

Preface

Low temperature fuel cells are electrochemical devices that convert chemical energy directly to electricity. They have great potential for both stationary and transportation applications and are expected to help address the energy and environmental problems that have become prevalent in our society. Despite their great promise, commercialization has been hindered by lower than predicted efficiencies and the high cost of electrocatalysts in the electrodes.

Highly dispersed Pt nanoparticles (2–3 nm) on carbon black are commonly used as electrocatalysts for both fuel oxidation (anode) and oxygen reduction (cathode) reactions in low temperature fuel cells. In a hydrogen fuel cell, hydrogen oxidation is an extremely fast reaction and requires low Pt catalyst loading ($<0.05 \text{ mg/cm}^2$). For more than five decades, the predominant work has been focused on the development of novel catalysts for the oxygen reduction reaction (ORR), which has sluggish kinetics and is responsible for the high overpotential observed in the low current region. Significant progress on Pt reduction (from $>1.0 \text{ mg/cm}^2$ to $\sim 0.4 \text{ mg/cm}^2$) in the cathode has been achieved by optimizing the membrane electrode assembly (MEA) over the past two decades. However, the rising price of Pt continues to offset this effort.

In direct alcohol fuels cells (DAFCs), some simple organic molecules such as methanol, ethanol, formic acid, and ethylene glycol are used as alternative fuels. Besides the slow kinetics of ORR in the cathode, the slow alcohol oxidation reaction on Pt is another major contribution to low DAFC performance.

Recent intensive research efforts have led to the development of less expensive and more abundant electrocatalysts for fuel cells. This book aims to summarize recent advances of electrocatalysis in oxygen reduction and alcohol oxidation, with a particular focus on low- and non-Pt electrocatalysts. The book is divided into two parts containing 24 chapters total. All the chapters were written by leading experts in their fields from Asia, Europe, North America, South America, and Africa. The first part contains six chapters and focuses on the electro-oxidation reactions of small organic fuels. The subsequent eighteen chapters cover the oxygen reduction reactions on low- and non- Pt catalysts.

Chapter 1 discusses the current status of electrocatalysts development for methanol and ethanol oxidation. Chapter 2 presents a systematic study of electrocatalysis of methanol oxidation on pure and Pt or Pd overlayer-modified tungsten carbide, which has similar catalytic behavior to Pt. Chapters 3 and 4 outline the understanding of formic acid oxidation mechanisms on Pt and non-Pt catalysts and recent development of advanced electrocatalysts for this reaction. The faster kinetics of the alcohol oxidation reaction in alkaline compared to acidic medium opens up the possibility of using less expensive metal catalysts. Chapters 5 and 6 discuss the applications of Pt and non-Pt-based catalysts for direct alcohol alkaline fuel cells.

Chapters 7–12 focus on the electrocatalysis of carbon-based non-precious metal catalysts. The unique properties and fuel cell applications of various carbon based catalysts are intensively discussed in these chapters. Chapter 7 summarizes the fundamental studies on the electrocatalytic properties of metallomacrocyclic and other non-macrocyclic complexes. Chapter 8 and 9 review the progress made in the past 5 years of pyrolyzed carbon-supported nitrogen-coordinated transition metal complexes. Chapter 10 gives a comprehensive discussion on the role of transitional metals in the ORR electrocatalysts in acidic medium. Chapter 11 introduces modeling tools such as density functional theory (DFT) and *ab initio* molecular dynamics (AIMD) simulation for chemical reaction studies. It also presents a theoretical point of view of the ORR mechanisms on Pt-based catalysts, non-Pt metal catalysts, and non-precious metal catalysts. Chapter 12 presents an overview on recent progresses in the development of carbon-based metal-free ORR electrocatalysts, as well as the correlation between catalyst structure and their activities.

Chapter 13 and 14 summarize the development of transitional metal oxides and transition metal chalcogenides for ORR, respectively. Chapter 15 is the only chapter in this book dedicated to the ORR catalysis of alkaline fuel cells. Electrocatalytic properties of various non-Pt catalysts including Ag, Pd, transition metal macrocycles, metal oxides, and multifunctional materials are presented. Fundamental issues related to the design of low-cost, high-performance electrocatalysts for alkaline fuel cells are discussed. Chapter 16 and 17 review the recent advances on the study of ORR on Au and Pd-based catalysts, respectively.

Chapters 18–21 discuss core–shell and advanced Pt alloy catalysts (which also can be considered to have a core–shell structure). Chapter 18 studies the fundamentals of Pt core–shell catalysts synthesized by selective removal of transition metals from transition metal-rich Pt alloys. Chapter 19 outlines the advances of core–shell catalysts synthesized by both electrochemical and chemical methods. The performance, durability, and challenges of core–shell catalyst in fuel cell applications are also discussed. Chapter 20 reviews the recent analyses of the various aspects intrinsic to the core–shell structure including surface segregation, metal dissolution, and catalytic activity, using DFT, molecular dynamics, and kinetic Monte Carlo. Chapter 21 presents the recent understanding of activity dependences on specific sites and local strains in the surface of bulk and core–shell nanoparticle based on DFT calculation results.

The last three chapters are dedicated to improving the durability of the catalyst/electrode. Chapter 22 reports the development and evaluation of bimetallic Pt–Ru (Ir) oxygen evolution catalysts on 3M's nanostructured thin film (NSTF). This type of catalyst may significantly reduce carbon corrosion and Pt dissolution during transient conditions of fuel cells. Chapter 23 discusses the unique properties of carbide-modified carbon as the support for fuel cell catalysts. The final chapter gives a comprehensive review of novel materials other than carbon black as catalyst support. The interactions between the supports and catalysts are intensively discussed in the last two chapters.

I believe this book includes most of the state-of-the-art development of low cost and high performance catalysts and our understanding of fuel cell reactions. I hope that this book can be a comprehensive reference for those who are interested in the related areas. I truly believe that some of the technologies described in this book will be applied in the mass-produced fuel cells in the not-too-distant future.

I would like to thank all the authors of each chapter for their great contributions and efforts to this project. I would also like to acknowledge the invitation from Dr. Anthony Doyle, Senior Editor at Springer to edit the book, and Ms. Christine Velarde and Grace Quinn for their kind help in the preparation of this book. Finally, I would like to express my appreciation to my family for their understanding and support of my work.

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