WILEY

Fuel Cell Systems Explained

James Larminie

Andrew Dicks

Fuel Cell Systems Explained

James Larminie
Oxford Brookes University, UK

Andrew Dicks
BG Technology, Loughborough, UK

JOHN WILEY & SONS, LTD
Chichester • Weinheim • New York • Brisbane • Singapore • Toronto

Baffins Lane, Chichester,
West Sussex, PO19 1UD, England

National 01243 779777
International (+44) 1243 779777
e-mail (for orders and customer service enquiries): cs-books@wiley.co.uk
Visit our Home Page on http://www.wiley.co.uk or http://www.wiley.com

Reprinted November 1999, October 2000, February 2001, June 2001, January 2002

Other Wiley Editorial Offices

John Wiley & Sons, Inc., 605 Third Avenue,
New York, NY 10158-0012, USA

Wiley-VCH Verlag GmbH
Pappelallee 3, D-69469 Weinheim, Germany

Jacaranda Wiley Ltd, 33 Park Road, Milton,
Queensland 4064, Australia

John Wiley & Sons (Canada) Ltd, 22 Worcester Road
Rexdale, Ontario, M9W 1L1, Canada

John Wiley & Sons (Asia) Pte Ltd, 2 Clementi Loop #02-01,
Jin Xing Distripark, Singapore 129809

British Library Cataloguing in Publication Data

A catalogue record for this book is available from the British Library

ISBN 0 471 49026 1

Produced from camera-ready copy supplied by the authors
Printed and bound in Great Britain by TJ International Ltd, Padstow, Cornwall
This book is printed on acid-free paper responsibly manufactured from sustainable forestry, in which at least two trees are planted for each one used for paper production.

Foreword

By Dr Gary Acres OBE, formerly Director of Research, Johnson Matthey Plc.

A significant time generally elapses before any new technological development is fully exploited. The fuel cell, first demonstrated by Sir William Grove in 1839, has taken longer than most, despite the promise of clean and efficient power generation.

Following Bacon's pioneering work in the 1950s fuel cells were successfully developed for the American manned space programme. This success, together with a policy to commercialise space technology, led to substantial development programmes in America and Japan in the 1970 and 80s, and more recently in Europe. Despite these efforts, which resulted in considerable technical progress, fuel cell systems were seen to be "always five years away from commercial exploitation".

During the last few years of the 20th century much changed to stimulate new and expanding interest in fuel cell technology. Environmental concerns about global warming and the need to reduce CO_2 emissions provided the stimulus to seek ways of improving energy conversion efficiency. The motor vehicle industry, as well as seeking higher fuel efficiencies, is also required to pursue technologies capable of eliminating emissions: the ultimate goal being the zero emission car. The utility industries, following the impact of privatisation and deregulation, are seeking ways to increase their competitive position while at the same time contributing to reduced environmental emissions.

As these developments have occurred, interest in fuel cell technology has expanded. Increased numbers of people from disciplines ranging from chemistry through engineering to strategic analysis, not familiar with fuel cell technology, have needed to become involved. The need by such people for a single, comprehensive and up to date exposition of the technology and its applications has become apparent, and is amply provided for by this book.

While the fuel cell itself is the key component and an understanding of its features is essential, a practical fuel cell system requires the integration of the stack with fuel processing, heat exchange, power conditioning and control systems. The importance of each of these components and their integration is rightly emphasised in sufficient detail for the chemical and engineering disciplines to understand the system requirements of this novel technology.

Fuel cell technology has largely been the preserve of a limited group consisting primarily of electro and catalyst chemists and chemical engineers. There is a need to develop more people with a knowledge of fuel cell technology. The lack of a comprehensive review of fuel cells and their applications has been a limiting factor in the inclusion of this subject in academic undergraduate and graduate student science and engineering courses. This book, providing as it does a review of the fundamental aspects of the technology, as well as its applications, forms an ideal basis for bringing fuel cells into appropriate courses and postgraduate activities.

The first three chapters describe the operating features of a fuel cell and the underlying thermodynamics and physical factors that determine their performance. A good understanding of these factors is essential to an appreciation of the benefits of fuel cell systems and their operating characteristics compared with conventional combustion based technology. A feature of fuel cell technology is that it gives rise to a range of five main types of system, each with its own operating parameters and applications. These are described in Chapters 4 to 6.

The preferred fuel for a fuel cell is hydrogen. While there are applications where hydrogen can be used directly, such as in space vehicles and local transport, in the foreseeable future, for other stationary and mobile applications, the choice of fuel and its conversion into hydrogen rich gas are essential features of practical systems. The range of fuels and their processing for use in fuel cell systems are described in Chapter 7. Chapters 8 and 9 describe the mechanical and electrical components that make up the complete fuel cell plant for both stationary and mobile applications.

This book offers those new to fuel cells a comprehensive, clear exposition and review to further their understanding, and also provides those familiar with the subject a convenient reference. I hope it will also contribute to a wider knowledge about, and a critical appreciation of, fuel cell systems, and thus to the widest possible application of an exciting 21st century technology that could do much to move our use of energy onto a more sustainable basis.

Gary Acres

February 2000

Acknowledgements

The point will frequently be made in this book that fuels cells are highly interdisciplinary, involving many aspects of science and engineering. This is reflected in the number and diversity of companies that have helped with advice, information and pictures in connection with this project. The authors would like to put on record their thanks to the following companies or organisations who have made this book possible:-

Advanced Power Sources Ltd, UK
Alstom Ballard GmbH,
Armstrong International Inc, USA
Ballard Power Systems Inc, Canada
BG Technology Ltd, UK
DaimlerChrysler Corporation
DCH Technology Inc, USA
Eaton Corporation, USA
Epyx, USA
GfE Metalle und Materialien GmbH, Germany
International Fuel Cells, USA
Johnson Matthey Plc, UK
Hamburgische Electricitäts-Werke AG, Germany
Lion Laboratories Ltd., UK
MTU Friedrichshafen GmbH, Germany
ONSI Corporation, USA
Paul Scherrer Institute, Switzerland
Siemens Westinghouse Power Corporation, USA
Sulzer Hexis AG, Switzerland
SR Drives Ltd, UK
Svenska Rotor Maskiner AB, Sweden
W.L.Gore and Associates Inc, USA
Zytek Group Ltd, UK

In addition, a number of people have helped with advice and comments to the text. In particular we would like to thank Felix Büchi of the Paul Scherrer Institute, Richard Stone and Colin Snowdon, both from the University of Oxford, and Tony Hern and Jonathan Bromley of Oxford Brookes University, who have all provided valuable comments and suggestions for different parts of this work. Special thanks is also due to Juliet Barrett who did a good deal of manuscript typing. Finally we are also indebted to family, friends and colleagues who have helped us in many ways, and put up with us while we devoted time and energy to this project.

James Larminie, Oxford Brookes University, Oxford

Andrew Dicks, BG Technology, Loughborough

Abbreviations

AC	Alternating current
AES	Air electrode supported
AFC	Alkaline (electrolyte) fuel cell
ASR	Area specific resistance, the resistance of 1 cm^2 of fuel cell. (N.B. total resistance is ASR *divided* by area.)
BLDC	Brushless DC (motor)
BOP	Balance of plant
CFM	Cubic feet per minute
CHP	Combined heat and power
CPO	Catalytic partial oxidation
DC	Direct current
DIR	Direct internal reforming
EC	European Community
EMF	Electro-motive-force
EVD	Electrochemical vapour deposition
FCV	Fuel cell vehicle
GT	Gas turbine
GTO	Gate turn off
HDS	Hydrodesulphurisation
HHV	Higher heating value
IEC	International Electrotechnical Commission
IGBT	Insulated gate bipolar transistor
IIR	Indirect internal reforming
LHV	Lower heating value
LH_2	Liquid (cryogenic) hydrogen
LPG	Liquid petroleum gas
LSGM	Lanthanum, strontium, gallium, and magnesium oxide mixture
MCFC	Molten carbonate (electrolyte) fuel cell
MEA	Membrane electrode assembly
MOSFET	Metal oxide semiconductor field effect transistor
NASA	National Aeronautics and Space Administration
NL	Normal litre, 1 litre at NTP
NTP	Normal temperature and pressure (20 °C and 1 atm.)
OCV	Open circuit voltage
PAFC	Phosphoric acid (electrolyte) fuel cell
PEM	Proton exchange membrane or polymer electrolyte membrane – different names for the same thing which fortunately have the same abbreviation.
PEMFC	Proton exchange membrane fuel cell or polymer electrolyte membrane fuel cell
PFD	Process flow diagram
PM	Permanent Magnet
ppb	Parts per billion

ppm	Parts per million
PURPA	Public utilities regulatory policies act
PTFE	Polytetrafluoroethylene
PSI	Pounds per square inch
PWM	Pulse width modulation
SCG	Simulated coal gas
SL	Standard litre, 1 litre at STP
SOFC	Solid oxide fuel cell
SPFC	Solid polymer fuel cell (= PEMFC)
SPP	Small power producer
SRM	Switched reluctance motor
SRS	Standard reference state (25 °C and 1 bar)
STP	Standard temperature and pressure (= SRS)
TEM	Transmission electron microscope
t/ha	Tonnes per hectare annual yield
THT	Tetrahydrothiophene ($C_4H_8O_2S$)
TOU	Time of use
UL	Underwriters' Laboratory
YSZ	Yttria stabilised zirconia

Symbols

a	Coefficient in base 10 logarithm form of Tafel equation also Chemical activity
a_x	Chemical activity of substance x
A	Coefficient in natural logarithm form of Tafel equation also Area
B	Coefficient in equation for mass transport voltage loss
C	Constant in various equations also Capacitance
c_p	Specific heat capacity at constant pressure, in $J.K^{-1}.kg^{-1}$
$\bar{c}_p$	Molar specific heat capacity at constant pressure, in $J.K^{-1}.mol^{-1}$
d	separation of charge layers in a capacitor
e	Magnitude of the charge on one electron, 1.602×10^{-19} Coulombs
E	EMF or open circuit voltage
E^0	EMF at standard temperature and pressure, and with pure reactants
F	Faraday constant, the charge on one mole of electrons, 96 485 Coulombs
G	Gibbs free energy
ΔG^0	Change in Gibbs free energy at standard temperature and pressure, and with pure reactants
ΔG_{T_A}	Change in Gibbs free energy at ambient temperature
$\bar{g}$	Gibbs free energy per mole
$\bar{g}_f$	Gibbs free energy of formation per mole
$(\bar{g}_f)_X$	Gibbs free energy of formation per mole of substance X
H	Enthalpy
$\bar{h}$	Enthalpy per mole
$\bar{h}_f$	Enthalpy of formation per mole
$(\bar{h}_f)_X$	Enthalpy of formation per mole of substance X
I	Current
i	Current density, current per unit area
i_l	Limiting current density
i_o	Exchange current density at an electrode/electrolyte interface
i_{oc}	Exchange current density at the cathode
i_{oa}	Exchange current density at the anode
m	Mass
$\dot{m}$	Mass flow rate
m_x	Mass of substance x

N	Avagadro's number, 6.022×10^{23} also Revolutions per second
n	Number of cells in a fuel cell stack
P	Pressure
P_1, P_2	The pressure at different stages in a process
P_X	Partial pressure of gas X
P^0	Standard pressure, 100 kPa
P_{SAT}	Saturated vapour pressure
P_e	Electrical power, only used when context is clear that pressure is not meant.
R	Molar or 'universal' gas constant, 8.314 $J.K^{-1}.mol^{-1}$ also Electrical resistance
r	Area specific resistance, resistance of unit area
S	Entropy
$\bar{s}$	Entropy per mole
$(\bar{s})_X$	Entropy per mole of substance X
T	Temperature
T_1, T_2	Temperatures at different stages in a process
T_A	Ambient temperature
T_c	Combustion temperature
t	Time
V	Voltage
V_c	Average voltage of one cell in a stack
V_a	Activation overvoltage
V_r	Ohmic voltage loss
W	Work done
W'	Work done under isentropic conditions
$\dot{W}$	Power
z	Number of electrons transferred in a reaction
α	Charge transfer coefficient
Δ	Change in ...
ε	Electrical permitivity
γ	Ratio of the specific heat capacities of a gas
η	Efficiency
η_c	Isentropic efficiency (or compressor or turbine)
ϕ	Relative humidity
λ	Stoichiometric ratio
ω	Humidity ratio
μ_f	Fuel utilisation

Contents

Appendices

1

Introduction

1.1 Hydrogen Fuel Cells - Basic Principles

The basic operation of the hydrogen fuel cell is extremely simple. The first demonstration of a fuel cell was by lawyer-cum-inventor William Grove in 1839, using an experiment along the lines of that shown in Figures 1.1a and 1.1b. In Figure 1.1a water is being electrolysed into hydrogen and oxygen by passing an electric current through it. In Figure 1.1b the power supply has been replaced with an ammeter, and a small current is flowing. The electrolysis is being reversed – the hydrogen and oxygen are recombining, and an electric current is being produced.

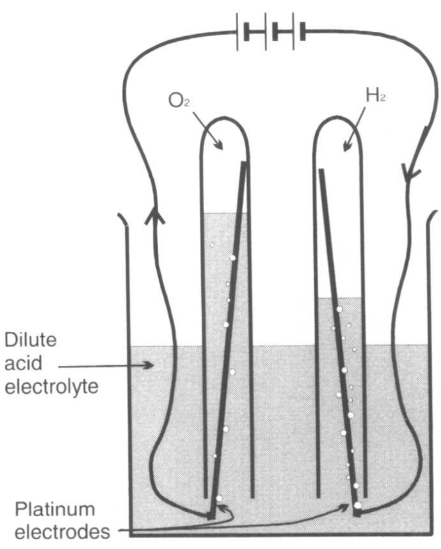

Figure 1.1a The electrolysis of water. The water is separated into hydrogen and oxygen by the passage of an electric current.

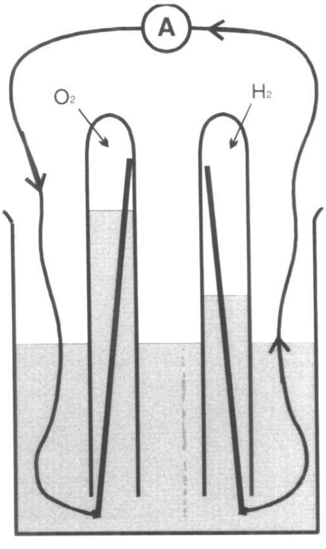

Figure 1.1b A small current flows. The oxygen and hydrogen are recombining.

Note, the arrows show the direction of flow of the ***negative electrons***, from – to +.

Another way of looking at the fuel cell is to say that the hydrogen fuel is being "burnt" or combusted in the simple reaction:

$$2H_2 + O_2 \rightarrow 2H_2O \qquad [1.1]$$

However, instead of heat energy being liberated, electrical energy is produced.

The experiment of Figures 1.1a and 1.1b makes a reasonable demonstration of the basic principle of the fuel cell, but the currents produced are very small. The main reasons for the small current are:

- the low 'contact area' between the gas, the electrode and the electrolyte – basically just a small ring where the electrode emerges from the electrolyte.
- the large distance between the electrodes - the electrolyte resists the flow of electric current.

To overcome these problems the electrodes are usually made flat, with a thin layer of electrolyte as in Figure 1.2. The structure of the electrode is porous, so that both the electrolyte from one side and the gas from the other can penetrate it. This is to give the maximum possible contact between the electrode, the electrolyte and the gas.

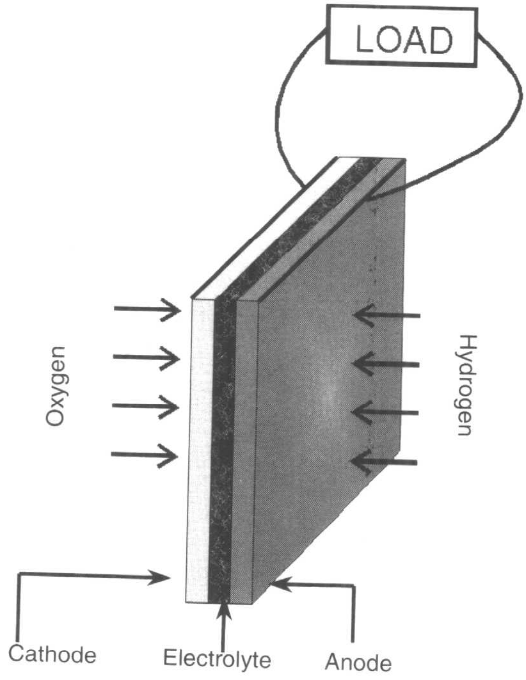

Figure 1.2 Basic cathode-electrolyte-anode construction of a fuel cell