Fuel cell electrocatalsis : oxygen reduction on Pt-based nanoparticle catalysts

Vliet, D.F. van der

Fuel Cell Electrocatalysis

Oxygen Reduction on Pt-based Nanoparticle Catalysts

Proefschrift

ter verkrijging van
de graad van Doctor aan de Universiteit Leiden,
op gezag van Rector Magnificus Prof. Mr. P.F. van der Heijden,
volgens besluit van het College voor Promoties
te verdedigen op dinsdag 21 september 2010
klokke 16.15 Uur

door

Dennis Franciscus van der Vliet

geboren te Tilburg in 1981

Promotiecommissie:

Promotor:	Prof. Dr. M. T. M. Koper
Copromotor:	Dr. N. M. Markovič (Argonne National Lab, USA)
Overige Leden:	Prof. Dr. J. Brouwer
	Prof. Dr. B. E. Nieuwenhuys
	Prof. Dr. J. W. N. Frenken
	Prof. Dr. G. A. Attard (University of Cardiff, UK)
	Prof. Dr. J. A. R. van Veen (Shell)
	Dr. N. P. Lebedeva (ECN)

Table of Contents

Preface 6

Chapter 1
Introduction 9
- **1.1 History of Fuel Cells** 10
- **1.2 Working principle of a Fuel Cell** 11
- **1.3 Towards better Fuel Cells** 13
- **1.4 Outline of this thesis** 13

Chapter 2
On the Importance of Correcting for the Uncompensated Ohmic Resistance in Model Experiments of the Oxygen Reduction Reaction 19

- **2.1 Introduction** 20
- **2.2 Experimental** 21
- **2.3 Results and discussion** 22
  - 2.3.1 IR-Drop 22
  - 2.3.2 Consequences on data interpretation 28
    - 2.3.2.1 Influence of adsorption processes 28
    - 2.3.2.2 Influence of Ohmic drop 29
- **2.4 Conclusion and Recommendations** 31

Chapter 3
Monodisperse Pt_3Co Nanoparticles as a Catalyst for the Oxygen Reduction Reaction: Size-Dependent Activity 35

- **3.1 Introduction** 36
- **3.2 Experimental** 36
- **3.3 Results and Discussion** 38
- **3.4 Conclusion** 42
- **3.5 Appendix** 42
  - 3.5.1 Synthesis of Pt3Co nanoparticles 42
  - 3.5.2 Characterization 43
  - 3.5.3 Electrochemical Measurements 43

Chapter 4
Monodisperse Pt_3Co Nanoparticles as Electrocatalysts: the effects of Particle Size and Pretreatment on Electrocatalytic Reduction of Oxygen **49**

4.1 Introduction **50**
4.2 Experimental **52**
4.2.1 NP synthesis 52
4.2.2 Characterizations 52
4.2.3 Electrochemical measurements 52
4.2.4 Simulation 53
4.3 Results and discussion **53**
4.3.1 Size controlled synthesis of Pt_3Co NPs 54
4.3.2 Size-dependent activity 56
4.3.3 Annealing temperature 56
4.3.4 Modeling and mechanisms 60
4.4 Summary **64**

Chapter 5
Multimetallic Au/$FePt_3$ Nanoparticles as Highly Durable Electrocatalyst **67**

5.1 Introduction **68**
5.2 Results **69**
5.3 Core shell particle synthesis and analysis **72**
5.4 Electrochemical characterization **78**
5.5 Discussion **80**
5.6 Summary **84**
5.7 Appendix **85**
5.7.1 Part 1 Experimental Methods and Characterizations 85
5.7.1.1 Nanoparticle Synthesis 85
5.7.1.1.1 7 nm Au NPs 85
5.7.1.1.2 7/1.5 nm Au/FePt3 NPs 85
5.7.1.2 Material Characterizations 86
5.7.1.3 Electrochemical Study 86
5.7.1.4 Theory and Simulations 86
5.7.2 Part 2 Electrochemical Properties of Well-Defined Surfaces 87
5.7.2.1 Electrochemical characterization of Pt and $FePt_3$ thin films on Au(111) substrate 87
5.7.2.1.1 Au(111)-Pt 87
5.7.2.1.2 Au(111)-$FePt_3$ 88
5.7.2.1.3 The absence of Au atoms on the Au(111)-$FePt_3$ surface 90
5.7.3 Part 3 Properties of Multimetallic Nanoparticles 92

5.7.3.1 Elemental analysis of Au/$FePt_3$ nanoparticles: 92
5.7.3.2 Electrochemical Characterization 93
5.7.4 Part 4 Mechanism of Stability Enhancement 94
5.7.4.1 Nanoparticle Shape 94
5.7.4.2 Stability enhancement through adsorbate induced segregation of Pt 95
5.7.4.3 Stabilization of Pt surface atoms through the hindered place exchange mechanism 96
5.7.4.4 DFT calculations of the subsurface atomic oxygen adsorption in $FePt_3$(111) alloys with subsurface Au 97

Chapter 6
Platinum-alloy Nanostructured Thin Film Catalysts for the Oxygen Reduction Reaction 101

6.1 Introduction 102
6.2 Experimental 103
6.3 Results and Discussion 104
6.3.1 Microscopy 104
6.3.2 Determination of proper platinum loading 105
6.3.3 Blank Cyclic Voltammetry 107
6.3.4 Oxygen Reduction Reaction 110
6.4 Conclusion 114

Chapter 7
Multimetallic Nanotubes as Catalysts for the Oxygen Reduction Reaction 117

7.1 Introduction 118
7.2 Experimental 119
7.3 Results 120
7.3.1 Catalyst preparation and characterization 120
7.3.2 Electrochemical characterization 123
7.3.3 ORR 124
7.4 Conclusion 128
7.5 Appendix 129
7.5.1 General observations during the annealing 129
7.5.2 Effect of annealing temperature 129
7.5.3 Different annealing environments 131
7.5.4 Effect of annealing time 132
7.5.5 Effect on Active Surface Area 133

Chapter 8
Electrochemistry of Pt (100) in Alkaline Media: A Voltammetric Study **137**

8.1 Introduction **138**
8.2 Materials and Methods **139**
8.3 Results **140**
8.3.1 Effect of electrode preparation method 140
8.3.2 Effect of potential cycling 145
8.3.3 Cation and Anion effects 147
8.4 Discussion **151**
8.5 Conclusion **154**

Summary **157**

Nedelandse Samenvatting **160**

List of Publications **163**

Curriculum Vitae **164**

Nawoord **165**

Preface

This thesis was prepared in cooperation between Argonne National Laboratory (ANL) and Leiden University. The density functional theory calculations set forth in this thesis were performed by Jeff Greeley at the center for nanoscale materials at ANL and the Monte Carlo simulations were performed by Guofeng Wang at Indiana University-Purdue University.
The synthesis of the nanoparticles as described in chapters 3-5 was performed by Dr. Chao Wang at ANL