Electrochemical Impedance Spectroscopy in PEM Fuel Cells

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Fundamentals and Applications

Springer

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ISBN 978-1-84882-845-2 e-ISBN 978-1-84882-846-9
DOI 10.1007/978-1-84882-846-9
Springer London Dordrecht Heidelberg New York

British Library Cataloguing in Publication Data
A catalogue record for this book is available from the British Library

Library of Congress Control Number: 2009940583

Cover design: eStudioCalamar, Figueres/Berlin

Printed on acid-free paper

Springer is part of Springer Science+Business Media (www.springer.com)

Preface

Proton exchange membrane (PEM) fuel cells hold the promise of environmentally friendly power generation due to their low/zero emissions in comparison with internal combustion engines. PEM fuel cells also have several other advantages over conventional energy converting devices, including both high efficiency and power density, which make them unique across a wide range of portable, stationary, and transportation power applications. However, several challenges remain, including cost and reliability/durability. Intensive R&D is therefore still needed to address these challenges in order to achieve sustainable commercialization. In this ongoing R&D, fuel cell testing and diagnostics play a critical role in material characterization, performance optimization, design validation, and fundamental understanding for further development. Among the testing and diagnostic tools used in fuel cell R&D, AC impedance spectroscopy (or electrochemical impedance spectroscopy, EIS) is regarded by scientists and engineers as a powerful technique.

In recent years, EIS has been widely used in studies of electrochemical systems, including batteries and materials corrosion, and is also being increasingly employed by researchers in PEM fuel cell studies. During the last few decades this technique has emerged as a primary tool in PEM fuel cell diagnosis.

Because PEM fuel cells are being developed at an increasingly rapid rate, with many new researchers entering the field, an overview of EIS methods is warranted to describe the basic principles, measurement techniques, and applications of this tool. Current researchers may or may not be electrochemists. Indeed, as fuel cells grow in popularity among students in mechanical, chemical, and electrical engineering, in environmental studies and engineering, as well as in materials science and engineering, fuel cell courses are being offered worldwide at many universities and research institutes, as well as in industry settings. The need for a text or reference book on fuel cell EIS has motivated the writing of this volume.

Each of the authors is closely involved in PEM fuel cell technology, including the areas of design, materials, components, operation, diagnostics, and systems. The present publication is therefore a direct result of many years' experience working on EIS diagnosis of PEM fuel cells. The authors hope this book will provide a general understanding of EIS techniques, as well as detailed guidance in the application of this technology to PEM fuel cells. The volume is also designed with the intention that other potential readers, especially non-electrochemists, will find it an accessible and useful introduction to EIS techniques, will gain basic knowledge of EIS testing, and after reading it will be well prepared for experimental result analysis. Although the book's primary audience is intended to be fuel cell researchers and practising engineers in universities, research institutes, and industries who perform PEM fuel cell testing and diagnostics, some undergraduate students, as well as M.Sc. and Ph.D. candidates in mechanical engineering, chemical and electrochemical engineering, environmental engineering, and materials science and engineering may also find this book a very useful reference source.

The book comprises six chapters and contains comprehensive information on the fundamentals of PEM fuel cells, as well as the basic principles of EIS electronics, measurements, and applications. Chapter 1 introduces readers to the general field of PEM fuel cells, including an overview of fuel cell history, the different types of fuel cells, and electrochemical approaches in fuel cell studies. Chapter 2 provides the electrical fundamentals that are the foundation for understanding spectra analysis based on electric equivalent circuits. Chapter 3 gives a brief overview of EIS fundamentals, covering topics such as impedance and its physical and chemical processes, and the relationships between impedance spectroscopy and other electrochemical techniques. Chapter 4 describes the equivalent circuits frequently used in PEM fuel cell diagnosis and their corresponding AC impedance spectra. Following this coverage of fundamentals in the first four chapters, progress in EIS techniques and applications is reviewed in Chapters 5 and 6, accompanied by some typical example analyses. These two chapters are more related to the practice and state-of-the-art development of EIS applications in PEM fuel cells. Literature published in scientific journals has been cited in this book up to the time of writing the final draft for each specific chapter.

We would like to take this opportunity to thank the many outstanding engineers and scientists who made direct contributions to the writing of this book at the National Research Council of Canada's Institute for Fuel Cell Innovation. Special thanks go to Dr. Yanghua Tang for his constructive contribution to Chapter 2, to Mr. Jason Ng Cheng Hin for his efficient editing of all the images, and to Dr. Dania Sheldon for her effective editing and indexing services. We also wish to thank the family members of all the authors for their continued patience, understanding, encouragement, and support throughout the writing of this monograph. Finally, it is our pleasure to acknowledge with gratitude the financial support provided by the NRC-Helmholtz Project, which made possible the editing and publication of this work.

If technical errors are found, all of the authors would deeply appreciate readers' constructive comments for correction and further improvement.

Vancouver, BC, Canada
May 2009

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Contents

Acronyms and Abbreviations

AC	Alternating current
AFC	Alkaline fuel cell
BCPE	Bounded constant phase element
BW	Bounded Warburg element
CB	Carbon black
CE	Counter electrode
CFE	Carbon fibre electrode
CL	Catalyst layer
CNLS	Complex non-linear least squares
CNT	Carbon nanotube
CPE	Constant phase element
DC	Direct current
DEFC	Direct ethanol fuel cell
DFAFC	Direct formic acid fuel cell
DFT	Discrete Fourier transform
DHE	Dynamic hydrogen electrode
DMFC	Direct methanol fuel cell
EDL	Electrical double layer
EIS	Electrochemical impedance spectroscopy
FFT	Fast Fourier transform
FRA	Frequency response analyzer
FT-EIS	Fourier transform EIS
GDE	Gas diffusion electrode
GDL	Gas diffusion layer
HF	High frequency
HFR	High-frequency resistance
HOR	Hydrogen oxidation reaction
IAE	Ionized air reference electrode
KCL	Kirchhoff's current law
K–K	Kramers–Kronig
KVL	Kirchhoff's voltage law
LANL	Los Alamos National Laboratory

LST	Linear systems theory
MCFC	Molten carbonate fuel cell
MEA	Membrane electrode assembly
NHE	Normal hydrogen electrode
NLLS	Non-linear least squares
OCV	Open circuit voltage
ORR	Oxygen reduction reaction
Ox	Oxidant
PAFC	Phosphoric acid fuel cell
PBI	Polybenzimidazole
PEFC	Polymer electrolyte fuel cell
PEM	Proton exchange membrane
PEMFC	Polymer electrolyte membrane fuel cell
PEO	Polyethylene oxide
PPY-PSS	Polypyrrole polystyrene sulfonate
PTFE	Polytetrafluoroethylene
RC	Resistor-capacitor
RCL	Resistor-capacitor-inductor
Rd	Reductant
RDE	Rotating disk electrode
RDS	Rate-determining step
RE	Reference electrode
RHE	Reversible hydrogen electrode
RL	Resistor-inductor
RRDE	Rotating ring-disk electrode
SCE	Saturated calomel electrode
SHE	Standard hydrogen reference electrode
SOFC	Solid oxide fuel cell
SWCNT	Single-walled carbon nanotube
TDS	Thermal desorption spectroscopy
W	Warburg
WE	Working electrode
XPS	X-ray photoelectron spectroscopy