ELSEVIER

Volume 1

Advances in Fuel Cells

T. S. Zhao
K-D. Kreuer
Trung Van Nguyen

VOLUME ONE

ADVANCES IN FUEL CELLS

Edited by

T. S. ZHAO (Editor-in-chief)
The Hong Kong University of Science & Technology
Hong Kong, China

K.-D. KREUER
Max Planck Inst Festkorperforsch, Germany

TRUNG VAN NGUYEN
University of Kansas, USA

ELSEVIER

Amsterdam • Boston • Heidelberg • London • New York • Oxford
Paris • San Diego • San Francisco • Singapore • Sydney • Tokyo

Elsevier
Linacre House, Jordan Hill, Oxford, OX2 8DP, UK
Radarweg 29, PO Box 211, 1000 AE Amsterdam, The Netherlands

First edition 2007
Reprinted 2008

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

Library of Congress Cataloging-in-Publication Data
A catalog record for this book is available from the Library of Congress

ISBN: 978-0-08-045394-1

For information on all Elsevier publications
visit our website at books.elsevier.com

Printed and bound in *Great Britain*

08 09 10 10 9 8 7 6 5 4 3 2

VOLUME ONE

ADVANCES IN FUEL CELLS

Contributors

Frank A. de Bruijn
Energy Research Centre of the Netherlands, P.O. Box 1, 1755 ZG Petten, The Netherlands.
University of Technology Eindhoven, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.

Patric Jannasch
Department of Polymer Science & Engineering, Lund University, P.O. Box 124, SE-221 00 Lund, Sweden.

Gaby J. M. Janssen
Energy Research Centre of The Netherlands, P.O. Box 1, 1755 ZG Petten, The Netherlands.

Dong Hyun Kim
Department of Chemical Engineering, Kyungpook National University, 1370 Sankyukdong, Daegu 702-701, Republic of Korea.

Yu Seung Kim
MST-11, Electronic and Electro-chemical Devices, Los Alamos National Laboratory, Los Alamos, NM 87545.

A. A. Kulikovsky
Institute for Materials and Processes in Energy Systems (IWV–3), Research Center "Jülich", D–52425 Jülich, Germany.

Arunabha Kundu
Department of Chemical Engineering, Yonsei University, 134 Shinchon Dong, Sudeamun-Ku, Seoul 120-749, Republic of Korea.

Benoît Lafitte
Department of Polymer Science & Engineering, Lund University, P.O. Box 124, SE-221 00 Lund, Sweden.

Xianguo Li
Fuel Cells and Green Energy Research Group, Department of Mechanical Engineering, University of Waterloo, Waterloo, Ontario, Canada.

Robert C. Makkus
Energy Research Centre of the Netherlands, P.O. Box 1, 1755 ZG Petten, The Netherlands.

Ronald K. A. M. Mallant
Energy Research Centre of The Netherlands, P.O. Box 1, 1755 ZG Petten, The Netherlands.

John Newman
Lawrence Berkeley National Laboratory and Department of Chemical Engineering, University of California, Berkeley, CA 94720-1462.

Bryan S. Pivovar
MST-11, Electronic and Electro-chemical Devices, Los Alamos National Laboratory, Los Alamos, NM 87545.

Yong Gun Shul
Department of Chemical Engineering, Yonsei University, 134 Shinchon Dong, Sudeamun-Ku, Seoul 120-749, Republic of Korea.

Adam Z. Weber
Lawrence Berkeley National Laboratory and Department of Chemical Engineering, University of California, Berkeley, CA 94720-1462.

PREFACE

Fuel cells have been recognized to be destined to form the cornerstone of energy technologies in the twenty-first century. The rapid advances in fuel cell system development have left current information available only in scattered journals and Internet sites. To be truly useful to both present and future workers in the field, this prodigious outpouring of new information needs to be brought together, deposited in one central resource and conveyed from a more global perspective. The establishment of this new book series, *Advances in Fuel Cells*, will answer the need and provide the forum.

Advances in Fuel Cells is intended to fill the information gap between regularly scheduled journals and university level textbooks by providing in-depth coverage over a broader scope than in journals or texts. Contributions by leading experts working in both academic and industrial research and development, will serve as a central source of reference for the fundamentals and applications of fuel cells, establishing the state of the art, disseminating the latest research discoveries, and providing potential textbooks to senior undergraduate and graduate students.

The present volume provides informative chapters on thermodynamic performance of fuel cells, macroscopic modeling of polymer-electrolyte membranes, the prospects for phosphonated polymers as proton-exchange fuel cell membranes, polymer electrolyte membranes for direct methanol fuel cells, materials for state of the art proton-exchange membrane fuel cells, and their suitability for operation above 100°C, analytical modeling of direct methanol fuel cells, and methanol reforming processes.

The editorial board expresses their appreciation to the contributing authors of Volume 1, who have opened up the high standards associated *Advances in Fuel Cells*. Last, but not least, the editors acknowledge the efforts of the professional staff at Elsevier for providing invaluable editorial assistance.

T. S. Zhao
The Hong Kong University of Science & Technology, Hong Kong, China

K.-D. Kreuer
Max Planck Inst Festkorperforsch, Germany

Trung Van Nguyen
University of Kansas, USA

Contents

CHAPTER ONE

Thermodynamic Performance of Fuel Cells and Comparison with Heat Engines

Xianguo Li

Contents

Fuel Cells and Green Energy Research Group, Department of Mechanical Engineering, University of Waterloo, Waterloo, Ontario, Canada

Advances in Fuel Cells
0080453945

Abstract

Heat engines based on fossil fuel combustion produce harmful pollutants and greenhouse gas emissions. Environmental concerns and sustainable development call for new technology for energy conversion and power generation, which is more efficient, environmentally friendly and compatible with alternative fuels and renewable energy sources and carriers. Fuel cells meet all these requirements, and are being developed as one of the primary energy technologies of the future. In this chapter, the thermodynamic performance of fuel cells is analyzed, energy conversion efficiency of fuel cells and heat engines is studied and compared, and misconceptions about fuel cell efficiency clarified. It is shown that both fuel cells and heat engines have the same maximum theoretical efficiency, which is equivalent to the Carnot efficiency, when operating on the same fuel and oxidant. However, fuel cells are free from the high temperature limit imposed by materials on heat engines and less irreversibilities associated with heat rejection. As a result, fuel cells can have higher practical efficiencies.

1.1 INTRODUCTION

Progress in human society, and especially modern civilization, has been marked by ever-increasing energy consumption and power requirements. The majority of the energy needs have been provided by combustion of fossil fuels since the industrial revolution. Heat engines utilizing fossil fuel combustion have resulted in severe local air pollution, threatening the health of millions of people living in many of the world's urban areas. They continue to contribute significantly to the increase in the atmospheric carbon dioxide concentrations, thus intensify the prospect of global warming. In addition to the health and environmental concerns, a steady depletion of the world's limited fossil fuel reserves and the very survival of humankind call for new generation technology for energy conversion and power generation, which is more efficient than the conventional heat engines with minimal or no pollutant emissions, and also compatible with renewable energy sources and carriers for sustainable development and energy security. Fuel cell has been identified as the most promising and potential energy conversion technology, which meets all of the above requirements. In fact, fuel cell technology has been successfully used in many specific areas, notably in space explorations, where fuel cell operates on pure hydrogen and oxygen with over 70% thermal to electrical energy efficiency and the only byproduct water constitutes the sole source of drinking water for the crew of the spacecraft. There are now several hundred fuel cell units for terrestrial applications, from stationary cogeneration, mobile transportation to portable applications, operating in over a dozen of countries, impressive technical progress has been achieved, and is driving the development of competitively priced fuel cell-based power generation systems with advanced features.

Besides being efficient, clean and compatible with future energy sources and carriers, fuel cell also offers many additional advantages for both mobile and stationary applications. Fuel cell is an electrochemical device and has no moving components except for peripheral compressors and motors. As a result, its operation is very quiet, and virtually without vibration and noise, thus capable of being sited at the premises of the consumer to eliminate power transmission lines. Its inherent modularity allows for simple construction and operation with possible applications for dispersed, distributed and portable power generation, because it may be made in any size from a few watts to megawatt scale plant with equal efficiency. Its fast response to the changing load condition while maintaining high efficiency makes it ideally suited to load following applications. Its high efficiency represents less chemical, thermal and carbon dioxide emissions for the same amount of energy conversion and power generation.

At present, fuel cell is being used routinely in space applications, and has been under intensive development for terrestrial use, such as for utilities and zero emission vehicles. There exist a variety of fuel cells, and they can be classified based on their operating temperature such as low and high temperature fuel cells, the type of ion migrating through the electrolyte, etc. However, the choice of electrolyte defines the properties of a fuel cell. Hence, fuel cell is often named by the nature of the electrolyte used. There are presently six major fuel cell technologies at varying stages of development and commercialization. They are alkaline, phosphoric acid, polymer electrolyte membrane, molten carbonate, solid oxide and direct methanol fuel cells. Their electrochemical reactions, operation fundamentals, construction and design, application and state of the art technology can be found elsewhere [1–7].

Although numerous studies aiming at developing fuel cell technology as a practical source of power have been conducted, some confusion and misconception exists about the thermodynamic performance of fuel cells and its comparison with heat engines [2,8–13]. For example, it is often said that fuel cells are not limited by the Carnot efficiency, therefore they have, or can achieve, higher energy efficiency than the conventional heat engines, e.g., Ref. [9]. Some even go so far as to state that fuel cells are not subject to "thermodynamic limitations." It is also often the practice that in proving a fuel cell has better performance, a reversible fuel cell is compared with the irreversible heat engine [9,11,13] – certainly an unfair comparison since a reversible energy conversion system is assured to have better performance than the irreversible energy system based on the second law of thermodynamics. Further, many analyses used the specific fluids involved, e.g., Ref. [11], and assumed constant properties, e.g., Refs. [2,8,11], leaving to questions regarding the generality of the conclusions reached. Furthermore, some studies even show the possibility of fuel cells that could achieve over 100% efficiency – a result some even cite as a proof that fuel cell is more efficient than conventional heat engine since heat engine is not possible to achieve over 100% efficiency. On the other hand, Li [14,15] only uses the thermodynamic laws without consideration of specific fluids involved and their property variations, and demonstrate that both fuel cells and heat engines have the same maximum possible efficiency when operating on the same fuel and oxidant, and this maximum efficiency and the Carnot efficiency are equal. But practical limitations (irreversibilities) result in fuel cells having higher practical efficiency than heat engines. Unique fuel cell operation at much lower temperatures also yields less or no pollutant emissions, thus leading to environmentally clean energy conversion. Finally, the riddle about the possibility of over 100% energy conversion efficiency for some reversible fuel cells was clarified. Li's approach has also been used by others in similar studies, e.g. [12].

In this chapter, the general approach by Li [14,15] will be followed in the analysis of fuel cell performance. The method of analysis will be general, without considering specific working fluids involved or their specific variations of properties with temperature, pressure and concentration, so that the results obtained and conclusions reached will be generally applicable. Specifically, the reversible cell potential will be derived by using the first and second laws of thermodynamics, and its variations with the operating conditions such as temperature, pressure and reactant concentrations in the reactant streams will be obtained with general thermodynamic relations. The issue of energy conversion efficiency will be presented with the help of the first and second laws of thermodynamics. The maximum possible efficiency for fuel cells will be investigated; a comparison will be made with Carnot efficiency, which is the maximum possible efficiency for heat engines against which fuel cells are competing for commercial success. Then the possibility of over 100% efficiency for fuel cells is examined. The energy conversion efficiency for a fuel cell system comprising fuel cells and auxiliary equipments will be considered, and efficiency loss mechanism for operating fuel cells will be discussed. It is the intention of preparing this chapter that the thermodynamic performance of fuel cell and its comparison with its rival heat engine is properly dealt with so that any future misunderstandings and misconceptions can be avoided.

1.2 Reversible Cell Potential

In a fuel cell, the chemical energy of a fuel and an oxidant is converted directly into electrical energy, which is exhibited in terms of cell potential and electrical current output. The maximum possible electrical energy output and the corresponding electrical potential difference between the cathode and anode are achieved when the fuel cell is operated under the thermodynamically reversible condition. This maximum possible cell potential is called reversible cell potential, one of the significantly important parameters for

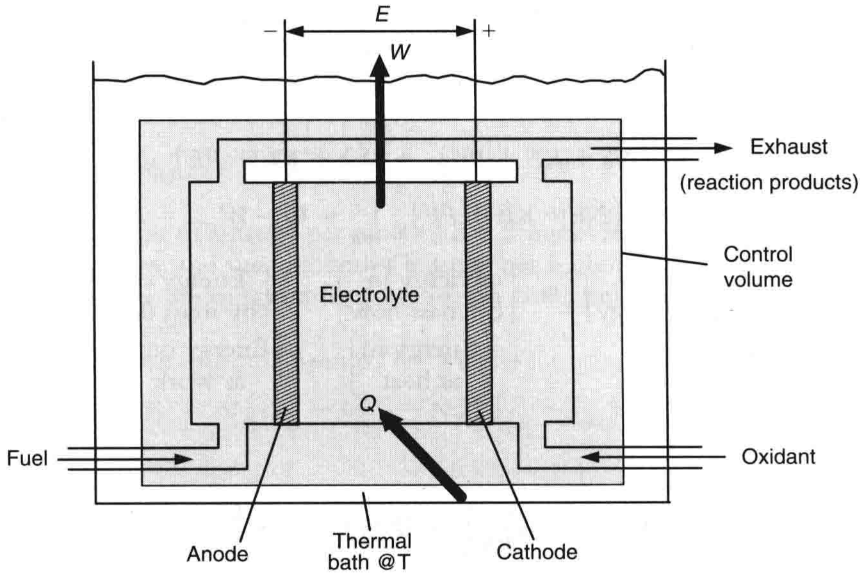

Figure 1.1 A thermodynamic model of fuel cell system.

fuel cells. We shall apply fundamental thermodynamic principles to derive the reversible cell potential in this section.

A thermodynamic system[1] model is shown in Figure 1.1 for the analysis of fuel cell performance. It is a control-volume system for the fuel cell to which fuel and oxidant streams enter and product or exhaust stream exits. The fuel cell is located inside a thermal bath in order to maintain the desired system temperature T. The reactant streams (fuel and oxidant) and the exhaust stream are considered to have the same temperature T and pressure P. It is assumed that the fuel and oxidant inflow and the exhaust outflow are steady; the kinetic and gravitational potential energy changes are negligible. Further, the overall electrochemical reactions occurring inside the fuel cell system boundary is described as follows:

$$\text{Fuel (e.g., } H_2) + \text{Oxidant (e.g., } O_2) \Rightarrow \dot{W} + \dot{Q} + \text{Product} \qquad (1.1)$$

where $\dot{W}$ is the rate of work done by the system and $\dot{Q}$ the rate of heat transferred into the system from the surrounding constant temperature thermal bath, which may, or may not, be in thermal equilibrium with the fuel cell system at the temperature T and pressure P. For hydrogen/oxygen

[1] A thermodynamic system, or simply system, is in thermodynamics a collection of matter under study (or analysis); whereas the jargon "fuel cell system" in fuel cell literature usually denotes the fuel cell power plant that consists of fuel cell stack(s) and auxiliary equipment. In this chapter, a fuel cell system may imply both meanings. However, the context will tell which it is meant to be.

fuel cells, the reaction product is usually water. Then, the first and second laws of thermodynamics can be written, respectively, for the present fuel cell system, as

$$\frac{dE_{C.V.}}{dt} = \left[\left(\dot{N}h + KE + PE\right)_F + \left(\dot{N}h + KE + PE\right)_{Ox}\right]_{in} - \left[\left(\dot{N}h + KE + PE\right)_{Ex}\right]_{out} + \dot{Q} - \dot{W} \tag{1.2}$$

$$\begin{pmatrix}\text{Increase in}\\ \text{system energy}\end{pmatrix} = \begin{pmatrix}\text{Energy in}\\ \text{by mass flow}\end{pmatrix} - \begin{pmatrix}\text{Energy out}\\ \text{by mass flow}\end{pmatrix} + \begin{pmatrix}\text{Energy in}\\ \text{as heat}\end{pmatrix} - \begin{pmatrix}\text{Energy out}\\ \text{as work}\end{pmatrix}$$

and

$$\frac{dS_{C.V.}}{dt} = \left[\left(\dot{N}s\right)_F + \left(\dot{N}s\right)_{Ox}\right]_{in} - \left[\left(\dot{N}s\right)_{Ex}\right]_{out} + \frac{\dot{Q}}{T} + \dot{\wp}_s \tag{1.3}$$

$$\begin{pmatrix}\text{Increase in}\\ \text{system entropy}\end{pmatrix} = \begin{pmatrix}\text{Entropy in}\\ \text{by mass flow}\end{pmatrix} - \begin{pmatrix}\text{Entropy out}\\ \text{by mass flow}\end{pmatrix} + \begin{pmatrix}\text{Entropy in by}\\ \text{heat transfer}\end{pmatrix} + \begin{pmatrix}\text{Entropy}\\ \text{generated}\end{pmatrix}$$

where $\dot{N}$ is the molar flow rate, h (absolute) enthalpy per unit mole, s the specific entropy on a mole basis and $\dot{\wp}_s$ the rate of entropy generation due to irreversibilities. The subscript "$_F$", "$_{Ox}$" and "$_{Ex}$" stand for fuel, oxidant and exhaust stream, respectively. "*KE*" and "*PE*" denote kinetic and gravitational potential energy that are being carried in and out of the system by the mass flow.

For a steady process, there are no temporal changes in the amount of energy $E_{C.V.}$ and entropy $S_{C.V.}$ within the control-volume system, hence, $dE_{C.V.}/dt = 0$ and $dS_{C.V.}/dt = 0$. Further, the changes in the kinetic and gravitational potential energy are negligible for the present process. Therefore, Eqs. (1.2) and (1.3) can be simplified as follows:

$$\dot{N}_F\left(h_{in} - h_{out}\right) + \dot{Q} - \dot{W} = 0 \tag{1.4}$$

$$\dot{Q} = -T\dot{\wp}_s - \dot{N}_F T\left(s_{in} - s_{out}\right) \tag{1.5}$$

where

$$h_{in} = \left(h_F + \frac{\dot{N}_{Ox}}{\dot{N}_F}h_{Ox}\right)_{in} \quad \text{and} \quad h_{out} = \frac{\dot{N}_{Ex}}{\dot{N}_F}h_{Ex} \tag{1.6}$$