

FUEL CELLS

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FUEL CELLS

Problems and Solutions

Second Edition

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PREFACE

The first edition of this book was published in December 2008. This second edition is updated with information published after this date up to October 2011. Two chapters of the first edition were rewritten: Chapter 15 (modeling of fuel cells) and Chapter 14—now Chapter 17 (small fuel cells for portable devices). In this edition three new chapters of high current interest are also included: Chapter 14 (structural and wetting properties of fuel cell components), Chapter 16 (experimental methods for fuel cell stacks), and Chapter 18 (nonconventional design principles for fuel cells).

My thanks go to Ms. Catherine Lysova for her help in editing some chapters of the book.

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PREFACE TO THE FIRST EDITION

When fuel cells were first suggested and discussed back in the nineteenth century, it was firmly hoped that distinctly higher efficiencies could be attained with them when converting the chemical energy of natural fuels to electric power. Now that the world supply of fossil fuels is seen to be finite, this hope turns into a need, into a question of maintaining advanced standards of life. Apart from conversion efficiency, fuel cells have other aspects which make them attractive: Their conversion process is clean, they may cogenerate useful heat, and can be used in many different fields. One worker in the field put it this way: “Fuel cells have the potential to supply electricity to power a wristwatch or a large city, replacing a tiny battery or an entire power generating station.”

With some important achievements made in the past, fuel cells today are a subject of vigorous R&D, engineering, and testing conducted on a broad international scale in universities, research centers, and private companies in different sectors of the economy. Between engineers, technicians, and scientists, several 10,000 workers contribute their efforts and skills to advance the field.

Progress in the field is fast. Hundreds of publications monthly report new results and discoveries. Important synergies exist with work done to advance the concepts of a hydrogen economy.

The book is intended for people who have heard about fuel cells but ignore the detailed potential and applications of fuel cells, and wish to obtain the information they need (as engineers in civil, industrial, and military jobs, R&D people of diverse profile, investors, decision makers in government, industry, trade, and all levels of administration, journalists, school and university teachers, students, and hobby scientists). It is also intended for people in industry and research who in their professional work are concerned with different special aspects of the

development and applications of fuel cells and want to gain an overview of fuel cell problems and their economic and scientific significance.

This book is thus focused on providing readers across the trades and life styles with a compact, readable introduction and explanation of what fuel cells do, how they do it, where they are important, where the problems are, how fuel cells will continue in the field, and how they can perform against air pollution and for portable devices. All this is done with a critical attitude based on a sufficiently detailed and advanced presentation. Problems and achievements are discussed at the level attained by the end of 2007.

Contradictions and a lack of consensus have existed in the field, along with ups and downs. In a field where the subject may range in size from milliwatt to megawatt output and many technical systems compete, this will not come as a surprise. To guide the reader through the maze, a sampling of literature references is provided. This sampling is intended to illustrate but had to be compiled while omitting a lot of work just as important as the work cited. Selection was also made difficult because of the strongly interdisciplinary character of fuel cell work.

The presentation is made against the historical background, and looks at future prospects, including those of synergy with a potential future hydrogen economy. Where views diverge, they are presented as such. Some of the ideas offered may well be open to further discussion.

My gratitude goes to my colleagues Dr. Nina Osetrova and Dr. Alexander Skundin, Moscow, for their help in selecting relevant literature, and to Timophei Pastushkin for preparing graphical representations. My thanks also go to Dr. Klaus Mueller, formerly at the Battelle Institute of Geneva, who transformed chapters written in Russian into English reading material, and contributed by making a number of very valuable suggestions.

I sincerely hope that what has inspired me during a long lifetime, of more than 50 years of research and teaching at the Moscow Quant Power Sources Institute and at the A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, will continue to inspire current and future specialists and people in general who work to improve our lives and solve our problems.

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SYMBOLS

Symbol	Meaning	Dimensions (Values)	Section Reference ^a
<i>Roman</i>			
c_j	concentration	mol/dm ³	
D_j	diffusion coefficient	cm ² /s	
E	electrode potential	V	1.4.3
E^0	equilibrium electrode potential	V	1.4.3
ε^0	electromotive force	V	1.4.4
F	Faraday constant	9485 C/mol	7.2
G	Gibbs energy	kJ/mol	1.1.2
H	enthalpy	kJ/mol	1.1.2
i	current density	mA/cm ²	1.4.3
i^0	exchange current density	mA/cm ²	1.4.3
I	current	A, mA	1.4.3
M	mass	kg	
M	molar concentration	mol/dm ³	
n	number of electrons in the reaction's elementary act	none	1.4.2
p	power density	W/kg	1.5.5
	power	W, kW	1.5.2

^a Sections where this symbol is used for the first time and/or where its definition is given.

Q	heat, thermal energy	J, kJ	1.1.1
q	heat (in eV)	eV	1.4.2
R	(1) resistance	Ω	1.4.3
	(2) molar gas constant	8.314 J/mol · K	7.2
S	(1) entropy	kJ/K	1.1.2
	(2) surface area	cm ²	
T	absolute temperature	K	1.1.1
U	cell voltage	V	1.4.4
w	energy density	kWh/kg	1.5.5
W	work, useful energy	W, kW	1.1.2

Greek

γ	roughness factor	none	
δ	thickness	cm	
λ_e	amount of coulombs	none	1.5.3
η	efficiency	none, %	
σ	conductivity	S/cm ²	

Subscripts

ads	adsorbed
app	apparent
e	electrical
exh	exhaust
ext	external
h.e.	hydrogen electrode
i	under current
j	any ion or substance
loss	energy loss
o.e.	oxygen electrode
ox	oxidizer
red	reducer
S	per unit area
V	per unit volume
0	without current
+	cation
-	anion

ABBREVIATIONS AND ACRONYMS

ac	alternating current
AFC	alkaline fuel cell
APU	auxiliary power unit
ATR	autothermal reforming
BET	Brunauer Emmett Teller
CD	current density
CHP	combined heat and power
CNT	carbon nanotube
CT	computed tomography
CTE	coefficient of thermal expansion
DBHFC	direct borohydride fuel cell
dc	direct current
DCFC	direct carbon fuel cell
DEFC	direct ethanol fuel cell
DFAFC	direct formic acid fuel cell
DHFC	direct hydrazine fuel cell
DLFC	direct liquid fuel cell
DMFC	direct methanol fuel cell
DSA	dimensionally stable anode
DVB	divinylbenzene
EM	electron microscopy

These abbreviations and acronyms are used in most chapters. Abbreviations for oxide materials used as electrolytes and electrodes in solid-oxide fuel cells are given in Chapter 8.

EMF	electromotive force
EPS	electrochemical power source
ET-PEMFC	elevated-temperature PEMFC
FCV	fuel cell vehicle
GDL	gas-diffusion layer
GDM	gas-diffusion medium
GLDL	gas-liquid diffusion layer
ICE	internal combustion engine
ICV	internal combustion vehicle
IRFC	internal reforming fuel cell
IT-SOFC	interim-temperature SOFC
LHV	lower heat value
LPG	liquefied petroleum gas
LT-SOFC	low-temperature SOFC
MCFC	molten carbonate fuel cell
MEA	membrane-electrode assembly
MMP	method of mercury porosimetry
MPL	microporous layer
MSCP	method of standard contact porosimetry
OCP	open-circuit potential
OCV	open-circuit voltage
ORR	oxygen reduction reaction
Ox,ox	oxidized form
PAFC	phosphoric acid fuel cell
PBI	polybenzimidazole
PCB	printed circuit board
PD	potential difference
PEEK	poly(ether ether ketone)
PEMFC	proton-exchange membrane fuel cell (<i>also</i> polymer electrolyte membrane fuel cell)
PFSA	perfluorinated sulfonic acid
POX	partial oxidation (reforming by)
PSDF	pore size distribution function
PTFE	polytetrafluoroethylene
PVD	physical vapor deposition
Red, red	reduced form
SC-SOFC	single-chamber solid-oxide fuel cell
SHE	standard hydrogen electrode
SOFC	solid-oxide fuel cell
SR	steam reforming
SSA	specific surface area
SWCNT	single-walled carbon nanotube
URFC	unitized regenerative fuel cell
UTC	United Technologies Corporation
WGSR	water-gas shift reaction

PART I

INTRODUCTION

INTRODUCTION

Fuel cells have the potential to supply electricity to power a wristwatch or a large city, replacing a tiny battery or an entire power generating station.

—George Wand, Fuel cell history, Part 1, *Fuel Cells Today*, April 2006

What Is a Fuel Cell? Definition of the Term

A *fuel cell* may be one of a variety of electrochemical power sources (EPSs), but is more precisely a device designed to convert the energy of a chemical reaction directly to electrical energy. Fuel cells differ from other EPSs: the primary galvanic cells called *batteries* and the secondary galvanic cells called *accumulators* or *storage batteries*, (1) in that they use a supply of gaseous or liquid reactants for the reactions rather than the solid reactants (metals and metal oxides) built into the units; (2) in that a continuous supply of the reactants and continuous elimination of the reaction products are provided, so that a fuel cell may be operated for a rather extended time without periodic replacement or recharging.

Possible reactants or fuels for the current-producing reaction are natural types of fuel (e.g., natural gas, petroleum products) or products derived by fuel processing, such as hydrogen produced by the reforming of hydrocarbon fuels or water gas (syngas) produced by treating coal with steam. This gave rise to their name: fuel cells.

Significance of Fuel Cells for the Economy

In this book we show that fuel cells, already used widely throughout the economy, offer:

- Drastically higher efficiency in the utilization of natural fuels for largescale power generation in megawatt power plants, and a commensurate decrease in the exhaust of combustion products and contaminants into the atmosphere from conventional thermal power plants
- Improved operation of power grids by load leveling with large-scale plants for temporary power storage
- A widely developed grid of decentralized, silent, local power plants with a capacity of tens to hundreds of kilowatts for use as a power supply or as a combined power and heat supply in remote locations, buildings, or installations not hooked up to the grid, such as stations for meteorological and hydrological observation; and for use as an emergency power supply in individual installations such as hospitals and control points
- Traction power plants with a capacity of tens of kilowatts for large-scale introduction of electric cars, leading to an important improvement in the ecological situation in large cities and densely populated regions
- Installations for power supply to spacecraft and submarines or other underwater structures, in addition to supplying crews with drinking water
- Small power units with a capacity of tens of watts or milliwatts, providing energy for extended continuous operation of portable or transportable devices used in daily life, such as personal computers, videocameras, and mobile communication equipment, or in industrial applications such as signaling and control equipment

For all these reasons, the development of fuel cells has received great attention since the end of the nineteenth century. In the middle of the twentieth century, interest in fuel cells became more general and global when dwindling world resources of oil and more serious ecological problems in cities were recognized. Space exploration provided a singular stimulus from the 1950s onward. An additional push was felt toward the end of the twentieth century in connection with the advent of numerous portable and other small devices used for civil and military purposes, that required an autonomous power supply over extended periods of use.

Today, numerous fuel cell-based power plants have been built and operated successfully, on a scale of both tens of megawatts and tens or hundreds of kilowatts. A great many small fuel cell units are in use that output between a few milliwatts and a few watts. Fuel cells are already making an important contribution to solving economic and ecological problems facing humankind. There can be no doubt that this contribution will continue to increase.

Large-scale research and development (R&D) efforts concerning the development and application of fuel cells are conducted today in many countries, in national laboratories, in science centers and universities, and in industrial establishments. Several hundred publications in the area of fuel cells appear every month in scientific and technical journals.