows forward scans of CVs of the three catalysts in 1M KOH + 1M $\text{C}_2\text{H}_5\text{OH}$

solution. It can be seen that $\text{PdAg/Nb}_{0.30}\text{Ti}_{0.70}\text{O}_2$ possesses the highest peak current density (6.1 mA cm^{-2}) for EOR compared with those of $\text{PdAg/mesoporous TiO}_2$ and $\text{PdAg/Ti}_n\text{O}_{2n-1}$ (4.5 and 4.1 mA cm^{-2} , respectively). This fact indicates that $\text{PdAg/Nb}_{0.30}\text{Ti}_{0.70}\text{O}_2$ has better EOR activity than $\text{PdAg/mesoporous TiO}_2$ and $\text{PdAg/Ti}_n\text{O}_{2n-1}$. It is possible that the combination of good electronic conductivity, hydroxyl adsorption improvement due to lattice mismatch and ordered mesoporous structure of the support helps $\text{PdAg/Nb}_{0.30}\text{Ti}_{0.70}\text{O}_2$ has higher EOR activity than the other two catalysts.

Figure 7-15 Corrosion curves of $\text{PdAg/mesoporous TiO}_2$, $\text{PdAg/Ti}_n\text{O}_{2n-1}$ and $\text{PdAg/Nb}_{0.30}\text{Ti}_{0.70}\text{O}_2$ in 1M KOH solution at 0.7 V, 1h

Figure 7-16 Normalized Pd ECSAs of PdAg/mesoporous TiO_2 , PdAg/ $\text{Ti}_n\text{O}_{2n-1}$ and PdAg/ $\text{Nb}_{0.30}\text{Ti}_{0.70}\text{O}_2$ after (a) fixed-potential test at 0.7 V and (b) multi-scan test

As shown in Fig. 7-15, the corrosion current density of PdAg/Ti_nO_{2n-1} is the highest while the lowest one is observed for PdAg/Nb_{0.30}Ti_{0.70}O₂ in the durability test at 0.7 V in the blank solution. As a result, Pd ECSA losses of 14 and 12 % are seen for PdAg supported on Ti_nO_{2n-1} and mesoporous TiO₂, respectively, whereas a Pd ECSA loss of 2 % is obtained for PdAg/Nb_{0.30}Ti_{0.70}O₂ (Fig. 16a). Similarly, Fig. 16b shows that the alloyed catalyst supported on Nb_{0.30}Ti_{0.70}O₂ only lost 9 % of its Pd ECSA after 2000 cycles while PdAg/Ti_nO_{2n-1} and PdAg/mesoporous TiO₂ lost 23 and 21 % of their Pd ECSAs, respectively. The results of both durability tests confirm the high corrosion-resistance property of Nb_{0.30}Ti_{0.70}O₂, which is possibly derived from the Nb-doping of the material.

7.4 Summary

In this chapter, several mesoporous Nb-doped TiO₂ materials were successfully synthesized and tested as catalyst supports for PdAg nanoparticles. 700°C was chosen as the suitable activation temperature for Nb-doped titania. The structure of Nb-doped TiO₂ activated at 700°C consists of a mixture of rutile and anatase phases. The addition of Nb into TiO₂ structure significantly improves the electronic conductivity of TiO₂. It was found that an increase of Nb content in Nb-doped TiO₂ results in an increase in electrical conductivity of the material. PdAg supported on various Nb_xTi_{1-x}O₂ with x=0.02, 0.05, 0.10, 0.20 and 0.30 were synthesized and compared their activity and durability for ethanol electrooxidation in alkaline solutions with those of PdAg/C and PdAg/commercial TiO₂. The PdAg/Nb_xTi_{1-x}O₂ displayed better performance for EOR than PdAg/C and PdAg/TiO₂. PdAg supported on Nb_{0.20}Ti_{0.80}O₂ and Nb_{0.30}Ti_{0.70}O₂ showed the highest catalytic activity towards EOR as well as excellent durability in basic solutions. In addition, a comparison of

PdAg supported on mesoporous TiO_2 , $\text{Ti}_n\text{O}_{2n-1}$ and $\text{Nb}_{0.30}\text{Ti}_{0.70}\text{O}_2$ showed that PdAg/ $\text{Nb}_{0.30}\text{Ti}_{0.70}\text{O}_2$ has better electrocatalytic activity for EOR and higher durability in alkaline condition than PdAg/ $\text{Ti}_n\text{O}_{2n-1}$ and PdAg/mesoporous TiO_2 . The results indicated that $\text{Nb}_x\text{Ti}_{1-x}\text{O}_2$ materials can be used as an effective replacement for carbon black in the role of catalyst support for ADEFC.

Chapter 8 CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

The research presented in this thesis focused on the development of effective non-platinum electrocatalysts for EOR and non-carbon catalyst support materials as alternatives to carbon-based catalyst supports for alkaline direct ethanol fuel cell (ADEFC). The non-platinum catalysts were designed by modifying Pd with Ag or Tb while titanium oxide – based materials were synthesized and examined as potential replacements for carbon black in the role of catalyst support. The following achievements were obtained in this work:

- 1) Alloyed PdAg nanoparticles deposited on carbon black were successfully prepared and showed excellent ethanol oxidation activity in tested solutions compared with Pd/C and Pt/C. Among several investigated PdAg/C electrocatalysts, 10%Pd-10%Ag/C displayed the highest catalytic activity for EOR in basic solutions and the best poisoning tolerance.
- 2) The addition of Tb to Pd/C gave a promotion effect on the EOR activity of Pd in alkaline media. Tb compounds facilitated the adsorption of hydroxyl onto the catalysts, resulting in the enhanced activity for EOR. The highest performance was observed for the PdTb/C catalyst with 2% of Tb. It was found that 10%Pd-2%Tb/C is somewhat less active for EOR than 10%Pd-10%Ag/C.
- 3) Mesoporous titania was prepared by a hydrothermal method and used as a support for Pd in comparison with carbon black and commercial TiO₂. The

peak current density of EOR on Pd/mesoporous TiO_2 is 2.6 and 4.4 times those of Pd/commercial TiO_2 and Pd/C. Durability tests with fixed-potentials and multi scans revealed that Pd/C suffered the worst corrosion with the highest Pd ECSA loss, whereas the lowest loss of Pd ECSA was observed for Pd/mesoporous TiO_2 .

- 4) Besides mesoporous TiO_2 , sub-stoichiometric $\text{Ti}_n\text{O}_{2n-1}$ was synthesized from commercial TiO_2 and tested its ability for acting as a support for Pd towards EOR in alkaline condition. The material showed its effective promotion for EOR and good durability through a 50 mV left shift of the onset potential, the highest current density for EOR and the lowest Pd ECSA loss of Pd/ $\text{Ti}_n\text{O}_{2n-1}$ compared with those of Pd/commercial TiO_2 and Pd/C.
- 5) Nb-doping was used to improve the electronic conductivity of titania. Nb-doped TiO_2 was successfully prepared with different contents of Nb. The materials showed clear N_2 adsorption/desorption isotherms of mesoporous structures and significantly enhanced electrical conductivities. PdAg/Nb-doped TiO_2 presented improved EOR activity compared with PdAg/C and PdAg/commercial TiO_2 . The best EOR behavior was seen for the PdAg/Nb-doped TiO_2 catalysts with 20 and 30 % of Nb. Excellent durability was observed for Nb-doped TiO_2 supported PdAg catalysts. Besides, it was found that PdAg/ $\text{Nb}_{0.30}\text{Ti}_{0.70}\text{O}_2$ has better electrocatalytic activity for EOR and higher durability in alkaline condition than PdAg/ $\text{Ti}_n\text{O}_{2n-1}$ and PdAg/mesoporous TiO_2 . These results indicate that Nb-doped TiO_2 materials

can be used as alternative catalyst supports for ADEFC.

8.2 Recommendations

This research was successful in designing effective Pd-based nanocatalysts for the ethanol electrooxidation in alkaline media and durable titania-based catalyst supports for ADEFC. However, more work should be performed to develop the current project.

For a further development of the study, it is recommended that the following should be investigated:

- To better understand the mechanism of the EOR, in situ techniques such as in situ FTIR spectroscopy or differential electrochemical mass spectrometry (DEMS) should be employed to detect intermediates formed during the oxidation process of ethanol on different catalysts in alkaline solutions.
- X-ray photoelectron spectroscopy (XPS) should be used to explore the effect of additives and supports to the electronic structure of the main catalyst component, which results in the enhancement of catalytic activity.
- It has been found that morphology of catalysts has a strong effect on their catalytic property. Therefore, different morphologies of the catalysts, i.e, core-shell, nanowire, nanorod, should be investigated for the ethanol electrooxidation.
- In addition to Ag, the combination of Pd with other metals, such as Au, also shifts up the d-band center of Pd [50]. Hence, alloyed or core-shell structures of PdAu should be examined for their activity for EOR in alkaline media.

- Apart from titania-based materials, other non-carbon based compounds, such as tungsten carbide, tungsten oxide, tin oxide, titanium nitride, have been found to be stable in corrosive environments [25, 147, 179]. These materials should be investigated as catalyst supports for ADEFC.
- Besides using half-cell tests to examine the catalytic activity of the catalysts, the investigation of the catalysts' behavior in single cells should be done for the practical application of the catalysts.

REFERENCES

- [1] T. Zhao, K.-D. Kreuer, T.V. Nguyen, *Advances in Fuel Cells*, Elsevier Inc., 2007.
- [2] F. Barbir, *PEM Fuel Cells: Theory and Practice*, Elsevier Inc., 2005.
- [3] W. Jung-Ho, *Journal of Power Sources* 161 (2006) 1-10.
- [4] S.S.V.A. A. S. Aricò, *Fuel Cells* 1 (2001) 133-161.
- [5] S.Q. Song, Z.X. Liang, W.J. Zhou, G.Q. Sun, Q. Xin, V. Stergiopoulos, P. Tsiakaras, *Journal of Power Sources* 145 (2005) 495-501.
- [6] E. Antolini, *J. Power Sources* 170 (2007) 1-12.
- [7] F. Hu, C. Chen, Z. Wang, G. Wei, P.K. Shen, *Electrochimica Acta* 52 (2006) 1087-1091.
- [8] C. Lamy, S. Rousseau, E.M. Belgsir, C. Coutanceau, J.M. Leger, *Electrochimica Acta* 49 (2004) 3901-3908.
- [9] U.B. Demirci, *Environment International* 35 (2009) 626-631.
- [10] H. Li, G. Sun, L. Cao, L. Jiang, Q. Xin, *Electrochimica Acta* 52 (2007) 6622-6629.
- [11] F. Delime, J.M. Leger, C. Lamy, *Journal of Applied Electrochemistry* 28 (1997) 27-35.
- [12] J. Ribeiro, D.M. Dos Anjos, J.M. Leger, F. Hahn, P. Olivi, A.R. De Andrade, G. Tremiliosi-Filho, K.B. Kokoh, *Journal of Applied Electrochemistry* 38 (2008) 653-662.
- [13] N. Wagner, M. Schulze, E. Gulzow, *Journal of Power Sources* 127 (2004) 264-272.
- [14] C. Xu, L. Cheng, P. Shen, Y. Liu, *Electrochem. Commun.* 9 (2007) 997-1001.
- [15] H. Liu, W. Li, A. Manthiram, *Applied Catalysis B: Environmental* 90 (2009) 184-194.
- [16] A. Serov, C. Kwak, *Applied Catalysis B: Environmental* 90 (2009) 313-320.
- [17] E. Antolini, *Applied Catalysis B: Environmental* 88 (2009) 1-24.
- [18] T. Ioroi, Z. Siroma, N. Fujiwara, S.I. Yamazaki, K. Yasuda, *Electrochem. Commun.* 7 (2005) 183-188.
- [19] J. Wang, G. Yin, Y. Shao, S. Zhang, Z. Wang, Y. Gao, *J. Power Sources* 171 (2007) 331-

339.

- [20] X. Wang, W. Li, Z. Chen, M. Waje, Y. Yan, J. Power Sources 158 (2006) 154-159.
- [21] P.K. Shen, C. Xu, Electrochemistry Communications 8 (2006) 184-188.
- [22] C. Xu, P.K. Shen, Y. Liu, Journal of Power Sources 164 (2007) 527-531.
- [23] H.T. Zheng, Y. Li, S. Chen, P.K. Shen, Journal of Power Sources 163 (2006) 371-375.
- [24] J. Ye, J. Liu, C. Xu, S.P. Jiang, Y. Tong, Electrochemistry Communications 9 (2007) 2760-2763.
- [25] E. Antolini, E.R. Gonzalez, Solid State Ionics 180 (2009) 746-763.
- [26] H. Chhina, S. Campbell, O. Kesler, J. New Mater. Electrochem. Syst. 12 (2009) 177-185.
- [27] T.B. Do, M. Cai, M.S. Ruthkosky, T.E. Moylan, Electrochim. Acta 55 (2010) 8013-8017.
- [28] R.E. Fuentes, B.L. Garcia, J.W. Weidner, J. Electrochem. Soc. 158 (2011) B461-B466.
- [29] S.Y. Huang, P. Ganesan, S. Park, B.N. Popov, J. Am. Chem. Soc. 131 (2009) 13898-13899.
- [30] S.Y. Huang, P. Ganesan, B.N. Popov, Applied Catalysis B: Environmental 96 (2010) 224-231.
- [31] T. Ioroi, H. Senoh, S.I. Yamazaki, Z. Siroma, N. Fujiwara, K. Yasuda, J. Electrochem. Soc. 155 (2008) B321-B326.
- [32] S. Minter, Acoholic Fuels, Taylor & Francis Group, 2006.
- [33] Z.X. Liang, T.S. Zhao, J.B. Xu, L.D. Zhu, Electrochim. Acta 54 (2009) 2203-2208.
- [34] Direct Alcohol Fuel Cell Group - Dalian Institute of Chemical Physics
, <http://dafc.dicp.ac.cn/fields.htm>, 2007.
- [35] S. Song, P. Tsiakaras, Applied Catalysis B: Environmental 63 (2006) 187-193.
- [36] C. Lamy, A. Lima, V. LeRhun, F. Delime, C. Coutanceau, J.M. Leger, Journal of Power Sources 105 (2002) 283-296.
- [37] C. Lamy, E.M. Belgsir, J.M. Leger, Journal of Applied Electrochemistry 31 (2001) 799-

809.

- [38] A.V. Tripkovic, K.D. Popovic, J.D. Lovic, *Electrochimica Acta* 46 (2001) 3163-3173.
- [39] C. Xu, Z. Tian, P. Shen, S.P. Jiang, *Electrochimica Acta* 53 (2008) 2610-2618.
- [40] D. Chu, J. Wang, S. Wang, L. Zha, J. He, Y. Hou, Y. Yan, H. Lin, Z. Tian, *Catalysis Communications* 10 (2009) 955-958.
- [41] Q. He, W. Chen, S. Mukerjee, S. Chen, F. Laufek, *Journal of Power Sources* 187 (2009) 298-304.
- [42] J. Bagchi, S.K. Bhattacharya, *Transition Metal Chemistry* 32 (2007) 47-55.
- [43] J. Bagchi, S.K. Bhattacharya, *Transition Metal Chemistry* 33 (2008) 113-120.
- [44] F. Vigier, S. Rousseau, C. Coutanceau, J.M. Leger, C. Lamy, *Topics in Catalysis* 40 (2006) 111-121.
- [45] F. Delime, J.M. Léger, C. Lamy, *Journal of Applied Electrochemistry* 29 (1999) 1249-1254.
- [46] J.M. Leger, S. Rousseau, C. Coutanceau, F. Hahn, C. Lamy, *Electrochimica Acta* 50 (2005) 5118-5125.
- [47] G. Li, P.G. Pickup, *Electrochimica Acta* 52 (2006) 1033-1037.
- [48] F. Vigier, C. Coutanceau, F. Hahn, E.M. Belgsir, C. Lamy, *Journal of Electroanalytical Chemistry* 563 (2004) 81-89.
- [49] U.B. Demirci, *J. Power Sources* 173 (2007) 11-18.
- [50] B. Hammer, J.K. Nørskov, *Advances in Catalysis* 45 (2000) 71-129.
- [51] J. Zhang, M.B. Vukmirovic, Y. Xu, M. Mavrikakis, R.R. Adzic, *Angewandte Chemie - International Edition* 44 (2005) 2132-2135.
- [52] J. Greeley, J.K. Nørskov, *Surf. Sci.* 592 (2005) 104-111.
- [53] J. Greeley, J.K. Nørskov, M. Mavrikakis, *Electronic structure and catalysis on metal surfaces*, *Annu. Rev. Phys. Chem.*, 2002, pp. 319-348.
- [54] V. Stamenkovic, B.S. Mun, K.J.J. Mayrhofer, P.N. Ross, N.M. Markovic, J. Rossmeisl, J. Greeley, J.K. Nørskov, *Angewandte Chemie - International Edition* 45 (2006) 2897-2901.

- [55] B. Hammer, J.K. Nørskov, *Surf. Sci.* 343 (1995) 211-220.
- [56] F.H.B. Lima, J. Zhang, M.H. Shao, K. Sasaki, M.B. Vukmirovic, E.A. Ticianelli, R.R. Adzic, *Journal of Physical Chemistry C* 111 (2007) 404-410.
- [57] A. Ruban, B. Hammer, P. Stoltze, H.L. Skriver, J.K. Nørskov, *J. Mol. Catal. A: Chem.* 115 (1997) 421-429.
- [58] T. Bligaard, J.K. Nørskov, *Electrochimica Acta* 52 (2007) 5512-5516.
- [59] A.U. Nilekar, Y. Xu, J. Zhang, M.B. Vukmirovic, K. Sasaki, R.R. Adzic, M. Mavrikakis, *Top. Catal.* 46 (2007) 276-284.
- [60] M.H. Shao, T. Huang, P. Liu, J. Zhang, K. Sasaki, M.B. Vukmirovic, R.R. Adzic, *Langmuir* 22 (2006) 10409-10415.
- [61] E. Antolini, E.R. Gonzalez, *Journal of Power Sources* 195 (2010) 3431-3450.
- [62] G. Chen, S.R. Bare, T.E. Mallouk, *J. Electrochem. Soc.* 149 (2002) A1092-A1099.
- [63] H. Chhina, S. Campbell, O. Kesler, *J. Electrochem. Soc.* 156 (2009) B1232-B1237.
- [64] M.D. Koninck, P. Manseau, B. Marsan, *J. Electroanal. Chem.* 611 (2007) 67-79.
- [65] X. Chen, S.S. Mao, *Chem. Rev.* 107 (2007) 2891-2959.
- [66] N.R. Elezovic, B.M. Babic, L. Gajic-Krstajic, V. Radmilovic, N.V. Krstajic, L.J. Vracar, *J. Power Sources* 195 (2010) 3961-3968.
- [67] S.C. Padmanabhan, S.C. Pillai, J. Colreavy, S. Balakrishnan, D.E. McCormack, T.S. Perova, S.J. Hinder, J.M. Kelly, *Chem. Mater.* 19 (2007) 4474-4481.
- [68] S. Yin, R. Li, Q. He, T. Sato, *Mater. Chem. Phys.* 75 (2002) 76-80.
- [69] S.L. Gojkovic, B.M. Babic, V.R. Radmilovic, N.V. Krstajic, *J. Electroanal. Chem.* 639 (2010) 161-166.
- [70] S.Y. Huang, P. Ganesan, B.N. Popov, *Applied Catalysis B: Environmental* 102 (2011) 71-77.
- [71] N. Wagner, M. Schulze, E. Gu?lzow, *Journal of Power Sources* 127 (2004) 264-272.
- [72] A. Serov, C. Kwak, *Applied Catalysis B: Environmental* In Press, Corrected Proof (2009).

- [73] F.P. Hu, P.K. Shen, *Journal of Power Sources* 173 (2007) 877-881.
- [74] L.D. Zhu, T.S. Zhao, J.B. Xu, Z.X. Liang, *Journal of Power Sources* 187 (2009) 80-84.
- [75] R.N. Singh, A. Singh, Anindita, *Carbon* 47 (2009) 271-278.
- [76] W.F. Smith, *Principles of Materials Science and Engineering*, 3rd ed., McGraw-Hill, Inc., New York, 1996.
- [77] E.E. Switzer, T.S. Olson, A.K. Datye, P. Atanassov, M.R. Hibbs, C.J. Cornelius, *Electrochimica Acta* 54 (2009) 989-995.
- [78] A. Pozio, M. De Francesco, A. Cemmi, F. Cardellini, L. Giorgi, *Journal of Power Sources* 105 (2002) 13-19.
- [79] R. Pattabiraman, *Applied Catalysis A: General* 153 (1997) 9-20.
- [80] M. Lukaszewski, M. Grden, A. Czerwinski, *Journal of Solid State Electrochemistry* 9 (2005) 1-9.
- [81] W.J. Zhou, W.Z. Li, S.Q. Song, Z.H. Zhou, L.H. Jiang, G.Q. Sun, Q. Xin, K. Poulitanitis, S. Kontou, P. Tsiakaras, *Journal of Power Sources* 131 (2004) 217-223.
- [82] T. Lopes, E. Antolini, F. Colmati, E.R. Gonzalez, *Journal of Power Sources* 164 (2007) 111-114.
- [83] Z. Liu, X.Y. Ling, X. Su, J.Y. Lee, *Journal of Physical Chemistry B* 108 (2004) 8234-8240.
- [84] E. Antolini, F. Colmati, E.R. Gonzalez, *Electrochemistry Communications* 9 (2007) 398-404.
- [85] G. Cao, *Nanostructures & Nanomaterials: Synthesis, Properties & Applications*, Imperial College Press, London, 2004.
- [86] A. Muramatsu, in: Y. Waseda, A. Muramatsu (Eds.), *Morphology Control of Materials and Nanoparticles*, Springer, Berlin, 2004, p. 30.
- [87] H. Abe, F. Matsumoto, L.R. Alden, S.C. Warren, H.D. Abruna, F.J. DiSalvo, *Journal of the American Chemical Society* 130 (2008) 5452-5458.
- [88] B.B. Blizanac, P.N. Ross, N.M. Markovic, *Journal of Physical Chemistry B* 110 (2006) 4735-4741.

- [89] S.L. Horswell, A.L.N. Pinheiro, E.R. Savinova, M. Danckwerts, B. Pettinger, M.-S. Zei, G. Ertl, *Langmuir* 20 (2004) 10970-10981.
- [90] F.H.B. Lima, J.F.R. de Castro, E.A. Ticianelli, *Journal of Power Sources* 161 (2006) 806-812.
- [91] H. Qinggang, C. Wei, M. Sanjeev, C. Shaowei, F. Laufek, *Journal of Power Sources* 187 (2009) 298-304.
- [92] Y. Chen, L. Zhuang, J. Lu, *Chinese Journal of Catalysis* 28 (2007) 870-874.
- [93] J. Prabhuram, R. Manoharan, H.N. Vasan, *Journal of Applied Electrochemistry* 28 (1998) 935-941.
- [94] B.B. Blizanac, P.N. Ross, N.M. Markovic, *Electrochimica Acta* 52 (2007) 2264-2271.
- [95] I. Boskovic, S.V. Mentus, M. Pjescic, *Electrochimica Acta* 51 (2006) 2793-2799.
- [96] M. Gustavsson, H. Ekstrom, P. Hanarp, L. Eurenus, G. Lindbergh, E. Olsson, B. Kasemo, *J. Power Sources* 163 (2007) 671-678.
- [97] A.N. Gavrilov, E.R. Savinova, P.A. Simonov, V.I. Zaikovskii, S.V. Cherepanova, G.A. Tsirlina, V.N. Parmon, *Physical Chemistry Chemical Physics* 9 (2007) 5476-5489.
- [98] J.L. Cohen, D.J. Volpe, H.D. Abruna, *Physical Chemistry Chemical Physics* 9 (2007) 49-77.
- [99] S. Basri, S.K. Kamarudin, W.R.W. Daud, Z. Yaakub, *International Journal of Hydrogen Energy* 35 (2010) 7957-7970.
- [100] C. Xu, P.K. Shen, *Journal of Power Sources* 142 (2005) 27-29.
- [101] M. Takahashi, T. Mori, F. Ye, A. Vinu, H. Kobayashi, J. Drennan, *Journal of the American Ceramic Society* 90 (2007) 1291-1294.
- [102] J. Zhao, W. Chen, Y. Zheng, *Materials Chemistry and Physics* 113 (2009) 591-595.
- [103] D.J. Guo, S.K. Cui, H. Sun, *Journal of Nanoparticle Research* 11 (2008) 707-712.
- [104] D.J. Diaz, N. Greenleach, A. Solanki, A. Karakoti, S. Seal, *Catalysis Letters* 119 (2007) 319-326.
- [105] M.A. Scibioh, S.K. Kim, E.A. Cho, T.H. Lim, S.A. Hong, H.Y. Ha, *Applied*

Catalysis B: Environmental 84 (2008) 773-782.

- [106] S. Uhm, Y. Yi, J. Lee, Catalysis Letters 138 (2010) 46-49.
- [107] E. Antolini, Energy and Environmental Science 2 (2009) 915-931.
- [108] C. Xu, K.S. Pei, Chemical Communications 10 (2004) 2238-2239.
- [109] Y. Wang, T.S. Nguyen, C. Wang, X. Wang, Dalton Transactions (2009) 7606-7609.
- [110] A.O. Neto, A.Y. Watanabe, M. Brandalise, M.M. Tusi, R.M. de S. Rodrigues, M. Linardi, E.V. Spinace, C.A.L.G.O. Forbicini, Journal of Alloys and Compounds 476 (2009) 288-291.
- [111] A.O. Neto, A.Y. Watanabe, R.M.D.S. Rodrigues, M. Linardi, C.A.L.G.O. Forbicini, E.V. Spinace, Ionics 14 (2008) 577-581.
- [112] S.T. Nguyen, H.M. Law, H.T. Nguyen, N. Kristian, S. Wang, S.H. Chan, X. Wang, Applied Catalysis B: Environmental 91 (2009) 507-515.
- [113] T. Ungar, J. Gubicza, G. Tichy, C. Pantea, T.W. Zerda, Composites Part A: Applied Science and Manufacturing 36 (2005) 431-436.
- [114] K.W. Lux, E.J. Cairns, Journal of the Electrochemical Society 153 (2006) A1132-A1138.
- [115] C. Feng, R. Zhang, P. Yin, L. Li, L. Guo, Z. Shen, Nanotechnology 19 (2008) 305601.
- [116] J.L. Lu, C. Xu, S.P. Jiang, International Journal of Nanoscience 8 (2009) 203-207.
- [117] C.W. Liu, Y.W. Chang, Y.C. Wei, K.W. Wang, Electrochimica Acta 56 (2011) 2574-2581.
- [118] J.A. Isaacs, A. Tanwani, M.L. Healy, L.J. Dahlben, J. Nanopart. Res. (2009) 1-12.
- [119] G. Selvarani, S. Maheswari, P. Sridhar, S. Pitchumani, A.K. Shukla, J. Electrochem. Soc. 156 (2009) B1354-B1360.
- [120] H. Song, X. Qiu, F. Li, W. Zhu, L. Chen, Electrochem. Commun. 9 (2007) 1416-1421.
- [121] S. Shanmugam, A. Gedanken, Journal of Physical Chemistry C 113 (2009) 18707-

18712.

- [122] D.S. Kim, S.J. Han, S.Y. Kwak, *J. Colloid Interface Sci.* 316 (2007) 85-91.
- [123] D.S. Kim, S.Y. Kwak, *Applied Catalysis A: General* 323 (2007) 110-118.
- [124] Y. Suo, I.M. Hsing, *Electrochim. Acta* 55 (2009) 210-217.
- [125] L. Sifang, Y. Guoliang, C. Guoqin, *Journal of Physical Chemistry C* 113 (2009) 4031-4037.
- [126] S.Y. Choi, M. Mamak, N. Coombs, N. Chopra, G.A. Ozin, *Adv. Funct. Mater.* 14 (2004) 335-344.
- [127] H. Chen, J. Yan, Z. Ye, L. Zhang, J. Gao, J. Shi, D. Yan, *Journal of Materials Science* 44 (2009) 6531-6537.
- [128] F. Bosc, A. Ayral, P.A. Albouy, C. Guizard, *Chem. Mater.* 15 (2003) 2463-2468.
- [129] J.B. Condon, *Surface Area and Porosity Determinations by Physisorption: Measurements and Theory*, 1st ed., Elsevier, Amsterdam, 2006.
- [130] J.H. Kim, H.I. Lee, *Korean J. Chem. Eng.* 21 (2004) 116-122.
- [131] S. Kaewgun, C.A. Nolph, B.I. Lee, L.Q. Wang, *Mater. Chem. Phys.* 114 (2009) 439-445.
- [132] Y. Le Page, P. Strobel, *J. Solid State Chem.* 44 (1982) 273-281.
- [133] B. Babic, J. Gulicovski, L. Gajic-Krstajic, N. Elezovic, V.R. Radmilovic, N.V. Krstajic, L.M. Vracar, *J. Power Sources* 193 (2009) 99-106.
- [134] X. Li, A.L. Zhu, W. Qu, H. Wang, R. Hui, L. Zhang, J. Zhang, *Electrochim. Acta* 55 (2010) 5891-5898.
- [135] F.C. Walsh, R.G.A. Wills, *Electrochim. Acta* 55 (2010) 6342-6351.
- [136] E. Slavcheva, V. Nikolova, T. Petkova, E. Lefterova, I. Dragieva, T. Vitanov, E. Budevski, *Electrochim. Acta* 50 (2005) 5444-5448.
- [137] L.M. Vračar, N.V. Krstajić, V.R. Radmilović, M.M. Jakšić, *Journal of Electroanalytical Chemistry* 587 (2006) 99-107.
- [138] R.F. Bartholomew, D.R. Frankl, *Physical Review* 187 (1969) 828-833.

- [139] K. Kolbrecka, J. Przyluski, *Electrochim. Acta* 39 (1994) 1591-1595.
- [140] G.B. Shan, G.P. Demopoulos, *Nanotechnology* 21 (2010) 025604.
- [141] T. Ioroi, H. Senoh, Z. Siroma, S. Yamazaki, N. Fujiwara, K. Yasuda, *ECS Transactions* 11 (2007) 1041-1048.
- [142] W. Li, C. Liang, W. Zhou, J. Qiu, Z. Zhou, G. Sun, Q. Xin, *J. Phys. Chem. B* 107 (2003) 6292-6299.
- [143] J.-S. Choi, H.-H. Kwon, W.S. Chung, H.-I. Lee, *Journal of Korean Powder Metallurgy Institute* 12 (2005) 117-121.
- [144] K. Lee, J. Zhang, H. Wang, D.P. Wilkinson, *J. Appl. Electrochem.* 36 (2006) 507-522.
- [145] D. Pantea, H. Darmstadt, S. Kaliaguine, L. Summchen, C. Roy, *Carbon* 39 (2001) 1147-1158.
- [146] K.W. Park, K.S. Seol, *Electrochem. Commun.* 9 (2007) 2256-2260.
- [147] Y. Shao, J. Liu, Y. Wang, Y. Lin, *J. Mater. Chem.* 19 (2009) 46-59.
- [148] A.A. Gusev, E.G. Avvakumov, A.Z. Medvedev, A.I. Masliy, *Science of Sintering* 39 (2007) 51-57.
- [149] A.A. Gusev, E.G. Avvakumov, *Science of Sintering* 39 (2007) 295-299.
- [150] L.M. Vracar, N.V. Krstajic, V.R. Radmilovic, M.M. Jaksic, *Journal of Electroanalytical Chemistry* 587 (2006) 99-107.
- [151] J. Greeley, J.K. Nørskov, M. Mavrikakis, *Annual Review of Physical Chemistry* 53 (2002) 319-348.
- [152] J.R. Smith, F.C. Walsh, R.L. Clarke, *J. Appl. Electrochem.* 28 (1998) 1021-1033.
- [153] A.V. Murugan, V. Samuel, V. Ravi, *Mater. Lett.* 60 (2006) 479-480.
- [154] J.M. Jaksic, N.V. Krstajic, L.M. Vracar, S.G. Neophytides, D. Labou, P. Falaras, M.M. Jaksic, *Electrochim. Acta* 53 (2007) 349-361.
- [155] J.M. Jaksic, C.M. Lacnjevac, N.V. Krstajic, M.M. Jaksic, *Chemical Industry and Chemical Engineering Quarterly* 14 (2008) 119-136.

- [156] M.M. Jaksic, *Electrochim. Acta* 45 (2000) 4085-4099.
- [157] M.M. Jaksic, *Solid State Ionics* 136-137 (2000) 733-746.
- [158] M.M. Jaksic, *Int. J. Hydrogen Energy* 26 (2001) 559-578.
- [159] N.V. Krstajic, L.M. Vracar, V.R. Radmilovic, S.G. Neophytides, M. Labou, J.M. Jaksic, R. Tunold, P. Falaras, M.M. Jaksic, *Surf. Sci.* 601 (2007) 1949-1966.
- [160] S.G. Neophytides, K. Murase, S. Zafeiratos, G. Papakonstantinou, F.E. Paloukis, N.V. Krstajic, M.M. Jaksic, *J. Phys. Chem. B* 110 (2006) 3030-3042.
- [161] S.G. Neophytides, S. Zafeiratos, G.D. Papakonstantinou, J.M. Jaksic, F.E. Paloukis, M.M. Jaksic, *Int. J. Hydrogen Energy* 30 (2005) 393-410.
- [162] B.L. Garcia, R. Fuentes, J.W. Weidner, *Electrochem. Solid-State Lett.* 10 (2007) B108-B110.
- [163] V. Bambagioni, C. Bianchini, J. Filippi, W. Oberhauser, A. Marchionni, F. Vizza, R. Psaro, L. Sordelli, M.L. Foresti, M. Innocenti, *ChemSusChem* 2 (2009) 99-112.
- [164] N. Fujiwara, Z. Siroma, S.i. Yamazaki, T. Ioroi, H. Senoh, K. Yasuda, *J. Power Sources* (2008).
- [165] C. Bock, C. Paquet, M. Couillard, G.A. Botton, B.R. MacDougall, *J. Am. Chem. Soc.* 126 (2004) 8028-8037.
- [166] A.S. Attar, M.S. Ghamsari, F. Hajiesmaeilbaigi, S. Mirdamadi, K. Katagiri, K. Koumoto, *Journal of Materials Science* 43 (2008) 5924-5929.
- [167] S.Y. Huang, P. Ganesan, P. Zhang, B.N. Popov, *ECS Transactions* 25 (2009) 1893-1902.
- [168] Y. Liu, J.M. Szeifert, J.M. Feckl, B. Mandlmeier, J. Rathousky, O. Hayden, D. Fattakhova-Rohlfing, T. Bein, *ACS Nano* 4 (2010) 5373-5381.
- [169] P.S. Archana, R. Jose, T.M. Jin, C. Vijila, M.M. Yusoff, S. Ramakrishna, *J. Am. Ceram. Soc.* 93 (2010) 4096-4102.
- [170] Y. Wang, B.M. Smarsly, I. Djerdj, *Chem. Mater.* 22 (2010) 6624-6631.
- [171] F. Ettingshausen, A. Weidner, S. Zils, A. Wolz, J. Suffner, M. Michel, C. Roth, *ECS Transactions* 25 (2009) 1883-1892.

- [172] W. Kraus, G. Nolze, J. Appl. Crystallogr. 29 (1996) 301-303.
- [173] P.A. Desario, M.E. Graham, R.M. Gelfand, K.A. Gray, Thin Solid Films 519 (2011) 3562-3568.
- [174] D. Morris, Y. Dou, J. Rebane, C.E.J. Mitchell, R.G. Egdell, D.S.L. Law, A. Vittadini, M. Casarin, Physical Review B - Condensed Matter and Materials Physics 61 (2000) 13445-13457.
- [175] S.B. Zhang, S.H. Wei, A. Zunger, Physica B: Condensed Matter 273-274 (1999) 976-980.
- [176] A. Zunger, Appl. Phys. Lett. 83 (2003) 57-59.
- [177] C.S. Chen, F.M. Pan, Applied Catalysis B: Environmental 91 (2009) 663-669.
- [178] Z. Liu, X.Y. Ling, X. Su, J.Y. Lee, L.M. Gan, J. Power Sources 149 (2005) 1-7.
- [179] M.M.O. Thotiyl, T.R. Kumar, S. Sampath, Journal of Physical Chemistry C 114 (2010) 17934-17941.