

Contents

Chapter 1

CHARACTERIZATION OF ALLOY ELECTROCATALYSTS BY COMBINED LOW-ENERGY ION SCATTERING SPECTROSCOPY AND ELECTROCHEMISTRY

Stephanus Axnanda, Kyle D. Cummins,
D. Wayne Goodman, and Manuel P. Soriaga

I. Introduction.....	1
II. Experimental Aspects	
1. Low Energy Ion Scattering Spectroscopy.....	4
2. Preparation of Pt-Co Alloy Films	7
3. Electrochemical Characterization	7
4. Instrumentation	8
III. Case Study: Pt-Co Alloy Electrocatalysts for Oxygen Reduction	10
1. Pt-Co Films and Alloys.....	10
2. Surface Elemental Composition and Surface Phase Diagrams	12
3. Long-Range Surface Order	14
4. Electrochemical Properties	16
(i) OCP Values.....	16
(ii) Cyclic Voltammogram of the Pt ₃ Co Alloy	17
(iii) <i>Potential-Dependent Dissolution of Pt₃Co</i>	18
5. Bulk Properties of the Pt ₃ Co Alloy	20
(i) <i>Relevance to Published Work</i>	20
IV. Summary	21
Acknowledgment	22
References	22

*Chapter 2*RECENT ADVANCES IN THEORETICAL ASPECTS OF
ELECTROCATALYSIS

Elizabeth Santos and Wolfgang Schmickler

I. Introduction	25
II. Classification of Electrochemical Reactions	27
III. Previous Approaches to Catalysis from the Surface Science	31
IV. Previous Approaches to Bond Breaking Electrochemical Reactions	34
V. Model Hamiltonian	36
VI. Interactions of the Atomic Orbitals of the Reactant with the Electronic States of the Electrode	40
VII. Occupation Probability of the Electronic State of the Reactant.....	45
VIII. 1-D And 3-D Potential Energy Representations.....	53
IX. Electrocatalysis by a Narrow d Band	59
X. Application to Real Systems – Hydrogen Evolution / Oxidation Reactions	67
XI. DFT Quantum Chemical Calculations as Input for the SKS- Hamiltonian.....	70
XII. Electrocatalysis at Nanostructures.....	78
XIII. Conclusions	84
Acknowledgements	86
References	86

*Chapter 3*COMPUTATIONAL SIMULATIONS ON THE OXYGEN
REDUCTION REACTION IN ELECTROCHEMICAL
SYSTEMS

John A. Keith and Timo Jacob

I. Introduction.....	89
II. Experimental Studies on the Oxygen Reduction Reaction.....	90
1. On Unmodified Pt Single Crystal Electrodes and Carbon Supports	90
2. On Bimetallic Surfaces and Alloys on Different Supports	92
III. Theoretical Studies on the Oxygen Reduction Reaction.....	94
1. Mechanistic Studies on the ORR	95
2. Treating Electrolyte Effects	98
3. Simulations on Bimetallic Alloy Surfaces	99
4. Simulations on Low-Pt Electrocatalysts	102
IV. Methods	103
1. DFT Calculations	103
(i) Finite Systems	103
(ii) Periodic Systems	104
2. Thermodynamic Considerations	105
V. Results and Discussion.....	106
1. Electrochemical Phase Diagram	107
2. Oxygen Reduction Reaction (ORR)	110
(i) O ₂ Dissociation	111
(ii) OOH/H ₂ O ₂ Formation.....	117
(iii) Influence of Water Solvation	118
(iv) Eley–Rideal Mechanisms.....	122
VI. Conclusions.....	123
Acknowledgements.....	126
References.....	127

Chapter 4

MOLECULAR-LEVEL MODELING OF THE STRUCTURE
AND PROTON TRANSPORT WITHIN THE MEMBRANE
ELECTRODE ASSEMBLY OF HYDROGEN PROTON
EXCHANGE MEMBRANE FUEL CELLS

Myvizhi Esai Selvan and David J. Keffer

I. Introduction.....	133
II. Morphology.....	137
1. Introduction.....	137
2. Molecular Models and Simulation Details.....	141
3. Results and Discussions.....	147
(i) Visualization	147
(ii) Cluster Size Distribution and Connectivity.....	150
(iii) Pair Correlation Function.....	156
(iv) Hydronium Hydration Histogram	161
(v) Water Density Profile	163
(vi) Hydronium Orientation at the Interface	168
(vii) Critical Gap.....	169
III. Transport.....	172
1. Introduction.....	172
2. Coarse-Grained Reactive Molecular Dynamics Algorithm.....	176
3. Proton Transport in Bulk Water.....	177
(i) Input from Macroscopic Model	177
(ii) Input from Quantum Mechanical Studies	178
(iii) Instantaneous Reaction and Local Equilibration..	182
(iv) Simulation Details.....	183
(v) Results and Discussions.....	184
4. Transport in Nafion.....	192
(i) Water and Vehicular Hydronium Diffusivities	192
(ii) Structural Diffusion of Protons	193
IV. Conclusions.....	195
Acknowledgements.....	197
References.....	198

Chapter 5

**SOME RECENT STUDIES ON THE LOCAL REACTIVITY OF
O₂ ON PT₃ NANOISLANDS SUPPORTED ON MONO- AND
BI-METALLIC BACKGROUNDS**

Juan C. Sotelo and Jorge M. Seminario

I. Introduction	203
II. Methodology	205
III. The Nanosystems	209
1. Clusters and Complexes.....	210
2. Reactive Sites.....	210
IV. DOS of BUBulkLK Co, Pt, Co ₃ Pt, Ni, and Fe	219
V. Electronic Characterization of the O ₂ -Substrate System (LDOS).....	222
VI. Local Reactivity of a Bimetallic Surface: Co ₃ Pt	225
1. Electronic Characterization.....	225
VII. Local Reactivity of Supported Pt ₃ Islands	230
1. Electronic Characterization.....	230
2. Structural Characterization	232
3. Binding and Dissociation Adsorption Energies	234
VII. Conclusions.....	237
Acknowledgements.....	238
References.....	239

Chapter 6

**METHANOL ELECTRO-OXIDATION BY METHANOL
DEHYDROGENASE ENZYMATIC CATALYST:
A COMPUTATIONAL STUDY**

N. B. Idupulapati and D. S. Mainardi

I. Introduction	243
1. Enzymatic Catalysts for Fuel Cell Applications	243
2. Methanol Dehydrogenase Enzyme	245

3. Methanol Electro-oxidation by Methanol Dehydrogenase Enzymes	246
II. Methodology	252
III. Results and Discussion.....	254
1. Methanol Dehydrogenase Active Site Models.....	254
2. Methanol Electro-Oxidation Mechanisms	256
(i) Addition-Elimination Mechanism.....	256
(ii) Hydride Transfer Mechanism	260
(iii) Methanol A-E versus H-T Electro-Oxidation Mechanisms by MDH	267
IV. Conclusions.....	269
References	272

Chapter 7

ELECTROCATALYTIC REACTIONS OF CHEMISORBED AROMATIC COMPOUNDS: STUDIES BY ES, DEMS, STM AND EC

Jean Sanabria-Chinchilla, Youn-Geun Kim, Xiaole Chen, Ding Li, Helmut Baltruschat, and Manuel P. Soriaga

I. Introduction.....	275
II. Experimental Protocols	276
1. Preparation of Single-Crystal Electrode Surfaces.....	277
2. Interfacial Characterization	279
(i) Electron Spectroscopy (ES).....	279
(ii) Scanning Tunneling Microscopy (STM)	282
(iii) Differential Electrochemical Mass Spectrometry (DEMS)	285
III. The Chemisorption and Electrocatalytic Reactivity of Aromatic Compounds	286
1. Benzene	286
(i) EC-STM.....	286
(ii) HREELS	292
(iii) DEMS	294
2. Hydroquinone/Benzoquinone	299
(i) HREELS	299

(ii) EC-STM.....	302
(iii) DEMS	304
IV. The Case for a Langmuir-Hinshelwood Mechanism	308
Acknowledgements.....	312
References.....	312

Chapter 8

A REVIEW OF CONTINUUM ELECTROCHEMICAL ENGINEERING MODELS AND A NOVEL MONTE CARLO APPROACH TO UNDERSTAND ELECTROCHEMICAL BEHAVIOR OF LITHIUM-ION BATTERIES

Vinten D. Diwakar, S. Harinipriya and
Venkat R. Subramanian

I. Introduction.....	315
II. Continuum Models for Predicting Battery Behavior	316
1. Variables and Governing Equations in the Macro Scale.....	318
(i) Cathode	318
(ii) Separator	320
(iii) Anode.....	321
2. Variables and Governing Equations on the Micro Scale.....	322
3. Micro-Macro Scale Coupled Continuum Models	324
4. Capabilities of Continuum Models	327
5. Limitations of Continuum Models	332
III. Modeling of Electrochemical Processes at the Micro and Nano Scale	334
1. Performance Characteristics of Cathode Materials for Lithium Ion Batteries	336
2. Methodology	338
3. Parameters Employed	340
4. Results and Discussion	340
(i) Discharge Behavior of LiCoO_2	341
(ii) Discharge Behavior of LiFePO_4	343

5. Perspectives	345
6. Conclusions of the Present Work.....	345
IV. Scope for Future Work.....	346
List of Symbols	346
References.....	348

Chapter 9

CHALLENGES IN THE DESIGN OF ACTIVE AND DURABLE ALLOY NANOCATALYSTS FOR FUEL CELLS

P. B. Balbuena, S. R. Calvo, R. Callejas-Tovar, Z. Gu, G. E. Ramirez-Caballero, P. Hirunsit, and Y. Ma

I. Introduction.....	351
II. Activity of Nanoalloy Catalysts Towards the ORR	355
III. Surface Atomic Distribution of an Alloy Nanoparticle.....	372
IV. Dissolution of Surface Atoms in Acid Medium.....	385
V. Conclusions.....	391
Acknowledgements.....	391
References.....	391

Chapter 10

DETERMINATION OF REACTION MECHANISMS OCCURRING AT FUEL CELL ELECTROCATALYSTS USING ELECTROCHEMICAL METHODS, SPECTROELECTROCHEMICAL MEASUREMENTS AND ANALYTICAL TECHNIQUES

C. Coutanceau, S. Baranton, and C. Lamy

I. Introduction.....	397
II. Coupled Experimental Methods.....	399

1. Infrared Reflectance Spectroscopy	399
2. Electrochemical Quartz Crystal Microbalance (EQCM)	401
3. Differential Electrochemical Mass Spectrometry (DEMS).....	402
4. Radiochemical Labeling	403
5. High Performance Liquid Chromatography (HPLC)....	405
III. CO Oxidation at Platinum Based Electrocatalysts	406
1. Adsorption and Electro-Oxidation of CO at Pure Platinum Catalysts	406
2. Adsorption and Electro-Oxidation of CO at Platinum Based Bimetallic Electrocatalysts	416
IV. Alcohol Oxidation at Platinum-Based Electrocatalysts	422
1. The Electro-Oxidation of Methanol	423
(i) IR Studies of CH ₃ OH Adsorption and Oxidation at Smooth Pt Electrodes	423
(ii) FTIR Studies of CH ₃ OH Adsorption and Oxidation at Pt-Ru Bulk Alloys	426
(iii) EQCM Studies of Methanol Adsorption and Oxidation	431
(iv) DEMS Study of Methanol Adsorption and Oxidation	434
(v) Radiochemical Labeling of Methanol Adsorption	439
(vi) Mechanism of the Electro-Oxidation of Methanol	449
2. The Electro-Oxidation of Ethanol.....	452
(i) IR Study of the Adsorption and Oxidation of Ethanol on Pt/C Catalysts	453
(ii) Comparison of Ethanol Electro-Oxidation on Pt and PtSn Catalysts	456
(iii) DEMS Study of Ethanol Electro-Oxidation on Pt- Based Catalysts	460
(iv) HPLC Investigation of Ethanol Electro-Oxidation on Pt Electrodes	466
(v) HPLC Analysis of Ethanol Oxidation on Dispersed Pt-Based Anodes of a DEFC.....	469
(vi) Detailed Mechanisms of Ethanol Oxidation at Pt- Based Electrodes	474

V. Oxygen Reduction Reaction (ORR).....	477
1. Electrochemical Methods: Rotating Disk Electrode (RDE) and Rotating Ring Disk Electrodes (RRDE)	477
2. Electrochemical Quartz Crystal Microbalance (EQCM)	484
3. Electrochemistry Coupled with Fourier Transform Infrared Spectroscopy (FTIRS).....	490
VI. Conclusions.....	493
References.....	494

Chapter 11

IN-SITU SYNCHROTRON SPECTROSCOPIC STUDIES OF ELECTROCATALYSIS ON HIGHLY DISPERSED NANO-MATERIALS

Sanjeev Mukerjee and Thomas Arruda

I. Introduction.....	503
II. Current State of the Art in Surface Science Tailored for Electrocatalysis Investigations	504
III. Synchrotron Methods as a Probe of Metal Reaction Centers at an Electrochemical Interface.....	506
IV. In-Situ Synchrotron Spectroscopy: Methodology and Practice	509
1. Overview of the Underlying Principle and Data Analysis	510
(i) XANES.....	513
(ii) New In-Situ Site Specific Surface Probe Using Synchrotron Based XANES Spectroscopy: Some Recent Results.....	516
2. EXAFS.....	519
V. Electrocatalysis for Low-Temperature Acid-Based Fuel Cells	523
1. Oxygen Reduction Reaction on Pt and Pt Alloy Electrocatalysts	523
2. Electrocatalysts for Anode Electrodes Using Pt Alloys.....	526
(i) Reformate Tolerant Electrocatalysts	526

(ii) Direct Methanol Oxidation	528
3. Non Pt-Based Electrocatalysts	530
(i) Current State of the Art in Non-Pt Chalcogenide Electrocatalyst Systems.....	530
(ii) Oxygen Reduction on Unique Enzymatic Active Centers	531
VI. Understanding Electrocatalytic Pathways.....	533
1. Nanocluster Morphology and Unique Reaction Environment.....	533
(i) Highly Dispersed Pt based Electrocatalysts: Issue of Particle Size.....	533
(ii) Nanophase Electrocatalysts: Surface Structure of Small Particles	534
(iii) Structural Effects on Electrocatalysis by Pt: Effect of Particle Size	536
2. Alloy Electrocatalysts: Electronic and Structural Effects on Electrocatalytic Properties of Platinum Alloys.....	542
(i) Cathode	544
(ii) Water Activation Studies	546
(iii) Anode.....	548
3. Chalcogenide Electrocatalysts	553
4. Co-Porphyrin Systems	557
5. XAS as a Probe in Enzymatic Fuel Cells.....	559
References.....	565
Index	573

Theory and Experiment in Electrocatalysis

Balbuena, P.B.; Subramanian, V.R. (Eds.)

2010, XXIV, 578 p., Hardcover

ISBN: 978-1-4419-5593-7