Edited by Hansan Liu and Jiujun Zhang

# Electrocatalysis of Direct Methanol Fuel Cells

From Fundamentals to Applications



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# **Electrocatalysis of Direct Methanol Fuel Cells**

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#### **Preface**

In today's world, human energy demands are continually on the rise, and the prospect of an energy shortage, or even crisis, is likely in the near future. Among the various efforts being made to meet global energy needs, the energy carried by hydrogen and liquid biofuels such as methanol and ethanol has become an attractive option in terms of sustainability and low environmental impact. Within this category of energy conversion technologies, the fuel cell is one of the most environmentally friendly and sustainable possibilities. In the past several decades, governments, along with academic communities and industries, have made enormous investments to develop fuel cells, especially proton exchange membrane fuel cells (PEMFCs), into a viable technology for stationary, portable, and transportation applications. As a result, great advances have been achieved in fuel cell technology in recent years. To date, several kinds of fuel cells, including direct methanol fuel cells (DMFCs), have shown great promise for near-term commercialization.

DMFCs, using renewable liquid methanol as fuel, have some advantages over the hydrogen-fuelled PEMFCs, such as easy fuel production, storage, and transportation, simple feed strategy, as well as system simplification. In comparison with other advanced energy devices such as lithium ion batteries, DMFCs show one order of magnitude higher energy density, making them a better choice for meeting the high energy density requirement of traditionally battery-powered devices. In the past two decades, great progress has been made in DMFC technology. For example, a few precommercial products based on this technology are currently emerging in the portable device category, including laptop computers and cell phones. However, several challenges still hinder commercialization, such as inadequate performance and high cost. The sluggish electrocatalytic reactions, that is, the anodic methanol oxidation reaction (MOR) and the cathodic oxygen reduction reaction (ORR), are largely responsible for this low performance. Methanol crossover from anode to cathode through the membrane can also cause performance deterioration. In order to overcome these technical difficulties, high-loading and high-cost Pt and Pt alloy catalysts must currently be used in DMFCs to mitigate the negative effects of the sluggish MOR and ORR, as well as the methanol crossover. In the past few years, numerous studies have been devoted to developing DMFC electrocatalysis, in an effort to further understand the reaction mechanisms, develop cost-effective and

high-performance or methanol-tolerant catalysts, and optimize the fabrication of catalyst layers and membrane electrode assemblies membrane electrode assembly

This book is designed to draw a clear picture of the current status of DMFC technology, with a particular focus on the technical progress, challenges, and perspectives in the field of DMFC electrocatalysis. A group of top fuel cell scientists and engineers, who have not only excellent academic records but also strong industrial fuel cell expertise, were invited to contribute chapters. These leading researchers from universities, government laboratories, and fuel cell industry companies in North America, Europe, and Asia share in this volume their knowledge, information, and insights on recent advances in the fundamental theories, experimental methodologies, and research achievements in DMFC electrocatalysis.

In the first chapter, Arico and his colleagues provide a comprehensive review of DMFC history, the current status of fundamental studies, and the technical advances that have been made in catalyst preparation, MEA fabrication, as well as stack/ system design. They also give a global summary of DMFC prototypes in portable and transportation applications, and discuss the techno-economic challenges still confronting DMFC technology. In Chapter 2, Liu and his co-workers describe various methods of synthesizing nanostructured electrocatalysts for DMFCs, including both conventional carbon-supported, Pt-based catalysts and novel unsupported catalyst nanostructures. In Chapter 3, Sarma and Hwang give an overview of versatile characterization techniques for elucidating nanoscale characteristics and activity validation methodologies for DMFC electrocatalysts. In Chapter 4, Jiang and Chu introduce the principles and modern technologies of combinatorial methods used in the synthesis and high throughput screening of electrocatalyst libraries for DMFCs. In Chapter 5, Lei and his co-workers introduce DMFC catalyst development in industry, particularly focusing on Cabot's spray conversion reaction (SCR) platform for the discovery and manufacturing of high-performance fuel cell electrocatalysts. In Chapter 6, Antolini surveys the progress in preparation methods, activity validation, and stability studies of Pt binary and ternary alloys for DMFC anodes. In Chapter 7, Lamy and his colleagues discuss the thermodynamics and kinetics of the oxygen reduction reaction on DMFC cathodes, and introduce strategies to mitigate the methanol-crossover effect; they also describe the progress made in developing methanol-tolerant catalysts. In Chapter 8, Chen and his co-authors review recent advances in carbon nanotube (CNT)-supported DMFC catalysts. In Chapter 9, Pak and Chang cover studies of mesoporous carbon-supported DMFC catalysts. In Chapter 10, Kim and Guiver discuss strategies for making proton exchange membranes with high proton conductivity and lower methanol permeability, mainly describing their own work on developing hydrocarbon-based copolymers containing sulfonic acid groups for DMFC membranes. In Chapter 11, Xing and his co-authors review the progress that has been made in the fabrication and optimization of DMFC catalyst layers and membrane electrode assemblies, with an emphasis on the effects of catalyst layer components, structures, and fabrication methods on DMFC performance. In Chapter 12, Kulikovsky and Wippermann present their experimental and modeling efforts to understand local current distribution during DMFC operation. In Chapter 13, Scott and Yu provide a detailed description of direct methanol alkaline fuel cells in terms of MOR catalysts, ORR catalysts, and membranes in alkaline circumstances. In Chapter 14, Blair and Law introduce electrocatalysis in other direct liquid fuel cells, mainly focusing on direct ethanol fuel cells and on their own work with direct formic acid fuel cells at Tekion Inc.

It is our hope that this volume will prove to be a good resource for electrochemists, chemical engineers, material scientists, students, and the public, providing up-todate information on DMFC principles, the current status of DMFC electrocatalysis, and the future prospects for DMFC technology. We anticipate that this book will also be used as a reference by undergraduate and graduate post-secondary students, as well as scientists and engineers who work in the areas of energy, electrochemistry science/technology, fuel cells, and electrocatalysis.

We would like to express our appreciation to Wiley-VCH for inviting us to lead this book project, and we thank Dr. Elke Maase and Dr. Heike Noethe for their guidance and support in smoothing the book preparation process. We also extend our thanks to all our colleagues at the National Research Council of Canada's Institute for Fuel Cell Innovation (IFCI), and especially to the members of the catalysis team, for their support and help. We gratefully acknowledge all the chapter authors for their enthusiastic, collaborative, and reliable contributions. Special thanks go to Prof. Arico, Dr. Lei, Dr. Chang, and Dr. Kulikovsky for providing raw materials for the book's cover design. (Kulikovsky's current distribution picture and IFCI's mesoporous catalysts pictures were incorporated into the cover art.) Finally, our special appreciation goes to our families, for their understanding and their ongoing support of our work.

Vancouver, Canada February 2009

Hansan Liu and Jiujun Zhang

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#### **Contents**

Preface XVList of Contributors XIX

1	Direct Methanol Fuel Cells: History, Status and Perspectives 1
	Antonino Salvatore Aricò, Vincenzo Baglio, and Vincenzo Antonucci
1.1	Introduction 1
1.2	Concept of Direct Methanol Fuel Cells 2
1.2.1	Principles of Operation 2
1.2.1.1	DMFC Components 2
1.2.1.2	DMFC Operation Mode 3
1.2.1.3	Fuel Cell Process 3
1.2.2	Performance, Efficiency and Energy Density 4
1.2.2.1	Polarization Curves and Performance 4
1.2.2.2	Fuel Utilization 5
1.2.2.3	Cathode Operating Conditions 7
1.2.2.4	Heat Production 8
1.2.2.5	Cell Efficiency 9
1.2.2.6	Energy Density 9
1.3	Historical Aspects of Direct Methanol Fuel Cell Development
	and State-of-the-Art 10
1.3.1	Historical Development of Methanol Oxidation Catalysts 10
1.3.2	Status of Knowledge of Methanol Oxidation Process and
	State-of-the-Art Anode Catalysts 14
1.3.2.1	Oxidation Mechanism 14
1.3.2.2	Pt-Ru Catalysts 15
1.3.2.3	Alternative Anode Formulations 19
1.3.2.4	Practical Anode Catalysts 19
1.3.2.5	Anode Catalysts for Alkaline DMFC Systems 20
1.3.3	Technological Advances in Electrolyte Development for DMFCs 21
1.3.4	State-of-the-Art DMFC Electrolytes 24
1.3.4.1	General Aspects of DMFC Electrolyte Development 24

/1	Contents	
	1.3.4.2	Proton Conducting Membranes 24
	1.3.4.3	Membranes for High Temperature Applications 26
	1.3.4.4	Alkaline Membranes 29
	1.3.4.5	Effects of Crossover on DMFC Performance and Efficiency 32
	1.3.5	Historical Development of Oxygen Electroreduction in DMFCs 33
	1.3.6	Status of Knowledge of Oxygen Reduction Electrocatalysis and
		State-of-the-Art Cathode Catalysts 33
	1.3.6.1	Oxygen Reduction Process 33
	1.3.6.2	Pt-Based Catalysts and Non-noble Metal Electrocatalysts 35
	1.3.6.3	Alternative Cathode Catalysts 37
	1.3.7	DMFC Power Sources in the 'Pre-1990 Era' 39
	1.4	Current Status of DMFC Technology for Different
		Fields of Application 40
	1.4.1	Portable Power Sources 40
	1.4.2	Transportation 53
	1.4.3	Technology Development 60
	1.4.3.1	DMFC Technology 60
	1.4.3.2	Catalyst Preparation 61
	1.4.3.3	Electrode Manufacturing and Membrane Electrode
		Assemblies Membrane Electrode Assembly (MEAs) 61
	1.4.3.4	Stack Hardware and Design 62
	1.4.3.5	DMFC Systems 64
	1.5	Perspectives of Direct Methanol Fuel Cells and
		Techno-Economical Challenges 65
		References 70
	2	Nanostructured Electrocatalyst Synthesis: Fundamental
		and Methods 79
		Nitin C. Bagkar, Hao Ming Chen, Harshala Parab, and Ru-Shi Liu
	2.1	Introduction 79
	2.2	Fundamental Understanding of the Structure–Activity Relationship 80
	2.2.1	Particle Size Effect 81
	2.2.2	Crystal Facet Effect 82
	2.3 2.3.1	Synthetic Methods of Conventional Carbon-Supported Catalysts 85
	2.3.1	Impregnation Method 87 Colloidal Method 88
	2.3.2.1	Colloidal Method 88 Polyol Synthesis 89
	2.3.2.1	
	2.3.3	
	2.4.1	
	2.4.1.1	Template-Based Synthesis 95 Soft Template 96
	2.4.1.2	Hard Template 96
	2.4.2	Galvanic Replacement Reaction 99
	2.4.2.1	Platinum Nanospheres 99
	2.4.2.2	Platinum Nanotubes 99

2.4.2.3	Nanoporous Platinum 101
2.4.2.4	Hollow Platinum Nanochannels 102
2.4.2.5	Bimetallic Clusters 103
2.4.3	Electrochemical Synthesis 104
2.4.3.1	Spherical Platinum Clusters 104
2.4.3.2	Nanoporous Platinum 105
2.4.3.3	Tetrahexahedral Platinum Nanostructures 106
2.5	Conclusions 108
	References 110
3	Electrocatalyst Characterization and Activity Validation – Fundamentals
	and Methods 115
	Loka Subramanyam Sarma, Fadlilatul Taufany, and Bing-Joe Hwang
3.1	Introduction 115
3.2	Direct Methanol Fuel Cells – Role of Electrocatalysts 117
3.2.1	Role of Anode Electrocatalysts – Methanol Oxidation
	Reaction (MOR) 118
3.2.2	Role of Cathode Electrocatalysts – Oxygen Reduction
	Reaction (ORR) 119
3.3	Characterization Techniques for Anode and Cathode Catalysts 121
3.3.1	Fundamental Aspects 121
3.3.2	Evaluation of Catalyst Crystallite Size, Elemental Composition,
	Morphology, Dispersion 122
3.3.2.1	X-ray Diffraction (XRD) 122
3.3.2.2	Transmission Electron Microscopy (TEM) 124
3.3.2.3	Scanning Electron Microscopy (SEM) 125
3.3.2.4	Atomic Force Microscopy (AFM) 125
3.3.2.5	Energy Dispersive X-ray Spectroscopy (EDS/EDX) 125
3.3.3	Elucidation of Nanostructural Characteristics of Electrocatalysts –
	Alloying Extent or Atomic Distribution, Electronic Structural
	Features, State of Catalyst Species, Surface Composition,
	Segregation Phenomena 126
3.3.3.1	X-ray Absorption Spectroscopy 126
3.3.3.2	X-ray Photoelectron Spectroscopy (XPS) 132
3.3.3.3	Electrochemical-Nuclear Magnetic Resonance Spectroscopy
	(EC-NMR) 133
3.3.3.4	Low-Energy Electron Diffraction (LEED) 134
3.3.3.5	Auger Electron Spectroscopy (AES) 134
3.3.3.6	Low-Energy Ion Scattering (LEIS) 135
3.3.3.7	Temperature Programmed Reduction (TPR) 135
3.4	Evaluation of Electrocatalyst Activity, Electrochemical Active Surface
	Area, Catalyst - Adsorbate Interactions, and Activity Validation
	Techniques 136
3.4.1	Cyclic Voltammetry (CV) 136
3.4.1.1	Applications 137

VIII	Contents	
	3.4.1.2	State of the Pt-Based Catalysts 137
	3.4.1.3	Qualitative Indicator for the Activity of Pt-Based Catalysts
		Towards ORR 139
	3.4.1.4	Qualitative Indicator for the Activity of Pt-Based Catalysts
		Towards MOR 139
	3.4.1.5	Reversibility of H <sub>ads/des</sub> Reaction and Roughness Factor (RF)
		of Pt-Based Catalysts 140
	3.4.1.6	Electrochemical Active Surface Area (ECASA) and Particle Size
	2.4.2	of Pt-Based Catalysts 140
	3.4.2	Adsorptive CO-Stripping Voltammetry (CO <sub>ads</sub> -SV) 141
	3.4.3 3.4.3.1	Underpotential Deposition (UPD) 143 Surface Composition of Pt-Based Catalysts Through the
	3.4.3.1	Cu-UPD method 145
	3.4.4	Rotating Disk Electrode (RDE) 146
	3.4.5	Rotating Ring-Disk Electrode (RRDE) Method 148
	3.4.6	Linear Sweep Voltammetry (LSV) 149
	3.5	Conclusions and Outlook 155
		References 156
	4	Combinatorial and High Throughput Screening of
		DMFC Electrocatalysts 165
		Rongzhong Jiang and Deryn Chu
	4.1	Introduction 165
	4.2	Common Procedures for the Development of DMFC Catalysts 168
	4.3	General Methods for Combinatorial and High
	4.4	Throughput Screening 169 Methods of Combinatorial Synthesis 171
	4.4.1	Chemical Synthesis 171
	4.4.2	Electrochemical Synthesis 173
	4.4.3	Physical Synthesis 174
	4.5	Electrode Arrays for High Throughput Screening 175
	4.5.1	Direct Electrode Array and Automated Screening Method 175
	4.5.2	Material Spot Array on a Single Electrode and Optical
		Screening Method 177
	4.5.3	Indirect Electrode Array on a Single Conductive Substrate and
		Electrolyte Probe Screening Methods 179
	4.6	Other Screening Methods for Catalyst Discovery 182
	4.6.1	Infrared (IR) Thermography 183
	4.6.2	Scanning Mass Spectrometry 183
	4.6.3	Scanning Electrochemical Microscope (SECM) 185
	4.7	Combinatorial Methods for DMFC Evaluation and Data Analysis 187
	4.7.1	Micro Fuel Cell Array 187
	4.7.2	A Method for High Throughput Screening of DMFC
	4.7.3	Single Cells 189  Data Analysis of Combinatorial Basults 180
	T./.J	Data Analysis of Combinatorial Results 190

4.8	References 193
5	State-of-the-Art Electrocatalysts for Direct Methanol Fuel Cells 197
	Hanwei Lei, Paolina Atanassova, Yipeng Sun, and Berislav Blizanac
5.1	Introduction 197
5.2	Electrocatalysis and Electrocatalysts for DMFC 198
5.2.1	Electrocatalysis for Methanol Oxidation 198
5.2.2	Electrocatalyst Development 199
5.2.3	Spray Conversion Reaction Platform for Electrocatalyst
	Manufacturing 202
5.3	DMFC Electrocatalyst Characterization and Evaluation 203
5.3.1	Physical Characterization 204
5.3.2	Electrochemical Evaluation 208
5.3.2.1	Thin Film Rotating Disc Electrode (TFRDE) Catalyst
	Characterization 208
5.3.2.2	Fuel Cell Evaluation 210
5.3.3	Durability Study 212
5.4	DMFC Performance Advancement via MEA Design 215
5.4.1	Electrocatalyst Layer Design 215
5.4.2	Hydrocarbon Membrane for DMFC Performance
	Improvement 217
5.4.3	Other Aspects of DMFC Catalyst Development 220
5.5	Prospects for DMFC 222
5.6	Conclusions 222
	References 224
6	Platinum Alloys as Anode Catalysts for Direct Methanol Fuel Cells 227
	Ermete Antolini
6.1	Introduction 227
6.2	Phase Diagram vs. Activity: New Chances for DMFC Anodes 229
6.2.1	PtRu Catalysts: The Effect of Alloying and Ru Oxide Presence 229
6.2.2	PtSn Catalysts: Activity of PtSn Alloys and Non-Alloyed
	$Pt-SnO_x$ 233
6.2.3	Pt-Co and Pt-Ni Catalysts: Effect of Alloying and $CoO_x$ and
	$NiO_x$ Presence 235
6.3	Preparation Methods of Pt Alloys 238
6.3.1	Unsupported Catalysts 238
6.3.2	Supported Catalysts 240
6.4	Activity Evaluation of Pt Alloys 242
6.4.1	Pt-Based Binary Catalysts 243
6.4.1.1	Pt-W 243
6.4.1.2	Pt-Mo 244
6.4.1.3	Pt-Au 245
6.4.2	Ternary Pt-Ru-Based Catalysts 246