3RD EDITION

FUEL CELL SYSTEMS EXPLAINED

ANDREW L. DICKS
DAVID A. J. RAND

WILEY

Fuel Cell Systems Explained

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Third Edition

Andrew L. Dicks
Griffith University
Brisbane, Australia

David A. J. Rand
CSIRO Energy
Melbourne, Australia

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Brief Biographies

Andrew L. Dicks

Andrew L. Dicks, PhD, CChem, FRSC, was educated in England and graduated from Loughborough University before starting a career in the corporate laboratories of the UK gas industry. His first research projects focused on heterogeneous catalysts in gas-making processes, for which he was awarded a doctorate in 1981. In the mid-1980s, BG appointed Andrew to lead a research effort on fuel cells that was directed predominantly towards molten carbonate and solid oxide systems. The team pioneered the application of process modelling to fuel-cell systems, especially those that featured internal reforming. This work, which was supported by the European Commission during the 1990s, involved collaboration with leading fuel-cell developers throughout Europe and North America. In 1994, Andrew was jointly awarded the Sir Henry Jones (London) Medal of the Institution of Gas Engineers and Managers for his studies on high-temperature systems. He also took an interest in proton-exchange membrane fuel cells and became the chair of a project at the University of Victoria, British Columbia, in which Ballard Power Systems was the industrial partner. In 2001, he was awarded a Senior Research Fellowship at the University of Queensland, Australia, that enabled further pursuit of his interest in catalysis and the application of nanomaterials in fuel-cell systems. Since moving to Australia, he has continued to promote hydrogen and fuel-cell technology, as director of the CSIRO National Hydrogen Materials Alliance and as a director of the Australian Institute of Energy. He is now consulted on energy and clean technology issues by governments and funding agencies worldwide.

David A. J. Rand

David A. J. Rand, AM, BA, MA, PhD, ScD, FTSE, was educated at the University of Cambridge where, after graduation, he conducted research on low-temperature fuel cells. In 1969, he joined the Australian government's CSIRO laboratories in Melbourne. After further exploration of fuel-cell mechanisms and then electrochemical studies of mineral beneficiation, he formed the CSIRO Novel Battery Technologies Group in the late 1970s and remained its leader until 2003. He was one of the six scientists who established the US-based Advanced Lead–Acid Battery Consortium in 1992 and served as its manager in 1994. He is the co-inventor of the UltraBattery^{TM}, which finds service in hybrid electric vehicle and renewable energy storage applications. As a chief research scientist, he fulfilled the role of CSIRO's scientific advisor on hydrogen and renewable energy until his retirement in 2008. He remains active within the organisation as an Honorary Research Fellow and has served as the chief energy scientist of the World Solar Challenge since its inception in 1987. He was awarded the Faraday Medal by the Royal Society of Chemistry (United Kingdom) in 1991, the UNESCO Gaston Planté Medal by the Bulgarian Academy of Sciences in 1996 and the R.H. Stokes Medal by the Royal Australian Chemical Institute in 2006. He was elected a fellow of the Australian Academy of Technological Sciences and Engineering in 1998 and became a member of the Order of Australia in 2013 for service to science and technological development in the field of energy storage.

Preface

Since publication of the first edition of *Fuel Cell Systems Explained*, three compelling drivers have supported the continuing development of fuel-cell technology, namely:

- The need to maintain energy security in an energy-hungry world.
- The desire to reduce urban air pollution from vehicles.
- The mitigation of climate change by lowering anthropogenic emissions of carbon dioxide.

New materials for fuel cells, together with improvements in the performance and lifetimes of stacks, are underpinning the emergence of the first truly commercial systems in applications that range from forklift trucks to power sources for mobile phone towers. Leading vehicle manufacturers have embraced the use of electric drivetrains and now see hydrogen fuel cells complementing the new battery technologies that have also emerged over the past few years. After many decades of laboratory development, a global — but fragile — fuel-cell industry is bringing the first products to market.

To assist those who are unfamiliar with fuel-cell electrochemistry, Chapter 1 of this third edition has been expanded to include a more detailed account of the evolution of the fuel cell and its accompanying terminology. In the following chapters, extensive revision of the preceding publication has removed material that is no longer relevant to the understanding of modern fuel-cell systems and has also introduced the latest research findings and technological advances. For example, there are now sections devoted to fuel-cell characterization, new materials for low-temperature hydrogen and liquid-fuelled systems, and a review of system commercialization. Separate chapters on fuel processing and hydrogen storage have been introduced to emphasize how hydrogen may gain importance both in future transport systems and in providing the means for storing renewable energy.

The objective of each chapter is to encourage the reader to explore the subject in more depth. For this reason, references have been included as footnotes when it is necessary to substantiate or reinforce the text. To stimulate further interest, however, some recommended further reading may be given at the end of a chapter.

There are now several books and electronic resources available to engineers and scientists new to fuel-cell systems. The third edition of *Fuel Cell Systems Explained* does not intend to compete with specialist texts that can easily be accessed via the Internet. Rather, it is expected that the book will continue to provide an introduction and overview for students and teachers at universities and technical schools and act as a primer for postgraduate researchers who have chosen to enter this field of technology. Indeed, it is hoped that *all* readers — be they practitioners, researchers and students in electrical, power, chemical and automotive engineering disciplines — will continue to benefit from this essential guide to the principles, design and implementation of fuel-cell systems.

December 2017

Andrew L. Dicks, Brisbane, Australia
David A. J. Rand, Melbourne, Australia

Acknowledgments

As emphasized throughout this publication, the research and development of fuel cells is highly interdisciplinary in that it encompasses many aspects of science and engineering. This fact is reflected in the number and diversity of companies and organizations that have willingly provided advice and information or given permission to use their images in the third edition of *Fuel Cell Systems Explained*. Accordingly, the authors are indebted to the following contributors:

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The authors also wish to express their thanks for the support and encouragement given by family, friends and colleagues during the course of this project.

Acronyms and Initialisms

ABPBI	phosphoric acid doped poly(2,5-benzimidazole)
AC	alternating current
ADP	adenosine 5'-triphosphate
AEM	alkaline-electrolyte membrane
AEMFC	alkaline-electrolyte membrane fuel cell
AES	air-electrode supported
AFC	alkaline fuel cell
AMFC	anion-exchange membrane fuel cell
ANL	Argonne National Laboratory
APEMFC	alkaline proton-exchange membrane fuel cell
APU	auxiliary power unit
ASR	area specific resistance
BCN	Dutch Fuel Cell Corporation
BG	British Gas
BIMEVOX	bismuth metal vanadium oxide ($Bi_4V_2O_{11}$)
BOP	balance-of-plant
BPS	Ballard Power Systems
BSF	Boudouard Safety Factor
CAN bus	Controller Area Network
CBM	coal-bed methane
CCS	carbon capture and storage
CFCL	Ceramic Fuel Cells Ltd
CGO	cerium–gadolinium oxide (same as GDC)
CHP	combined heat and power
CLC	chemical looping combustion
CNR	Consiglio Nazionale delle Ricerche (Italy)
CNT	carbon nanotube
CODH-1	carbon monoxide dehydrogenase
CPE	constant phase element
CPO	catalytic partial oxidation
CRG	catalytic rich gas
CSG	coal-seam gas
CSIRO	Commonwealth Scientific and Industrial Research Organisation

CSO cerium-samarium oxide (same as SDC)
CSZ calcia-stabilized zirconia
CV cyclic voltammetry
CVD chemical vapour deposition

DBFC direct borohydride fuel cell
DC direct current
DCFC direct carbon fuel cell
DEFC direct ethanol fuel cell
DEGFC direct ethylene glycol fuel cell
DFAFC direct formic acid fuel cell (also formic acid fuel cell, FAFC)
DFT density functional theory
DG distributed generator
DIR direct internal reforming
DIVRR directly irradiated, volumetric receiver–reactor
DLFC direct liquid fuel cell
DMFC direct methanol fuel cell
DOE Department of Energy (United States)
DPFC direct propanol fuel cell
DPFC(2) direct propan-2-ol fuel cell
DSSC dye-sensitized solar cell

EC evaporatively cooled
ECN Energy Research Centre of the Netherlands
EFOY Energy for You
EIS electrochemical impedance spectroscopy
EPFL Swiss Federal Institute of Technology
EU European Union
EVD electrochemical vapour deposition
EW membrane equivalent weight

FCE Fuel Cell Energy Inc.
FCES Fuel Cell Energy Solutions GmbH
FCV fuel cell vehicle
FRA frequency response analyser
FT Fischer–Tropsch

GDC gadolinium-doped ceria/gadolinia-doped ceria (same as CGO)
GDL gas-diffusion layer
GE General Electric
GHG greenhouse gas
GM General Motors
GPS Global Positioning System
GTL gas-to-liquid
GTO gate turn-off (thyristor)

HAZID hazard identification
HAZOP hazard and operability study

HCNG	hydrogen-compressed natural gas
HDS	hydrodesulfurization
HEMFC	hydroxide-exchange polymer membrane fuel cell
HEV	hybrid electric vehicle
HHV	higher heating value
HOR	hydrogen oxidation reaction
HPE	high-pressure proton-exchange membrane electrolyser
IBFC	indirect borohydride fuel cell
ICE	internal combustion engine
ICEV	internal combustion engine vehicle
IFC	International Fuel Cells
IGBT	insulated-gate bipolar transistor
IHI	Ishikawajima-Harima Heavy Industries Co., Ltd
IHP	inner Helmholtz plane
IIR	indirect internal reforming (also known as ‘integrated reforming’)
ITM	ion transport membrane, also refers to company ITM Power
IT-SOFC	intermediate-temperature solid oxide fuel cell
IUPAC	International Union of Pure and Applied Chemistry
KEPCO	Korea Electric Power Corporation
KIST	Korea Institute of Science and Technology
LAMOX	lanthanum molybdate ($La_2Mo_2O_9$)
LCA	life-cycle assessment (also known as ‘life-cycle analysis’ and ‘cradle-to-grave analysis’)
LCOE	levelized cost of electricity
LH_2	liquid hydrogen
LHV	lower heating value
LNG	liquefied natural gas
LPG	liquefied petroleum gas
LSCF	lanthanum strontium cobaltite ferrite
LSCV	strontium-doped lanthanum vanadate
LSGM	lanthanum gallate ($LaSrGaMgO_3$)
LSM	strontium-doped lanthanum manganite
LT-SOFC	low-temperature solid oxide fuel cell
MCFC	molten carbonate fuel cell
MCR	microchannel reactor
MEA	membrane–electrode assembly
MEMS	microelectromechanical systems
METI	Ministry of Economy, Trade and Industry (Japan)
MFC	microbial fuel cell
MFF	mass flow factor
MHPS	Mitsubishi Hitachi Power Systems
MIEC	mixed ionic–electronic conductor (oxides)
MOF	metal–organic framework
MOSFET	metal-oxide-semiconductor field-effect transistor

MPMDMS	(3-mercaptopropyl)methyldimethoxysilane
MRFC	mixed-reactant fuel cell
MSW	municipal solid waste
MTBF	mean time between failures
MWCNT	multiwalled carbon nanotube
NADP	nicotinamide adenine dinucleotide phosphate
NASA	National Aeronautics and Space Administration
NCPO	non-catalytic partial oxidation
NEDO	New Energy Development Organization (Japan)
NOMO	Notice of Market Opportunities
NTP	normal temperature and pressure
OCV	open-circuit voltage
OEM	original equipment manufacturer
OER	oxygen evolution reaction
OHP	outer Helmholtz plane
ORR	oxygen reduction reaction
P2G	power-to-gas
P3MT	poly(3-methylthiophene)
PAFC	phosphoric acid fuel cell
PANI	polyaniline
PAR	photosynthetically active radiation
PBI	polybenzimidazole
PBSS	poly(benzylsulfonic acid)siloxane
PC	phthalocyanine
PCT	pressure composition isotherm
PEC	photoelectrochemical cell
PEMFC	proton-exchange membrane fuel cell (also called 'polymer electrolyte membrane fuel cell' and same as SPEFC and SPFC)
PET	polyethylene terephthalate
PF	power factor, also PFC power factor correction
PFD	process flow diagram
PFSA	perfluorinated sulfonic acid
plc	programmable logic controller
POX	partial oxidation
PPA	polyphosphoric acid
PPBP	poly(1,4-phenylene), poly(4 phenoxybenzoyl-1,4-phenylene)
Ppy	polypyrrole
PROX	preferential oxidation
PrOx	preferential oxidation reactor
PSA	pressure swing adsorption
PTFE	polytetrafluoroethylene
PV	photovoltaic
PWM	pulse width modulation
QA	quaternary ammonium

RDE	rotating disc electrode
RFB	redox flow battery
RH	relative humidity
RHE	reversible hydrogen electrode
RRDE	rotating ring-disc electrode
RSF	rotational speed factor
SATP	standard ambient temperature and pressure
SCG	simulated coal gas
SCT-CPO	short contact time catalytic partial oxidation
SDC	samarium-doped ceria/samaria-doped ceria (same as CSO)
SECA	Solid State Energy Conversion Alliance
SFCM	standard cubic foot per minute
SHE	standard hydrogen electrode
SI	International System of Units (French: Système international d'unités)
SLM	standard litre per minute
SMR	steam reforming reaction
SNG	substitute natural gas (also synthetic natural gas)
SOFC	solid oxide fuel cell
m-SPAEEN-60	sulfonated poly(arylene ether ether nitrile)
SPEEK	sulfonated polyether ether ketone
SPEFC	solid polymer electrolyte fuel cell (same as PEMFC)
SPFC	solid polymer fuel cell (same as PEMFC)
SPOF	single point of failure
STP	standard temperature and pressure
SWPC	Siemens Westinghouse Power Corporation
TAA	tetraazaannulene
THT	tetrahydrothiophene
TMPP	tetramethoxyphenylporphyrin
TPP	tetraphenylporphyrin
TPTZ	2, 4, 6-tris(2-pyridyl)-1,3,5-triazine
TTW	tank-to-wheel
UCC	Union Carbide Corporation
UK	United Kingdom
ULP	unleaded petrol
UPS	uninterruptible power system; also uninterruptible power supply
URFC	unitized regenerative fuel cell
USA	United States of America
USB	universal serial bus
UTC	United Technologies Corporation
UV	ultraviolet
WGS	water–gas shift
WTT	well-to-tank
WTW	well-to-wheels
XPS	X-ray photoelectron spectroscopy

Symbols and Units

Subunits			*Multiple units*		
d	deci	10^{-1}	k	kilo	10^{3}
c	centi	10^{-2}	M	mega	10^{6}
m	milli	10^{-3}	G	giga	10^{9}
μ	micro	10^{-6}	T	tera	10^{12}
n	nano	10^{-9}	P	peta	10^{15}

A ampere
A electrode area (cm^2), also coefficient in natural logarithm form of the Tafel equation
Ah ampere hour
a chemical activity; also coefficient in base 10 logarithm form of the Tafel equation
a_x chemical activity of species x
atm atmosphere (=101.325 kPa)
B exergy (J)
ΔB change in exergy (J)
bbl barrel of oil: 35 imperial gallons (159.113 L), or 42 US gallons (158.987 L)
bar unit of pressure (=100 kPa)
bhp brake horsepower (=745.7 W)
C constant in various equations; also coulomb (=1A s), the unit of electric charge
°C degree Celsius
C_P specific heat capacity at constant pressure ($J\,kg^{-1}\,K^{-1}$)
C_V specific heat capacity at constant volume ($J\,kg^{-1}\,K^{-1}$)
$\overline{c_P}$ molar heat capacity at constant pressure ($J\,mol^{-1}\,K^{-1}$)
$\overline{c_V}$ molar heat capacity at constant volume ($J\,mol^{-1}\,K^{-1}$)
cm centimetre
D_m diffusion coefficient ($m^2\,s^{-1}$)
d separation of charge layers in a capacitor (mm)
E electrode potential (V)
$E°$ standard electrode potential (V)
E_r reversible electrode potential (V)
E_r° standard reversible electrode potential (V)

EW	(membrane) equivalent weight
e^-	electron, or the charge on one electron (=1.602×10^{-19} coulombs)
ΔE_{act}	activation overpotential (V)
F	farad, unit of electrical capacitance ($s^4 A^2 m^{-2} kg^{-1}$)
F	Faraday constant (=96 458 coulombs mol^{-1})
ft	foot (linear measurement = 305 mm)
G	Gibbs free energy (J)
ΔG	change in Gibbs free energy (J)
$\Delta G°$	change in standard Gibbs free energy (J)
G_f°	standard Gibbs free energy of formation (J)
ΔG_f°	change in standard Gibbs free energy of formation (J)
$\overline{g}$	molar Gibbs free energy ($J\,mol^{-1}$)
$\Delta\overline{g}$	change in molar Gibbs free energy ($J\,mol^{-1}$)
$\Delta\overline{g}^\circ$	change in standard molar Gibbs free energy ($J\,mol^{-1}$)
$\Delta\overline{g}_f$	change in molar Gibbs free energy of formation ($J\,mol^{-1}$)
$\Delta\overline{g}_f^\circ$	change in standard molar Gibbs free energy of formation ($J\,mol^{-1}$)
g	gram
g	acceleration due to gravity ($m\,s^{-2}$)
H	enthalpy (J)
ΔH	change in enthalpy (J)
$\Delta H°$	change in standard enthalpy (J)
H_f°	standard enthalpy of formation (J)
ΔH_f°	change in standard enthalpy (heat) of formation (J)
$\overline{h}$	molar enthalpy ($J\,mol^{-1}$)
$\Delta\overline{h}$	change in molar enthalpy ($J\,mol^{-1}$)
$\Delta\overline{h}^\circ$	change in standard molar enthalpy ($J\,mol^{-1}$)
$\Delta\overline{h}_f$	change molar enthalpy of formation ($J\,mol^{-1}$)
$\Delta\overline{h}_f^\circ$	change in standard molar enthalpy of formation ($J\,mol^{-1}$)
h	hour
$IR_e^/$	resistive loss in electrolyte (Ω)
$IR_t^/$	total resistive loss in electrodes (Ω)
I	current (A)
i	current density, i.e., current per unit area (usually expressed in $mA\,cm^{-2}$)
i_c	crossover current (A)
i_l	limiting current density (usually expressed in $mA\,cm^{-2}$)
i_o	exchange-current density (usually expressed in $mA\,cm^{-2}$)
J	joule (=1 W s)
K	kelvin (used as a measure of absolute temperature)
L	litre
MFF	mass flow factor ($kg\,s^{-1} K^{1/2} bar^{-1}$)
m	metre
$\dot{m}$	mass flow rate, e.g., of gas ($kg\,s^{-1}$) or of a liquid ($ml\,min^{-1}$)
m_x	mass of substance x (g)
mEq	milliequivalent (weight) ($mg\,L^{-1}$)
mol	mole, i.e., mass of 6.022×10^{23} elementary units (atoms, molecules, etc.) of a substance
N	newton (unit of force = 1 $kg\,m\,s^{-2}$)

N	rotor speed of fan (revolutions per minute)
N_A	Avogadro's number, $6.022140857 \times 10^{23}$
$N\text{-}m^3$	normal cubic metre of gas (i.e., that measured at NTP)
n	number of units (electrons, atoms, molecules) involved in a chemical or electrochemical reaction; also number of cells in fuel-cell stack
n_i	number of units or moles of species i
$\dot{n}_x$	molar flow rate of species x (mol s^{-1})
P	pressure (in Pa, or bar)
P_e	power (W), only used when context is clear that pressure is not under discussion
P°	standard pressure (=100 kPa)
P_{SAT}	saturated vapour pressure
P_x	partial pressure of species x
Pa	pascal (1 Pa = 1 N m^{-2} = 9.869×10^{-6} atm)
ppb	parts per billion
pH	numerical scale used to specify the acidity or basicity of an aqueous solution
ppm	parts per million
R	gas constant (=8.1345 J K^{-1} mol^{-1})
$R^{/}$	resistance (Ω)
$R_{DS,on}$	internal resistance of a transistor
RH	relative humidity (%); also denoted by the symbol ϕ (*v.i.*)
®	registered trademark/copyright
r	area specific resistance (Ω cm^2)
S	siemens, unit of conductance (Ω^{-1})
S	entropy (J K^{-1})
ΔS	change in entropy (J K^{-1})
ΔS°	change in standard entropy (J K^{-1})
S_f°	standard entropy of formation (J K^{-1})
ΔS_f°	change in standard entropy of formation (J K^{-1})
$\bar{s}$	molar entropy (J K^{-1} mol^{-1})
$\Delta\bar{s}$	change in molar entropy (J K^{-1} mol^{-1})
$\Delta\bar{s}^\circ$	change in standard molar entropy (J mol^{-1})
$\Delta\bar{s}_f$	change in molar entropy of formation (J mol^{-1})
$\Delta\bar{s}_f^\circ$	change in standard molar entropy of formation (J mol^{-1})
s	second
SLM	standard litre per minute
T	temperature
TM	trademark
t	tonne
$t_{1/2}$	half-life
V	volt
V_c	cell voltage (V)
V_r	reversible cell voltage; also known as 'open-circuit voltage' (V)
V_r°	reversible cell voltage (V) under standard conditions of temperature (298.15 K) and pressure (101.325 kPa)
ΔV_{gain}	voltage gain (V)
ΔV_{loss}	voltage loss (V)
vol.%	volume percent

W work done, e.g., in compressing a gas (J)
W' isentropic work (J)
W watt
W_{el} watt, electrical power
W_{th} watt, thermal power
Wh watt-hour
wt.% weight percent
x_i mole fraction of species i in solution
Z impedance (Ω)
z number of units (electrons, atoms, molecules) involved in a chemical or electrochemical reaction

α charge transfer coefficient
γ ratio of the specific heats of a gas C_P:C_V
δ_m thickness of proton exchange membrane (cm)
ε electrical permittivity ($F\,m^{-1}$)
ξ electro-osmotic coefficient
η electrode overpotential (V); also efficiency (%) (e.g., of a fuel cell)
η_+ overpotential at a positive electrode (V)
η_- overpotential at a negative electrode (V)
η_C isentropic compressor efficiency (%)
η_f fuel utilization coefficient (%), a 'figure of merit' for DMFCs
ϑ phase angle
λ stoichiometric ratio
μ_f fuel utilization coefficient
μ_i chemical potential of species i ($J\,kg^{-1}$ or $J\,mol^{-1}$)
μ gas viscosity (centipoise, $cP = 0.001\,kg\,m^{-1}\,s^{-1}$)
ϕ relative humidity (usually expressed as a percentage); also denoted by RH
ρ gas density ($kg\,m^{-3}$)
ω humidity ratio, also known as 'absolute humidity' and 'specific humidity'; symbol also used for radial frequency
Ω ohm