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Fuel Cell Engineering

Volume 41

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FUEL CELL ENGINEERING

VOLUME **41**

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CHEMICAL ENGINEERING

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PREFACE

Fuel cells are energy converters able to transform chemically stored energy directly to electrical energy at high thermodynamic efficiencies. From the point of view of chemical engineers, fuel cells are electrochemical membrane reactors featuring a high degree of complexity due to the interaction of multistep electrode reactions with simultaneous (and often multiphase) mass, charge, and energy transport phenomena. In spite of significant progress during the past two decades, further improvements of performance, durability, and controllability are necessary for translating fuel cell technologies into commercial products. For this purpose, a detailed understanding of the steady state and dynamic behavior of fuel cells—on electrode level, the single cell level, and the system level—is of fundamental importance. This can be achieved only by physical–chemical modeling of all relevant processes involved in the operation of fuel cell systems. Thus, the present issue of *Advances in Chemical Engineering* is focused on the model-based analysis, control, and optimization of fuel cells.

Chapter 1 gives an overview on different chemical routes for converting hydrocarbon fuels to hydrogen or hydrogen-rich gas mixtures usable for operating different types of fuel cells. Apart from fuels, fuel processors, and fuel requirements, quantitative modeling and simulation approaches are reported, aiming at the description of the molecular processes during fuel conversion and the prediction of chemical reactions on catalytic surfaces in combination with heat and mass transport phenomena between surfaces and gaseous fluids.

Chapter 2 is focused on polymer electrolyte fuel cells (PEFCs) which receive the most attention for automotive and small stationary applications because of their high electrical efficiency and power density. The governing conservation equations, transport equations, electrochemical reaction kinetics, and thermodynamic relations are examined with regard to performance-related issues. The chapter is written as a guide toward understanding the complex interactions that occur within PEFCs.

While conventional PEFCs are operated with high purity hydrogen gas as anode feed, direct methanol fuel cells (DMFCs) are fed with aqueous methanol solutions. This makes DMFCs attractive for mobile and portable applications. Chapter 3 reports the principles of operation and models which have been developed to create viable DMFCs.

In particular, models which describe the dynamic cell response are reviewed to aid in development of control strategies.

Chapter 4 is focused on PEFC fuel cell system modeling and controller design. The formulation of lumped parameter models, able to capture the essential dynamics of fuel cell stacks and systems, is discussed. The design of controllers for hydrogen purge, heat management, and air supply is described. Conventional PID controllers as well as advanced control methods (Model Predictive Control) are presented. Moreover, selected approaches for fuel cell fault diagnosis are presented.

Chapter 5 briefly summarizes the physical phenomena responsible for the degradation phenomena occurring in various parts of PEFC fuel cells. It is mainly targeted at the experimental techniques and models used by engineers for evaluating aging processes. The operating conditions applied in long-term tests of fuel cell components are presented and a selection of typical aging situations is discussed.

While Chapters 2–5 cover different aspects of low-temperature PEFCs, the following contributions are focused on high-temperature solid oxide fuel cells (SOFCs). Chapter 6 presents a modeling framework for SOFCs, including the transport phenomena and chemical and electrochemistry reactions. Using tubular and planar cells as examples, model problems are solved to illustrate and discuss both steady state and dynamical behaviors. The latter are highly relevant for the interpretation of electrochemical impedance spectra and for the development of control strategies, as well as for coordinating multiple sensors and actuators.

Chapter 7 discusses SOFCs at the system level, that is, the integration of a cell stack with the so-called balance-of-plant components (BoP: reformer, pumps, blowers, heat exchangers, burner, etc.). Understanding and predicting the exchange of matter and energy among the BoP components is essential for system design and control. In addition to system efficiency, one has to perform a careful analysis of the life-cycle costs in order to optimize the overall system performance.

Of course, this collection of chapters does not represent a comprehensive compendium of the whole area of fuel cell engineering. But I hope that this sampling of work will provide graduate students and experienced practitioners with a helpful introduction to the current state of model-based fuel cell analysis, control, and optimization.

Finally, I would like to thank the series editor Prof. Guy Marin and the publisher Elsevier for the invitation to organize this topical issue. And, of course, I am very thankful to the authors of the seven chapters for taking time to contribute to this volume.

Kai Sundmacher
Magdeburg
December 31, 2011

CONTENTS

CHAPTER 1

Fuel Processing for Fuel Cells

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Abstract This chapter focuses on processing the different fuels for the use in fuel cells, that is, the chemical conversion of different hydrocarbon fuels to hydrogen or hydrogen-rich synthesis gases. Aside from an overview on fuels, fuel processors, and fuel requirements from the perspective of different fuel cells, quantitative modeling and simulation approaches are presented. The models are based on the molecular chemical processes in heterogeneous fuel conversion and describe the interactions of chemical reactions on catalytic surfaces and in the gaseous fluid with mass and heat transport. Reforming of natural gas, gasoline, diesel, and ethanol are discussed.

ABBREVIATIONS

AC	alternating current
APU	auxiliary power unit
ATR	autothermal reforming
AUVs	autonomous undersea vehicles
BGBI	Federal Law Gazette
BOP	balance of plant
C/O	carbon-to-oxygen ratio

CHP	combined heat and power
CPOX	catalytic partial oxidation
CPU	central processor unit
D	dimension
DC	direct current
DFT	density functional theory
DIN	German Industry Standard
DMFC	direct methanol fuel cell
DR	dry reforming
E10	gasoline blended with 10 vol.% ethanol
E5	gasoline blended with 5 vol.% ethanol
E85	gasoline blended with 85 vol.% ethanol
EG	European Community
EN	European Standard
EPA	Environmental Protection Agency
Eq	equation
EU	European Union
FAME	fatty acid methyl ester
HDS	hydrodesulfurization process
HTS	high-temperature stage in WGS
ISO	International Organization for Standardization
LLNL	Lawrence Livermore National Laboratory
LNG	liquefied natural gas
LPG	liquefied petroleum gas
LTS	low-temperature stage in WGS
MCFC	molten carbonate fuel cell
MEA	membrane electrode assembly
MF	mean-field approximation
PAFC	phosphoric acid fuel cell
PAHs	polyaromatic hydrocarbons
PEM	proton exchange membrane
PEMFC	proton exchange membrane fuel cell
POX	partial oxidation
PrOX	preferential oxidation of carbon monoxide
R&D	research and development
S/C	steam-to-carbon ratio
SMET	selective methanation of carbon monoxide
SOFC	solid oxide fuel cell
SR	steam reforming
UBI-QEP	unity bond index–quadratic exponential potential method
WGS	water–gas shift

LIST OF UNITS AND SYMBOLS

%cal	caloric percentage
°C	degree celsius
kg	kilogram
kJ	kilojoule
kW	kilowatt
m	meter
mg	milligram
mm	millimeter
mm^2	square millimeter
MW	megawatt
mW	milliwatt
n	number of moles
ppm	parts per million
ppmv	parts per million by volume
ppmw	parts per million by weight
pS	pico-Siemens
vol.%	volume percentage
W	watt
A_i	name of species i
A_k	pre-exponential factor, mol, m, s
C(s)	surface carbon
c_i	species concentration, mol m^{-2}, mol m^{-3}
E_{a_k}	activation energy, J mol^{-1}
$F_{cat/geo}$	ratio of the total active catalytic surface area in relation to the geometric surface area of the fluid–solid interphase
$\vec{j}_i$	diffusion flux of species i, kg m^{-2} s^{-1}
k_{f_k}	rate coefficient of the forward reaction, mol, m, s
K_s	number of surface reactions
M_i	molar mass of species i, kg mol^{-1}
$\vec{n}$	(surface) normal
N_b	bulk species absorbed by the catalyst particle
N_g	species in the gas phase
N_s	species adsorbed on the top catalyst layer
R	gas constant, J K^{-1} kg^{-1}
R_i^{het}	local chemical source term species i
$\dot{s}_i$	molar net production rate of species i, mol m^{-2} s^{-1}
t	time, s
T	temperature, K
Y_i	mass fraction of species i
β_k	temperature exponent

Γ	site density, mol m^{-2}
ΔH^0_{298}	molar standard formation enthalpy, J mol^{-1}
ε_{i_k}	coverage-dependent activation energy parameter, J mol^{-1}
η	effectiveness factor based on the Thiele modulus
Θ_i	surface coverage of species i
μ_{i_k}	coverage-dependent reaction order parameter
ν'_{ik}	stoichiometric coefficient
ν''_{ik}	stoichiometric coefficient
$\vec{v}_{\text{Stef}}$	Stefan velocity, m s^{-1}
ρ	density, kg m^{-3}
σ_i	coordination number, gives the number of surface sites which are covered by the adsorbed species

1. INTRODUCTION

The first successful ascension of a balloon filled with hydrogen on December 1st, 1783, in Paris was possible, thanks to prior intensive fuel processing, because Jacques Charles was eventually able to sufficiently clean the hydrogen he gathered from the dissolution of metal in acid. In their experiments in the years before, Goethe, Lichtenberg, and Soemmering in Göttingen and Frankfurt also observed the hydrogen bubbles but failed to realize their dreams of filling a balloon with them due to insufficient fuel processing (Sandstede, 2000).

In this book, fuel processing is understood as the process in which the chemical composition of chemical energy carriers (primary fuels) is chemically converted to a composition with which a fuel cell can be operated. As hydrogen is the most commonly used fuel for fuel cells, fuel processing usually is the conversion of the primary fuel to hydrogen or hydrogen-rich gases and removal of components such as sulfur and carbon monoxide that may have hazardous effects on the fuel cell operation. Since a variety of primary fuels is of interest, and since there is a variety of fuel cell types with very different requirements regarding the fuel quality, various concepts of fuel processing have been developed, depending not only on the primary fuel and the fuel cell type, but also on the field of application and its operating and boundary conditions.

Today, the lack of an adequate infrastructure for hydrogen distribution requires the delivery of hydrogen stored in bottles and tanks to the location of the fuel cell. This hydrogen is mainly produced from natural gas by large-scale industrial steam reformers associated with the need of an extensive input of external energy and a tremendous output of the greenhouse gas carbon dioxide. Therefore, from a sustainable point of view, little is gained by using fuel cells for the production of electrical