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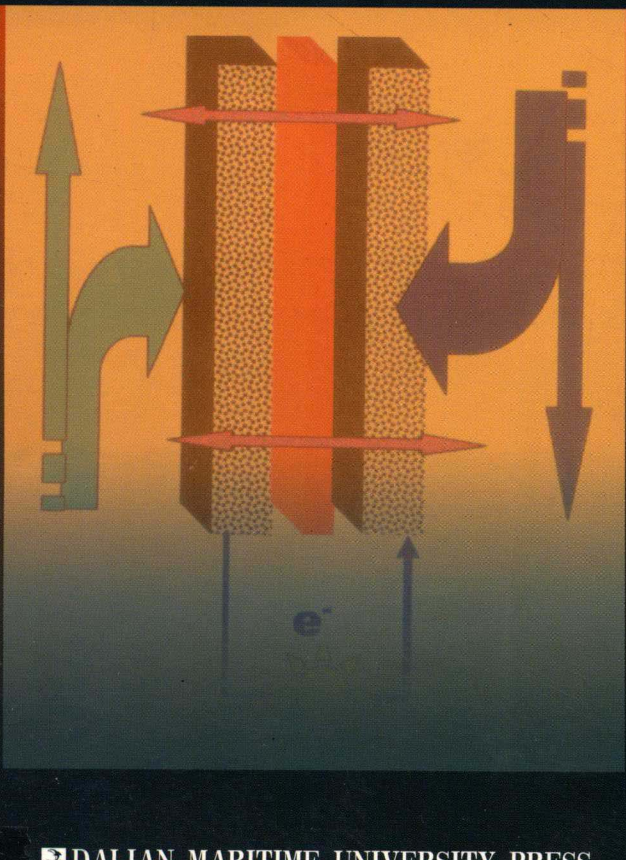

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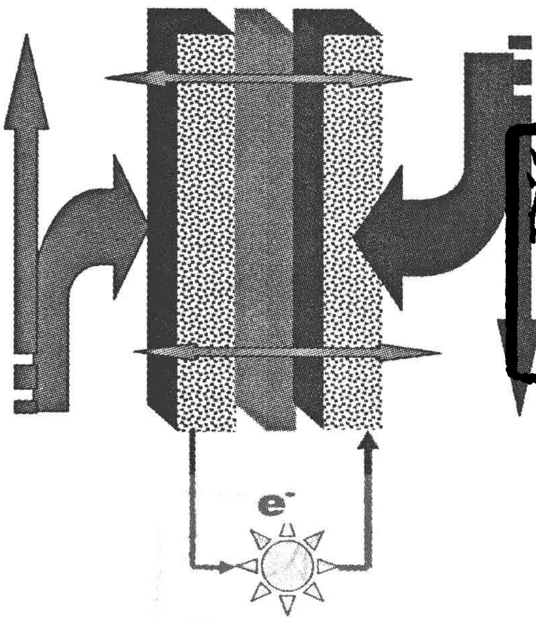


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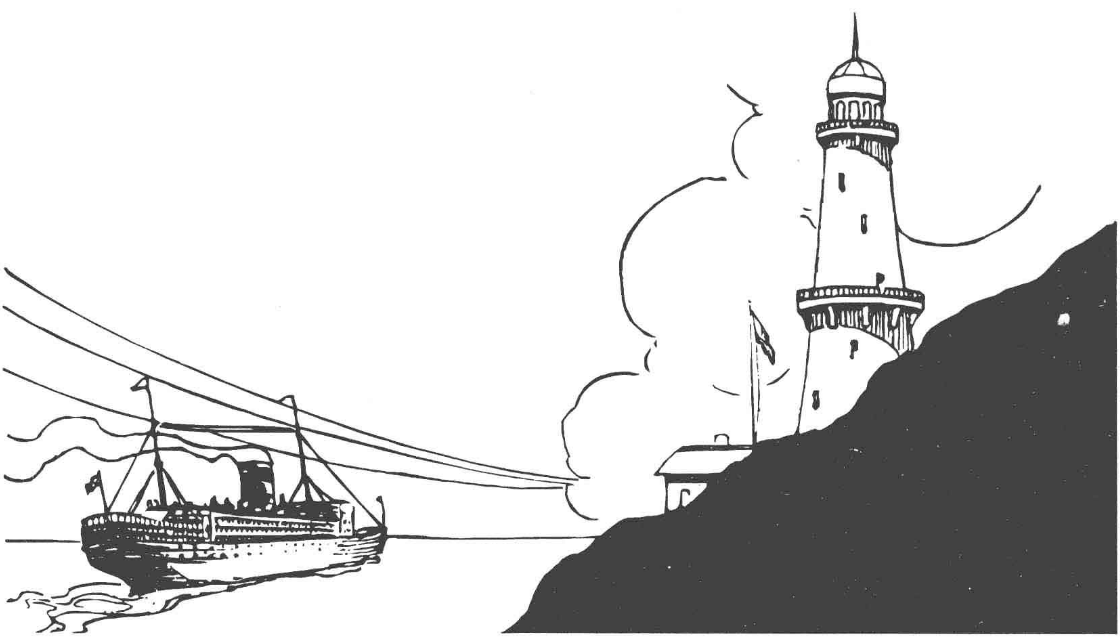

# 前 言

燃料电池是一种直接将储存在燃料(如氢气、天然气等)和氧化剂(如空气中的氧气)中的化学能高效地转化为电能的发电装置。采用氢气作为燃料，其转化过程的产物为水(气或液态)和热量，对环境无任何污染。在所有种类的燃料电池中，固体电解质燃料电池(SOFC)和质子交换膜燃料电池(PEMFC)具有独特的优势和特点，受到各国的普遍重视，被公认为21世纪重要的绿色能源。电池内的气(液)和热量传递及分配对燃料电池的性能有着重要的影响，历来被认为是影响燃料电池走向实用化的关键性技术之一。进一步提高燃料电池的重量/功率比、体积/功率比及电池的工作可靠性都强烈依赖于电池内气与热流动的优化设计和配送过程的研究，以确保电极各处均能得到充足的燃料和氧化剂供应及工作温度均匀。基于多年燃料电池的研究经验，本书对SOFC和PEMFC中各部件气体、热量流动及其压力、温度等参数的分布进行了深入的分析和讨论。本书是作者在多年科研工作的基础上编写的，可作为燃料电池有关专业研究生教科书，也可供相关工程技术人员参考。

此书的出版得到了大连海事大学学术著作出版基金的资助。大连海事大学孙俊才教授、殷佩海教授、岳丹婷教授等认真阅读了原稿，并提出了不少宝贵意见。作者在此表示衷心的感谢。

袁金良

2003年11月1日

# PREFACE

In a fuel cell, electrical energy is generated directly through the electro-chemical reaction of oxidant (oxygen from air) and fuels (such as natural gas, methanol or pure hydrogen) at two electrodes separated by an electrolyte. When pure hydrogen is used, the only products of this process are heat, electricity and water. Fuel cells are expected to play a significant role in the next generation of energy systems and road vehicles for transportation. There are various transport processes in solid oxide fuel cells (SOFCs) and proton exchange membrane fuel cells (PEMFCs), such as multi-dimensional flow and heat transfer in multi-phase flows, multi-component transport of gaseous species in porous media and electrochemical reactions including heat generation. However, substantial progress is required to understand the associated heat and mass transport processes for reducing manufacturing costs and improving the performance of fuel cells. Currently a large number of research activities are carried out for fuel cells worldwide, but there is no comprehensive book available to address the analysis of transport phenomena in fuel cells so far.

This book aims to understand the major transport processes in SOFCs and PEMFCs. It focuses on the modeling, simulation and numerical analysis of heat, mass transfer/species flow, two-phase transport and effects on the cell performance in SOFCs and PEMFCs based on their similarities/dissimilarities. The unique boundary conditions (thermal, mass) for the flow ducts appearing in fuel cells are recognized and applied. This book is based on the research experiences and results from fuel cell related projects, and several relevant topics published are included for detailed discussions.

This book are applicable for other investigations considering overall fuel cell modeling and system studies, as well as the emerging field of micro-reactor engineering.

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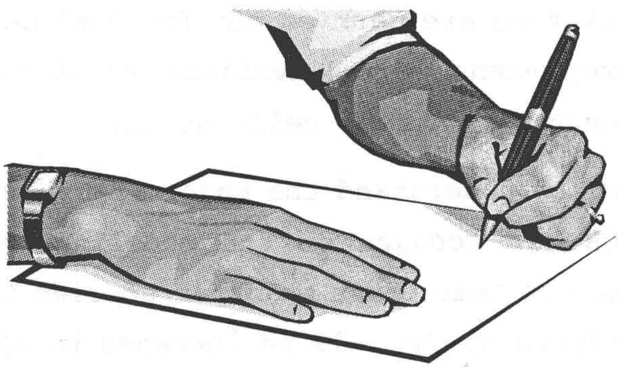
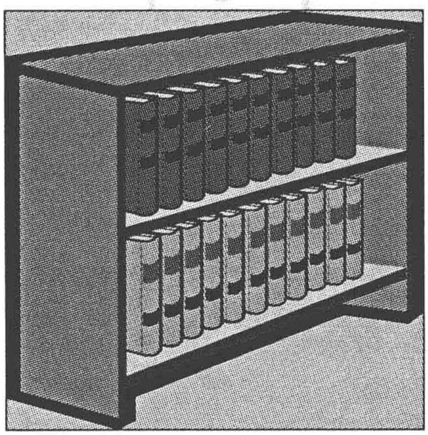
**YUAN Jinliang**

2003-11-01



# CONTENT



# 1 INTRODUCTION

Uniform supply of species to an active surface, where the electrochemical reaction happens, is important in a fuel cell duct. The most common ducts in fuel cells consist of a porous layer, the flow duct and solid current collector (or connector) with constant cross-section area. Understanding of various species (gas/liquid water) and heat transport processes is crucial for increasing power density, reducing manufacturing cost and accelerating commercialisation of fuel cell systems.

Analyses and simulations of gas utilization, produced power, energy efficiency, electrical current and temperature distribution, and mechanical stress in unit cells of a fuel cell stack have been presented in the literature for solid oxide fuel cells (SOFCs) and proton exchange membrane fuel cells (PEMFCs). The energy balance equation is usually employed in the thermal analysis and calculations of temperature distributions. However, the assumptions concerning the convective heat transfer coefficients for the flow of the fuel and the oxidant are usually based on constant Nusselt numbers which are available in the published literature. The unique mass transfer and thermal boundary conditions of fuel cells have not been considered properly. The flow ducts for the fuel and the oxidant are usually identical in the model and uniform throughout the entire fuel cell stack. This is not very appropriate if an even temperature distribution is attempted for and if the pressure drop for each fluid should be kept within certain limits. Thus there is a need to deepen and further develop such analyses to give a better understanding and achieve heat transfer coefficients which are valid for the fuel cell boundary conditions.

In fuel cells, heat is mainly transferred through one duct wall which will be clarified in this book, while the other three walls are kept at a uniform temperature or are thermally insulated. The heat transfer coefficient is influenced by this thermal boundary condition. In addition, mass transfer across one or more duct walls associated with the electrochemical reactions is another unique feature of fuel cells. Fuel (usually $H_2$) and part of the oxidant (usually air) are consumed in the anode and cathode ducts, respectively. However, later (further along the duct) the mass flow rate is increased due to the transfer of the water generated in the electrochemical reaction in the anode duct for SOFCs and in the cathode duct for PEMFCs. This mass transfer also affects the heat transfer and pressure drop (flow field) characteristics. Moreover, buoyancy effects are significant in some applications and should be considered. In addition, effects of species transport through a porous layer are significant in the PEMFCs and the moderate temperature (anode-supported) SOFCs, because the size of the porous layer is large compared to the flow duct in terms of thickness and cross-section area.

It is a widely accepted fact that the PEMFCs cathode is the performance-limiting component. It is so because the potential water flooding as discussed later in this book and occurrence of slower kinetics of the oxygen reduction reaction affect the cell performance. In addition, mass transfer limitations may happen due to the nitrogen barrier layer effects in the porous layer. Two-phase flow and its effects on the heat transfer, concentration variation and PEMFCs performance are very important.

The pressure drop is of particular importance as the thermal-hydraulic performance of the fuel cell should be established and as the fuel cell should be integrated with other units, such as a gas turbine or combined heat and power plants. The influences of the fuel cell on process coupling and on the choice of components in an energy system, such as pre-heaters, inter-coolers, and district heating heat exchangers and so on, depend on the characteristics of the fuel cell. The need for determination of temperature distribution, convective heat transfer, pressure drop and two-phase flow/water balance is thus significant. This is particularly true as optimization is requested and to enable the fuel cell to operate correctly.

The overall aim of this book is to analyze heat and mass transport, and fluid flow (two-phase) phenomena in fuel cell ducts. Numerical calculation methods have been further developed to enable predictions of convective heat transfer, pressure drop and two-phase flow in the flow ducts of the fuel and the oxidant. The following detailed objectives have been carefully considered as given below:

- To establish the state-of-the-art concerning thermal analysis and simulation of fuel cells in terms of methodologies and applications of detailed analysis of the heat transfer and gas flow, temperature distribution;
- To identify the heat and mass transfer/fluid mechanics problems and the unique thermal boundary conditions, interfacial conditions between flow duct and porous layer;
- To simulate and analyze effects of other unique fuel cell conditions of the composite fuel cell duct, including porous layer, solid structure and flow duct;
- To develop calculation procedures for pressure drop, heat and mass transfer, and two-phase flow and effects on the cell performance, so that the thermal hydraulic characteristics and heat/water management of fuel cells can be applied as system integration with a gas turbine and/or a combined process is considered.

This book aims to understand the major transport processes in SOFCs and PEMFCs. Fuel cells with high and moderate operating temperature (such as SOFCs) and low temperature (such as PEMFCs) are considered. It focuses on the modeling, simulation and numerical analysis of heat, mass transfer/species flow, two-phase transport and effects on the cell performance in SOFCs and PEMFCs based on their similarities/dissimilarities. This book is based on the research experiences and results from fuel cell related projects, and several relevant topics published are included for detailed discussions. This book are applicable for other investigations considering overall fuel cell modeling and system studies, as well as the emerging field of micro-reactor engineering.

# 2 FUNDAMENTALS AND DEVELOPMENTS OF FUEL CELLS

The invention of fuel cells as an electrical energy conversion system is attributed to Sir William Grove. However, the principle was discovered by Christin Friedrich Schönbein, who was a Professor at the University of Basle from 1829 to 1868, and in close contact with Sir Grove. It is no doubt that fuel cell is one of the oldest electrical energy conversion technologies known to people. The fuel cell development was very slow due to the lack of drives during the first century because primary energy sources were abundant, unrestricted and inexpensive. It was until the early of the 20th century, particularly during last decades, the conversion of chemical energy into electrical energy became more important due to the increase in the use of electricity. In the case of hydrogen/oxygen fuel cells, which are the focus of most research activities today, the only by-product is water and heat. The increase of the world's population has led to an increased interest in the development of more powerful and clean power generation as well. It is a fact that the increasing concern about the environmental consequences of fossil fuel use affected fuel cell developments in production of electricity and for the propulsion of vehicles and ships. Fuel cells may help to reduce our dependence on fossil fuels and diminish poisonous emissions into the atmosphere, since fuel cells have higher electrical efficiencies compared to internal combustion engines. The share of renewable energy from various sources, such as wind, water and sun, will increase further but these sources have limitations to cover the electrical base load due to their irregular availability. Consequently, the high efficiency of fuel cells and the prospects of generating electricity without pollution have made them a serious candidate to supply electricity and power for the next generation of vehicles and ships.

## 2.1 Fuel Cell Basics

Fuel cells are electricity generating devices, in which the free energy of a chemical reaction is converted into electrical energy (via an electrical current). The Gibbs free energy change of a chemical reaction is related to the cell voltage as follows,

$$\Delta G = -nF\Delta V_o \tag{2.1}$$

where $n$ is the number of electrons involved in the reaction, $F$ is the Faraday constant, and $\Delta V_o$ the voltage of the cell for thermodynamic equilibrium in the absence of a current flow.

The anode reaction in fuel cells is either the direct oxidation of hydrogen, or indirect oxidation via a reforming reaction when non pure hydrogen is used as fuels. While the cathode reaction in fuel cells is oxygen reduction, in most cases from air.

For the case of a hydrogen/oxygen fuel cell, the overall reaction is:

$$\mathrm{H_2} + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{H_2} \text{ with } \Delta G = 237 \text{ kJ/mol} \tag{2.2}$$

An equilibrium cell voltage is the difference of the equilibrium electrode potentials of cathode and anode which are determined by the electrochemical reaction taking place at the respective electrode:

$$\Delta V_o = \Delta V_{o,c} - \Delta V_{o,a} \tag{2.3}$$

The basic structure of all fuel cells is similar: the cell consists of two electrodes (**anode** for fuels and **cathode** for oxidant) which are separated by the electrolyte and which are connected in an external & electrically conducting circuit. The electrodes are exposed to gas or liquid flows to supply the electrodes with fuel or oxidant. The electrodes should be permeable to gas or liquid via a porous structure, while the electrolyte should possess gas permeability as low as possible.

## 2.2 Fuel Cell Developments

Several types of fuel cells are currently under development. In general, fuel cells can be classified according to the type of ionic conductor (electrolyte) they use and the temperature range at which they operate. Fig. 2.1 provides a brief summary of various types of fuel cells. Alkali fuel cell (AFC), being used for a long time by NASA on space missions, use alkaline potassium hydroxide as the electrolyte. In proton exchange membrane fuel cell (PEMFC) and phosphoric acid fuel cell (PAFC), hydrogen fuel dissociates into free electrons and protons (positive hydrogen ions). The hydrogen protons migrate through the electrolyte to the cathode. At the cathode, oxygen from air, electrons from the external circuit and protons combine to form pure water and heat. All these three types are low temperature fuel cells.

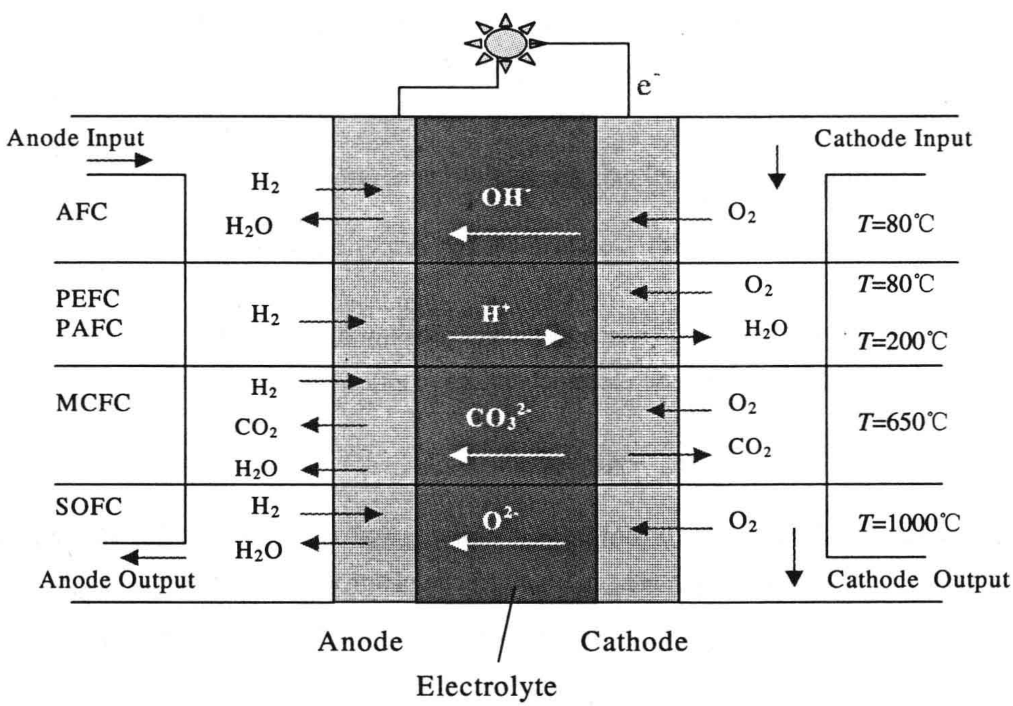



**Fig. 2.1 Various types of fuel cells**

High temperature fuel cells, such as solid oxide fuel cells (SOFCs) and molten carbonate ones (MCFC) are of particular interest, because operation at high temperatures allows usage of natural gas as a fuel, and hybrid concepts involving a combination of a fuel cell and a gas turbine. The overall system efficiency can be significantly increased. Operation at temperature about 1000℃ (conventional, electrolyte-supported design), 700℃ (inter-medium temperature, anode-supported design) and pressures greater than one atmosphere leads to solid oxide fuel cells (SOFCs) as the obvious choice[1].

In the anode duct, fuel (e.g., $H_2$) is supplied and air ($O_2+N_2$) is introduced in the cathode duct, and these ducts are separated by the electrolyte/electrode assembly. Reactants are transported by diffusion and/or convection to the electrode/electrolyte (SOFC) or catalyst/electrolyte (PEMFC) interfaces, where electrochemical reactions take place. An electrochemical oxidation reaction at the anode produces electrons that flow through the inter-collector (bipolar plate, for PEMFC) or inter-connector (for SOFC) to the external circuit, while the ions pass through the electrolyte to the opposing electrode. The electrons return from the external circuit to participate in the electrochemical reduction reaction at the cathode. In the electrochemical reaction process, part of the oxygen is consumed in the cathode duct, while the hydrogen is consumed in the anode duct. Heat and water ($H_2O$) are only the by-products during the process. The water generated is injected into the anode duct further along the duct in SOFCs, while in PEMFCs it enters into the cathode duct. The electrochemical reactions can be written as eqs. (2.4a-b) in SOFCs:

Cathode reaction $$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-} \tag{2.4a}$$

Anode reaction $$H_2 + O^{2-} \rightarrow H_2O + 2e^- \tag{2.4b}$$

Equations (2.5a-b) describe the reactions in PEMFCs:

Cathode reaction $$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \tag{2.5a}$$

Anode reaction $$H_2 \rightarrow 2H^+ + 2e^- \tag{2.5b}$$

The overall reaction is as follows:

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \tag{2.6}$$