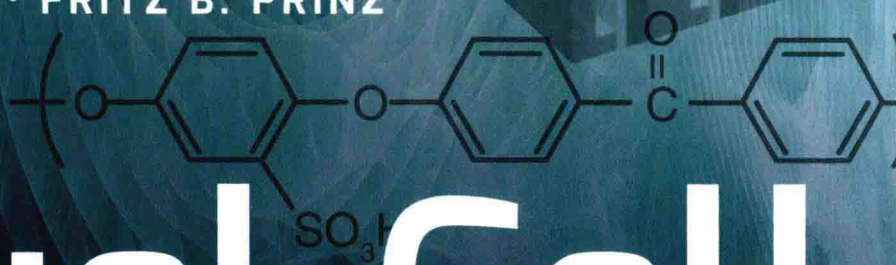


RYAN O'HAYRE · SUK-WON CHA

WHITNEY COLELLA · FRITZ B. PRINZ



# Fuel Cell Fundamentals

Third Edition

(fixed g

Air

(fixed ga

WILEY

---

# FUEL CELL FUNDAMENTALS

---

Third Edition

**RYAN O'HAYRE**

Department of Metallurgical and Materials Engineering  
Colorado School of Mines  
[PhD, Materials Science and Engineering, Stanford University]

**SUK-WON CHA**

School of Mechanical and Aerospace Engineering  
Seoul National University  
[PhD, Mechanical Engineering, Stanford University]

**WHITNEY G. COLELLA**

The G.W.C. Whiting School of Engineering and The Energy, Environment,  
Sustainability and Health Institute  
The Johns Hopkins University  
Gaia Energy Research Institute  
[Doctorate, Engineering Science, The University of Oxford]

**FRITZ B. PRINZ**

R.H. Adams Professor of Engineering  
Departments of Mechanical Engineering and Material Science and Engineering  
Stanford University

**WILEY**

This book is printed on acid-free paper. ∞

Copyright © 2016 by John Wiley & Sons, Inc. All rights reserved.  
Published by John Wiley & Sons, Inc., Hoboken, New Jersey.  
Published simultaneously in Canada.

No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning, or otherwise, except as permitted under Section 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, (978) 750-8400, fax (978) 646-8600, or on the web at [www.copyright.com](http://www.copyright.com). Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201) 748-6011, fax (201) 748-6008, or online at [www.wiley.com/go/permissions](http://www.wiley.com/go/permissions).

**Limit of Liability/Disclaimer of Warranty:** While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with the respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives or written sales materials. The advice and strategies contained herein may not be suitable for your situation. You should consult with a professional where appropriate. Neither the publisher nor the author shall be liable for damages arising herefrom.

For general information about our other products and services, please contact our Customer Care Department within the United States at (800) 762-2974, outside the United States at (317) 572-3993 or fax (317) 572-4002.

Wiley publishes in a variety of print and electronic formats and by print-on-demand. Some material included with standard print versions of this book may not be included in e-books or in print-on-demand. If this book refers to media such as a CD or DVD that is not included in the version you purchased, you may download this material at <http://booksupport.wiley.com>. For more information about Wiley products, visit [www.wiley.com](http://www.wiley.com).

**Library of Congress Cataloging-in-Publication Data is available:**

ISBN 9781119113805 (Cloth)  
ISBN 9781119114208 (ePDF)  
ISBN 9781119114154 (ePub)

Cover Design: Wiley  
Cover Illustrations: Ryan O'Hayre  
Cover Image: Glacial abstract shapes © ppart/iStockphoto

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

*To the parents who nurtured us.*

*To the teachers who inspired us.*



# PREFACE

---

Imagine driving home in a fuel cell car with nothing but pure water dripping from the tailpipe. Imagine a laptop computer that runs for 30 hours on a single charge. Imagine a world where air pollution emissions are a fraction of that from present-day automobiles and power plants. These dreams motivate today's fuel cell research. While some dreams (like cities chock-full of ultra-low-emission fuel cell cars) may be distant, others (like a 30-hour fuel cell laptop) may be closer than you think.

By taking fuel cells from the dream world to the real world, this book teaches you the *science* behind the technology. This book focuses on the questions "*how*" and "*why*." Inside you will find straightforward descriptions of *how* fuel cells work, *why* they offer the potential for high efficiency, and *how* their unique advantages can best be used. Emphasis is placed on the fundamental scientific principles that govern fuel cell operation. These principles remain constant and universally applicable, regardless of fuel cell type or technology.

Following this philosophy, the first part, "Fuel Cell Principles," is devoted to basic fuel cell physics. Illustrated diagrams, examples, text boxes, and homework questions are all designed to impart a unified, *intuitive* understanding of fuel cells. Of course, no treatment of fuel cells is complete without at least a brief discussion of the practical aspects of fuel cell technology. This is the aim of the second part of the book, "Fuel Cell Technology." Informative diagrams, tables, and examples provide an engaging review of the major fuel cell technologies. In this half of the book, you will learn how to select the right fuel cell for a given application and how to design a complete system. Finally, you will learn how to assess the potential environmental impact of fuel cell technology.

Comments or questions? Suggestions for improving the book? Found a typo, think our explanations could be improved, want to make a suggestion about other important concepts to discuss, or have we got it all wrong? Please send us your feedback by emailing us at [fcf3@yahoogroups.com](mailto:fcf3@yahoogroups.com). We will take your suggestions into consideration for the next edition. Our website <http://groups.yahoo.com/group/fcf3> posts these discussions, fliers for the book, and additional educational materials. Thank you.

# ACKNOWLEDGMENTS

---

The authors would like to thank their friends and colleagues at Stanford University and the former Rapid Prototyping Laboratory (RPL), now the Nano-Prototyping Laboratory (NPL), for their support, critiques, comments, and enthusiasm. Without you, this text would not have been written! The beautiful figures and illustrations featured in this textbook were crafted primarily by Marily Mallison, with additional illustrations by Dr. Michael Sanders—their artistic touch is greatly appreciated!

The authors would like to thank the Deans of the Stanford School of Engineering, Jim Plummer and Channing Robertson, and John Bravman, Vice Provost Undergraduate Education, for the support that made this book possible. We would also like to acknowledge Honda R&D, its representatives J. Araki, T. Kawanabe, Y. Fujisawa, Y. Kawaguchi, Y. Higuchi, T. Kubota, N. Kuriyama, Y. Saito, J. Sasahara, and H. Tsuru, and Stanford's Global Climate and Energy Project (GCEP) community for creating an atmosphere conducive to studying and researching new forms of power generation. All members of RPL/NPL are recognized for stimulating discussions. Special thanks to Dr. Tim Holme for his innumerable contributions, including his careful review of the text, integration work, nomenclature and equation summaries, and the appendixes. Thanks also to Professor Rojana Pornprasertsuk, who developed the wonderful quantum simulation images for Chapter 3 and Appendix D. The authors are grateful to Professor Yong-il Park for his help in the literature survey of Chapter 9 and Rami Elkhatab for his significant contributions in writing this section. Professor Juliet Risner deserves gratitude for her beautiful editing job, and Professor Hong Huang deserves thanks for content contribution. Dr. Jeremy Cheng, Dr. Kevin Crabb, Professor Turgut Gur, Shannon Miller, Masafumi Nakamura, and A. J. Simon also provided significant editorial advice. Thanks to Dr. Young-Seok Jee, Dr. Daeheung Lee, Dr. Yeageun Lee,



Dr. Wonjong Yu, and Dr. Yusung Kim for their contributions to Chapters 6 and 13. Special thanks to Rusty Powell and Derick Reimanis for their careful editing contributions to the second edition. Finally, thanks to colleagues at the Colorado School of Mines (CSM), including Bob Kee and Neal Sullivan for their helpful discussions and for a decade's worth of students at CSM for catching typos and identifying areas in need for clarification for this third edition.

We would like to extend our gratitude to Professor Stephen H. Schneider, Professor Terry Root, Dr. Michael Mastrandrea, Mrs. Patricia Mastrandrea, Dr. Gerard Ketafani, and Dr. Jonathan Koomey. We would also like to thank the technical research staff within the U.S. Department of Energy (DOE) complex, including researchers at DOE national laboratories [Sandia National Laboratories (SNL), Lawrence Berkeley National Laboratory (LBNL), Argonne National Laboratory (ANL), the National Renewable Energy Laboratory (NREL), and Lawrence Livermore National Laboratory (LLNL), among others]. We would also like to thank research participants within the International Energy Agency (IEA) Stationary Fuel Cell Annex, the American Institute of Chemical Engineers (AIChE) Transport and Energy Processes Division (TEP), and the National Academy of Engineering (NAE) Frontiers of Engineering (FOE) program.

For intellectually stimulating discussions on energy system design, we also would like to thank Dr. Salvador Aceves (LLNL), Dr. Katherine Ayers (ProtonOnsite Inc.), Professor Nigel Brandon (Imperial College London), Mr. Tom Brown (California State University Northridge), Dr. Viviana Cigolotti [Energy and Sustainable Economic Development (ENEA)], Professor Peter Dobson [University of Oxford (Oxon)], Dr. Elango Elangovan (Ceramtec Inc.), Professor Ferhal Erhun, Dr. Angelo Esposito (European Institute for Energy Research), Dr. Hossein Ghezel-Ayagh [FuelCell Energy Inc. (FCE)], Dr. Lorenz Gubler [Paul Scherrer Institut (PSI)], Dr. Monjid Hamdan (Giner Inc.), Dr. Joseph J. Hartvigsen (Ceramtec Inc.), Professor Michael Hickner (The Pennsylvania State University), Professor Ben Hobbs (Johns Hopkins University), Professor Daniel M. Kammen [University of California at Berkeley (UCB)], Professor Jon Koomey, Dr. Scott Larsen (New York State Energy Research and Development Authority), Mr. Bruce Lin (EnerVault Inc.), Dr. Ludwig Lipp (FCE), Dr. Bernard Liu (National Cheng Kung University), Professor V. K. Mathur (University of New Hampshire), Dr. Marianne Mintz (ANL), Professor Catherine Mitchell (University of Exeter), Dr. Cortney Mittelsteadt (Giner Inc.), Dr. Yasunobu Mizutani (ToHo Gas Co. Ltd.), John Molburg (Argonne National Laboratory), Dr. Angelo Moreno [Italian National Agency for New Technologies, Energy and Sustainable Economic Development (ENEA)], Professor Vincenzo Mulone (University of Rome Tor Vergata), Dr. Jim O'Brien (Idaho National Laboratory), Professor Joan Ogden (University of California at Davis), Dr. Pinakin Patel (FCE), Dr. Randy Petri (Versa Power Inc.), Professor Bruno Pollet (University of Ulster), Dr. Peter Rieke [Pacific Northwest National Laboratory (PNNL)], Dr. Subhash C. Singhal (PNNL), Professor Colin Snowden (Oxon), Professor Robert Socolow (Princeton University), Mr. Keith Spitznagel (KAS Energy Services LLC), Professor Robert Steinberger-Wilckens (University of Birmingham), Dr. Jeffry Stevenson (PNNL), Professor Richard Stone (Oxon), Professor Etim Ubong (Kettering University), Professor Eric D. Wachsman (University of Maryland), Professor Xia Wang (Oakland University), and Professor Yingru Zhao (Xiamen University).

Fritz B. Prinz wants to thank his wife, Gertrud, and his children, Marie-Helene and Benedikt, for their love, support, and patience.

Whitney G. Colella would like to thank her friends and family, especially the Bakers, Birchards, Chens, Colellas, Culvers, Efthimiades, Hoffmans, Jaquintas, Judges, Louies, Mavrovitis, Omlands, Pandolfis, Panwalkers, Qualtieris, Scales, Smiths, Spielers, Tepers, Thananarts, Tragers, Wasleys, and Wegmans.

Suk-Won Cha wishes to thank Unjung, William, and Sophia for their constant support, love, and understanding.

Ryan O'Hayre sends his thanks and gratitude to Lisa for her friendship, encouragement, confidence, support, and love. Thanks also to Kendra, Arthur, Morgan, little Anna, and little Robert. Ryan has always wanted to write a book ... probably something about dragons and adventure. Well, things have a funny way of working out, and although he ended up writing about fuel cells, he had to put the dragons in somewhere. ...



# NOMENCLATURE

---

Symbol	Meaning	Common Units
$A$	Area	$\text{cm}^2$
$A_c$	Catalyst area coefficient	Dimensionless
$a$	Activity	Dimensionless
ASR	Area specific resistance	$\Omega \cdot \text{cm}^2$
$C$	Capacitance	F
$C_{\text{dl}}$	Double-layer capacitance	F
$c^*$	Concentration at reaction surface	$\text{mol}/\text{cm}^2$
$c$	Concentration	$\text{mol}/\text{m}^3$
$c$	Constant describing how mass transport affects concentration losses	V
$c_p$	Heat capacity	$\text{J}/\text{mol} \cdot \text{K}$
$D$	Diffusivity	$\text{cm}^2/\text{s}$
$E$	Electric field	$\text{V}/\text{cm}$
$E$	Thermodynamic ideal voltage	V
$E_{\text{thermo}}$	Thermodynamic ideal voltage	V
$E_T$	Temperature-dependent thermodynamic voltage at reference concentration	V
$F$	Helmholtz free energy	J, J/mol
$F$	Faraday constant	96,485 C/mol
$F_k$	Generalized force	N
$f$	Reaction rate constant	$\text{Hz}, \text{s}^{-1}$
$f$	Friction factor	Dimensionless

Symbol	Meaning	Common Units
$G, g$	Gibbs free energy	J, J/mol
$g$	Acceleration due to gravity	m/s <sup>2</sup>
$\Delta G^\ddagger$	Activation energy barrier	J/mol, J
$\Delta G_{\text{act}}$	Activation energy barrier	J/mol, J
$H$	Heat	J
$H, h$	Enthalpy	J, J/mol
$H_C$	Gas channel thickness	cm
$H_E$	Diffusion layer thickness	cm
$h$	Planck's constant	$6.63 \times 10^{-34}$ J · s
$\hbar$	Reduced Planck constant, $h/2\pi$	$1.05 \times 10^{-34}$ J · s
$h_m$	Mass transfer convection coefficient	m/s
$i$	Current	A
$J$	Molar flux, molar reaction rate	mol/cm <sup>2</sup> · s
$\hat{J}$	Mass flux	g/cm <sup>2</sup> · s, kg/m <sup>2</sup> · s
$J_C$	Convective mass flux	kg/m <sup>2</sup> · s
$j$	Current density	A/cm <sup>2</sup>
$j_0$	Exchange current density	A/cm <sup>2</sup>
$j_0^0$	Exchange current density at reference concentration	A/cm <sup>2</sup>
$j_L$	Limiting current density	A/cm <sup>2</sup>
$j_{\text{leak}}$	Fuel leakage current	A/cm <sup>2</sup>
$k$	Boltzmann's constant	$1.38 \times 10^{-23}$ J/K
$L$	Length	m
$M$	Molar mass	g/mol, kg/mol
$\dot{M}$	Mass flow rate	kg/s
$M_{ik}$	Generalized coupling coefficient between force and flux	Varies
$m$	Mass	kg
$mc_p$	Heat capacity flow rate	kW/kg · °C
$N$	Number of moles	Dimensionless
$N_A$	Avogadro's number	$6.02 \times 10^{23}$ mol <sup>-1</sup>
$n$	Number of electrons transferred in the reaction	Dimensionless
$n_g$	Number of moles of gas	Dimensionless
$P$	Power or power density	W or W/cm <sup>2</sup>
$P$	Pressure	bar, atm, Pa
$Q$	Heat	J, J/mol
$Q$	Charge	C
$Q_h$	Adsorption charge	C/cm <sup>2</sup>
$Q_m$	Adsorption charge for smooth catalyst surface	C/cm <sup>2</sup>
$q$	Fundamental charge	$1.60 \times 10^{-19}$ C
$R$	Ideal gas constant	8.314 J/mol · K
$R$	Resistance	$\Omega$
$R_f$	Faradaic resistance	$\Omega$

Symbol	Meaning	Common Units
Re	Reynolds number	Dimensionless
$S, s$	Entropy	J/K, J/mol · K
$S/C$	Steam-to-carbon ratio	Dimensionless
Sh	Sherwood number	Dimensionless
$T$	Temperature	K, °C
$t$	Thickness	cm
$U$	Internal energy	J, J/mol
$u$	Mobility	cm <sup>2</sup> /V · s
$\bar{u}$	Mean flow velocity	cm/s, m/s
$V$	Voltage	V
$V$	Volume	L, cm <sup>3</sup>
$V$	Reaction rate per unit area	mol/cm <sup>2</sup> · s
$v$	Velocity	cm/s
$v$	Hopping rate	s <sup>-1</sup> , Hz
$v$	Molar flow rate	mol/s, mol/min
$W$	Work	J, J/mol
$X$	Parasitic power load	W
$x$	Mole fraction	Dimensionless
$x_v$	Vacancy fraction	mol vacancies/mol sites
$y_x$	Yield of element $X$	Dimensionless
$Z$	Impedance	$\Omega$
$z$	Height	cm

### Greek Symbols

Symbol	Meaning	Common Units
$\alpha$	Charge transfer coefficient	Dimensionless
$\alpha$	Coefficient for CO <sub>2</sub> equivalent	Dimensionless
$\alpha^*$	Channel aspect ratio	Dimensionless
$\beta$	Coefficient for CO <sub>2</sub> equivalent	Dimensionless
$\gamma$	Activity coefficient	Dimensionless
$\Delta$	Denotes change in quantity	Dimensionless
$\delta$	Diffusion layer thickness	m, cm
$\varepsilon$	Efficiency	Dimensionless
$\varepsilon_{FP}$	Efficiency of fuel processor	Dimensionless
$\varepsilon_{FR}$	Efficiency of fuel reformer	Dimensionless
$\varepsilon_H$	Efficiency of heat recovery	Dimensionless
$\varepsilon_O$	Efficiency overall	Dimensionless
$\varepsilon_R$	Efficiency, electrical	Dimensionless
$\varepsilon$	Porosity	Dimensionless
$\dot{\varepsilon}$	Strain rate	s <sup>-1</sup>

Symbol	Meaning	Common Units
$\eta$	Overvoltage	V
$\eta_{\text{act}}$	Activation overvoltage	V
$\eta_{\text{conc}}$	Concentration overvoltage	V
$\eta_{\text{ohmic}}$	Ohmic overvoltage	V
$\lambda$	Stoichiometric coefficient	Dimensionless
$\lambda$	Water content	Dimensionless
$\mu$	Viscosity	kg · m/s
$\mu$	Chemical potential	J, J/mol
$\tilde{\mu}$	Electrochemical potential	J, J/mol
$\rho$	Resistivity	$\Omega \text{ cm}$
$\rho$	Density	kg/cm <sup>3</sup> , kg/m <sup>3</sup>
$\sigma$	Conductivity	S/cm, ( $\Omega \cdot \text{cm}$ ) <sup>-1</sup>
$\sigma$	Warburg coefficient	$\Omega/\text{s}^{0.5}$
$\tau$	Mean free time	s
$\tau$	Shear stress	Pa
$\varphi$	Electrical potential	V
$\varphi$	Phase factor	Dimensionless
$\omega$	Angular frequency ( $\omega = 2\pi f$ )	rad/s

## Superscripts

Symbol	Meaning
0	Denotes standard or reference state
eff	Effective property

## Subscripts

Symbol	Meaning
diff	Diffusion
$E, e, \text{elec}$	Electrical (e.g., $P_e, W_{\text{elec}}$ )
$f$	Quantity of formation (e.g., $\Delta H_f$ )
(HHV)	Higher heating value
(LHV)	Lower heating value
$i$	Species $i$
$P$	Product
$P$	Parasitic
$R$	Reactant
rxn	Change in a reaction (e.g., $\Delta H_{\text{rxn}}$ )
SK	Stack
SYS	System

Nafion is a registered trademark of E.I. du Pont de Nemours and Company.

PureCell is a registered trademark of UTC Fuel Cells, Inc.

Honda FCX is a registered trademark of Honda Motor Co., Ltd.

Home Energy System is a registered trademark of Honda Motor Co., Ltd.

Gaussian is a registered trademark of Gaussian, Inc.

# CONTENTS

---

<b>PREFACE</b>	<b>xi</b>
<b>ACKNOWLEDGMENTS</b>	<b>xiii</b>
<b>NOMENCLATURE</b>	<b>xvii</b>

## **I FUEL CELL PRINCIPLES**

<b>1 Introduction</b>	<b>3</b>
1.1 What Is a Fuel Cell? / 3	
1.2 A Simple Fuel Cell / 6	
1.3 Fuel Cell Advantages / 8	
1.4 Fuel Cell Disadvantages / 11	
1.5 Fuel Cell Types / 12	
1.6 Basic Fuel Cell Operation / 14	
1.7 Fuel Cell Performance / 18	
1.8 Characterization and Modeling / 20	
1.9 Fuel Cell Technology / 21	
1.10 Fuel Cells and the Environment / 21	
1.11 Chapter Summary / 22	
Chapter Exercises / 23	



<b>2</b>	<b>Fuel Cell Thermodynamics</b>	<b>25</b>
2.1	Thermodynamics Review / 25	
2.2	Heat Potential of a Fuel: Enthalpy of Reaction / 34	
2.3	Work Potential of a Fuel: Gibbs Free Energy / 37	
2.4	Predicting Reversible Voltage of a Fuel Cell under Non-Standard-State Conditions / 47	
2.5	Fuel Cell Efficiency / 60	
2.6	Thermal and Mass Balances in Fuel Cells / 65	
2.7	Thermodynamics of Reversible Fuel Cells / 67	
2.8	Chapter Summary / 71	
	Chapter Exercises / 72	
<b>3</b>	<b>Fuel Cell Reaction Kinetics</b>	<b>77</b>
3.1	Introduction to Electrode Kinetics / 77	
3.2	Why Charge Transfer Reactions Have an Activation Energy / 82	
3.3	Activation Energy Determines Reaction Rate / 84	
3.4	Calculating Net Rate of a Reaction / 85	
3.5	Rate of Reaction at Equilibrium: Exchange Current Density / 86	
3.6	Potential of a Reaction at Equilibrium: Galvani Potential / 87	
3.7	Potential and Rate: Butler–Volmer Equation / 89	
3.8	Exchange Currents and Electrocatalysis: How to Improve Kinetic Performance / 94	
3.9	Simplified Activation Kinetics: Tafel Equation / 97	
3.10	Different Fuel Cell Reactions Produce Different Kinetics / 100	
3.11	Catalyst–Electrode Design / 103	
3.12	Quantum Mechanics: Framework for Understanding Catalysis in Fuel Cells / 104	
3.13	The Sabatier Principle for Catalyst Selection / 107	
3.14	Connecting the Butler–Volmer and Nernst Equations (Optional) / 108	
3.15	Chapter Summary / 112	
	Chapter Exercises / 113	
<b>4</b>	<b>Fuel Cell Charge Transport</b>	<b>117</b>
4.1	Charges Move in Response to Forces / 117	
4.2	Charge Transport Results in a Voltage Loss / 121	
4.3	Characteristics of Fuel Cell Charge Transport Resistance / 124	
4.4	Physical Meaning of Conductivity / 128	
4.5	Review of Fuel Cell Electrolyte Classes / 132	