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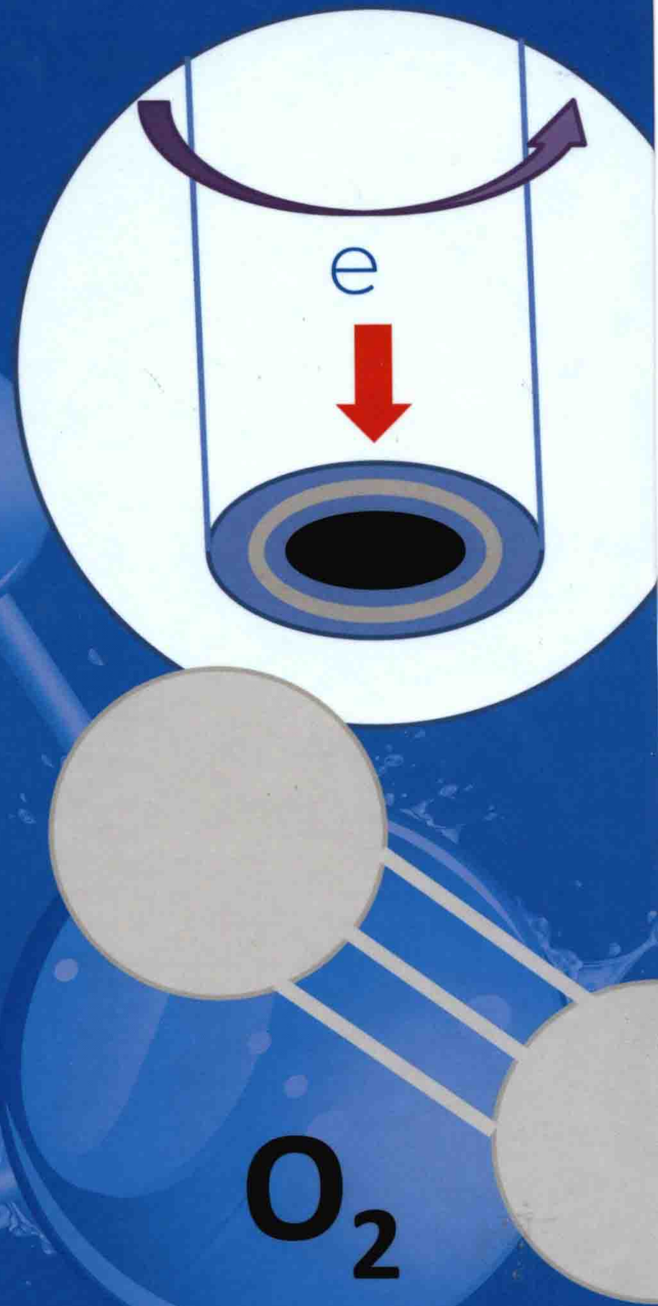

Rotating Electrode Methods and Oxygen Reduction Electrocatalysts

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ROTATING ELECTRODE METHODS AND OXYGEN REDUCTION ELECTROCATALYSTS

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PREFACE

Rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) techniques are one kind of the important and commonly used methods in electrochemical science and technology, particularly, in the fundamental understanding of electrochemical catalytic reaction mechanisms such as electrocatalytic oxygen reduction reaction (ORR). The kinetics and mechanisms of ORR catalyzed by both noble metal- and nonnoble metal-based electrocatalysts are the most important aspects in fuel cell and other ORR-related electrochemical technologies. Using RDE and RRDE to evaluate the activities of catalysts and their catalyzed ORR mechanisms is necessary and also one of the most feasible approaches in the development of ORR electrocatalysts.

In developing ORR electrocatalysts, significant challenges exist in achieving high catalyst activity and stability. To facilitate the effort to overcome these challenges, a book with focus on the catalyzed ORR and its associated testing and diagnosis of ORR catalysts is particularly useful. Although all researchers in the area of ORR-related electrocatalysts use RDE/RRDE as routine techniques to evaluate their catalysts and explore the catalyzed ORR mechanisms, based on our observation, however, a fundamental understanding of these methods seems not being fully achieved. Some confusion can be found in the literature when RDE/RRDE methods were used and the data explained. Therefore, a detailed and comprehensive description about these techniques from fundamentals to applications is definitely helpful and may be necessary.

In Chapter 1 of this book, the necessary parameters for both RDE/RRDE analysis in ORR study, such as O_2 solubility, O_2 diffusion coefficient, and the viscosity of the aqueous electrolyte solutions, are discussed in depth in terms of their definitions, theoretical background, and experimental measurements. The effects of type/concentration of electrolyte, temperature, and pressure on values of these parameters are also discussed. To provide the readers with useful information, the values of these parameters are collected from the literature, and summarized in several tables. In addition, the values of both the O_2 solubility and diffusion coefficient in Nafion® membranes or ionomers are also listed in the tables. Hopefully, this chapter would be able to serve as a data source for the later chapters of this book, and also the readers could find it useful in their experimental data analysis.

In Chapter 2, to facilitate understanding and preparing the basic knowledge for rotating electrode theory, both the electron transfer and reactant transport theories at the interface of electrode/electrolyte are presented. Regarding the reactant transport, three transportation modes such as diffusion, migration, and convection are described. A focusing discussion is given to the reactant diffusion near the electrode surface using both Fick's first and second laws. In addition, based on the approach in the literature, the kinetics of reactant transport near and within porous matrix electrode layer and its effect on the electron transfer process is also presented using a simple equivalent electrode/electrolyte interface.

In Chapter 3, to give some basic knowledge and concepts, some fundamentals about the catalyst activity and stability of ORR electrocatalysts, which are the targeted research systems by rotating electrode methods, are presented. A detailed description about the electrocatalysts and catalyst layers and their applications for ORR in terms of their types, structures, properties, catalytic activity/stability, as well as their research progress in the past several decades are also given. Furthermore, both the synthesis and characterization methods for ORR electrocatalysts, and the fabrication procedures for catalyst layers are also reviewed.

In Chapter 4, the fundamentals of ORR including thermodynamics and electrode kinetics are presented. The ORR kinetics including reaction mechanisms catalyzed by different electrode materials and catalysts including Pt, Pt alloys, carbon materials, and nonnoble metal catalysts are discussed based on literature in terms of both experiment and theoretical approaches. It is our belief that these fundamentals of ORR are necessary in order to perform the meaningful characterization of catalytic ORR activity using both RDE and RRDE methods.

In Chapter 5, to give readers the knowledge how to appropriately use RDE in their ORR study, fundamentals of both the electron transfer process on electrode surface and diffusion-convection kinetics near the rotating electrode are presented. Two kinds of RDE and their associated theories of the diffusion-convection kinetics and its coupling with the electron transfer process are presented, one is the smooth electrode surface, and the other is the catalyst-layer coated electrode. For measurements using RDE method, the apparatus of RDE and its associated devices such as rotator and electrochemical cell are described to give the readers the basic sense about this technique. The measurement procedure including RDE preparation, catalyst layer fabrication, current–potential curve recording, the data analysis, as well as the cautions in RDE measurements are also discussed in this chapter.

In Chapter 6, the importance of RRDE fundamentals and practical usage in ORR study is emphasized in terms of both the electron transfer process on electrode surface, diffusion-convection kinetics near the electrode, and the ORR mechanism, particularly the detection of intermediate such as peroxide. One of most important parameters of RRDE, the collection efficiency, is deeply described including its concept, theoretical expression, as well as experiment calibration. Its usage in evaluating the ORR kinetic parameters, the apparent electron transfer, and percentage of peroxide formation is also presented. In addition, the measurement procedure including RRDE preparation, current–potential curve recording, and the data analysis are also discussed in this chapter.

Chapter 7 reviews the applications of RDE and RRDE techniques in ORR research and its associated catalyst evaluation. Some typical examples for RDE and RRDE analysis in obtaining the ORR kinetic information such as the overall electron transfer number, electron transfer coefficiency, and exchange current density are also given in this chapter. It demonstrates that both RDE and RRDE methods are a powerful tool in ORR study, and using RDE and RRDE methods, ORR has been successfully studied on Pt electrode, carbon electrode, monolayer metal catalyst, Pt-based catalyst, and nonnoble metal-based catalysts.

It is our hope that this book could be used as a reference for college/university students including undergraduates and graduates, scientists and engineers who work in the areas of energy, electrochemistry science/technology, fuel cells, and batteries.

We would like to acknowledge with deep appreciation our families for their understanding and support of our work. If technical errors exist in this book, we would deeply appreciate the readers' constructive comments for correction and further improvement.

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BIOGRAPHY

Dr Wei Xing is a Professor and R&D Director at the Changchun Institute of Applied Chemistry, Chinese Academy of Sciences (CIAC-CAS). In 1987, Dr Xing received his PhD in Electrochemistry from CIAC-CAS. Dr Xing has more than 25 years of experience as an electrochemist in the area of oxygen reduction reaction and fuel cells, during which, as one of the key senior researchers, he established, and continues to lead the Laboratory of Advanced Power Sources at CIAC-CAS, which develops novel proton exchange membrane fuel cells (PEMFC) catalysts and technologies. His research is mainly concentrated on the R&D of fuel cell technologies including PEMFCs, direct methanol fuel cells (DMFCs), and direct formic acid fuel cells (DFAFCs), in which cathode catalyst development for oxygen reduction reaction is the major focus. To date, he has published more than 160 referred journal papers, 3 books, and 39 patents.

Dr Geping Yin is a Professor at Harbin Institute of Technology (HIT), China, the Vice-Dean of School of Chemical Engineering and Technology and the Director of HIT's Institute of Advanced Chemical Power Sources. She received her BS and PhD in Electrochemistry from HIT in 1982 and 2000, respectively. She has over 30 years of R&D experience in theoretical and applied electrochemistry, and over 15 years in fuel cells. After completing her BS, she took a Lecture position at HIT in 1988, and was promoted to associate and full professor in 1993 and 2000, respectively. Prof. Yin carried out two terms of visiting scholar research at Tokyo Institute of Technology (1985–1986) and Yokohama National University (2009–2010). Prof. Yin serves on several professional Committees or Associations in China, including the Power Sources Committee of Chinese Institute of Communications, and Chinese Industrial Association of Power Sources. She is also member of Editorial Boards for several journals, such as Journal of Chemical Engineering of Chinese Universities, Electrochemistry, Chinese Journal of Power Sources, Battery, and Carbon. Up to now, Prof. Yin has published more than 160 SCI papers, which have been cited for 3100 times (single most cited for 250 times, H-index 29). Some of these papers were selected as "Hot Papers in Engineering" by ISI Web of Knowledge, the top 50 most-cited articles by Chinese mainland authors published in Elsevier's Environmental Sciences journals, and "one hundred most influential international academic papers" in China by Institute of Scientific & Technical Information of China. Prof. Yin is an active member of Electrochemistry Committee of the Chinese Chemical Society and Lead-acid Batteries Committee of Electrotechnical Society of China.

Dr Jiujun Zhang is a Principal Research Officer and Fuel Cell Catalysis Core Competency Leader at the National Research Council of Canada (NRC) Institute for Fuel Cell Innovation (NRC-IFCI, now changed to Energy, Mining & Environment Portfolio (NRC-EME)). Dr Zhang received his BS and MSc in Electrochemistry from Peking University in 1982 and 1985, respectively, and his PhD in Electrochemistry from Wuhan University in 1988. After completing his PhD, he took a position as an associate professor at the Huazhong Normal University for 2 years. Starting in 1990, he carried out three terms of postdoctoral research at the California Institute of Technology, York University, and the University of British Columbia. Dr Zhang has over 30 years of R&D experience in theoretical and applied electrochemistry, including over 15 years of fuel cell R&D (among these 6 years at Ballard Power Systems and 10 years at NRC), and 3 years of electrochemical sensor experience. Dr Zhang holds several adjunct professorships, including one at the University of Waterloo, one at the University of British Columbia, and one at Peking University. Up to now, Dr Zhang has coauthored more than 300 publications including over 200 refereed journal papers with approximately 6200 citations, 11 edited/coauthored books, 11 conference proceeding papers, 12 book chapters, as well as 50 conference and invited oral presentations. He also holds over 10 US/EU/WO/JP/CA patents, 9 US patent publications, and produced in excess of 80 industrial technical reports. Dr Zhang serves as the editor/editorial board member for several international journals as well as Chief-in-Editor for book series (Electrochemical Energy Storage and Conversion, CRC press). Dr Zhang is an active member of The Electrochemical Society, the International Society of Electrochemistry, and the American Chemical Society.

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