MULTI-SCALE BRANCHING FLOW STRUCTURES OPTIMIZING HIGH-PERFORMANCE POLYMER ELECTROLYTE FUEL CELLS

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presented by

STEPHAN MARTIN SENN
Dipl. Masch.-Ing. ETH
born on September 24th, 1977
citizen of Boniswil AG, Switzerland

Accepted on the recommendation of

Prof. Dr. Dimos Poulakakos, examiner
Prof. Dr. Konstantinos Boulouchos, co-examiner
Prof. Dr. Aldo Steinfeld, co-examiner

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Summary

The scope of this thesis is the computational modeling and design/performance optimization of polymer electrolyte fuel cells and direct methanol fuel cells. Directly related to this goal, hence also a component of this thesis, is the investigation of the fundamental multiphase transport phenomena in the fuel cell, and the investigation of novel multi-scale flow structures, including tree network channels and porous materials, aiming at achieving higher power densities and efficiencies that are required to make the polymer electrolyte fuel cell a viable and competitive energy conversion device.

In chapter 1, branching, tree-like channel networks are introduced as a fuel cell fluid distribution concept. In order to perform quantitative calculations based on this concept, a one-dimensional model is used to predict the polarization curves of a so-constructed polymer electrolyte fuel cell. Pressure drop and pumping power required for the fluid circulation is estimated. Multiparametric genetic search is performed to maximize the net power density with respect to constructal parameters and operating conditions, leading to the optimized tree network. It is found that the use of tree networks instead of the traditional, non-bifurcating serpentine channels in rectangular systems can provide substantially improved cell performance due to their intrinsic advantage with respect to both mass transfer and pressure drop. In chapter 2, direct methanol fuel cells are investigated with the same concept of sequentially branching channels as fluid distributors, leading to pyramidal-shaped fuel cells. In chapter 3, a novel concept is investigated, according to which the traditional ribbed flow delivery systems are replaced with permeable porous fluid distributors, which circumvent a number of known performance hindering drawbacks. A thorough single-phase model, including the conservation of mass, momentum, energy, species, and electric current, using Butler-Volmer kinetics, is numerically solved in three dimensions, to investigate the impact of different flow configurations on the performance of hydrogen fuel cells. It is found that cells with porous gas distributors generate substantially higher current densities due to reduced mass transfer limitations. In chapter 4, a thorough non-isothermal multiphase model for the porous diffusion layer of a polymer electrolyte fuel cell is introduced. This model can be used in connection with the advanced concepts above in future investigations. The effect of downscaling of channel width, current collector rib width, and diffusion layer thickness on the performance of polymer electrolyte fuel cells is systematically investigated and optimal geometric length ratios (i.e., diffusion layer thickness / diffusion layer width, channel width / rib width) are identified at decreasing length scales. Based on this model it is found that
microchannels, e.g. as part of a tree network channel system, together with diffusion layers that are thinner than conventional layers can provide substantially improved current densities compared to conventional channels with diameters in the order of one millimeter, since the transport processes occur at reduced length scales. In chapter 5, a novel multistage polymer electrolyte fuel cell concept is introduced according to which the cell potential is subject to a stepwise or continuous variation along the channel direction. A common boundary condition in which the cell potential is uniformly distributed along the flow direction is replaced herein by a boundary condition in which the cell potential is nonuniformly distributed along the flow direction. It is shown that the optimum cell potential distribution function which maximizes the electric cell power density is a non-uniform function. In chapter 6, focusing on cooling issues in fuel cell stacks and employing the branching, tree-like channel concept for the coolant distribution, the laminar convective heat transfer and pressure drop characteristics in tree-like microchannel nets are numerically investigated and compared to the corresponding characteristics in traditional serpentine flow patterns, by solving the Navier-Stokes and energy equation for an incompressible fluid with constant properties in three dimensions. A constant heat flux is applied to the walls of the square cross-sectional channels. The intrinsic advantage of tree-like nets with respect to both heat transfer and pressure drop is demonstrated. In addition, secondary flow motions initiated at bifurcations and their important role on thermal mixing are identified and discussed.
Introduction

Computational modeling provides a more fundamental understanding of the physical phenomena occurring inside a thermodynamic system and forms the basis of thermodynamic optimization. Entropy generation minimization subject to physical constraints that are responsible for the irreversible operation of a device is the method of modeling and optimization of real devices for which the thermodynamic imperfection is due to heat transfer, mass transfer, and fluid flow irreversibilities. Entropy generation minimization is also known as thermodynamic optimization and finite time thermodynamics in the engineering and physics literature, respectively. A wide range of fuel cell models of different sophistication levels are available in the literature, targeted at improving the scientific understanding of the fundamental processes, while there is a lack of studies concerning constrained thermodynamic optimization in fuel cells [1]. The present thesis introduces the concept of constrained and purposeful optimization in fuel cell research. The first two chapters of this dissertation lay the foundation of such a novel direction in fuel cell science and the results reveal the importance to further pursue this direction. In this context, branching, constructal-inspired, tree-like channel networks are introduced as a fuel cell fluid distribution concept, which also optimizes the shape of polymer electrolyte fuel cells. The resulting double-staircase or pyramidal shape of the fuel cells differs from the traditional rectangular shape while maintaining simplicity and it is determined based on the functionality of the flow distribution system.

The models that are used and developed in the first two chapters are based on first principles. They are quasi two-dimensional and can be quickly solved, a prerequisite for solving multiparametric optimization problems. While three-dimensional models provide the most instructive insight into the fundamental mechanisms, today they still require substantial computational resources and computational time to be solved numerically with respect to entire cells. Multiparametric system optimization becomes even more expensive or impossible, especially if the number of optimization parameters within a certain objective function is large, requiring a lot of evaluations of the objective function. In contrast to three-dimensional models, quasi two-dimensional models can usually be quickly solved, either numerically or even analytically, and therefore open the possibility to address complex multidimensional system optimization issues. Starting with such basic models in the first two chapters, we proceed with the discussion of a more fundamental and thorough mathematical formulation in the third chapter. Herein, a fully three-dimensional single-phase model is considered and used to quantify losses attributed to the non-uniformity of the transport
phenomena in traditional ribbed flow delivery systems. Porous materials as fluid distributors are suggested in this context to replace the traditional channeled systems since they allow the reactive sites to be uniformly covered with high reactant concentrations. In such a system, the effective lengths at which the transport phenomena occur are reduced compared to the traditional ribbed flow delivery systems.

Transport and formation of liquid water plays an important role in polymer electrolyte fuel cells. On the one hand, the electrolyte phase needs to be sufficiently hydrated to provide a high proton conductivity. On the other hand, the presence of liquid water in the porous catalyst and diffusion layers can block pores and prevent gaseous reactant species from reaching the reaction sites, resulting in enhanced mass transfer limitations. In the fourth chapter, we therefore proceed to introduce a thorough multiphase model, based on which the transport phenomena in the diffusion zone are discussed. In contrast to the previous single-phase models, this formulation takes into account transport and formation of liquid water. The effect of downscaling of channel width, current collector rib width, and diffusion layer thickness on the performance of polymer electrolyte fuel cells is systematically investigated and optimum geometric length ratios are identified at decreasing length scales. Based on this model it is found that microchannels, e.g. as part of a tree network channel system, together with diffusion layers that are thinner than conventional layers can provide substantially improved current densities compared to conventional channels with diameters in the order of one millimeter, since the transport processes occur at reduced length scales. As in the previous chapter, it is shown that the reduction of the effective lengths at which the transport phenomena occur allows for substantial cell performance improvements. This is also the subject of the last chapter, which concerns the thermal management of the fuel cell, as done, for example, in fuel cell stacks.

Reference

1. Tree network channels as fluid distributors constructing double-staircase polymer electrolyte fuel cells

Abstract

In this paper, constructal tree-like channel networks are introduced as a fuel cell fluid distribution concept, which also optimizes the shape of polymer electrolyte fuel cells. This concept is the main contribution of the paper. To perform quantitative calculations based on this concept, a one-dimensional model, accounting for oxygen consumption in the feed channel, oxygen mass transfer between the channel and the backing layer, and oxygen mass transfer through the backing layer to the catalyst layer, is used to predict the polarization curve of a so constructed polymer electrolyte fuel cell. Pressure drop and pumping power required for the fluid circulation is estimated. Multiobjective genetic search is performed to maximize the net power density with respect to constructal parameters and operating conditions, leading to the optimized tree network. It is found that the use of tree networks instead of the traditional, non-bifurcating serpentine channels in rectangular systems can provide substantially improved cell performance due their intrinsic advantage with respect to both mass transfer and pressure drop. The resulting “double-staircase” shape of the fuel cells differs from the traditional rectangular shape while maintaining simplicity and it is determined based on the functionality of the flow distribution system.

1.1. Introduction

In polymer electrolyte fuel cells, chemical energy of hydrogen is directly converted to electric energy. A proton-conductive polymer membrane separates the anode and cathode side of the cell where each side includes a fluid distribution system, a gas diffusion layer and a catalyst layer. Hydrogen is fed to the fluid delivery system on the anode side and diffuses
through the gas diffusion layer to the catalyst layer where oxidation of hydrogen occurs. Protons are transported through the electrolyte phase of the catalyst layers and the membrane to react with oxygen in the cathode catalyst layer and to form water vapor. Oxygen is fed to the cathode fluid delivery system, usually by means of humidified air, and it is subject to diffuse through the cathode gas diffusion or backing layer to the reaction sites in the cathode catalyst layer.

The cell performance is reduced as a result of the various loss mechanisms prevailing in the system. Reaction, activation, and concentration overpotentials are identified in the catalyst layers. Ohmic losses are due to electron flux in the backing layers, the catalyst layers and the current collector plates, and due to proton flux through the polymer electrolyte phase of the catalyst layers and the membrane. Concentration overpotentials in the catalyst layers are caused by reactant species depletion and mass transfer limitations between the bulk fluid flow in the channels and the reaction sites in the catalyst layers. The influence of mass transfer resistances depends on operating conditions, material properties of the backing layer, geometry parameters, and structural parameters. These include the size and the shape of the channel cross-sections, the topology of the fluid delivery system, the thickness, structure, porosity and permeability of the diffusion and catalyst layers, and the width of the current collector shoulders. Operating a cell at elevated temperature and/or pressure levels provides higher diffusivities for reactant and product species and hence reduces diffusion losses. At high current densities, substantial amount of liquid water may form on the cathode side, blocking pores in the backing layer and adding further resistance to mass transfer. In ribbed fluid distributors, diffusion paths from the channels to the reaction sites under the current collector shoulders are longer than the diffusion paths from the channels to the reaction sites straight under the channels. As a result, resistance to mass transfer between the channel and the part of the catalyst layer under the current collector shoulders is higher, causing increased concentration overpotential losses in these regions.

One-dimensional to fully three-dimensional mathematical models have been developed in the past and solved analytically or numerically to obtain a better understanding of the fundamental transport phenomena inside the fuel cell. While three-dimensional models provide the most instructive insight into the fundamental mechanisms occurring in the cell, today they still require substantial computational resources and computational time to be solved numerically with respect to entire cells. Multiparametric system optimization becomes even more expensive or impossible, especially if the number of optimization parameters within a certain objective function is large, requiring a lot of evaluations of the objective
function. In contrast to three-dimensional models, one-dimensional models can usually be solved very fast, either numerically or even analytically, and therefore open the possibility to address complex multidimensional system optimization issues.

In this paper, the use of constructal tree-like channel networks of Bejan and co-workers [1-3], also termed as networks of branching tubes [4], is investigated as a fluid distribution concept in polymer electrolyte fuel cells and compared to traditional, non-bifurcating serpentine channel systems. Bejan and Errera [5] discussed a deterministic tree network for fluid flow with minimum flow resistance between a volume and a point, subjected to two constraints: fixed total volume and fixed channel volume. In this study, the entire geometric structure of the tree network is optimized with respect to maximum electric power output and minimum flow resistance, subject to the constraint of a fixed cell area, leading to an optimized tree network, which also defines the shape of the fuel cell. The corresponding multiparametric optimization problem is addressed by means of a genetic optimization algorithm.

1.2. Mathematical model

A one-dimensional analytical model originally proposed and experimentally validated by Kulikovsky and co-workers [6-8] is used and further developed in this study to more accurately account for mass transfer resistances on the cathode side. The extended model additionally accounts for mass transfer resistance between the bulk fluid flow in the channels and the channel/backing layer interface as well as for mass transfer resistance in the lateral direction, indicated by the y axis in Fig. 1.1. While the original model was developed for a cell with a single, non-bifurcating channel, the extended model is adapted to predict the current-voltage characteristics of a cell with a tree network fluid delivery system. In this model, flow resistance in the tree network is further estimated taking also into account effects from bifurcations. The model comprises a variety of assumptions [6-8]: The anode kinetics is assumed to be fast such that overpotential losses on the anode side are not significant. The fluid velocity is assumed to be constant along a channel of a certain branching level. A Tafel-like expression is used to describe the electrochemical reaction rate of oxygen reduction on the cathode side, which for large current densities of practical interest is a valid approach. It is further assumed that the cathode overpotential is constant throughout the cell. Variation of the overpotential across the catalyst layer is neglected. Water transport through the membrane is not accounted for and it is assumed that the membrane is ideally hydrated which is justified for high stoichiometric flow ratios and highly humidified inlet streams. A backing layer with
a high electrical conductivity is considered such that Ohmic losses can be neglected in this layer.

Fig. 1.1. Geometric structure of the cell, including the current collector plate, flow channels, backing layer, catalyst layer and the membrane. The length \( h_k \) is the channel width, \( l_b \) is the backing layer thickness, \( l_c \) is the catalyst layer thickness, \( l_n \) is the membrane thickness, and the difference \( b_k - h_k \) represents the width of the current collector shoulders. The direction \( z \) indicates the flow direction and \( y \) indicates the lateral direction.

The above model is chosen for its effectiveness, if one takes into account its simplicity, and it will be used to quantify the main contribution of the present work: The concept of tree based optimization of the fluid distributors, the functionality of which will also determine the final shape of the fuel cell. The geometric structure of a cell with the proposed tree network fluid distribution system is outlined in Figs. 1.1 and 1.2. Channels with square cross-sections of width \( h_k \) are considered, where the subscript \( k \) indicates the branching level. The length \( l_b \) indicates the backing layer thickness, \( l_c \) indicates the catalyst layer thickness, and \( l_n \) indicates the membrane thickness. The lengths \( l_b \), \( l_c \), and \( l_n \) are independent of the branching level \( k \). The length \( b_k \) represents the current collector width which is associated with the considered channel, such that the width of the current collector shoulder equals \( b_k - h_k \) in parallel channel assembly, as shown in Fig. 1.1. The tree network has one inlet channel at the zeroth branching level and a number of \( 2^m \) outlet channels at the \( m \)th branching level, where the number of channels increases by a factor of two between two consecutive branching levels, as shown in Fig. 1.2. It is assumed that the flow at the interface between two consecutive branching levels is subject to redistribute uniformly to the channels of the higher branching level. In practice, this can be simply achieved with a gap of small flow resistance,
for example. Such manufacturing issues however are not the main theme of this work which focuses on the basic mass transfer and fluid dynamic aspects of the problem.

Fig. 1.2. Geometric structure of the tree network. The boundary of the cell is indicated by the dashed lines. Channels are indicated as black rectangles and are arranged in parallel.

1.2.1. Governing equations: Branching level $k$

A cell with a tree network fluid delivery system is considered in which the channel width ratio $\varphi$ between two consecutive branching levels is constant such that the channel width at the $k$th branching level,

$$h_k = h_0 \varphi^k,$$  

(1)
can be expressed in terms of the channel width \( h_0 \) at the zeroth branching level where \( h_{k+1} = h_k \varphi \) holds. The same is assumed for the current collector width,

\[
b_k = b_0 \varphi^k, \tag{2}\]

where an identical ratio \( \varphi \) is used resulting in a constant \( b_k / h_k \) ratio throughout the net. A different ratio \( \phi \) relates the channel lengths between consecutive branching levels, such that the channel length at the \( k \)th branching level reads

\[
L_k = L_0 \phi^k. \tag{3}\]

Mass balance at the interface between two branching levels relates the fluid velocities in the consecutive branches,

\[
v_k h_k^2 = 2 v_{k+1} h_{k+1}^2, \tag{4}\]

and the fluid velocity at the \( k \)th branching level reads

\[
v_k = 2^{-k} \varphi^{2k} v_0. \tag{5}\]

The flux of oxygen mass transfer from the bulk fluid flow in the channel to the channel/backing layer interface may be written as

\[
N_{O_2,k} = \kappa_{h,k} \left( c_{O_2,h,k} - c_{O_2,i,k} \right), \tag{6}\]

where \( c_{O_2,h,k} \) is the mean molar concentration of oxygen in the channel, \( c_{O_2,i,k} \) is the oxygen concentration at the channel/backing layer interface, and \( \kappa_{h,k} \) is the corresponding mass transfer coefficient. For a square duct with three adiabatic walls and a wall with a uniform heat flux, the Nusselt number \( \text{Nu} \) is constant for laminar fully developed flow, i.e. \( \text{Nu} = 2.712 \) (see Ref. [9]). According to the Chilton-Colburn analogy [10,11], the Sherwood number \( \text{Sh} \) can be related to the Nusselt number \( \text{Nu} \) as \( \text{Sh} = \text{Nu} \text{Le} (\text{Pr}/\text{Sc})^{2/3} \), where \( \text{Le} = a / D \) is the Lewis number, \( \text{Pr} = \nu / a \) is the Prandtl number, \( \text{Sc} = \nu / D \) is the Schmidt number, \( a \) is the thermal diffusivity, \( \nu \) is the kinematic viscosity, and \( D \) is the diffusion.
coefficient. For the fluid properties in this study, $\text{Le} (\text{Pr}/\text{Sc})^{2/3} = 1$, and the mass transfer coefficient $\kappa_{h,k}$ can be obtained from

$$S_{h} = \kappa_{h,k} h_k / D_h = 2.7 . \quad (7)$$

The diffusive flux of oxygen from the channel/backing layer interface to the catalyst layer is formulated as

$$N_{\text{O}_2,k} = \kappa_{h,k} \left( c_{\text{O}_2,i,k} - c_{\text{O}_2,c,k} \right) \quad (8)$$

where $c_{\text{O}_2,i,k}$ is the molar concentration of oxygen at the channel/backing layer interface and $c_{\text{O}_2,c,k}$ is the oxygen concentration in the catalyst layer. Since the catalyst layer is much thinner than the backing layer, mass transfer resistance in this layer can be safely neglected compared to mass transfer resistance in the backing layer. Therefore, the oxygen concentration $c_{\text{O}_2,i,k}$ in the catalyst layer is assumed to be constant in the vertical $x$ direction.

The oxygen mass transfer coefficient $\kappa_{b,k}$ in the backing layer is given as

$$\kappa_{b,k} = D_b / l_{b,k} \quad (9)$$

in which $D_b$ is the effective diffusion coefficient of oxygen in the porous backing layer. The Bruggeman model [12,13] relates the free-stream diffusion coefficient $D_h$ to the effective diffusion coefficient $D_b$ through the backing layer porosity $\varepsilon$ according to

$$D_b = D_h \varepsilon^{3/2} \quad (10)$$

with a tortuosity factor of $3/2$. The minimum diffusion length for oxygen between the channel/backing layer interface and the catalyst layer is $l_b$ in the vertical $x$ direction, as seen in Fig. 1.1. However, oxygen diffuses not only along the vertical $x$ direction to the part of the catalyst layer situated directly below the channel, it is also subject to diffuse in the lateral $y$ direction to the parts of the catalyst layers situated under the current collector shoulders. Since in this study a one-dimensional approach to the problem is required, this issue is accounted for by defining an effective diffusion length $l_{b,k}$, i.e.
\[
L_{b,k} = \left\{ \begin{array}{ll}
\sum_{i=0}^{3} q_i \eta^i, & h_k = (0.1, 0.05, 0.025) \text{cm}, \quad 0.6 \leq \eta \leq 1.0 \\
\frac{1}{2} \left[ L_0 + \left[ L_0 + (h_k - h_k) / 2 \right] \right], & h_k < 0.025 \text{cm}, \quad \forall \eta
\end{array} \right.
\]  

with \( b_k = 2h_k \), \( L_{b,k} (\eta < 0.6 \text{V}) = L_{b,k} (\eta = 0.6 \text{V}) \) and \( L_{b,k} (\eta > 1.0 \text{V}) = L_{b,k} (\eta = 1.0 \text{V}) \) for \( h_k = (0.1, 0.05, 0.025) \text{cm} \), where \( q_i \) are polynomial coefficients, \( \eta \) is the cathode overpotential, and \( h_k \) is the channel width. The coefficients \( q_i \) are given in Table 1.1 and they are based on the operating condition parameters of Table 1.2. Linear interpolation between the three polynomials is used to provide a continuous correlation for \( L_{b,k} \). This correlation was obtained from three-dimensional numerical solutions of the Navier-Stokes and species conservation equations in a single straight cathode channel including the backing layer, where the method of local volume averaging was used to describe transport through porous media. A surface reaction was applied to the backing layer wall describing a source of water vapor and a sink of oxygen following the kinetics of this study. Kinetic gas theory and JANAF tables were used to compute the local mixture properties. In addition, \( Sh_b = 2.7 \) and \( Le(Pr/Sc)^{2/3} \approx 1 \) was found to be in excellent agreement with the three-dimensional numerical results. The latter were computed based on the finite volume method using central scheme discretization. The oxygen flux between the channel and the catalyst layer can be written then as

\[
N_{O_2,k} = \frac{1}{K_{h,k}^{-1} + K_{b,k}^{-1}} (c_{O_2,h,k} - c_{O_2,c,k})
\]  

Table 1.1. Polynomial coefficients \( q_i \).

<table>
<thead>
<tr>
<th>( h_k ) (cm)</th>
<th>( q_0 ) (cm)</th>
<th>( q_1 ) (cm/V)</th>
<th>( q_2 ) (cm/V^2)</th>
<th>( q_3 ) (cm/V^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>-0.322 65</td>
<td>1.5640</td>
<td>-2.0786</td>
<td>0.866 67</td>
</tr>
<tr>
<td>0.05</td>
<td>-0.030 920</td>
<td>0.240 83</td>
<td>-0.300 00</td>
<td>0.116 67</td>
</tr>
<tr>
<td>0.025</td>
<td>0.014 511</td>
<td>0.033 762</td>
<td>-0.042 143</td>
<td>0.016 667</td>
</tr>
</tbody>
</table>
Table 1.2. Invariable geometry and operating condition parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of electrons participating in the reaction $n$</td>
<td>4</td>
</tr>
<tr>
<td>Stoichiometric coefficient of oxygen $S$</td>
<td>1</td>
</tr>
<tr>
<td>Transfer coefficient $\alpha$</td>
<td>0.5 $^a$</td>
</tr>
<tr>
<td>Cell temperature $T$ (K)</td>
<td>363 $^a$</td>
</tr>
<tr>
<td>Open circuit potential $U$ (V)</td>
<td>1.23 $^a$</td>
</tr>
<tr>
<td>Reference molar concentration of oxygen $c_{\text{ref}}$ (mol/cm$^3$)</td>
<td>3.31 x 10$^{-5}$ $^a$</td>
</tr>
<tr>
<td>Volumetric exchange current density $i_*$ (A/cm$^3$)</td>
<td>3.5 x 10$^{-3}$ $^a$</td>
</tr>
<tr>
<td>Membrane conductivity $\sigma$ (Ω$^{-1}$cm$^{-1}$)</td>
<td>0.1 $^b$</td>
</tr>
<tr>
<td>Diffusion coefficient of O$_2$ in the gas channel $D_h$ (cm$^2$/s)</td>
<td>0.356 $^c$</td>
</tr>
<tr>
<td>Diffusion coefficient of O$_2$ in the backing layer $D_b$ (cm$^2$/s)</td>
<td>0.0318 $^d$</td>
</tr>
<tr>
<td>Backing layer wet porosity $\varepsilon$</td>
<td>0.2 $^e$</td>
</tr>
<tr>
<td>Friction factor $f_s/Re_k$</td>
<td>56.9 $^f$</td>
</tr>
<tr>
<td>Dynamic viscosity $\mu$ (Pa s)</td>
<td>2.12 x 10$^{-5}$ $^f$</td>
</tr>
<tr>
<td>Oxygen molar fraction at the inlet $\xi$</td>
<td>0.0627 $^g$</td>
</tr>
<tr>
<td>Total molar concentration of the gas mixture $c$ (mol/cm$^3$)</td>
<td>3.31 x 10$^{-5}$ $^a$</td>
</tr>
<tr>
<td>Backing layer thickness $l_b$ (cm)</td>
<td>0.017 $^a$</td>
</tr>
<tr>
<td>Catalyst layer thickness $l_c$ (cm)</td>
<td>0.006 $^a$</td>
</tr>
<tr>
<td>Membrane thickness $l_m$ (cm)</td>
<td>0.01 $^a$</td>
</tr>
<tr>
<td>Total flow-field area $A$ (cm$^2$)</td>
<td>9 $^h$</td>
</tr>
</tbody>
</table>

$^a$ Reference [7].
$^b$ Reference [6].
$^c$ Reference [10].
$^d$ Obtained through Eq. (10).
$^e$ Reference [16].
$^f$ Reference [9].
$^g$ Corresponding to 100% relative humidity at the cathode inlet [15].
$^h$ Assumed.

and it is coupled to the local transfer current density $j_{T,k}$ in the catalyst layer through the stoichiometric coefficient, $S = 1$, and the number of electrons, $n = 4$, involved in the cathode reaction,
\[ N_{O_2,k} = \frac{S}{nF} j_{T,k}, \]  

where \( F \) denotes the Faraday constant. The transfer current density

\[ j_{T,k} = \frac{F}{e} \left( \frac{Q_{k}}{nF} \right) \]  

is obtained from the volumetric transfer current density

\[ Q_{T,k} = \frac{c_{O_2,e,k}}{c_{\text{ref}}} \exp \left( \frac{\alpha F}{RT} \eta \right), \]

assuming a reaction order of one [6]. Herein, \( i_e \) is the volumetric exchange current density, \( c_{\text{ref}} \) is the reference molar concentration of oxygen, \( \alpha \) is the Tafel constant, \( R \) is the universal gas constant, \( T \) is the temperature, and \( \eta \) is the cathode overpotential. From Eqs. (12)-(15) it follows

\[ c_{O_2,e,k} = \frac{c_{O_2,h,k}}{1 + \beta_k} \]  

where

\[ \beta_k = \frac{S}{nF} i_e \left( \frac{1}{\kappa_{h,k}} + \frac{1}{\kappa_{b,k}} \right) \exp \left( \frac{\alpha F}{RT} \eta \right). \]

Mass conservation of oxygen along the channel reads

\[ v_k h_k \frac{dc_{O_2,h,k}}{dz_k} = -\frac{S}{nF} j_{T,k} b_k \]  

where \( z_k \) indicates the flow direction. Note that \( j_{T,k} \) depends on \( z_k \). The latter is zero at the beginning of branching level \( k \) and equals \( L_k \) at the end of branching level \( k \). Integration of Eq. (18) gives the distribution of the oxygen molar concentration along a channel of the \( k \)th branching level,
\[ c_{O_2,b,k}(z_k) = c_{O_2,b,k}(0) \exp\left( -\frac{z_k}{L_{C,k} + L_{D,k}} \right) \]  \hspace{1cm} (19)

where the first factor on the right hand side indicates the oxygen concentration in the channel at the beginning of branching level \( k \). Note that

\[ L_{C,k} = \frac{nF}{S} \frac{h_k^2 v_k c_{\text{inf}}}{b_k I_k} \exp\left( -\frac{\alpha F}{RT} \eta \right) \]  \hspace{1cm} (20)

is the characteristic length of oxygen consumption related to the \( k \)th branching level and that

\[ L_{D,k} = \frac{h_k^2 v_k}{b_k} \left( \frac{1}{\kappa_{b,k}} + \frac{1}{\kappa_{\text{b,k}}} \right) \]  \hspace{1cm} (21)

is the characteristic length of diffusion losses related to the \( k \)th branching level where

\[ \beta_k = \frac{L_{D,k}}{L_{C,k}} \]  \hspace{1cm} (22)

applies. Equations (14)-(16), (19), and (22) lead to the distribution of the local current density along a channel of the \( k \)th branching level,

\[ j_{l,k}(z_k) = \frac{L_k}{L_{C,k} + L_{D,k}} \exp\left( -\frac{z_k}{L_{C,k} + L_{D,k}} \right) \]  \hspace{1cm} (23)

with the stoichiometric current density

\[ j_{\lim,k} = \frac{nF}{S} \frac{h_k^2 v_k}{b_k I_k} c_{O_2,b,k}(0) . \]  \hspace{1cm} (24)

Averaging the local transfer current density along the entire channel length,

\[ \bar{j}_k = \frac{1}{L_k} \int_0^{L_k} j_{l,k}(z_k) dz_k , \]  \hspace{1cm} (25)

yields a length-averaged transfer current density of the \( k \)th branching level,
1.2.2 Governing equations: Tree network

This concept is now extended to a cell with an entire tree network to predict the corresponding current-voltage behavior. The cell current density

\[
J = \frac{I_m}{\pi A} \quad \text{Eq. (27)}
\]

is defined as the ratio between the cell current

\[
I_m = \sum_{k=0}^{m} \bar{J}_k L_k b_k 2^k \quad \text{Eq. (28)}
\]

and the total cell area

\[
A = \sum_{k=0}^{m} L_k b_k 2^k \quad \text{Eq. (29)}
\]

Note that \( L_k b_k 2^k \) represents the part of the cell area which belongs to the \( k \)th branching level and that the average current density at the \( k \)th branching level \( \bar{J}_k \) is given by Eq. (26). The total cell area \( A \) is given if the parameters \( L_0, b_0, \phi, \varphi, \) and \( m \) are fixed. In order to compare different tree network geometries with respect to cell performance, one may alternatively want to fix the total cell area \( A \) and consider \( L_0 \) as a dependent parameter, i.e.

\[
L_0 = \frac{A}{b_0 \sum_{k=0}^{m} \phi^k \varphi^k 2^k} \quad \text{Eq. (30)}
\]

The oxygen concentration at the beginning of a channel of the \( k \)th branching level is derived from Eq. (19) and is written as
\[ c_{O_2,h,k} = \begin{cases} c_{O_2,h,0}, & \text{if } k = 0 \\ c_{O_2,h,0} \prod_{i=1}^{k} \exp \left( -\frac{L_{i-1}}{L_{c,i-1} + L_{D,i-1}} \right), & \text{if } 0 < k \leq m \end{cases} \]  

(31)

where

\[ c_{O_2,h,0} = \xi c \]  

(32)

is the oxygen concentration at the channel inlet of the zeroth branching level. Herein, \( \xi \) is the molar fraction of oxygen at the inlet and \( c \) is the total molar concentration of the gas mixture. Equations (31) and (32) can be written alternatively as

\[ c_{O_2,h,k} = \xi c \left[ \exp \left( \frac{L_{-1}}{L_{c,-1} + L_{D,-1}} \right) \right] \prod_{i=0}^{k} \exp \left( -\frac{L_{i-1}}{L_{c,i-1} + L_{D,i-1}} \right). \]  

(33)

Note that \( L_{-1}, L_{c,-1}, \) and \( L_{D,-1} \) are obtained from Eqs. (3), (20), and (21), respectively, with \( k = -1 \).

The limiting current density of the cell is obtained by evaluating the limits of Eq. (27) where the cathode overpotential \( \eta \) tends to infinity. The local limiting current density at the inlet of the tree network is determined by further taking the limit where the inlet velocity tends to infinity, leading to

\[ \lim_{\eta \to \infty} \lim_{\eta \to \infty} J_m = \frac{1}{A} \frac{nF}{S} \xi c \sum_{k=0}^{m} \frac{1}{\kappa_{h,k} + \kappa_{b,k}} L_{-1} b_{h,k} 2^k \]  

(34)

This limit may also be referred to as a maximum limiting current density which is obtained for very high inlet flow rates of oxygen such that the consumption of oxygen along the network is negligibly small and that the current density is not subject to decay along the flow direction. For a tree network with zero branching levels, i.e. \( m = 0 \) and \( L_0 = A/b_0 \), which essentially corresponds to a traditional, non-bifurcating channel of length \( L_0 \), the limiting current density reads

\[ \lim_{\eta \to \infty} J_m = \frac{nF}{S} \frac{b_{h,0} v_0}{b_{D,0} L_0} \xi c \left[ 1 - \exp \left( -\frac{b_{h,0} L_0}{h_0 v_0 \left( \kappa_{h,0} + \kappa_{b,0} \right)} \right) \right]. \]  

(35)
and the maximum limiting current density is simply given by

$$\lim_{n \to \infty} \lim_{s \to \infty} J_{m=0} = \frac{nF}{S} \xi c \frac{1}{\kappa_{b,0}^{-1} + \kappa_{t,0}^{-1}}.$$  \hfill (36)

If the flow direction is reversed, Eqs. (31)-(33) are to be replaced by

$$c_{O_2,h,k} = \begin{cases} c_{O_2,h,m} \prod_{i=1}^{m-1} \exp \left( - \frac{L_{m-i+1}}{I_{C,m-i+1} + I_{D,m-i+1}} \right), & \text{if } 0 \leq k < m \\ c_{O_2,h,m}, & \text{if } k = m \end{cases}, \hfill (37)$$

and

$$c_{O_2,h,m} = \xi c, \hfill (38)$$

respectively. Reversed flow direction means that the inlet mass flow rate is fed to the $m$ channels of the highest branching level instead of being fed to the channel of the zeroth branching level. It is then assumed that the inlet mass flow rate is uniformly divided to the $m$ channels. By straightforward manipulations it can be shown that the average cell current density is not altered if the flow direction is reversed. Thus, the cell current-voltage behavior does not depend on the flow direction in this context.

### 1.2.3. Pressure drop and pumping power

Increasing the inlet velocity provides a higher limiting current density of the cell, approaching asymptotically the maximum limiting current density if the inlet velocity tends to infinity. The following is clear from the above set of equations: Very high inlet velocities imply that the oxygen concentration reduction along the flow direction is negligibly small and therefore the effect of concentration overpotential due to oxygen concentration depletion downstream the channels becomes insignificant. However, for higher inlet velocities, the losses due to pressure drop and the related pumping power required for fluid circulation increase, and they may not be negligibly small any more, compared to the electric power generated by the cell. The net power available to the user can then be substantially reduced if a considerable amount of electric energy is required for pumping power and as a result,
overall cell efficiency is reduced. In order for the polymer electrolyte fuel cell to become firmly established as a competitive form of electric power generation in a host of engineering applications, such as powering of vehicles, laptop computers, cell phones, general portable power systems, and remote power generations, the overall cell efficiency must be maximized, i.e. the chemical energy of the respective fuel needs to be converted to net available electric energy at high efficiency. Consequently, it is indispensable that the pressure drop is accounted for as a loss mechanism when trying to optimize the fluid delivery system of a polymer electrolyte fuel cell towards maximum net power densities.

In the following, the pressure drop of the tree network is estimated assuming geometrically similar shapes of channel cross-sections throughout the network. Pressure drop of a tree network with m branching levels having one inlet at the zeroth branching level and a number of m outlets at the nth branching level can be written then as

\[
\Delta p_{\text{tot},m} = \sum_{k=0}^{m} \frac{C L_k v_k}{h_k^2} + \sum_{k=0}^{m-1} \zeta_t \rho v_k^2 / 2
\]

\[
= C \frac{L_0 v_0}{h_0^2} \frac{1 - \phi^{m+1}/[2^{m+1} \phi^{4(m+1)}]}{1 - \phi/(2\phi^4)} + \frac{\zeta_{t} \rho v_0^2}{2} \frac{1 - (4\phi^4)^{-m}}{1 - (4\phi^4)^{-1}}, \quad \text{if } m \geq 1
\]

\[
\Delta p_{\text{tot},0} = C \frac{L_0 v_0}{h_0^2} + \chi \zeta_{s} \rho v_0^2 / 2, \quad \text{if } m = 0
\]

Note that the tree network with zero branching levels essentially corresponds to one single, non-bifurcating channel, representing a traditional serpentine fluid delivery system. The constant C is particular to the considered channel cross-sectional shapes and fluid properties, \( \rho \) is the fluid density, \( \zeta_t \) is a resistance coefficient that accounts for pressure drop due to bifurcations in the tree network, \( \zeta_s \) is a resistance coefficient that accounts for pressure drop due to turns in a serpentine fluid delivery system, and \( \chi \) is the number of turns. For the serpentine fluid delivery system, smooth half circular turns are assumed for which a loss coefficient \( \zeta_s = 1.0 \) is given in Ref. [14]. For the tree network, \( \zeta_t = 1.0 \) is identically assumed. In order to compare pressure drop of different tree networks with identical area \( A \), the length \( L_0 \) in Eq. (40) is substituted with Eq. (30) in this study. The constant C is given as \( C = \mu f_k \text{Re}_k / 2 \) where the friction factor for a square cross-sectional channel under fully developed flow conditions reads [9].
\[ f_k \text{Re}_k = 24 \left[ 1 - \frac{192}{\pi^3} \sum_{\zeta = 1}^{\infty} \frac{1}{\zeta^3} \tanh \left( \frac{\zeta \pi}{2} \right) \right] = 56.9. \quad (41) \]

Herein, \( f_k \) is the friction factor, \( \text{Re}_k \) is the Reynolds number, and \( \mu \) is the dynamic viscosity of the fluid mixture. The pumping power density, defined as pumping power per cell area, of a tree network with \( m \) branching levels is given then as

\[ P_m = h_0^2 \nu_0 \Delta \rho_{tot,m} A^{-1}. \quad (42) \]

### 1.2.4. Electric power density and net power density

The cell potential \( V_m \) is determined by subtracting the main voltage losses, i.e. the cathode overpotential and the membrane potential loss, from the open-circuit potential \( U \),

\[ V_m = U - \eta - J_m \sigma^{-1}, \quad (43) \]

in which \( \eta \) is the membrane thickness and \( \sigma \) is the ionic conductivity of the membrane. The resulting electric power density, defined as electric power per cell area, reads

\[ E_m = J_m V_m. \quad (44) \]

Subtracting the pumping power density yields a net power density

\[ \Pi_m = E_m - P_m \quad (45) \]

which is obtained from a cell with a tree network fluid delivery system with \( m \) branching levels. Note that \( E_{m(0)} \) and \( \Pi_{m(0)} \) represent the electric power density and the net power density of a cell with a single, non-bifurcating square cross-sectional channel of width \( h_0 \) and length \( L_0 \), building up a traditional serpentine fluid distribution system with a number of \( \chi \) turns.

### 1.3. Network optimization

The net power density \( \Pi_m \) depends on a variety of operating condition and geometry parameters. The question arising is how to find a parameter set for which the net power
density, considered as an objective function, provides a global maximum. One may want to
distinguish between fixed or invariable parameters and optimization parameters to reduce the
dimension of the optimization problem. In this study, a constant cell area $A$ is considered and
one seeks a tree network geometry, an inlet velocity, and a certain cathode overpotential
which together provide a global maximum of the net power density function. This maximum
can then be compared to the one of a cell with identical area $A$ and with a single, non-
bifurcating channel. The net power density can then be written as a function of two vectors,

$$\Pi_m(\lambda, \theta) = g(\lambda, \theta)$$

(46)

where the vector

$$\lambda = (n, F, S, \alpha, R, T, U, c_{\text{ref}}, i_\infty, \sigma, D_b, \varepsilon, f \Re_e, \zeta, \eta, \chi, \mu, \xi, c, l_h, l_c, l_n, A)$$

(47)

contains all invariable parameters, and the vector

$$\theta = (b, h, v, \eta, m, \varphi, \phi)$$

(48)

contains all the variable or optimization parameters such that the optimization problem can be
formulated as: Find a vector $\theta_{\text{max}} \in \Xi$ such that

$$\Pi_m(\lambda, \theta_{\text{max}}) \geq \Pi_m(\lambda, \theta), \quad \forall \theta \in \Xi,$$

(49)

where $\Xi$ is the space of the variable parameters of the function $\Pi_m(\lambda, \theta)$. Note that $\Pi_{m(\cdot)}$
does not depend on $\varphi$ and $\phi$.

1.4. Results and discussion

The effect of optimization parameter variations on the polarization curve, the electric
power density curve, and the net power density curve is discussed in this section. For this
purpose, a base case is considered with $b_0 = 0.14$ cm, $h_0 = 0.07$ cm, $v_0 = 20$ m/s
($Re_0 = 462$), $m = 6$, $\varphi = 2^{-1/3}$, and $\phi = 2^{-1/3}$. Invariable parameters of the vector $\lambda$ are listed
in Table 1.2. Individual optimization parameters are varied and the respective impact on the
target curves is discussed. In addition, the multiparametric optimization problem is further
addressed by means of a genetic algorithm to search for a global maximum of the objective function leading to an optimized tree network.

1.4.1. Characteristics of parameter variations

For the base case, the impact of the variation of $v_0$, $m$, $\varphi$, and $\phi$ on the polarization and power density curves is shown in Figs. 1.3-1.6. Herein, the cell area $A = 9 \text{ cm}^2$ is kept constant, as well as the channel width $h_0$ and the current collector width $b_0$ of the zeroth branching level.

By increasing the inlet velocity $v_0$, the high current density end of the polarization curve is shifted to the right generating a higher maximum electric power density, as shown in Fig. 1.3. For low inlet velocities $v_0$, most oxygen is consumed along the channels such that the polarization curves of a channel system with $m = 6$ (dashed lines) and of a channel system with $m = 0$ (solid line) are close together. By reducing $v_0$ towards zero, the polarization curve of a channel system with $m = 6$ will approach the polarization curve of a channel system with $m = 0$ from the right side. If the inlet mass flow rate is so small that almost all of the oxygen is consumed along the channels, then it is clear that the tree network fluid delivery system cannot provide higher performance than a traditional fluid delivery system. By increasing the inlet velocity $v_0$, the high current density end of the polarization curve of the network system is shifted more to the right than that of the traditional system. Both ends asymptotically approach the polarization curves corresponding to the respective maximum limiting current densities as the inlet velocity $v_0$ tends to infinity. The analogous characteristic behavior is observed for the electric power density variation and it is seen that for high inlet mass flow rates of oxygen the tree network system allows for substantially higher maximum electric power densities than the traditional system. For inlet velocities $v_0$ of 10 m/s, 20 m/s, 30 m/s, 40 m/s, 50 m/s, and $\infty$ m/s, it is seen that compared to the traditional system, the tree network system provides a 8.6%, 12%, 13%, 14%, 14%, and 15% higher maximum electric power density, respectively. Note that the inlet velocities $v_0$ of 10 m/s, 20 m/s, 30 m/s, 40 m/s, 50 m/s, and $\infty$ m/s correspond to inlet Reynolds numbers $Re_0$ of 231, 462, 693, 924, 1155, and $\infty$, respectively. The inlet Reynolds number is defined as $Re_0 = cM v_0 h_0 / \mu$ where $M$ is the molecular weight of the fluid mixture. In practice, the Reynolds number is usually not beyond the critical Reynolds number ($\approx 2 \times 10^5$) to avoid increased pressure drop in the turbulent flow.
Fig. 1.3. Performance of a cell with a traditional fluid distributor (solid lines) and a cell with tree network fluid distributors (dash-dotted lines) for different inlet velocities $v_0$, i.e. $v_0 = (10, 20, 30, 40, 50, \infty) \text{ m/s}$ corresponding to $Re_0 = (231, 462, 693, 924, 1155, \infty)$ and with $b_0 = 0.14 \text{ cm}$, $h_0 = 0.07 \text{ cm}$, $m = 6$, $\varphi = 2^{-1/3}$, $\phi = 2^{-1/3}$, and $\chi = 6$. Labels indicate values of $v_0$. (a) Polarization curves. (b) Electric power density curves. (c) Net power density curves.

regime. For the traditional system with an inlet velocity of $v_0 = 20 \text{ m/s}$ ($Re_0 = 462$), a maximum electric power density of 0.12 W/cm$^2$ is obtained at a current density of 0.41 A/cm$^2$ [see Fig. 1.3(b)] corresponding to a stoichiometric flow ratio of $\psi = 2.1$. The stoichiometric flow ratio $\psi = v_0 h_0 \xi cnF/(JmA)$ defines the ratio of the oxygen fed to the fuel cell to the amount of oxygen electrochemically converted. For the tree network system with an identical inlet velocity of $v_0 = 20 \text{ m/s}$ ($Re_0 = 462$), a maximum electric power density of 0.14 W/cm$^2$
is obtained at a current density of 0.47 A/cm² [see Fig. 1.3(b)] corresponding to a stoichiometric flow ratio of $\psi = 1.9$. Note that for the Reynolds numbers at consecutive branching levels the relation $\frac{Re_{k+1}}{Re_k} = 1/(2\varphi)$ holds. For $\varphi = 2^{-1/3}$, $\frac{Re_{k+1}}{Re_k} = 0.63$ results, which means that the Reynolds number decays from one branching level to the next higher. However, increasing the inlet velocity also increases pressure drop such that a larger pumping power is required for the feed gas circulation, thus reducing the net power density at high inlet mass flow rates. This effect is clearly seen from the net power density curves in Fig. 1.3. While for the traditional system the maximum net power density already drops down for inlet velocities larger than roughly $v_0 = 20$ m/s ($Re_0 = 462$), the maximum net power density of the network system can still be slightly increased for higher inlet velocities. By further increasing the inlet velocity, this maximum is subject to decrease very fast in the traditional systems, in contrast to the network system. To exemplify, for an inlet velocity of $v_0 = 50$ m/s ($Re_0 = 1155$), the maximum net power density of the network system still remains at a high level while the maximum net power density of the traditional system is almost zero, where most of the curve is even in the negative net power density range. For inlet velocities $v_0$ of 10 m/s, 20 m/s, 30 m/s, 40 m/s, and 50 m/s, it is seen that compared to the traditional system, the tree network system provides a 12%, 26%, 51%, 114%, and 485% higher maximum net power density, respectively.

The effect of varying the number of branching levels $m$ is demonstrated in Fig. 1.4. A network with zero branching levels $m = 0$ corresponds to the traditional non-bifurcating system. Note that for a network system with $m$ branching levels the flow is subject to bifurcate $m$ times. By increasing the number of branching levels $m$, the high current density end of the polarization curve is shifted to the right, hence increasing the limiting current density and the maximum electric power density. The higher the number of branching levels $m$, the lower the performance improvement by further increasing $m$. This means that the polarization curve and the electric power density curve asymptotically approach limiting curves if $m$ tends to infinity. For values of $m$ of 1, 2, 3, 4, 5, 6, and $\infty$, it is seen that compared to the traditional system, the tree network system provides a 1.7%, 3.6%, 5.8%, 7.8%, 9.7%, 12%, and 26% higher maximum electric power density, respectively. The higher the number of branching levels, the lower the effect of losses due to mass transfer limitations between the channels and the channel/backing layer interface as well as due to mass transfer limitations in the lateral direction, since most of the channels in the network system would become very
thin, thus reducing the lateral diffusion length towards zero. In the particular theoretical case of an infinite number of branching levels \( m \), the mentioned mass transfer losses would become zero.

![Diagram](image_url)

**Fig. 1.4. Performance of a cell with a traditional fluid distributor (solid line) and a cell with tree network fluid distributors (dash-dotted lines) for different numbers of branching levels \( m \), i.e. \( m = (1,2,3,...,8,9,\infty) \) with \( b_0 = 0.14 \text{ cm} \), \( h_0 = 0.07 \text{ cm} \), \( v_0 = 20 \text{ m/s} \) \((\text{Re}_0 = 462)\), \( \varphi = 2^{-1/3} \), and \( \varphi = 2^{-1/3} \). Labels indicate values of \( m \). Electric power density curves.**

In Fig. 1.5, the channel width ratio \( \varphi = h_k/h_k \) is varied between 0.1 and 0.9. Since the cell area \( A \) is kept constant, small \( \varphi \) implies that \( L_0 \) must be large or that a long inlet channel is required at the zeroth branching level since the channel diameter decays very fast. On the other hand, large \( \varphi \) requires that \( L_0 \) be rather small or that a short inlet channel is required at the zeroth branching level. In the limiting cases of \( \varphi \rightarrow 0 \) and \( \varphi = 1 \), the polarization curve and the electric power density curve of the traditional fluid delivery system are recovered. In between, there exists an optimum channel width ratio for which the high current density end of the polarization curve is shifted most to the right and the maximum of the electric power density curve is highest. This represents the network configuration with minimum losses due to mass transfer limitations between the channels and the channel/backing layer interface and due to mass transfer limitations in the lateral direction. From the net power density curves it is seen that for high channel width ratios \( \varphi \) the pumping power is small and that for low \( \varphi \),
pressure drop becomes dominant. Note that the net power density curves for $\varphi < 0.7$ are below the negative bound of the graph. The optimum channel width ratio corresponding to the maximum net power density is slightly higher than the optimum channel width ratio corresponding to the maximum electric power density.

![Graph showing performance of a cell with a traditional fluid distributor (solid line) and a cell with tree network fluid distributors (dash-dotted lines) for different channel width ratios $\varphi$, i.e. $\varphi = (0.1, 0.2, 0.3, ..., 0.9)$ with $h_0 = 0.14$ cm, $h_0 = 0.07$ cm, $v_0 = 20$ m/s ($Re_0 = 462$), $m = 6$, $\phi = 2^{-1/3}$, and $\chi = 6$. Labels indicate values of $\varphi$. (a) Electric power density curves. (b) Net power density curves.]

Fig. 1.5. Performance of a cell with a traditional fluid distributor (solid line) and a cell with tree network fluid distributors (dash-dotted lines) for different channel width ratios $\varphi$, i.e. $\varphi = (0.1, 0.2, 0.3, ..., 0.9)$ with $h_0 = 0.14$ cm, $h_0 = 0.07$ cm, $v_0 = 20$ m/s ($Re_0 = 462$), $m = 6$, $\phi = 2^{-1/3}$, and $\chi = 6$. Labels indicate values of $\varphi$. (a) Electric power density curves. (b) Net power density curves.
Finally, the variation of the channel length ratio $\phi = \frac{I_{k+1}}{I_k}$ is discussed with Fig. 1.6 where $\phi$ is varied between 0.1 and 1.5. For $\phi = 0$, the polarization curve and the electric power density curve of the traditional fluid delivery system is recovered. By increasing $\phi$, the high current density end of the polarization curve is shifted to the right and the maximum electric power density increases, approaching asymptotically a maximum polarization and electric power density curve. In such a case where $\phi$ is large or tends to infinity, losses due to mass transfer limitations between the channel and the channel/backing layer interface and due to mass transfer limitations in the lateral direction become negligibly small.

Fig. 1.6. Performance of a cell with a traditional fluid distributor (solid line) and a cell with tree network fluid distributors (dash-dotted lines) for different channel length ratios $\phi$, i.e. $\phi = (0.1, 0.2, 0.3, ..., 1.5)$ with $h_0 = 0.14$ cm, $h_b = 0.07$ cm, $v_0 = 20$ m/s ($Re_0 = 462$), $m = 6$, and $\phi = 2^{-1/3}$. Electric power density curves.

1.4.2. The optimized tree network

Given a certain cell area $A$, the question arises which geometric structure of the constructal tree network and which operating conditions can provide the highest net power density for the specific cell area under consideration. In order to resolve this important issue, a genetic algorithm [17] has been implemented to address the multiparametric optimization problem stated above. A fixed cell area of $A = 9$ cm$^2$ is considered with the constraint $b_0 = 2h_0$ and the parameter set $\lambda$ is assumed to be fixed to the values given in Table 1.2. The
optimization parameter space shall be limited to the ranges indicated in the bottom row of Table 1.3. For genetic search, the ranges of the six parameters $h_0$, $v_0$, $\eta$, $m$, $\varphi$, and $\Phi$ are discretized into a finite number of equidistant points. Each discretized parameter is binary-coded and represents one binary gene such that a chromosome contains six genes, i.e. one for each parameter. The binary length of a gene includes 20 digits and therefore the length of a chromosome contains 120 digits. As a result, each parameter range is divided into a number of $2^{20} - 1 = 1,048,575$ equidistant intervals and therefore is discretized into $2^{20}$ discrete points. A population size of 500 chromosomes is used. The probability for crossover is set to 0.6 and the probability for mutation is set to 0.004. An example of the course of the maximum, minimum and average fitness of the population as a function of the generation number is shown in Fig. 1.7. Note that the fitness of a chromosome equals the net power density. For negative net power densities, the fitness is artificially set to zero. The initial population is created randomly. It is seen that the maximum and average fitness grow very

Table 1.3. Genetic optimization of the tree network structure and operating conditions. In each row the decoded chromosome with the maximum overall fitness $\Pi_m$ that was obtained up to the respective generation is listed. This chromosome contains the properties of the optimum tree network and operating conditions with respect to the current generation number.

<table>
<thead>
<tr>
<th>Generation</th>
<th>$h_0$ (cm)</th>
<th>$v_0$ (cm/s)</th>
<th>$\eta$ (V)</th>
<th>$m$</th>
<th>$\varphi$</th>
<th>$\Phi$</th>
<th>$\Pi_m$ (W/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0882</td>
<td>2084</td>
<td>0.8979</td>
<td>2</td>
<td>0.8422</td>
<td>0.2209</td>
<td>0.1200</td>
</tr>
<tr>
<td>10</td>
<td>0.0882</td>
<td>2886</td>
<td>0.8979</td>
<td>5</td>
<td>0.8050</td>
<td>0.7902</td>
<td>0.1389</td>
</tr>
<tr>
<td>$10^2$</td>
<td>0.0985</td>
<td>2442</td>
<td>0.8972</td>
<td>6</td>
<td>0.8320</td>
<td>0.7896</td>
<td>0.1473</td>
</tr>
<tr>
<td>$10^3$</td>
<td>0.0997</td>
<td>2438</td>
<td>0.8962</td>
<td>6</td>
<td>0.8151</td>
<td>0.7892</td>
<td>0.1476</td>
</tr>
<tr>
<td>$10^4$</td>
<td>0.0999</td>
<td>2664</td>
<td>0.8966</td>
<td>6</td>
<td>0.8226</td>
<td>0.7928</td>
<td>0.1479</td>
</tr>
<tr>
<td>$5 \times 10^4$</td>
<td>0.0998</td>
<td>2679</td>
<td>0.8960</td>
<td>6</td>
<td>0.8260</td>
<td>0.7936</td>
<td>0.1479</td>
</tr>
</tbody>
</table>

$0.0 \leq h_0 \leq 0.1$, $0.0 \leq v_0 \leq 5000$, $0.0 \leq \eta \leq 1.2$, $0 \leq m \leq 6$, $0.0 \leq \varphi \leq 1.0$, $0.0 \leq \Phi \leq 0.7937$. 
fast within a few generations, and then stagnate or do not increase substantially any more. The peaks on the bottom of the graph represent the variation of the minimum fitness of the population which is subject to increase and drop down to zero again due to mutation. The decoded chromosome which provides the maximum fitness within the first generation is listed in the first row of Table 1.3. This chromosome is stored and replaced by the chromosome with the maximum fitness of the next generation if the latter provides a higher fitness. The decoded stored chromosome is then listed in Table 1.3 for higher generation numbers. This chromosome includes information concerning the geometric structure and the operating conditions of an optimized tree network at the respective generation. A net power density of 0.148 W/cm² is found for the optimized tree network [see Table 1.3].

![Graph showing fitness variation](image)

**Fig. 1.7. Genetic optimization of the tree network. Maximum fitness (upper curve), average fitness (middle curve), and minimum fitness (lower curve). The fitness equals the net power density of the tree network.**

For the traditional non-bifurcating fluid delivery system, a maximum net power density of 0.119 W/cm² is obtained at an inlet velocity \( v_0 = 16.2 \text{ m/s} \) \( (Re_0 = 374) \) and a channel width \( h_0 = 0.1 \text{ cm} \). As a result, the concept of tree network channels allows for a 24% improvement in net power density.

It is seen from Table 1.3 that during the course of the optimization procedure the values of the parameters \( m \) and \( \phi \) tend towards the values of their higher parameter bounds. From the previous discussion it is clear that for the optimized tree network structure the values of the parameters \( m \) and \( \phi \) must correspond to the higher bound of their ranges, since
the higher these parameters the higher the resulting net current density. From a practical point of view, the maximum number of branching levels however must be limited since only a limited number of branching levels can be manufactured onto a plate of fixed area, thus justifying the artificial upper parameter bounds for $m$ and $\phi$. Continuing the optimization procedure towards higher generation numbers than the ones listed in Table 1.3 does not provide further substantial improvement. In view of the accuracy of the analytical model employed, this would also not be consistent. The implemented genetic optimization algorithm proves to be very efficient in this context. The results of Table 1.3 have been obtained within a few minutes on a standard Unix workstation.

1.5. Conclusions

Constructal tree networks, introduced by Bejan and his co-workers in recent years, were investigated herein, as a fluid distribution concept in polymer electrolyte fuel cells. The channel distribution was allowed to also determine the shape of the fuel cell, resulting in double-staircase design, based on functionality alone and without imposing a priori the traditional rectangular shape. The one dimensional fuel cell model utilized to quantify the concept, accounts for oxygen consumption along the channel, mass transfer losses between the channel and the channel/backing layer interface, and mass transfer losses in the normal and lateral direction in the backing layer. In addition to the current-voltage behavior, pressure drop is estimated for both systems. It is shown that it is indispensable to consider pressure drop and the related pumping power as a loss mechanism when trying to optimize the cell towards high net efficiency.

It is found that the tree network fluid distribution system allows for substantially increased electric and net power densities compared to the traditional non-bifurcating systems, due to reduced mass transfer losses in the lateral direction in the backing layer, reduced mass transfer losses between the channels and the channel/backing layer interface, and reduced pumping power. In addition to the higher electric power density, the tree network system can also provide substantially reduced pressure drop and pumping power, leading to a higher net power density. This aspect becomes important for low diameter channels and high mass flow rates, both of which are required for high electric current densities. The influence of a host of operating condition parameters is discussed. An optimized tree network which provides a maximum net power density is then derived by means of a genetic optimization algorithm. Due to their intrinsic advantage with respect to both mass transfer and pressure
drop, constructal tree networks have the potential to significantly improve the performance of polymer electrolyte fuel cells at different length scales.

References


2. Pyramidal direct methanol fuel cells

Abstract

The main concept of this article is to allow for the optimized tree-like design of the flow distributors to actually define the shape of the fuel cell, thereby eliminating problems associated with the mismatch between a predecided rectangular shape and a functionally preferred channel distribution system. The work focuses on direct methanol fuel cells (DMFC). A one-dimensional across-the-cell model is extended to a two-dimensional along-the-channel model and numerically solved to predict the polarization curves of a direct methanol fuel cell with tree network channels and of a cell with traditional serpentine channels. For both flow configurations, pressure drop and pumping power are estimated. Net power densities are computed in terms of constructal parameters and operating conditions. In contrast to the traditional rectangular shape of fuel cells, the resulting “pyramidal” or “double-staircase” shape is based on the functionality of the fluid distribution system. It is found that tree network channels can provide substantially improved electric and net power densities compared to the traditional nonbifurcating single serpentine channels, as a result of their intrinsic advantage with respect to both mass transfer and pressure drop. For six (twelve) branching levels and inlet channel diameters of 0.05, 0.04, and 0.03 cm, the tree network channels allow for 14% (21%), 17% (26%), and 30% (46%) higher net power densities, respectively.

Nomenclature

\[ A \] total cell area \((\text{cm}^2)\)

\[ b \] current collector width \((\text{cm})\)

\[ c^a \] molar concentration of methanol \((\text{mol cm}^{-3})\)

---

\[ ^b \] This chapter has been submitted for publication:
\( c \)  molar concentration of oxygen (mol cm\(^{-3}\))

\( D \)  diffusion coefficient (cm\(^2\) s\(^{-1}\))

\( E \)  electric power density (W cm\(^{-2}\))

\( F \)  Faraday constant, 96485 C mol\(^{-1}\)

\( h \)  channel width (cm)

\( i_x \)  exchange current density (A cm\(^{-3}\))

\( J \)  average cell current density (A cm\(^{-2}\))

\( j \)  local proton current density (A cm\(^{-2}\))

\( k \)  concentration factor

\( L \)  channel length (cm)

\( l_b \)  backing layer thickness (cm)

\( l_m \)  membrane thickness (cm)

\( l_t \)  catalyst layer thickness (cm)

\( N \)  molar flux (mol cm\(^{-2}\) s\(^{-1}\))

\( Nu \)  Nusselt number

\( n \)  total number of branching levels

\( n_z \)  drag coefficient

\( P \)  pumping power density (W cm\(^{-2}\))

\( p \)  pressure (Pa)

\( Q \)  local rate of electrochemical reaction (A cm\(^{-3}\))

\( R \)  universal gas constant, 8.314 J K\(^{-1}\) mol\(^{-1}\)

\( Re \)  Reynolds number

\( Sh \)  Sherwood number

\( T \)  cell temperature (K)

\( V_{cell} \)  cell potential (V)

\( v \)  bulk velocity in the channel (cm s\(^{-1}\))

\( x \)  coordinate across the membrane (cm)

\( y \)  coordinate (cm)

\( z \)  coordinate along the channel (cm)

Greek symbols

\( \alpha \)  transfer coefficient
\( \chi \) number of turns in the serpentine channel
\( \varepsilon \) effective porosity
\( \phi \) channel length ratio
\( \varphi \) channel width ratio
\( \gamma \) effective order of reaction
\( \eta \) local overpotential in the catalyst layer (V)
\( \eta_i \) overpotential at the membrane/catalyst layer interface (V)
\( \eta_{\infty} \) open circuit potential (V)
\( \kappa \) mass transfer coefficient (cm s\(^{-1}\))
\( \mu \) dynamic viscosity (Pa s)
\( \Pi \) net power density (W cm\(^{-2}\))
\( \sigma \) proton conductivity (\( \Omega^{-1}\)cm\(^{-1}\))
\( \xi \) loss coefficient

Subscripts
- \( b \) in the backing layer
- \( h \) in the channel
- \( i \) value at the membrane/catalyst layer interface
- \( k \) at the \( k \)th branching level
- \( \text{lim} \) limiting
- \( m \) in bulk membrane
- \( \text{max} \) maximum
- \( \text{ref} \) reference
- \( s \) stoichiometric
- \( t \) in the catalyst layer
- \( w \) water
- \( 0 \) at the zeroth branching level
- \( \chi \) characteristic

Superscripts
- \( a \) on the anode side
- \( c \) on the cathode side
2.1. Introduction

In this article, constructal tree network channels introduced by Bejan [1-3] are investigated not only as a fluid distribution concept for the anode and cathode side of liquid-feed direct methanol fuel cells but also as a means to functionally define the shape of the fuel cells. A simple two-dimensional model is numerically solved to predict polarization curves, electric power density curves, and net power density curves of a direct methanol fuel cell with tree network channels as fluid distributors, and compare them to the respective curves of a cell with a traditional nonbifurcating serpentine channel. Variation of cell performance in terms of constructal and operating condition parameters is discussed and optima are identified. Characteristic variations along the channel of methanol and oxygen concentration, anode and cathode overpotential, and electric current density are discussed for both tree network channels and traditional nonbifurcating serpentine channels. Three-dimensional models [4] provide the most comprehensive and fundamental insight into the transport phenomena in fuel cells. However, their numerical solution still requires substantial computational time and resources, making them inappropriate for multiparametric optimization studies that usually require a large number of evaluations of an objective function. The functionality-optimized pyramidal fuel cell design was recently introduced by Senn and Poulikakos [5] with respect to hydrogen polymer electrolyte fuel cells, showing excellent promise compared to traditional alternatives. The fundamental characteristics of laminar mixing, heat transfer, and pressure drop in tree network channels were also investigated numerically [6], along with their application for thermal management in polymer electrolyte fuel cells. Vargas and Bejan [7] recently presented an elemental level thermodynamic optimization study for the electrodes of alkaline fuel cells. Entropy generation minimization [8] at the global level presents a major challenge in fuel cell research.
Fig. 2.1. Schematic drawing of methanol and oxygen concentration distributions across the cell, including anode channel (I), anode backing layer (II), anode catalyst layer (III), membrane (IV), cathode catalyst layer (V), cathode backing layer (VI), and cathode channel (VII).

2.2. Mathematical formulation

A one-dimensional across-the-cell model originally developed and experimentally validated by Kulikovsky [9,10] is utilized to predict the polarization curves and the electric power density curves of a direct methanol fuel cell with tree network channels as fluid distributors. The original model [9,10] accounts for methanol and oxygen mass transfer through the backing layers, methanol permeation through the membrane, and non-uniform overpotential distributions across the finite-size catalyst layers. The model is extended to a
two-dimensional model that additionally takes into account methanol and oxygen consumption along the channels, mass transfer between the channels and the backing layers, mass transfer in the lateral direction indicated by the y axis in Fig. 2.1, as well as overpotential variations along the channel. In addition, pressure drop and pumping power required for the fluid circulation are estimated considering also effects from bifurcations. Diffusion mass transport along the streamwise direction z (see Fig. 2.1) is neglected due to the high Peclet number. The model is based on a variety of other assumptions [9,10]: Ohmic losses due to electron transport are neglected, thus a high electrical conductivity of the current collector plates, backing layers, and catalyst layers is assumed. Reactant concentrations are assumed to be constant across the finite-size catalyst layers. A constant diffusion coefficient of methanol is assumed inside the membrane. Methanol permeated through the membrane is assumed to completely react with oxygen in the cathode catalyst layer. The methanol concentration on the cathode side is assumed to be much smaller than the methanol concentration on the anode side. The electrolyte phase is assumed to be ideally hydrated and constant proton conductivities are assumed inside the membrane and the catalyst layers. The fluid velocity is assumed to remain constant along the channel of a certain branching level. The model is a single-phase one, two-phase flow [11,12] issues are not considered. Tafel-like expressions are used to predict the electrochemical reaction rates at the anode and cathode.

The geometric structure of a cell with tree network channels as fluid distributors on the anode and cathode side is outlined in Figs. 2.1 and 2.2. The anode tree network and the cathode tree network are identical and congruently superimposed. Schematic distributions of reactant concentrations across the cell are shown in Fig. 2.1. The white areas in Fig. 2.2 represent schematically the channels of the tree network having one inlet at the zeroth branching level and a number of $2^n$ outlets at the nth branching level, where n is the total number of branching levels. This means that the flow is subject to redistribute n times. Square cross-sectional channels of width $h_k$ are considered, where the subscript k indicates the branching level. From the current collector width $b_k$, the current collector shoulder width $b_k - h_k$ follows. The backing layer thicknesses $l_{ba}^a$ and $l_{ba}^c$, the catalyst layer thicknesses $l_t^a$ and $l_t^c$, and the membrane thickness $l_m$ are constant whereas $h_k$ and $b_k$ vary from one branching level to the next higher. The superscripts a and c refer to the anode and cathode side, respectively. The subscripts b, t, and m refer to the backing layer, the catalyst layer, and the membrane, respectively. It is assumed that at the interface between two consecutive branching levels, the flow is subject to redistribute uniformly to the channels of the higher branching
level. This can be achieved with a gap of small flow resistance, for example. However, such manufacturing issues are not the main subject of this study. The aim of the present study is to investigate the fundamental mass transfer and fluid dynamics aspects of the problem. The model is based on first principles and it is chosen for its effectiveness if one takes into account its simplicity.

Fig. 2.2. Geometric structure of the pyramidal tree network fluid delivery system including channels (white) and current collector shoulders (black).

2.2.1. Governing equations: Branching level $k$

In direct methanol fuel cells, methanol and water are converted to carbon dioxide and protons at the anode, according to

$$\frac{1}{6} \text{CH}_3\text{OH} + \frac{1}{6} \text{H}_2\text{O} \rightarrow \frac{1}{6} \text{CO}_2 + \text{H}^+ + \text{e}^-.$$  \hspace{1cm} (1)

Protons are transported through the electrolyte phase of the catalyst layers and the membrane to react with oxygen in the cathode catalyst layer, according to
\[
\frac{1}{4} \text{O}_2 + \text{H}^+ + \text{e}^- \rightarrow \frac{1}{2} \text{H}_2\text{O}.
\]

(2)

In this study, the case where dry air is fed on the cathode side is considered. A constant channel width ratio \( \phi \) between two consecutive branching levels is imposed, such that the channel width at the \( k \)th branching level \( h_k \) can be related to the channel width at the zeroth branching level \( h_0 \) as

\[
h_k = h_0 \phi^k,
\]

(3)

where \( h_{k+1} = h_k \phi \). The current collector width scales identically and

\[
b_k = b_0 \phi^k
\]

(4)

holds, where \( b_{k+1} = b_k \phi \). The constant length ratio \( \phi \) relates the channel length at the \( k \)th branching level, given by

\[
L_k = L_0 \phi^k,
\]

(5)

to the channel length at the zeroth branching level \( L_0 \), where \( L_{k+1} = L_k \phi \). It is assumed that the number of channels increases by a factor of two from one branching level to the next higher. A mass balance at the interface between two consecutive branching levels then leads to

\[
v^a_k h^2_k = 2v^a_{k+1} h^2_{k+1},
\]

(6)

where \( v^a_k \) represents the bulk velocity in an anode channel of the \( k \)th branching level that can be expressed in terms of the anode inlet velocity \( v^a_0 \) at the zeroth branching level, given by

\[
v^a_k = 2^{-k} \phi^{-2k} v^a_0.
\]

(7)

In this study, \( \phi = 2^{-1/3} \) is assumed and therefore the fluid velocity is subject to decrease by a factor of \( 2^{-1} \phi^{-2} \approx 0.79 \) from one branching level to the next higher branching level. Replacing the superscript \( a \) by \( c \) in Eqs. (6) and (7) leads to analogous relations on the cathode
side. Herein, it is implicitly assumed that the bulk velocities are constant along the channels of a certain branching level, that is, \( v_k = \text{const.} \) and \( v^c = \text{const.} \). Conservation of electric current in the anode catalyst layer is formulated as

\[
\frac{\partial j_k}{\partial x_k} = Q^a_k, \tag{8}
\]

where \( j_k \) is the local proton current density in the catalyst layer, \( x_k \) is the across-the-cell coordinate, and \( Q^a_k \) is the volumetric transfer current density. Ohm’s law relates the local current density to the local electric field through the catalyst layer proton conductivity \( \sigma^a \), that is

\[
j_k = \sigma^a \frac{\partial \eta^a}{\partial x_k}, \tag{9}
\]

where the anode overpotential \( \eta^a \) substitutes the local electrolyte phase potential. Note that \( \eta^a \) is defined as the difference between the solid phase potential and the local electrolyte phase potential, where the solid phase potential is assumed to be constant. The volumetric transfer current density can be written as

\[
Q^a_k = i^a \left( \frac{c^\alpha_{c,k}}{c^\alpha_{ref}} \right)^{\gamma^a} \exp \left( \frac{\alpha^a F \eta^a}{RT} \right), \tag{10}
\]

where \( i^a \) is the exchange current density, \( c^\alpha_{c,k} \) is the methanol concentration in the anode catalyst layer, \( c^\alpha_{ref} \) is the reference concentration, \( \gamma^a \) is the reaction order, \( \alpha^a \) is the transfer coefficient, \( F \) is the Faraday constant, \( R \) is the universal gas constant, and \( T \) is the temperature. Identical relations can be formulated for the cathode catalyst layer, that is

\[
\frac{\partial j_k}{\partial x_k} = -Q^c_k, \tag{11}
\]

where

\[
j_k = -\sigma^a \frac{\partial \eta^c_k}{\partial x_k}. \tag{12}
\]
where \( c_{\text{i},k}^{c} \) is the oxygen concentration in the cathode catalyst layer. Note that the local cathode overpotential \( \eta_{c}^{k} \) is defined as the difference between the local electrolyte phase potential and the solid phase potential, where the latter is assumed to be constant. The flux of methanol mass transfer from the bulk fluid flow in the channel to the catalyst layer can be written as

\[
\frac{c_{h,k}^{a} - c_{\text{i},k}^{c}}{(\kappa_{0,k}^{a})^{\frac{1}{2}} + (\kappa_{0,k}^{a})^{\frac{1}{2}}} = \frac{j_{i,k}}{6F} + N_{k},
\]

where \( c_{h,k}^{a} \) is the mean molar concentration of methanol in the anode channel (the subscript \( h \) refers to the channel), \( \kappa_{h,k}^{a} \) is the mass transfer coefficient between the bulk fluid flow and the channel/backing layer interface, \( \kappa_{h,k}^{a} \) is the mass transfer coefficient between the channel/backing layer interface and the catalyst layer, \( j_{i,k} \) is the value of the local proton current density at the membrane/catalyst layer interface (the subscript \( i \) refers to the membrane/catalyst layer interface), and

\[
N_{k} = \frac{D_{m} c_{\text{i},k}^{c}}{l_{m}} + n_{d} \frac{j_{i,k} c_{\text{i},k}^{c}}{F w^{a}},
\]

denotes the flux of methanol through the membrane. Herein, \( D_{m} \) is the diffusion coefficient of methanol in the membrane, \( n_{d} \) is a drag coefficient that defines the number of methanol molecules transported through the membrane by one proton, and \( w^{a} \) is the water concentration on the anode side. In the first term on the right-hand side of Eq. (15) it is assumed that the methanol concentration in the cathode catalyst layer is much smaller than in the anode catalyst layer. Similarly, the flux of oxygen mass transfer from the bulk fluid flow in the channel to the cathode catalyst layer can be formulated as

\[
Q_{k}^{c} = i_{k}^{c} \left( \frac{c_{\text{i},k}^{c}}{c_{\text{ref}}} \right)^{\frac{1}{2}} \exp \left( \frac{\alpha^{c} F}{RT} \eta_{c}^{k} \right),
\]
where $c_{h,k}^c$ is the mean oxygen concentration in the cathode channel. It is assumed that methanol transported through the membrane completely reacts with oxygen in the cathode catalyst layer, according to

$$\text{CH}_3\text{OH} + \frac{3}{2} \text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}. \quad (17)$$

For laminar fully developed flow in a square duct with three adiabatic walls and a wall with a uniform heat flux, the Nusselt number $Nu$ is constant, that is, $Nu = 2.712$ (see Ref. [13]). The Sherwood number $Sh$ can be related to the Nusselt number $Nu$ according to the Reynolds analogy [14,15], $Sh = Nu Le$, where $Le = Sc / Pr$ is the Lewis number, $Sc$ is the Schmidt number, and $Pr$ is the Prandtl number. For dry air that is fed on the cathode side, $Le \approx 1$ applies. For the liquid that is fed on the anode side, the Chilton–Colburn analogy [14,15], $Sh = Nu Le (Pr / Sc)^{2/3}$, suggests that the Sherwood number and the Nusselt number are of the same order of magnitude in this study. In order to remain consistent in accuracy, $Sh / Nu = 1$ is assumed in this analysis. The Sherwood number for mass transfer between the bulk fluid flow in the channel and the channel/backing layer interface is given then by

$$Sh_{h,k}^a = 2.7 \quad (18)$$

and the corresponding mass transfer coefficient at the $k$th branching level reads

$$\kappa_{h,k}^a = Sh_{h,k}^a D_h^a / h_k, \quad (19)$$

where $D_h^a$ denotes the methanol diffusion coefficient in the anode channel. The Sherwood number for mass transfer between the channel/backing layer interface and the catalyst layer shall be empirically defined as

$$Sh_{h,k}^s = \left[1 + (b_k - h_k) / \left(A_{k}^s \right)^{-1} \right]^{-1}. \quad (20)$$
The corresponding mass transfer coefficient at the \( k \)th branching level reads

\[
\kappa_{b,k}^c = \frac{S\chi_{b,k}^c D_{b}^c}{l_b^c} = \frac{D_{b}^c}{\left\{l_b^c + \left[l_b^c + (b_k - h_k)/2\right]/2\right\}/2}
\]  

(21)

where \( D_{b}^c \) is the effective methanol diffusion coefficient in the anode backing layer. The effective diffusion length scale in Eq. (21), denoted by the denominator, is defined as the mean value between a minimum diffusion length \( l_b^c \) and a maximum diffusion length \( l_b^c + (b_k - h_k)/2 \) between the channel/backing layer interface and the catalyst layer (see Fig. 2.1). In a previous study [5], three-dimensional solutions of the Navier–Stokes and species conservation equations showed that the mass transfer correlation given in Eq. (20) is a good approximation for low–diameter channels and \( b_k = 2h_k \). The Bruggeman correction [16,17] relates the free-stream diffusion coefficient \( D_{b}^a \) to the effective diffusion coefficient \( D_{b}^c \) through the backing layer porosity \( \epsilon \), according to

\[
D_{b}^c = D_{b}^a \epsilon^{3/2}
\]

(22)

with a tortuosity factor of 3/2. Similar relations hold on the cathode side and can be written as

\[
S\chi_{b}^c = 2.7,
\]

(23)

\[
\kappa_{b,k}^c = S\chi_{b,k}^c D_{b}^c/h_k,
\]

(24)

\[
S\chi_{b,k} = \left[1 + (b_k - h_k)/(4h_k)\right]^{-1},
\]

(25)

\[
\kappa_{b,k}^c = \frac{S\chi_{b,k}^c D_{b}^c}{l_b^c} = \frac{D_{b}^c}{\left\{l_b^c + \left[l_b^c + (b_k - h_k)/2\right]/2\right\}/2}
\]

(26)

and

\[
D_{b}^c = D_{b}^c \epsilon^{3/2}.
\]

(27)
From Eqs. (8)–(10) and Eqs. (14) and (15) a simple relation between the local anode overpotential $\eta_{i,k}^a$ and the local proton current density $j_{i,k}$, both evaluated at the membrane/anode catalyst layer interface, can be obtained [9,10]:

$$j_{i,k}/j_{a,k}^a = X_k^a \tan X_k^a,$$

where

$$X_k^a = \left[ k_x^a \exp\left( \frac{\eta_{i,k}^a}{\eta_x^a} \right) \left(1 - \frac{j_{i,k}}{j_{i,\lim,k}^a}\right)^{\phi} \right] \times \left[1 + \beta_k^n \frac{j_{i,k}}{j_{w,k}^a}\right]^{\phi - \frac{1}{\sqrt{2}}},$$

$$\eta_x^a = \frac{RT}{\alpha^a F^a}, \quad j_x^a = \frac{2\sigma_x^a \eta_x^a}{i_1^a},$$

$$k_x^a = \frac{i_1^a j_x^a}{j_x^a} \left( \frac{\epsilon_{h,k}^a}{\epsilon_{c,ref}^a} \right)^{\phi},$$

$$j_{i,\lim,k}^a = 6F \frac{\epsilon_{h,k}^a}{\left( \kappa_{h,k}^a \right)^{-1} + \left( \kappa_{h,k}^a \right)^{-1}},$$

$$\beta_k = \frac{D_m}{l_m} \left[ \left( \kappa_{h,k}^a \right)^{-1} + \left( \kappa_{h,k}^a \right)^{-1} \right],$$

$$j_{w,k}^a = F \frac{w^a}{\left( \kappa_{h,k}^a \right)^{-1} + \left( \kappa_{h,k}^a \right)^{-1}},$$

and

$$N_k = \frac{j_{i,\lim,k}^a}{6F} \left[ \frac{\beta_k + n_{b,i,k} / j_{w,k}}{1 + \beta_k + n_{b,i,k} / j_{w,k}} \right] \times \left(1 - j_{i,k}/j_{i,\lim,k}^a\right).$$

A detailed derivation of Eq. (28) is given by Kulikovsky [9,10]. From Eqs. (11)–(16) a simple relation between the local cathode overpotential $\eta_{i,k}^c$ and the local proton current density $j_{i,k}$, both evaluated at the membrane/cathode catalyst layer interface, can be obtained [9,10]:
\[ \frac{j_{i,k}}{j_{z,k}} = \frac{X_{c,k}^i}{X_{c,k}^z} \tan X_{c,k}^z, \quad (36) \]

where

\[ X_{c,k}^z = \left[ k^c_k \exp \left( \frac{\eta_{c,k}^c}{\eta_{c,k}^z} \right) \right] \times \left[ \left(1 - \frac{j_{i,k}}{j_{\text{lim},k}} - r_k \right)^\gamma - \left( \frac{j_{i,k}}{j_{z}} \right)^2 \right]^{1/2}, \quad (37) \]

\[ \eta_{c,k}^z = \frac{RT}{\alpha \xi F}, \quad j_{z} = \frac{2\sigma_{c}^c \eta_{c,k}^z}{r_c}, \quad (38) \]

\[ k^c_k = \frac{j_{\text{lim},k}^c}{j_{z}^c} \left( \frac{c_{h,k}^c}{c_{\text{ref}}} \right)^{\gamma'}, \quad (39) \]

\[ j_{\text{lim},k}^c = 4F \frac{c_{h,k}^c}{\left( \kappa_{h,k}^c \right)^{-1} + \left( \kappa_{h,k}^c \right)^{-1}}, \quad (40) \]

\[ r_k = \frac{j_{\text{lim},k}^a}{j_{\text{lim},k}^c} \left( \frac{\beta_k + n_{a,i,k}}{j_{i,k}^a / j_{w,k}} \right) \left(1 + \beta_k + n_{a,i,k} / j_{w,k} \right) \times \left(1 - \frac{j_{i,k}}{j_{\text{lim},k}^a} \right). \quad (41) \]

The derivation of Eq. (36) is given by Kulikovsky [9,10]. Note that Eq. (36) is formulated at a certain position \( z_k \). The latter is the coordinate along the flow direction, it is zero at the beginning of branching level \( k \), and equals \( L_k \) at the end of branching level \( k \). Mass conservation of methanol and oxygen along the channel reads

\[ \frac{d\left( c_{h,k}^c / c_{h,k}^z (z_k = 0) \right)}{d\left( z_k / L_k \right)} = - \frac{j_{i,k}}{j_{\text{lim},k}^c} - 6F \frac{N_k}{j_{\text{lim},k}^a}, \quad (42) \]

and

\[ \frac{d\left( c_{h,k}^c / c_{h,k}^z (z_k = 0) \right)}{d\left( z_k / L_k \right)} = - \frac{j_{i,k}}{j_{\text{lim},k}^c} - 6F \frac{N_k}{j_{\text{lim},k}^a}. \quad (43) \]
respectively. Herein, the quantities

\[ j_{s,k} = 6F \frac{h^2 v^s c_{e,k}^s (z_k = 0)}{b_k I_k} \]  

and

\[ j_{c,k} = 4F \frac{h^2 v^c c_{e,k}^c (z_k = 0)}{b_k I_k} \]  

represent the stoichiometric current densities of the \( k \)th branching level on the anode and cathode side, respectively. They are related to the cell stoichiometric current densities \( j^a_s \) and \( j^c_s \) as

\[ j^a_s = j_{s,k} \frac{1}{\sum_{k=0}^{n} \phi^k \phi^k 2^k} \]  

and

\[ j^c_s = j_{c,k} \frac{1}{\sum_{k=0}^{n} \phi^k \phi^k 2^k} \]  

respectively, where \( j^a_s = j^a_{s,0} b_0 I_0 / A \) and \( j^c_s = j^c_{s,0} b_0 I_0 / A \) further applies. In Eqs. (42) and (43) it is assumed that the bulk velocities are constant along the channels of a certain branching level, that is, \( v^a_k = \text{const.} \) and \( v^c_k = \text{const.} \). Diffusion mass transport along the streamwise direction \( z_k \) is neglected due to the high Peclet numbers \( Pe^a_k = v^a_k I_k / D^a_h \) and \( Pe^c_k = v^c_k I_k / D^c_h \) in this study. Averaging the local current density \( j_{i,k} \) along the channel yields an average current density of the \( k \)th branching level, given by

\[ j_{i,k} = I_k \left[ \int_0^{l_k} j_{i,k} dz_k \right] \]  

2.2.2. Governing equations: Tree network

The model describing the transport phenomena at a certain branching level \( k \), as discussed in the last subsection, is used to predict the current–voltage behavior of a cell with
an entire tree network channel system including \( n \) branching levels. The average cell current density can then be written as

\[
J = A^{-1} \sum_{k=0}^{n} J_{k} b_{k} 2^{k}, \tag{49}
\]

where

\[
A = \sum_{k=0}^{n} L_{k} b_{k} 2^{k} \tag{50}
\]

is the total cell area. The factor \( L_{k} b_{k} 2^{k} \) in Eq. (49) represents the cell area that belongs to the \( k \)th branching level. If the cell potential \( V_{\text{cell}} \) is constant along the tree network channels, then \( J \) and \( V_{\text{cell}} \) describe the current–voltage behavior of a cell with tree network fluid distributors on the anode and cathode side.

2.2.3. Pressure drop and pumping power

Electrochemical reaction rates depend on local reactant concentrations. Since the reactant concentrations decrease downstream the channels, the local current density also decreases along the flow direction. The higher the fluid inlet velocities, the lower the relative reduction in reactant concentrations along the channels is, for a constant cell potential. In the limiting case where the inlet velocities tend to infinity, the reactant concentrations remain constant along the flow direction and the average cell current density corresponds to the local current density at the inlet. Hence, the electric power density can be enhanced by increasing the anode and cathode inlet flow rates or the stoichiometric flow ratios, however, the pumping power required for the fluid circulation is increased at the same time. If a considerable amount of electric power is required for pumping power, the net power available to the user can be substantially reduced, implying reduced overall fuel cell efficiency. Consequently, there exists a thermodynamic optimum in this context. For the optimization of the fluid distribution system of direct methanol fuel cells, it is therefore imperative that pressure drop be considered as a loss mechanism.

The pressure drop in the tree network channels can be estimated by assuming geometrically similar shapes of channel cross sections. On the anode side, the overall pressure drop can be written as
\[ \Delta p^a = \sum_{k=0}^{n} C^a \frac{v_k^a}{h_i^k} + \sum_{k=0}^{n} \xi \rho^a (v_k^a)^2 / 2, \quad \text{if } n \geq 1, \quad (51) \]

or

\[
\Delta p^a = C^a \frac{I_0 v_0^a}{h_i^0} \frac{1 - \phi^{n+1} \left( \frac{2^{n+1} \phi^{n+1}}{2 \phi^a} \right)}{1 - \phi^a (2 \phi^a} \\
+ \xi \rho^a(v_0^a)^2 \frac{1 - \left( \frac{4 \phi^a}{1} \right)^n}{1 - \left( \frac{4 \phi^a}{1} \right)^n}, \quad \text{if } n \geq 1, \quad (52)
\]

and

\[
\Delta p^a = C^a \frac{I_0 v_0^a}{h_i^0} + \xi \rho^a(v_0^a)^2 / 2, \quad \text{if } n = 0, \quad (53)
\]

where \( n = 0 \) indicates a tree network with zero branching levels which essentially corresponds to a single nonbifurcating channel, representing a traditional serpentine fluid delivery system. The resistance coefficient \( \xi \) accounts for the pressure drop due to bifurcations in the tree network. An identical resistance coefficient \( \xi \) is assumed to account for the pressure drop due to turns in the traditional nonbifurcating channel. The factor \( \chi \) indicates the number of turns and \( \rho^a \) is the fluid density. The coefficient \( C^a \) is given as

\[
C^a = \mu^a f Re / 2, \quad (54)
\]

where the friction factor for a square cross-sectional channel under fully developed flow conditions is given as \( f Re = 56.9 \) (see Ref. [13]). The pumping power density on the anode side, defined as pumping power per cell area \( A \), is given then as

\[
P^a = h_i^0 v_0^a \Delta p^a A^{-1}, \quad (55)
\]

where \( h_i^0 v_0^a \) is the volumetric inlet flow rate on the anode side. Replacing the superscript \( a \) by \( c \) in Eqs. (51)–(55) leads to the pumping power density \( P^c \) on the cathode side.
2.2.4. Electric and net power density

The cell potential $V_{\text{cell}}$ is obtained by subtracting the main voltage losses, that is, the anode overpotential, the cathode overpotential, and the membrane potential loss, from the open-circuit potential $\eta_{\text{oc}}$, and may be written as

$$V_{\text{cell}} = \eta_{\text{oc}} - \frac{\eta_{\text{an}}}{\eta_{\text{oc}}} - \frac{\eta_{\text{cat}}}{\eta_{\text{oc}}} - j_m$$

with $j_m = \sigma_m \eta_{\text{oc}} / l_m$, where $\sigma_m$ is the proton conductivity in the membrane and $l_m$ is the membrane thickness. The electric power density $E$ of the cell, defined as the total electric power per cell area $A$, is given then as

$$E = JV_{\text{cell}}.$$  (57)

Finally, a net power density

$$\Pi = E - P^a - P^c$$  (58)

can be defined as the difference between the electric power density and the power density required for fluid circulation on the anode and cathode sides.

2.3. Solution method

The model is solved numerically along the tree network. The methanol concentration at the anode inlet, the oxygen concentration at the cathode inlet, and the cell potential $V_{\text{cell}}$ are prescribed first. The equations governing transport in the across-the-cell direction $x_k$ are then solved numerically. Herein, the local proton current density $j_{i,k}$ at the membrane/catalyst layer interface is first estimated, based on which the anode overpotential $\eta_{i,k}^a$ and the cathode overpotential $\eta_{i,k}^c$ can be numerically obtained through Eqs. (28) and (36), respectively, using the secant method. The resulting cell potential can then be calculated from Eq. (56). If it does not coincide with the prescribed cell potential, then a new value for $j_{i,k}$ is estimated and the previous steps are repeated until convergence is achieved. This outer iteration loop is addressed again with the secant method. The initial value problem given by Eqs. (42) and (43)
is numerically solved with a standard Runge-Kutta method, where the just described across-
the-cell procedure is repeated at each integration step. The numerical solution converges very
quickly due to the fourth order error of the Runge-Kutta method.

2.4. Results and discussion

In this section, the effect of geometric and operating parameter variations on the
polarization curve, the electric power density curve, and the net power density curve is
discussed. In addition, the characteristic variations along the tree network of methanol and
oxygen concentration, anode and cathode overpotential, and current density are compared to
the respective characteristics of a single nonbifurcating channel. A constant cell area $A$ is
considered for both flow distribution systems. The numerical results are based on the
parameters listed in Table 2.1.

2.4.1. Concentration variation along the channels

The variation of the methanol concentration $c_{h,k}$ and the oxygen concentration $c_{h,k}^o$
along the channels of a tree network with $n = 6$ number of branching levels is shown in Fig.
2.3(a) for different anode inlet velocities $v_{0a}$ and cathode inlet velocities $v_{0c}$. The inlet
Reynolds numbers on the anode and cathode side are defined as $Re_{a} = \rho a v_{0a} / \mu a$ and
$Re_{c} = \rho c v_{0c} h_{c} / \mu c$, respectively. Labels indicate values of $v_{0c}$ where $v_{0c} = 0.02v_{0a} / 5$.
Note that the along-the-channel coordinate $z$ is defined as $z = z_{k} + L_{k-1} + L_{k-2} + \ldots + L_{0}$
and that the total length $L$ is defined as $L = L_{0} + L_{1} + L_{2} + \ldots + L_{n}$, such that $z / L = 0$ and $z / L = 1$ refer to the
inlet and outlets of the tree network, respectively. Concentration variations along a single
nonbifurcating channel covering the same cell area $A$ are shown in Fig. 2.3(b) for different
inlet velocities. The two graphs indicate how the characteristic concentration profiles along
the tree network fundamentally differ from the characteristic concentration profiles along a
single nonbifurcating channel. In the tree network channels, the reactant concentrations decay
faster towards the outlets than near the inlet [see Fig. 2.3(a)]. The opposite is the case for the
nonbifurcating channel [see Fig. 2.3(b)]. The characteristic concentration profiles along a
single branching level reflect the characteristics of a traditional channel, whereas the sequence
of profiles including more than one branching level has a different characteristic. This
fundamental difference is due the fact that the channel cross section and the Reynolds number
Table 2.1. Parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell temperature $T$ (K)</td>
<td>363 $^d$</td>
</tr>
<tr>
<td>Anode pressure level $p^n$ (bar)</td>
<td>1 $^d$</td>
</tr>
<tr>
<td>Cathode pressure level $p^c$ (bar)</td>
<td>1 $^e$</td>
</tr>
<tr>
<td>Open circuit potential $\eta_{oc}$ (V)</td>
<td>1.21</td>
</tr>
<tr>
<td>Membrane thickness $l_m$ (cm)</td>
<td>0.0206 $^d$</td>
</tr>
<tr>
<td>Anode catalyst layer thickness $l^n_a$ (cm)</td>
<td>0.0015 $^d$</td>
</tr>
<tr>
<td>Cathode catalyst layer thickness $l^c_c$ (cm)</td>
<td>0.005 $^d$</td>
</tr>
<tr>
<td>Backing layer thickness $l_b^n$, $l_b^c$ (cm)</td>
<td>0.03 $^d$</td>
</tr>
<tr>
<td>Membrane proton conductivity $\sigma_m$ ($\Omega^{-1}$ cm$^{-1}$)</td>
<td>0.1 $^d$</td>
</tr>
<tr>
<td>Catalyst layer proton conductivity $\sigma_i$ ($\Omega^{-1}$ cm$^{-1}$)</td>
<td>0.01 $^d$</td>
</tr>
<tr>
<td>Reference molar concentration $c_{ref}^a$ (mol cm$^{-3}$)</td>
<td>1.0x10$^{-3}$ $^d$</td>
</tr>
<tr>
<td>Reference molar concentration $c_{ref}^c$ (mol cm$^{-3}$)</td>
<td>3.2x10$^{-5}$ $^d$</td>
</tr>
<tr>
<td>Anode exchange current density $i^n_x$ (A cm$^{-3}$)</td>
<td>1.1x10$^{-2}$ $^d$</td>
</tr>
<tr>
<td>Cathode exchange current density $i^c_x$ (A cm$^{-3}$)</td>
<td>1.1x10$^{-2}$ $^d$</td>
</tr>
<tr>
<td>Effective order of anode reaction $\gamma^a$</td>
<td>0.5 $^d$</td>
</tr>
<tr>
<td>Effective order of cathode reaction $\gamma^c$</td>
<td>1 $^d$</td>
</tr>
<tr>
<td>Anode transfer coefficient $\alpha^a$</td>
<td>0.8 $^d$</td>
</tr>
<tr>
<td>Cathode transfer coefficient $\alpha^c$</td>
<td>0.7 $^d$</td>
</tr>
<tr>
<td>Backing layer effective porosity $\epsilon$</td>
<td>0.2 $^e$</td>
</tr>
<tr>
<td>Dynamic viscosity $\mu^a$ (Pa s)</td>
<td>3.2x10$^{-4}$ $^f$</td>
</tr>
<tr>
<td>Dynamic viscosity $\mu^c$ (Pa s)</td>
<td>2.1x10$^{-5}$ $^f$</td>
</tr>
<tr>
<td>Loss coefficient $\xi$</td>
<td>1.0 $^g$</td>
</tr>
<tr>
<td>Drag coefficient $n_d$</td>
<td>1.0 $^d$</td>
</tr>
<tr>
<td>Inlet methanol concentration $c_{h,0}^a(0)$ (mol cm$^{-3}$)</td>
<td>1.5x10$^{-3}$ $^e$</td>
</tr>
<tr>
<td>Inlet oxygen concentration $c_{h,0}^c(0)$ (mol cm$^{-3}$)</td>
<td>6.96x10$^{-6}$</td>
</tr>
<tr>
<td>Total flow-field area $A$ (cm$^2$)</td>
<td>9 $^{d,h}$</td>
</tr>
<tr>
<td>Diffusion coefficient of methanol</td>
<td></td>
</tr>
</tbody>
</table>
in the channel $D_{ch}^a$ (cm$^2$ s$^{-1}$) $2.0 \times 10^{-4}$

in the anode backing layer $D_{bl}^a$ (cm$^2$ s$^{-1}$) $1.8 \times 10^{-5}$

in the membrane $D_{m}$ (cm$^2$ s$^{-1}$) $1.0 \times 10^{-5}$

Diffusion coefficient of oxygen

in the channel $D_{ch}^c$ (cm$^2$ s$^{-1}$) $0.29$

in the cathode backing layer $D_{cl}^c$ (cm$^2$ s$^{-1}$) $2.6 \times 10^{2}$

\textsuperscript{d} Reference [9].
\textsuperscript{e} Assumed.
\textsuperscript{f} Reference [19].
\textsuperscript{g} Reference [20].
\textsuperscript{h} Reference [21].
\textsuperscript{i} Obtained through Eq. (22).
\textsuperscript{j} Reference [14].
\textsuperscript{k} Obtained through Eq. (27).
Fig. 2.3. Variation of the methanol concentration $c_{h,k}^i$ (solid lines) and the oxygen concentration $c_{h,k}^o$ (dashed lines) along the flow direction for different inlet velocities $v_0^i$ and $v_0^o$ [i.e., $v_0^i = (0.01, 0.02, 0.04, 0.08)$ m/s and $v_0^o = (2.5, 5, 10, 20)$ m/s] corresponding to $Re_0^i = (15, 30, 60, 120)$ and $Re_0^o = (57, 115, 229, 459)$, with $h_0 = 0.1$ cm, $h_o = 0.05$ cm, and $V_{cell} = 0.3$ V. Labels indicate values of $v_0^i = 0.01v_0^o / 2.5$. (a) Tree network fluid distributor with $n = 6$, $\phi = 2^{-1/3}$, and $\phi = 2^{-1/3}$. (b) Traditional fluid distributor.
decrease in the tree network from one branching level to the next higher. The Reynolds numbers of consecutive branching levels are related as $Re_{k+1} / Re_k = 1/(2\varphi)$. For a channel width ratio $\varphi = 2^{-1/3}$, $Re_{k+1} / Re_k = 0.63$ results.

2.4.2. Current density variation along the channels

The variation of the local current density along the channels is shown in Fig. 2.4 for both flow configurations and different inlet flow rates. For the tree network, local discontinuities appear at the interface between two consecutive branching levels, since the geometric details of the transition are not taken into account and a sudden change in channel width is considered. The lower the inlet flow rates, the more the local current density decays along the tree network. For low inlet flow rates, the distribution of the local current density has its maximum at the inlet. For high inlet flow rates, the maximum of the local current density distribution is shifted downstream the channels. It should be noted that if the inlet flow rates tend to infinity, the variation of the local current density along the tree network is described by a right-angled monotonically increasing staircase shaped “curve” with its maximum near the outlet. The term “staircase-shaped” or “pyramidal” as part of the name of the herein proposed fuel cell fluid distribution concept refers in fact not only to the geometric structure but also to the intrinsic nature of the entire transport phenomena. The variation of the local current density along the tree network is shown in Fig. 2.5 for different numbers of branching levels $n$. 
Fig. 2.4. Variation of the current density $j_{i,k}$ along the flow direction for different inlet velocities $v_0^i$ and $v_0^e$ [i.e., $v_0^i = (0.01, 0.02, 0.04, 0.08) \text{ m/s and } v_0^e = (2.5, 5, 10, 20) \text{ m/s} ]$ with $h_0 = 0.1 \text{ cm}, \ h_e = 0.05 \text{ cm}, \ and \ V_{cel} = 0.3 \text{ V}$. Labels indicate values of $v_0^e$ where $v_0^e = 0.01v_0^i / 2.5$. (a) Tree network fluid distributor with $n = 6, \ \phi = 2^{-1/3}, \ and \ \phi = 2^{-1/3}$. (b) Traditional fluid distributor.
Fig. 2.5. Variation of the local current density $j_{i,k}$ along the flow direction for different numbers of branching levels $n$ [i.e., $n=(0,1,2,3,...,7)$] with $v_0^a = 0.01$ m/s, $v_0^c = 2.5$ m/s, $b_0 = 0.1$ cm, $h_0 = 0.05$ cm, $\varphi = 2^{-1/3}$, $\phi = 2^{-1/3}$, and $V_{cell} = 0.3$ V.
Fig. 2.6. Performance of a cell with a traditional fluid distributor (solid lines) and a cell with a tree network fluid distributor (dashed lines) for different inlet velocities $v_0$ and $v_0^c$ [i.e., $v_0^c = (0.02, 0.04, 0.08, 0.12, 0.2, \infty) \text{ m/s and } v_0^c = (5, 10, 20, 30, 50, \infty) \text{ m/s }$ for $h_0 = 0.1 \text{ cm}$, $h_0 = 0.05 \text{ cm}$, $n = 6$, $\phi = 2^{-1/3}$, $\psi = 2^{-1/3}$, and $\chi = 6$. Labels indicate values of $v_0^c$ where $v_0^c = 0.02v_0^c / 5$. (a) Polarization curves. (b) Electric power density curves. (c) Net power density curves.
2.4.3. Electric and net power densities

The polarization curves of a cell with tree network channels as fluid distributors are shown in Fig. 2.6(a) for different inlet flow rates, together with the polarization curves of a cell with a single nonbifurcating channel. If the flow rate is increased, the high current density end of the polarization curve is shifted to the right, that is, the limiting current density is increased, approaching asymptotically a maximum limiting current density at infinite inlet flow rates. It can be seen that for a constant cell potential the tree network channels provide higher cell current densities than the traditional channels. The corresponding electric power density curves are plotted in Fig. 2.6(b). For inlet velocities $v_0$ of 5, 10, 20, 30, 50, and $\infty$ m/s, it is seen that compared to the traditional system, the tree network system provides 3.9%, 4.9%, 5.3%, 5.4%, 5.5%, and 5.5% higher maximum electric power densities, respectively. Herein, the maxima of the electric power density curves are compared. The net power density curves are shown in Fig. 2.6(c). For inlet velocities $v_0$ of 5, 10, and 20 m/s, it is seen that compared to the traditional system, the tree network system provides 6.3%, 14%, and 59% higher maximum net power densities, respectively. For $n = 9$, this last sequence reads 7.7%, 17%, and 69% [see Fig. 2.7(a)]. For $n = 12$, the sequence reads 8.3%, 19%, and 77% [see Fig. 2.7(b)]. For $n = 15$, the sequence reads 8.7%, 21%, and 83% [see Fig. 2.7(c)].

2.4.4. Maximum electric and net power densities

A fixed geometry of a tree network channel system shall be considered first, for which the net power density is to be optimized in terms of two optimization parameters: the inlet flow rate and the average cell current density. From Fig. 2.6(c) it can be seen that there exists an optimum pair, that is, an optimum inlet flow rate and an optimum average current density, which together provide a maximum net power density. This maximum can be obtained from the maximum of the envelope enclosing the continuous set of constant velocity curves in Fig. 2.6(c). The same holds for the traditional fluid distribution system. Note that the maximum electric power density is simply obtained from the maximum of the curve for which the inlet flow rates tend to infinity [see Fig. 2.6(b)].

The maxima of such envelopes are plotted in Fig. 2.8 for different inlet channel diameters $h_0$ and different numbers of branching levels $n$. In Fig. 2.8(a), absolute values are plotted for the electric power density and the net power density. In Fig. 2.8(b), these absolute
Fig. 2.7. Performance of a cell with a traditional fluid distributor (solid lines) and a cell with a tree network fluid distributor (dashed lines) for different inlet velocities $v_0^i$ and $v_0^c$ i.e., $v_0^i = (0.02, 0.04, 0.08, 0.12, 0.2) \text{ m/s and } v_0^c = (5, 10, 20, 30, 50) \text{ m/s }$ with $b_0 = 0.1 \text{ cm}$, $h_0 = 0.05 \text{ cm}$, $\phi = 2^{-1/3}$, $\phi = 2^{-1/3}$, and $\chi = n$. Labels indicate values of $v_0^c$ where $v_0^c = 0.02v_0^c/5$. (a) Net power density curves for $n = 9$. (b) Net power density curves for $n = 12$. (c) Net power density curves for $n = 15$. 
Fig. 2.8. Maximum electric power density (dashed lines) and maximum net power density (solid lines) based on $h_0 = 2h_0$, $\varphi = 2^{-1/3}$, $\phi = 2^{-1/3}$, and $v_0^* = 0.02v_0^* / 5$. (a) Absolute values for the tree network system ($n > 0$) and the traditional system ($n = 0$). (b) Values for the tree network system ($n > 0$) are scaled with the corresponding values of the traditional system ($n = 0$).
values are scaled with the corresponding values of a traditional nonbifurcating channel, to compare the two flow distribution systems. From Fig. 2.8(a), it can be seen that the higher the number of branching levels, the higher the electric power density is, and the same holds for the net power density. The net power density increases for increasing inlet channel diameters $h_0$ due to a reduced pressure drop. In contrast, the electric power density decreases for increasing channel diameters due to enhanced resistances to mass transfer. The graphs suggest that in trying to maximize the net power density, the number of branching levels must be maximized and the inlet channel diameter must correspond to the higher bound of the parameter range considered here. A finite inlet channel diameter range of practical interest is discussed. If the higher bound of the inlet channel diameter range in Figs. 2.8(a) and 2.8(b) is extended towards higher values, the net power density curves in Fig. 2.8(a) are expected to have a maximum and the scaled net power density curves in Fig. 2.8(b) are expected to have a minimum, since the electric power density is monotonically decreasing for increasing inlet channel diameters. The number of branching levels is limited by a manufacturing constraint; that is, there exists a maximum number of branching levels that can be manufactured onto a plate of finite size, although with today’s MEMS techniques [18] channels of diameters as small as of the order of 100 nm do not present particular manufacturing challenges. For a tree network with $n = 6$, it is seen from Figs. 2.8(a) and 2.8(b) that compared to the traditional system with $n = 0$ and $\chi = 6$, the tree network system provides 30%, 17%, and 14% higher maximum net power densities for inlet channel diameters $h_0$ of 0.03, 0.04, and 0.05 cm, respectively. For a tree network with $n = 12$, it is seen that compared to the traditional system with $n = 0$ and $\chi = 12$, the tree network system provides 46%, 26%, and 21% higher maximum net power densities for inlet channel diameters $h_0$ of 0.03, 0.04, and 0.05 cm, respectively.

It should be noted that the effect of bubbles on the anode side was neglected in this study. In cases where it occurs, the formation of bubbles is expected to increase the volumetric flow rate in the channel, according to conservation of mass. The presence of bubbles will also affect friction, in particular at high void fractions. In addition, the dynamic wetting behaviour between the liquid phase, the gaseous phase, and the solid phase of the wall or the porous channel/backing layer interface will play a role in this context, especially for the smaller channels of the higher branching levels. In the smaller channels, the pressure differences between the gaseous and liquid phases may not be negligible. Furthermore,
different two-phase flow regimes are to be expected within the proposed tree network channel system containing multiple length scales.

2.5. Conclusions

Pyramidal direct methanol fuel cells were designed from tree network distribution channels. In contrast to the traditional a priori imposed rectangular shapes of fuel cells, the resulting pyramidal shape of the fuel cell is based on the functionality of the fluid distribution system. A one-dimensional across-the-cell model was utilized and extended in this study to a two-dimensional model. The current–voltage behavior was predicted for both flow distribution systems and it was shown that it is imperative that the pressure drop and the related pumping power be considered as a loss mechanism when optimizing the fuel cell with respect to maximum net power densities. It was found that tree network channels can provide substantially improved electric and net power densities compared to the traditional nonbifurcating serpentine channels, due to reduced mass transfer resistance between the channel and the channel/backing layer interface, reduced mass transfer resistance in the lateral direction of the backing layer, and reduced pressure drop and pumping power. The influence of the variation of geometric and operating parameters on the electric and net power density were discussed and optima identified. It was shown that tree network channels on pyramidal shaped plates have the potential to significantly improve the performance of direct methanol fuel cells due to their intrinsic advantage with respect to both mass transfer and pressure drop.

References


3. Polymer electrolyte fuel cells with porous materials as fluid distributors and comparisons with traditional channeled systems

Abstract
In this study, a novel concept is investigated, according to which the traditional ribbed flow delivery systems are replaced with permeable porous fluid distributors, which circumvent a number of known performance hindering drawbacks. A thorough single-phase model, including the conservation of mass, momentum, energy, species and electric current, using Butler-Volmer kinetics, is numerically solved in three dimensions, to investigate the impact of different flow configurations on the performance of hydrogen fuel cells. It is found that cells with porous gas distributors generate substantially higher current densities and therefore are more advantageous with respect to mass transfer. Another advantage of porous flow distributors is the potential for higher power densities and reduced stack weight.

Nomenclature
Latin letters

\( a \)  effective surface to volume ratio \((\text{m}^2\text{m}^{-3})\)

\( c \)  molar concentration \((\text{mol m}^{-3})\)

\( D_i \)  binary diffusivity of \( i \) in a multicomponent mixture \((\text{m}^2\text{s}^{-1})\)

\( D_{ij} \)  diffusivity of the pair \( i-j \) in a binary mixture \((\text{m}^2\text{s}^{-1})\)

\( d \)  average pore diameter \((\text{m})\)

\( F \)  Faraday constant, 96485.309 \((\text{C mol}^{-1})\)

\( h \)  specific enthalpy of gas mixture \((\text{J kg}^{-1})\)

\( I \)  identity matrix \((-)\)

\( ^c \)  This chapter is published in:
Electric current density (A m\(^{-2}\))

Exchange current density (A m\(^{-2}\))

Reference current density (A m\(^{-2}\))

Electric current density (A m\(^{-2}\))

Transfer current density (A m\(^{-3}\))

Diffusive flux of species \(i\) (kg m\(^{-2}\) s\(^{-1}\))

Thermal conductivity (W m\(^{-1}\) K\(^{-1}\))

Channel length (m)

Molecular weight (kg mol\(^{-1}\))

Total number of species (-)

Pressure (Pa)

Heat flux (W m\(^{-2}\))

Reaction source term of species \(i\) (kg m\(^{-3}\) s\(^{-1}\))

Universal gas constant, 8.314510 (J K\(^{-1}\) mol\(^{-1}\))

Temperature (K)

Cell potential (V)

Mixture velocity (m s\(^{-1}\))

Mole fraction of species \(i\) (-)

Greek letters

\(\alpha_a\) anodic transfer coefficient (-)

\(\alpha_c\) cathodic transfer coefficient (-)

\(\gamma\) concentration exponent (-)

\(\varepsilon\) porosity (-)

\(\zeta\) water activity (-)

\(\eta\) overpotential (V)

\(\kappa\) permeability (m\(^2\))

\(\lambda\) water content in the membrane

\(\mu\) dynamic viscosity (Pa s)

\(\rho\) mixture density (kg m\(^{-3}\))

\(\rho_i\) mass concentration of species \(i\) (kg m\(^{-3}\))
3.1. Introduction

Polymer electrolyte fuel cells (PEFC) have the potential to become firmly established as a competitive form of electric power generation in a host of engineering applications, such as powering of vehicles, portable power systems and remote power generations. Even though low temperature fuel cells have very high theoretical efficiencies, there are several challenges
to overcome in the way of making the PEFC a competitive, efficient and environmentally friendly alternative energy conversion device. Current issues in PEFC research are strongly interdisciplinary and are related to transport phenomena, thermal management, water management, electrochemistry, materials and manufacturing.

Numerical modeling provides an improved understanding of the fundamental transport phenomena inside the fuel cell and therefore allows for efficient, scientifically based optimization which is necessary to aid the PEFC on the road to success. Therefore, substantial research effort has been focused on the development of mathematical models and their analytical or numerical solution during the last decade. One-dimensional models [1-4], pseudo-two-dimensional models [5-8] as well as fully two-dimensional models [9-13] are not able to predict with the needed accuracy the three-dimensional transport phenomena in a PEFC and therefore are not ideally appropriate for design or material optimization. Three-dimensional modeling [14-19] is crucial to capture performance-limiting effects such as mass transfer limitations to and from the portion of the diffusion layer which is not covered by flow channels as well as Ohmic losses in the membrane-electrode assembly. In most of these three-dimensional models [14-18] the catalyst layers are modeled as infinitely thin interfaces, whereas in Ref. [19] the finite size of the catalyst layers was considered. The existence of two different electric potential fields, i.e. a solid potential field governing the electron flux and a membrane potential field governing the proton flux is not accounted for. A two-dimensional approach is used for the membrane in [15-17]. In contrast, the present mathematical model accounts for the finite thickness of the catalyst layers as well as of the membrane and the governing equations inside each of these layers are solved in three dimensions. Two different electric potential fields are considered, i.e. a solid potential field and a membrane potential field. In addition, kinetic gas theory is used to determine the thermal conductivity of the gas mixture, which strongly depends on the mixture composition.

The mathematical model is solved for porous flow distributors, put forth by Bejan and co-workers [20,21], as well as for the classical parallel and serpentine flow distributors, for the sake of comparison. Validation of the code at different operating pressures and temperatures was performed using experimental data from Ticianelli et al. [22]. Parallel and serpentine flow-fields exhibit limited reactant/product mass transfer to and from the part of the diffusion and catalyst layer which is not covered by flow channels (i.e. under the current collector “shoulders”). This effect is most distinct on the cathode side due to the low diffusivity of oxygen. Removal of water vapor from these regions is also limited. In this paper
it is shown that porous flow distributors circumvent this drawback which is particular to ribbed flow-fields and therefore are more advantageous in terms of mass transfer.

Porous materials such as carbon or metal foams are available at porosities up to 98% which implies the possibility of a reduction in stack weight – a key quantity for applications in transportation. However, the higher the porosity of the foam, the lower the effective electrical conductivity is. On the other hand, mass transfer limitations are higher at the lower porosities due to reduced effective species diffusivities. Parametric studies are performed to investigate these interactions. Finally, appropriate foam materials currently available on the market are suggested.

3.2. Mathematical model

Transport phenomena in the PEFC are described by the formulation of mass, momentum, energy, species and electric current conservation equations. The method of local volume averaging [23-26] is applied to equations governing transport in porous media which means that the equations are spatially smoothed over a representative elementary volume. Its
diameter has to be much larger than the pore diameter as well as much smaller than the macroscopic dimension of the corresponding porous layer. The computational domain $\Omega$ consists of three coupled subdomains $\Omega_1$, $\Omega_{II}$ and $\Omega_{III}$, as shown in Fig. 3.1. The first subdomain $\Omega_1$ (fluid subdomain) incorporates flow channels, gas diffusion layers, catalyst layers and the membrane. Inhomogeneous distributions of material properties inside this subdomain are defined in order to account for different physical layers. Mass, momentum, energy, species and electric current conservation is formulated for this subdomain. The second and third subdomain (solid subdomains), $\Omega_{II}$ and $\Omega_{III}$, include the current collector on the cathode and anode side, respectively, for which conservation of energy and electric current is formulated. Rates of electrochemical reactions in the catalyst layers are described by Butler-Volmer equations.

An ideal gas mixture is assumed inside the fluid subdomain $\Omega_1$,

$$p = \frac{\rho}{M}RT, \quad p = p_i / x_i, \quad \rho = \sum_{i=1}^{N} \rho_i, \quad M = \sum_{i=1}^{N} x_i M_i,$$

where pressure is defined in terms of partial pressure and mole fraction of species $i$, mixture density is expressed in terms of mass concentrations and mixture molecular weight is given by the molecular weight of individual species. For the ideal gas mixture, the specific enthalpy is a function of temperature and species mass fractions,

$$h(T, \omega_1, ..., \omega_N) = \sum_{i=1}^{N} \omega_i h_i(T),$$

where specific enthalpies $h_i$ of individual species, defined as the sum of the enthalpy of formation at the standard reference state and the sensible enthalpy, depend on temperature only and are approximated using JANAF tables [27]. In the following, volume-averaged conservation equations are formulated to describe transport in porous media. Mass conservation for the ideal gas mixture reads

$$\nabla \cdot (\varepsilon \rho \mathbf{v}) = 0.$$  

For a porosity of $\varepsilon = 1$, mass conservation of a free-stream gas mixture is recovered. Momentum conservation is written as
\[
\n\nabla \cdot (\varepsilon p \mathbf{v}) = -\nabla (\varepsilon p) - \nabla \cdot (\varepsilon \mathbf{\tau}) - \frac{\mu}{\kappa} \varepsilon^2 \mathbf{v}
\]

with the stress tensor

\[
\mathbf{\tau} = -\mu \left( \nabla \mathbf{v} + (\nabla \mathbf{v})^T \right) + \frac{2}{3} \mu \left| \nabla \cdot \mathbf{v} \right| \mathbf{I}.
\]

The last term in Eq. (4) represents an additional source term, Darcy’s drag, for porous media regions in order to account for increased flow resistance. Note that Eq. (4) is a generalized form of Darcy’s law [23-26]. For \( \varepsilon = 1 \) and \( \kappa \to \infty \), momentum conservation for a free-stream gas mixture is recovered. The local dynamic viscosity of the gas mixture

\[
\mu = \sum_{j=1}^{N} \frac{x_j \mu_j}{\sum_{j=1}^{N} x_j \Theta_j}
\]

with

\[
\Theta_j = \frac{1}{\sqrt{8}} \left( 1 + \frac{M_{j,k}}{M_j} \right)^{-1/2} \left[ 1 + \left( \frac{\mu_k}{\mu_j} \right)^{1/2} \left( \frac{M_{j,k}}{M_j} \right)^{1/4} \right]^2
\]

is determined based on the Chapman-Enskog theory, extended to multicomponent gas mixtures at low density [28-30]. Within this framework, dynamic viscosities of individual species are given as

\[
\mu_j = 2.6693 \times 10^{-6} \sqrt{\frac{10^3 M_j T}{\sigma_j^2 \Omega_{j,s}}}.
\]

The volume-averaged conservation equation of energy is written as [30]

\[
\nabla \cdot (\varepsilon p \mathbf{v}) = -\nabla \cdot \mathbf{q} - (\varepsilon \mathbf{\tau} : \nabla \mathbf{v}) + \mathbf{v} \cdot \nabla (\varepsilon p) - J \eta \mathbf{z} + \frac{\dot{z}_s \mathbf{z} \cdot \dot{z} \mathbf{z}}{\sigma_s} + \frac{\dot{z}_r \mathbf{z} \cdot \dot{z} \mathbf{z}}{\sigma_r}
\]

where
\[ q = -k_{\text{eff}} \nabla T + \sum_{i=1}^{N} h_i \mathbf{j}_i \]  

(10)

is the heat flux, accounting for heat conduction and energy transport by species diffusion. The second term on the right hand side of Eq. (9) manifests the irreversible rate of viscous dissipation and the third term includes the reversible rate compression work. The fourth term accounts for electric work due to volumetric electric current transfer between the solid potential field \( \Phi_s \) and the pore potential field \( \Phi_r \) in the catalyst layers, where the volumetric transfer current density \( J \) is given by Eqs. (23) and (26) below and \( \eta \) is the overpotential. This term appears only in the catalyst layers. The fifth term stands for Joule heating due to electron flux and the last term accounts for Joule heating due to proton flux in the catalyst layers and the membrane. Heat generation due to reactions, i.e. conversion of chemical energy to heat energy, is implicitly accounted for in Eq. (9) through the fourth term on the right hand side, since enthalpy \( h_i \) is defined as the sum of the enthalpy of formation at the standard reference state and the sensible enthalpy [30]. The effective thermal conductivity in porous media is determined based on the variational approach using composite spheres for macroscopically homogeneous and isotropic multiphase materials, as introduced by Hashin and Shtrikman [31], where the higher bound reads

\[ k_{\text{eff}} = \frac{1}{\frac{1-\varepsilon}{3k_s} + \frac{\varepsilon}{2k_s + k_i}} - 2k_s. \]  

(11)

Note that \( k_{\text{eff}} (\varepsilon = 1) = k_i \) and \( k_{\text{eff}} (\varepsilon = 0) = k_s \) applies. The thermal conductivity of the fluid phase strongly depends on the composition of the gas mixture and is determined within the framework of the Chapman-Enskog theory [32], i.e.

\[ k_i = \frac{\sum_{i=1}^{N} x_i k_i}{\sum_{i=1}^{N} x_i \Theta_i} \]  

(12)

Conservation of species reads

\[ \nabla \cdot (\varepsilon \rho \mathbf{u} \mathbf{y}) = -\nabla \cdot \mathbf{j}_i + r_i, \quad i \in [1, 2, 3, ..., N] \]  

(13)
with the diffusive flux of species $i$,

$$\dot{j}_i = -\rho D_{i,\text{eff}} \nabla \omega_i.$$  \hfill (14)

Note that the species source terms $r_i$ on the right hand side of Eq. (13) only appear in the catalyst layers. Effective diffusion coefficients account for reduced mass transport in porous media and are determined in terms of the free-stream diffusion coefficients,

$$D_{i,\text{eff}} = \varepsilon^2 D_i,$$  \hfill (15)

according to the Bruggeman correction [23,25]. The diffusion coefficient of species $i$,

$$D_i = \frac{1 - x_i}{\sum_{j=1, j \neq i}^{n} \frac{x_j}{D_j}},$$  \hfill (16)

is expressed in terms of binary diffusion coefficients which in turn are obtained from the Chapman-Enskog theory [30,33],

$$D_y = 0.018829 \sqrt{\frac{T^3 \left( \frac{1}{10^4 M_i} + \frac{1}{10^4 M_j} \right)}{p \sigma_{y}^2 \Omega_{13,ij}}}.$$  \hfill (17)

Note that Eq. (17) is written here in terms of quantities with SI units as declared in the nomenclature. The electric current flow through the cell is due to electron flux in the current collectors, the solid phase of the gas diffusion layers, the solid phase of the catalyst layers and due to proton flux in the polymer electrolyte phase of the catalyst layers and the membrane. The electron flux is governed by the electric potential field $\Phi_e$ and the proton flux is governed by the electric potential field $\Phi_f$. The steady conservation equation of electric current in conjunction with Gauss’s law for irrotational electric fields leads to

$$\nabla \cdot \dot{i}_s = -\nabla \cdot (\sigma_s \nabla \Phi_s) = \begin{cases} +J^+, & \text{cathode catalyst layer} \\ -J^-, & \text{anode catalyst layer} \\ 0, & \text{else} \end{cases}$$  \hfill (18)
and

\[ \mathbf{V} \cdot \mathbf{i}_t = -\mathbf{V} \cdot (\sigma_t \nabla \Phi_t) = \begin{cases} -J^+, & \text{cathode catalyst layer} \\ +J^+, & \text{anode catalyst layer} \\ 0, & \text{else} \end{cases} \]  

(19)

From the sum of Eqs. (18) and (19),

\[ \mathbf{V} \cdot \mathbf{i}_s + \mathbf{V} \cdot \mathbf{i}_t = 0, \]

(20)

it is seen that conservation of charge is accomplished. Electrochemical surface reaction rates are determined with Butler-Volmer equations [34,35]. The surface specific transfer current in the catalyst layer on the cathode side is given then as

\[ i = i_0 \exp \left( \frac{\alpha F}{RT} (\Phi_s - \Phi_t) \right) - \exp \left( -\frac{\alpha F}{RT} (\Phi_s - \Phi_t) \right) \]

(21)

with the overpotential \( \eta = \Phi_s - \Phi_t \), where the exchange current density

\[ i_0^+ = -i_0^{\text{ref}} \left( \frac{c_{O_2,w}}{c_{O_2,w}^{\text{ref}}} \right)^{\gamma_{O_2}} \left( \frac{c_{H_2O_w}}{c_{H_2O_w}^{\text{ref}}} \right)^{\gamma_{H_2O}} \]

(22)

is expressed in terms of the reference current density and the reactant and product concentrations \( c_{r,w} = \omega_{r,w} \rho / M_i \) at the interface. Multiplying with the surface to volume ratio \( a^+ \) in the catalyst layer leads to the volumetric transfer current density

\[ J^+ = a^+ i^+ \]

(23)

on the cathode side, where \( a^+ \) is a direct representation of catalyst loading. Similarly, electrochemical reaction rates on the anode side are expressed as

\[ i^- = i_0 \exp \left( \frac{\alpha F}{RT} (\Phi_s - \Phi_t) \right) - \exp \left( -\frac{\alpha F}{RT} (\Phi_s - \Phi_t) \right) \]

(24)
\[ i_0^- = i_0^{\text{ref}}, \left( \frac{c_{H_2,w}^{\text{ref}}}{c_{H_2,w}} \right)^{n_{H_2}} \]  

and

\[ J^- = \alpha^* i^- . \]  

The stoichiometric reactant coefficients of the cathode reaction

\[ \frac{1}{4} O_2 + H^+ + e^- \rightarrow \frac{1}{2} H_2O \]  

and of the hydrogen oxidation on the anode side

\[ \frac{1}{2} H_2 \rightarrow H^+ + e^- \]  

are needed to couple the surface specific transfer current density to mass transfer at the solid-fluid interface in the catalyst layers. This is written as

\[ M_{O_2} \frac{i^+}{4F} = + \rho D_{O_2,\text{eff}} \frac{\omega_{O_2} - \omega_{O_2,w}}{d^+} \]  

and

\[ M_{H_2O} \frac{i^+}{2F} = - \rho D_{H_2O,\text{eff}} \frac{\omega_{H_2O} - \omega_{H_2O,w}}{d^+} \]  

where \( \omega_i \) denotes the mass fraction of species \( i \) in the middle of the fluid pore, \( \omega_{i,w} \) is the mass fraction at the solid-fluid interface where surface reactions occur, \( d^+ \) is the average pore diameter and \( D_{i,\text{eff}} / d^+ \) represents the mass transfer coefficient. Numerical solution of the set of nonlinear equations (21), (22) and (29) for \( \omega_{i,w} \) [36] allows to determine the volumetric source terms

\[ r_{O_2} = -\alpha^* \rho D_{O_2,\text{eff}} \frac{\omega_{O_2} - \omega_{O_2,w}}{d^+} \]  

and
\[ r_{\text{H}_2\text{O}} = -a^+ \rho D_{\text{H}_2\text{O}, \text{eff}} \frac{\omega_{\text{H}_2\text{O}} - \omega_{\text{H}_2\text{O}, \text{w}}}{d^+} \]  

which are used in Eq. (13). Similarly, formulation of these constraints on the anode side yields

\[ M_{\text{H}_2} \frac{i^-}{2F} = +\rho D_{\text{H}_2, \text{eff}} \frac{\omega_{\text{H}_2} - \omega_{\text{H}_2, \text{w}}}{d^-} \]  

and

\[ r_{\text{H}_2} = -a^- \rho D_{\text{H}_2, \text{eff}} \frac{\omega_{\text{H}_2} - \omega_{\text{H}_2, \text{w}}}{d^-}. \]  

For determining the proton conductivity \( \sigma_f \) in the membrane, the correlation by Springer et al. [1] is used,

\[ \sigma_f = 100 \exp \left[ 1286 \left( \frac{1}{303} - \frac{1}{T} \right) \right] (0.005139 \lambda - 0.00326) \]  

where the water content in the membrane

\[ \lambda = \begin{cases} 0.043 + 17.81 \zeta - 39.85 \zeta^2 + 36.0 \zeta^3 & \text{if } 0 < \zeta \leq 1 \\ 14 + 1.4(\zeta - 1) & \text{if } 1 < \zeta \leq 3 \end{cases} \]  

is correlated in terms of the water activity

\[ \zeta = \frac{x_{\text{H}_2\text{O}} P}{P_{\text{sat}}}. \]

The saturation pressure of water vapor is approximated with [1]

\[ \log_{10} \left( P_{\text{sat}} \times 10^{-3} \right) = -2.1794 + 0.02953 (T - 273.15) \]
\[ -9.1837 \times 10^{-5} (T - 273.15)^2 \]
\[ +1.4454 \times 10^{-7} (T - 273.15)^3. \]
3.3. Numerical solution

3.3.1. Models and boundary conditions

The performance of fuel cells with porous flow distributors is numerically investigated and compared with fuel cells having either parallel or serpentine flow-fields. For the cell with the parallel flow-field, one single half-channel assembly is modeled in three dimensions, as shown in Fig. 3.1(a), using symmetry boundary conditions at \( \xi_1 = \xi_{1,\text{min}} \) and \( \xi_1 = \xi_{1,\text{max}} \). Dirichlet boundary conditions are used for temperature on the top, bottom and front sides with a constant value corresponding to the temperature of the inlet gas streams. These settings represent the case of a perfectly cooled flow-field. Newman boundary conditions with zero flux are used for \( \Phi_i \) on \( \partial \Omega \). At the top and bottom boundaries of the channel, Dirichlet boundary conditions with constant values are set for \( \Phi_s \), where zero-flux conditions are applied to the inlet and outlet front. The difference between the top and bottom boundary condition value of \( \Phi_s \) is obviously the sum of all the potential losses inside the cell. Constant mass flow rates and fixed pressure boundary conditions are applied to inlets and outlets, respectively. The serpentine flow-field is of quadratic shape; its width is equal to the length of the parallel flow-field and therefore includes exactly seven connected channels. For the porous flow distributors, no variations in the direction of \( \xi_1 \) are assumed, cf. Fig. 3.1(b). Therefore, it is modeled in two dimensions.

3.3.2. Solution method

The coupled set of partial differential equations is numerically solved with a finite-volume central scheme on a structured grid using the licensed solver CFD-ACE distributed by CFDRC of Huntsville, USA. Coupling of the set of partial differential equations including the strongly non-linear Butler-Volmer equations requires advanced source term linearization techniques [37]. Algebraic multigrid solver is used in conjunction with a convergence criterion of \( 1 \times 10^{-10} \). A first order upwind scheme is chosen to obtain a preliminary numerical solution for the model with the serpentine flow-field consisting of 647,360 finite volumes, which is further used as an initial condition for the application of the central scheme.

The computational grid of the two-dimensional model of the porous gas distributor consists of 2,700 cells. By increasing the cell number to 5,400 (10,800), the average current density increases by \( 5.9 \times 10^{-4} \% \) (7.6 \times 10^{-4} \%). When comparing species contours, the three
Table 3.1. Geometry data for the half-channel assembly representing the parallel flow-field.

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current collector thickness (mm) *</td>
<td>0.762</td>
</tr>
<tr>
<td>Gas channel thickness (mm) [11]</td>
<td>0.762</td>
</tr>
<tr>
<td>Gas diffuser thickness (mm) [11]</td>
<td>0.254</td>
</tr>
<tr>
<td>Catalyst layer thickness (mm) [11]</td>
<td>0.0287</td>
</tr>
<tr>
<td>Membrane thickness (mm) [11]</td>
<td>0.230</td>
</tr>
<tr>
<td>Gas channel length $L$ (mm) *</td>
<td>10.6681</td>
</tr>
<tr>
<td>Gas channel width (half-width) (mm) *</td>
<td>0.762 (0.381)</td>
</tr>
<tr>
<td>Current collector or shoulder width (half-width) (mm) *</td>
<td>0.762 (0.381)</td>
</tr>
</tbody>
</table>

* assumed

Table 3.2. Material properties.

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity of the diffusion layers, $\varepsilon$ [11,3]</td>
<td>0.4</td>
</tr>
<tr>
<td>Porosity of the catalyst layers, $\varepsilon$ [11,3]</td>
<td>0.4</td>
</tr>
<tr>
<td>Porosity of the membrane, $\varepsilon$ [11,3]</td>
<td>0.28</td>
</tr>
<tr>
<td>Permeability of the diffusion layers, $\kappa$ (m$^2$) [11]</td>
<td>1.76x10^{-11}</td>
</tr>
<tr>
<td>Permeability of the catalyst layers, $\kappa$ (m$^2$) [11]</td>
<td>1.76x10^{-11}</td>
</tr>
<tr>
<td>Permeability of the membrane, $\kappa$ (m$^2$) [11,3]</td>
<td>1.8x10^{-18}</td>
</tr>
<tr>
<td>Tortuosity of the diffusion and catalyst layers, $\tau$ [11,3]</td>
<td>1.5</td>
</tr>
<tr>
<td>Solid thermal conductivity of the diffusion layers, $k_s$ (W m$^{-1}$ K$^{-1}$) [44]</td>
<td>169</td>
</tr>
<tr>
<td>Solid thermal conductivity of the catalyst layers, $k_s$ (W m$^{-1}$ K$^{-1}$) [44]</td>
<td>169</td>
</tr>
<tr>
<td>Solid electrical conductivity of the diffusion layers, $\sigma_s$ (Ω$^{-1}$ m$^{-1}$) [3,22]</td>
<td>53</td>
</tr>
<tr>
<td>Solid electrical conductivity of the catalyst layers, $\sigma_s$ (Ω$^{-1}$ m$^{-1}$) [3,22]</td>
<td>53</td>
</tr>
<tr>
<td>Thermal conductivity of the current collector, $k_s$ (W m$^{-1}$ K$^{-1}$) [44]</td>
<td>169</td>
</tr>
<tr>
<td>Electrical conductivity of the current collector, $\sigma_s$ (Ω$^{-1}$ m$^{-1}$) [44]</td>
<td>1.25x10^{5}</td>
</tr>
</tbody>
</table>

grids yield practically indistinguishable results. For the three-dimensional model of the parallel flow-field, a computational grid consisting of 43,200 cells is used. By increasing the cell number to 86,400 (172,800), the average current density increases by 0.015% (0.022%). Again, comparison of species contours yields practically indistinguishable results. The grid
resolution of the serpentine flow-field (647,360 cells) is consistent with the one of the parallel flow-field.

Table 3.3. Operating conditions and kinetic constants.

<table>
<thead>
<tr>
<th></th>
<th>Anode</th>
<th>Cathode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative humidity of inlet streams [11,3]</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>N₂/O₂ mole fraction of dry air</td>
<td></td>
<td>0.79/0.21</td>
</tr>
<tr>
<td>O₂ stoichiometric flow ratio [11]</td>
<td></td>
<td>2.8 A/cm² equivalent</td>
</tr>
<tr>
<td>H₂ stoichiometric flow ratio [11]</td>
<td>2.6 A/cm² equivalent</td>
<td></td>
</tr>
<tr>
<td>Anodic transfer coefficient αₐ *</td>
<td>1/2</td>
<td>3/2</td>
</tr>
<tr>
<td>Cathodic transfer coefficient αₑ *</td>
<td>1/2</td>
<td>3/2</td>
</tr>
<tr>
<td>Concentration exponent γ₉₂ [18]</td>
<td>1/2</td>
<td></td>
</tr>
<tr>
<td>Concentration exponent γ₀₂ [18]</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Concentration exponent γ₉₂₀ [18]</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Reference current density a⁻i₀⁺ref⁻ / [ (c₀₂ref)γ₀₂ (c₉₂₀ref)γ₉₂₀ ] *</td>
<td>2.92x10⁷ (A/m³)/(mol/m³)³/²</td>
<td></td>
</tr>
<tr>
<td>Reference current density a⁺i₀⁺ref⁺ / [ (c₀₂ref)γ₀₂ (c₉₂₀ref)γ₉₂₀ ] *</td>
<td>1.05x10³ (A/m³)/(mol/m³)</td>
<td></td>
</tr>
</tbody>
</table>

* calibration parameter

3.4. Validation

The mathematical model is validated on a wide range of operating conditions using data from experiments conducted at Los Alamos National Laboratory, cf. Ticianelli et al. [22]. In their work, the effect of temperature and of pressure on the cell potential-current density behavior was investigated as part of a comprehensive analysis of electrode kinetics of single cells. Among other things, cell potential-current density measurements were recorded at 323K and 1/1Atm (inlet pressure at anode / inlet pressure at cathode), 323K and 3/5Atm, 353K and 3/5Atm, for Prototech electrodes (20 wt% Pt/C in supported electrocatalyst plus 50 nm sputtered film of Pt, 0.45 mg/cm² of Pt), as shown in Fig. 3.2. The numerical results in Fig. 3.2 were obtained from the three-dimensional parallel flow-field. Corresponding geometry data are given in Table 3.1, material properties and operating conditions are listed in Table 3.2 and Table 3.3, respectively. Material properties of graphite are used for the current collector.
plates. The reference current densities and Tafel constants listed in Table 3.3 were obtained by calibration at low current densities, because they are not known from the experiment. Since the performance of the cell is rate-limited at low current densities, this is a valid procedure. The open-circuit potentials reported by Ticianelli et al. [22] were used to determine the cell potentials.

![Polarization curves for three different operating conditions: 1) 323K, 1/1Atm; 2) 323K, 3/5Atm; 3) 353K, 3/5Atm.](image)

**Fig. 3.2. Comparison of numerical results with experimental results from Ticianelli et al. [22].**

The comparison shows good agreement between numerical and experimental results, especially at 323K and 3/5Atm, 353K and 3/5Atm. For the case with 323K and 1/1Atm, cell performance is over-predicted at current densities higher than 0.6A/cm². This bound corresponds to the maximum power output of the cell. The discrepancy is assumed to appear due to the fact that the current mathematical model does not take into account effects caused by water vapor condensation which are highest at the high current densities. The presence of liquid water blocking the pores of the gas diffusion and catalyst layers is expected to add additional mass transport limitations [38–40]. At the higher temperature and pressure levels, these limitations become significant at current densities higher than 1A/cm² [22] due to enhanced species diffusivities and electrochemical reaction rates.

3.5. Numerical results and discussion

In cells with ribbed flow distributors, the mass transfer rate to and from the reacting zones under the current collector shoulders is reduced compared to the mass transfer rate to
zones under the flow channels, due to longer diffusion paths. This phenomenon is most prominent on the cathode side of fuel cells operated with air and hydrogen due to the low diffusivity of oxygen in nitrogen. For saturated inlet streams, the diffusivity of hydrogen in water vapor is much higher and therefore the issue of mass transfer limitations on the anode side is of minor importance. The limitations on the cathode side manifest themselves in reduced oxygen mole fractions, increased mole fractions of water vapor and increased overpotential losses (activation and concentration) under the current collector shoulders, as shown clearly in Figs. 3.3(b) and 3.4(b). Obviously, removal of water vapor from these regions is also limited. Therefore, a higher saturation level is observed under the shoulders which is expected to lead to further mass transfer limitations due to pores clogged with liquid water which cannot be captured since the current model does not account for condensation. Therefore, the performance assessment of the porous flow distributors with respect to the ribbed flow distributors is expected to be a conservative one, especially at the higher current densities where the saturation level is highest. It is shown in Figs. 3.3(a) and 3.4(a) that the mole fraction of oxygen in the reacting zone under the shoulders can be markedly smaller (approximately down to half) compared to the concentration under the flow channels. In addition, a significant reduction in the oxygen concentration in the downstream region of the serpentine flow distributor of Fig. 3.4(a) is observed.

Replacing the traditional ribbed flow distributors with distributors made out of a porous medium eliminates the above mentioned drawback of mass transfer non-uniformity, since the diffusion layers are continuously covered with the bulk flow through the permeable porous matrix. Therefore, the oxygen mole fraction and all other quantities vary in the flow direction $\xi_3$ only, cf. Fig. 3.5, and not in the cross-direction $\xi_1$.

There are three key properties of the porous medium of the flow distributors which need consideration in this context: porosity, permeability and effective electrical conductivity. High permeability and porosity of the foam are required to avoid excessive pressure drop in the flow-field. However, the higher the porosity, the lower the effective electrical conductivity, which results in increased Ohmic losses across the foam. Further, mass transfer through the porous matrix is limited at lower porosities due to reduced effective diffusivities, as a consequence of the Bruggeman correction (Eq. 15). Both, pressure drop and Ohmic losses need to be minimized to maximize overall fuel cell efficiency.
Fig. 3.3. Parallel flow-field at 323K, 1/1 Atm and $U = 0.3V$. (a) Cross-sectional distribution of the oxygen mole fraction $x_{O_2}$ in three different planes, i.e. $\xi_3 = 0.1L$ (left side), $\xi_3 = 0.5L$ (middle) and $\xi_3 = 0.9L$ (right side). The subdomains $\Omega_{13}$, $\Omega_{15}$ and $\Omega_{15}$ are shown from the bottom to the top. (b) Distribution of the overpotential $\eta = \Phi_3 - \Phi_1$ in the middle of the cathode catalyst layer ($\xi_2 = -129.35 \mu m$). The picture is shrunk in the flow direction $\xi_3$. (c) Cross-sectional distribution of the water vapor mole fraction $x_{H_2O}$ in the three planes, i.e. $\xi_3 = 0.1L$ (left side), $\xi_3 = 0.5L$ (middle) and $\xi_3 = 0.9L$ (right side). (d) Cross-sectional distribution of the relative humidity $x_{H_2O}P / p_{sat}$ in the three planes, i.e. $\xi_3 = 0.1L$ (left side), $\xi_3 = 0.5L$ (middle) and $\xi_3 = 0.9L$ (right side).
Fig. 3.4. Serpentine flow-field at 323K, 1/1Atm and $U = 0.3V$. (a) Distribution of the oxygen mole fraction $x_{O_2}$ in the middle of the cathode diffusion layer ($\xi_2 = -270.7\mu m$). (b) Distribution of the overpotential $\eta = \Phi_s - \Phi_i$ in the middle of the cathode catalyst layer ($\xi_2 = -129.35\mu m$). (c) Distribution of the water vapor mole fraction $x_{H_2O}$ in the middle of the cathode diffusion layer ($\xi_2 = -270.7\mu m$). (d) Distribution of the relative humidity $x_{H_2O}p / p_{sat}$ in the middle of the cathode diffusion layer ($\xi_2 = -270.7\mu m$).
Fig. 3.5. Porous gas distributor at 323K, 1/1Atm, $U = 0.3V$, $\varepsilon = 0.9$, $\kappa = 1.76 \times 10^{-9} m^2$ and $\sigma = 1.250 \Omega^{-1} m^{-1}$. (a) Distribution of the oxygen mole fraction $x_{O_2}$ throughout the cell ($\xi = $ const.). The picture is shrunk in the flow direction $\xi$. (b) Distribution of the water vapor mole fraction $x_{H_2O}$ in the same plane. (c) Distribution of the relative humidity $x_{H_2O} p / p_{sat}$ in the same plane.
Fig. 3.6. Average current density of a fuel cell with a porous gas distributor for different effective electrical conductivities and porosities $\varepsilon$ of the foam at 323K, 1/1Atm, $U=0.5V$, $\kappa=1.76x10^{-9} m^2$. The effective electrical foam conductivity $\sigma_s$ is nondimensionalized with the electrical conductivity of the solid material $(125,000 \Omega^{-1} m^{-1})$, i.e. $\sigma_d = \sigma_s/(125,000 \Omega^{-1} m^{-1})$.

The average current density $i_{avg}$ of the cell with the porous gas distributor is nondimensionalized with the average current density obtained from the parallel flow-field operated at identical conditions, i.e. $i_{avg.d} = i_{avg}/(0.62A/cm^2)$. The position of a cell in which reticulated vitreous carbon ($\varepsilon=0.9$, 100 ppi) is used for the porous gas distributors is indicated by the cross-marker.
experimental numerical (parallel channel flow-field) numerical (porous gas distributor) \( \sigma_d = 10\% \) numerical (porous gas distributor) \( \sigma_d = 1.0\% \) numerical (porous gas distributor) \( \sigma_d = 0.227\% \) numerical (porous gas distributor) \( \sigma_d = 0.1\% \)

**Fig. 3.7.** Polarization curves. Comparison of the parallel channel flow-field with the porous gas distributors for different effective electrical conductivities \( \sigma_s \) of the foam at 323K, 1/1Atm, \( \varepsilon = 0.9 \), \( \kappa = 1.76 \times 10^{-9} \) m\(^2\) with \( \sigma_d = \sigma_s / (125,000 \Omega^{-1} \text{m}^{-1}) \). The position of reticulated vitreous carbon (\( \varepsilon = 0.9 \), 100 ppi) is indicated as a specific example.
In order to explore the influence of each quantity parametric studies have been performed on the porous flow distributors. It is seen from Fig. 3.6 that the porous gas distributors can generate up to 13% higher average current densities than the parallel flow-field. This improvement is achieved for porosities higher than 0.7. If the effective electrical conductivity of the foam is about two thousandths of the conductivity of the solid material, then the same average current density is obtained from the porous gas distributors as from the parallel flow-field, for foam porosities higher than 0.7. Mass transfer limitations due to reduction of foam porosity can be neglected at porosities higher than 0.7 but become important at lower values. If the electrical conductivity of the foam is $10^3$ times smaller than that of the solid matrix, Ohmic losses are dominant compared to the losses caused by these mass transfer limitations, as shown in Fig. 3.6.

Reticulated vitreous carbon (RVC) [41] is one example of a potential material to be used as a porous fluid distributor, due to its high electrical conductivity and low resistance to flow. It is available down to a recommended thickness of 1.5mm with a maximum of 100 pores per inch (ppi). The performance of reticulated vitreous carbon ($\varepsilon = 0.9$, 100ppi, $\kappa = 1.76 \times 10^9 \text{m}^{-2}$, $\sigma_s = 1,250 \Omega^{-1}\text{m}^{-1}$) is marked by a cross-marker in Fig. 3.6.

Polarization curves for cells with the porous flow distributors are given in Fig. 3.7 for different effective electrical conductivities of the foam and constant foam porosity and permeability. For performance assessment of the porous flow distributors, the numerically obtained polarization curve of the parallel flow-field is given in the same graph in conjunction with the corresponding experimentally obtained curve [22]. These two curves are the same as the lowest curves in Fig. 3.2. With increasing electrical conductivity of the foam, the polarization curve is shifted upwards and therefore higher cell power output is achieved. If the effective electric foam conductivity is higher than about 0.2% of the conductivity of the solid material, then the cell power output from the porous gas distributors is higher than the one from the parallel flow-field. At lower conductivities, Ohmic losses across the foam increase such that the parallel flow-field becomes more advantageous in terms of cell power output. The performance of reticulated vitreous carbon is also shown as a specific example.

Phase change and transport of liquid water driven by pressure, capillary and gravity forces are not considered in the present model. Consequently, transport of liquid water through the membrane by means of electro-osmotic drag is also not accounted for. The effect of electro-osmotic drag in the membrane is expected to cause a higher water saturation level in the cathode catalyst layer which may lead to further mass transport limitations for gas
species to the reaction sites due to enhanced blocking of pores by liquid water [39]. Mazumder and Cole recently showed with their three-dimensional mathematical model accounting for transport and formation of liquid water [37,39] that in the investigated cases the effect of electro-osmotic drag on cell performance is not significant.

Pressure drops of 1.56 Pa (0.315 Pa), 74.2 Pa (13.4 Pa) and 9.40 Pa (1.92 Pa) are obtained for the cathode (anode) side of the parallel, serpentine and macro-porous flow-field \((\varepsilon = 0.9, \, \kappa = 1.76 \times 10^{-9} \text{ m}^2, \, \sigma = 1.250 \Omega^{-1} \text{ m}^{-1}, \, U = 0.5 \text{ V})\), respectively. Hence, pressure drop in the porous gas distributor is roughly an order of magnitude higher than in the parallel flow-field but an order of magnitude lower than in the serpentine flow-field. Experimental and numerical studies on flow characteristics in metal foams [42,43] also report that the pressure drop in flows through high porosity porous foams is not prohibitively high.

3.6. Conclusions

A thorough mathematical model describing the transport phenomena in a PEFC has been presented and numerically solved. A central point of the study was to investigate the performance of porous flow distributors as a possible replacement for the currently used ribbed flow distributors of various shapes. As a consequence, the solution of both porous and ribbed flow distributors was accomplished, which allowed for the necessary comparisons. Numerical results were validated against experimental data from Ticianelli et al. [22]. Mass transfer limitations in cells with ribbed flow-fields such as parallel and serpentine flow-fields were investigated. It has been shown numerically that porous gas distributors are advantageous in terms of mass transfer and therefore exhibit substantially higher cell performance. Reticulated vitreous carbon has been suggested as one example of a potential porous material to be used in this context. The replacement of ribbed flow-fields with macro-porous gas distributors would also allow for a reduction in stack weight. Finally, the manufacturing cost could be substantially reduced since the expensive process of machining the ribbed flow-field would no longer be necessary.

References


[41] 2002, Duocel RVC physical characteristics data sheet, ERG Materials and Aerospace, Oakland.


4. Multiphase transport phenomena in the diffusion zone of a PEM fuel cell\textsuperscript{d}

Abstract

In this paper, a thorough model for the porous diffusion layer of a polymer electrolyte fuel cell (PEFC) is presented that accounts for multicomponent species diffusion, transport and formation of liquid water, heat transfer, and electronic current transfer. The governing equations are written in nondimensional form to generalize the results. The set of partial differential equations is solved based on the finite volume method. The effect of downscaling of channel width, current collector rib width, and diffusion layer thickness on the performance of PEM fuel cells is systematically investigated and optimum geometric length ratios (i.e., optimum diffusion layer thicknesses, optimum channel and rib widths) are identified at decreasing length scales. A performance number is introduced to quantify losses attributed to mass transfer, the presence of liquid water, charge transfer, and heat transfer. Based on this model it is found that microchannels (e.g., as part of a tree network channel system in a double-staircase PEM fuel cell) together with diffusion layers that are thinner than conventional layers can provide substantially improved current densities compared to conventional channels with diameters in the order of one millimeter, since the transport processes occur at reduced length scales. Possible performance improvements of 29\%, 53\%, and 96\% are reported.

Nomenclature

Latin letters
\[ a \quad \text{stoichiometric coefficient} \]
\[ b \quad \text{current collector width (m)} \]

\textsuperscript{d}This chapter is published in:
\( c \)  molar concentration (mol m\(^{-3}\))
\( D_{ij} \)  effective binary diffusion coefficient (m\(^2\) s\(^{-1}\))
\( D_{ij,0} \)  binary diffusion coefficient (m\(^2\) s\(^{-1}\))
\( \mathbf{e}_y \)  unit vector in \( y \) direction
\( \mathbf{e}_z \)  unit vector in \( z \) direction
\( F \)  Faraday constant, 96,485 (C mol\(^{-1}\))
\( f(\varepsilon) \)  porosity function
\( g(s) \)  saturation function
\( h \)  channel width (m)
\( h_{lg} \)  latent heat of condensation (J mol\(^{-1}\))
\( i \)  exchange current density (A m\(^{-2}\))
\( J(S) \)  Leverett \( J \)-function
\( j \)  transfer current density (A m\(^{-2}\))
\( K \)  parameter
\( k \)  effective thermal conductivity (W m\(^{-1}\) K\(^{-1}\))
\( L \)  diffusion layer thickness (m)
\( M \)  molecular weight (kg mol\(^{-1}\))
\( N \)  mass flux (mol m\(^{-2}\) s\(^{-1}\))
\( Nu \)  Nusselt number
\( n_d \)  effective drag coefficient
\( p \)  pressure (Pa)
\( p_c \)  capillary pressure (Pa)
\( Q \)  condensation rate (mol m\(^{-3}\) s\(^{-1}\))
\( R \)  universal gas constant, 8.314 J K\(^{-1}\) mol\(^{-1}\)
\( S \)  reduced liquid water saturation
\( \Delta s \)  entropy change (J K\(^{-1}\) mol\(^{-1}\))
\( s \)  liquid water saturation
\( s_{im} \)  immobile saturation
\( T \)  temperature (K)
\( w \)  coordinate (m)
$x$ mole fraction
$y$ coordinate (m)
$z$ coordinate (m)

Greek letters

$\alpha$ Tafel constant
$\beta$ heat transfer coefficient (W m$^{-2}$ K$^{-1}$)
$\chi$ effective electrical conductivity ($\Omega^{-1}$ m$^{-1}$)
$\delta$ film thickness (m)
$\epsilon$ porosity
$\phi$ electric potential (V)
$\gamma$ condensation rate constant (s$^{-1}$)
$\kappa$ absolute permeability (m$^2$)
$\kappa_r$ relative permeability
$\mu_L$ viscosity of liquid water (Pa s)
$\Pi$ performance number
$\Omega$ collision integral
$\sigma$ collision diameter (Angstroem)
$\theta$ contact angle (rad)
$\rho_L$ density of liquid water (kg m$^{-3}$)
$\sigma$ surface tension (N m$^{-1}$)
$\xi$ parameter

Subscripts

avg average
F fluid
G gas phase
H2O water vapor
h top boundary
L liquid water
O2 oxygen
S solid
4.1. Introduction

Thermodynamic optimization of finite-size components and finite-time processes subject to physical constraints is currently emerging as a challenging field in polymer electrolyte membrane (PEM) fuel cell research [1,2]. The method combines modeling and optimization of real devices subject to physical constraints which actually cause the thermodynamic imperfection and irreversible operation of the device [3,4].

Tree network channels constructing double-staircase PEM fuel cells have been recently introduced as a novel fluid distribution concept [1,5]. The proposed flow architecture [1] has resulted from a multiparametric genetic optimization analysis subject to physical constraints. Compared to traditional non-bifurcating serpentine channel systems, the suggested tree-network-based channel system has demonstrated promise to achieve higher maximum electric power densities while minimizing the required pumping power for fluid circulation at the same time, due to its intrinsic advantage with respect to both mass transfer and pressure drop. It has been shown that the effect of channel size and rib width has a major influence on the magnitude of mass transfer resistances. The smaller these lengths, the lower the mass transfer resistance between the channel and the catalyst layer is, due to a reduced effective length of the diffusion paths. Herein, equal channel and rib widths have been considered along with a constant diffusion layer thickness. However, channels of smaller diameters cause a higher pressure drop and require a higher pumping power for fluid circulation. Compared to non-bifurcating serpentine channels, the suggested multi-scale tree network channel system provides more favorable downscaling laws, enabling to minimize mass transfer resistances and pressure drop at the same time. The term “multi-scale” is used since an intrinsic length scale does not exist in such a tree network channel system. Intrinsic length scales can be defined at a certain branching level, but they change as we go from one branching level to the next higher.

Besides diffusion mass transfer, other transport phenomena can be important in the diffusion layer, such as transport of liquid water, electronic current transfer, and heat transfer.
Multicomponent diffusion in the diffusion and catalyst layers of PEM fuel cells was investigated by Kulikovsky and co-workers [6-8] considering two different electric potential fields governing the transport of electrons and protons. These two-dimensional models were extended to a quasi three-dimensional approach [9] taking further into account liquid water in the membrane phase. Herein, the presence of liquid water in voids and in the porous diffusion layer was neglected and isothermal conditions were assumed in all their studies [6-9]. Nguyen and co-workers investigated mass transfer in the porous electrodes of a PEM fuel cell using the interdigitated gas distributor [10]. They also introduced two-dimensional models [11,12] and a three-dimensional model [13] for the cathode of a PEM fuel cell taking into account multicomponent diffusion and transport of liquid water. Their models [10-13] are isothermal and electronic current transfer in the diffusion layer is not considered, that is, infinite thermal and electronic conductivities are assumed. Two-phase flow and transport under isothermal conditions along the cathode channel and the cathode diffusion layer were studied in two dimensions [14,15], neglecting gradients in the direction parallel to the membrane underneath the current collector ribs. A three-dimensional, nonisothermal, two-phase flow model was presented by Berning and Djilali [16]. However, one single geometric configuration is considered in their work and the effect of channel width, rib width, and diffusion layer thickness on the performance of PEM fuel cells is not investigated. A one-dimensional study on nonisothermal two-phase transport in the diffusion layer of a PEM fuel cell was presented by Nam and Kaviany [17]. Another detailed, isothermal, one-dimensional analysis of two-phase transport in the anode and cathode was presented by Weber et al. [18], taking further into account transport within the membrane.

In this paper, a model for the porous diffusion layers of a PEM fuel cell is introduced in which all the governing macroscopic transport phenomena, including multicomponent diffusion, transport of liquid water, electronic current transfer, and heat transfer are considered at the same time. While the model can also be used to investigate the transport phenomena in the anode diffusion layer, it is only applied to the cathode diffusion layer in this study. The governing equations are written in nondimensional form to generalize the results. The model is solved in two dimensions, neglecting gradients in the streamwise direction along the channel. The effect of downscaling of channel width, current collector rib width, and diffusion layer thickness on the performance of PEM fuel cells is systematically investigated and optimum length ratios (i.e., diffusion layer thickness / diffusion layer width, channel width / rib width) are identified. A performance number is introduced to quantify losses in the
diffusion layer attributed to mass transfer, the presence of liquid water, charge transfer, and heat transfer.

### 4.2. Mathematical formulation

A nonisothermal, multicomponent, two-phase diffusion layer model is presented in this section. A two-dimensional rectangular computational domain including the porous cathode diffusion layer is considered, as shown in Fig. 4.1. Isotropic porous media are investigated in this study. The catalyst layer is assumed to be very thin and therefore is treated as a boundary condition. The $y$-coordinate indicates the direction parallel to the membrane where $z$ indicates the direction perpendicular to the membrane. In fuel cell channels, the Peclet number (defined based on the channel length) is usually very large and concentration gradients in the diffusion layer along the flow direction $w$ (i.e., in the direction perpendicular to $y$ and $z$) are much smaller than the corresponding gradients along $y$ and $z$. This implies that in the case of high Peclet numbers the transport phenomena between the anode and cathode channel exhibit a strongly two-dimensional character. Based on this concept, the previously mentioned quasi three-dimensional models [9] were established.

![Fig. 4.1. Schematic drawing of the cathode diffusion layer (DL) and the cathode channel (CH). The catalyst layer (CL) is treated as a boundary condition. The computational domain is indicated by the dotted rectangle, where $b$ is the diffusion layer width, $L$ is the diffusion layer thickness, and $h$ is the channel width.](image-url)
4.2.1 Governing equations

A fluid consisting of two phases, i.e. a gas phase and a liquid phase, is considered. In the gas phase, an ideal three-component gas mixture is assumed, consisting of oxygen, water vapor, and nitrogen. The liquid phase contains only water. Between the phases, mass transfer can occur by means of condensation and evaporation of water. Ordinary diffusion in multicomponent ideal gases at low density can be described by the Stefan-Maxwell equations [19], given by

$$\nabla x_i = \sum_{j=1}^n \frac{x_i N_j - x_j N_i}{cD_{i,j}},$$

(1)

where $x_i$ is the mole fraction of species $i$, $N_i$ is the molar flux of species $i$ with respect to stationary coordinates, $c$ is the total molar concentration, and $D_{i,j}$ is the effective binary diffusion coefficient between species $i$ and $j$. For the three-component gas mixture, Eq. (1) yields

$$\nabla x_{O2} = \frac{x_{O2} N_{H2O} - x_{H2O} N_{O2}}{cD_{O2,H2O}} + \frac{x_{O2} N_{N2} - x_{N2} N_{O2}}{cD_{O2,N2}},$$

(2)

and

$$\nabla x_{H2O} = \frac{x_{H2O} N_{O2} - x_{O2} N_{H2O}}{cD_{O2,H2O}} + \frac{x_{H2O} N_{N2} - x_{N2} N_{H2O}}{cD_{H2O,N2}},$$

(3)

where

$$x_{N2} = 1 - x_{O2} - x_{H2O}.$$  

(4)

Note that $x_{O2}$, $x_{H2O}$, and $x_{N2}$ are the mole fractions of oxygen, water vapor, and nitrogen, respectively. Conservation of mass requires [19]

$$0 = -\nabla \cdot N_{O2},$$

(5)

$$0 = -\nabla \cdot N_{H2O} - Q,$$

(6)

and
where $Q$ is a source term that accounts for condensation and evaporation of water. Nitrogen does not participate in the electrochemical reaction and it does not cross the membrane due to its low diffusivity in the membrane. In the steady state, nitrogen is therefore motionless with respect to stationary coordinates and $N_{N_2} \equiv 0$ applies in the diffusion layer [20]. Using Eqs. (2)-(4), the molar fluxes of oxygen and water vapor can then be written as

$$N_{O_2} = \frac{cD_{O_2,N_2}}{(-1 + x_{O_2} + x_{H_2O})} \left[ -D_{O_2,N_2} x_{H_2O} + D_{O_2,H_2O} \frac{\nabla x_{H_2O}}{x_{H_2O}} \left( -1 + x_{O_2} + x_{H_2O} \right) \right]$$

and

$$N_{H_2O} = \frac{cD_{H_2O,N_2}}{(-1 + x_{O_2} + x_{H_2O})} \left[ -D_{O_2,N_2} x_{H_2O} + D_{O_2,H_2O} \frac{\nabla x_{H_2O}}{x_{H_2O}} \left( -1 + x_{O_2} + x_{H_2O} \right) \right],$$

respectively. In this study, transport of liquid water in hydrophobic porous media is investigated. Herein, the capillary pressure equals the difference between the liquid (non-wetting) phase pressure and the gas (wetting) phase pressure, given by

$$p_c = p_L - p_g.$$  

A uniform gas phase pressure is assumed [17,18] such that the capillary pressure gradient equals the liquid water pressure gradient. The molar flux of liquid water may be written as [17]

$$N_L = -\frac{D_L}{M_L} \frac{\kappa \kappa_r L}{\mu_L} \nabla p_L,$$

where $\nabla p_L \equiv \nabla p_c = (dp_{c}/dS)\nabla S$. Note that $\rho_L$ is the liquid water density, $M_L$ is the molecular weight, $\kappa$ is the absolute permeability, $\kappa_r$ is the relative permeability, $\mu_L$ is the dynamic viscosity, $p_c$ is the capillary pressure, and
\[ S = \frac{s - s_{im}}{1 - s_{im}} \]  

is the reduced water saturation, expressed in terms of the liquid water saturation \( s \) and the immobile saturation \( s_{im} \). Herein, \( s \) is defined as the ratio between the pore volume occupied by liquid water and the entire pore volume. It is assumed that the capillary pressure \( p_c \) can be written as a function of the reduced water saturation [17,21],

\[ p_c = \frac{\sigma |\cos \theta|}{(\kappa/\varepsilon)^{1/2}} J(S), \]  

where \( \sigma \) is the surface tension, \( \theta \) is the contact angle, and \( \varepsilon \) is the porosity. The Leverett \( J \)-function [17,22,23]

\[ J(S) = 1.417S - 2.120S^2 + 1.263S^3 \]  

is used to describe the relation between the capillary pressure and the reduced water saturation. This correlation is based on experimental imbibition capillary pressure data obtained by Leverett [24]. He suggested that the semi-empirical nondimensional form \( J(S) = (p_c/\sigma)(\kappa/\varepsilon)^{1/2} \) can be used to describe capillary versus saturation behavior [17,21,25], where \( p_c/\sigma \) represents a mean interfacial curvature of a meniscus in a pore and \( (\kappa/\varepsilon)^{1/2} \) is a pore length scale. Based on Eq. (14), heat transfer considering phase change and capillarity in porous sand packs (spherical grain shape) was investigated by Udell [23]. For the relative permeability,

\[ \kappa_{rel}(S) = S^3 \]  

is used [17]. The derivative of the capillary pressure with respect to the reduced water saturation is given by

\[ \frac{dp_c}{dS} = \frac{\sigma |\cos \theta|}{(\kappa/\varepsilon)^{1/2}} \frac{dJ}{dS}. \]
Conservation of mass for liquid water reads

\[ 0 = -\nabla \cdot \mathbf{N}_L + Q, \]  

(17)

where \( Q \) is a condensation source or an evaporation sink. Heat transfer in the porous electrode is assumed to be dominated by heat conduction, such that conservation of energy can be formulated as

\[ 0 = \nabla \cdot (k \nabla T) + \chi (\nabla \phi)^2 + Q h_{lg}, \]  

(18)

where \( k \) is an effective thermal conductivity, \( T \) is the local temperature, \( \chi \) is an effective electrical conductivity, \( \phi \) is the electric potential, and \( h_{lg} \) is the latent heat of condensation. The first term on the right hand side of Eq. (18) accounts for heat conduction, the second term accounts for joule heating due to electron transfer in the diffusion layer, and the last term accounts for the latent heat of condensation. Electron transport is governed by an electric potential field \( \phi \), according to

\[ 0 = \nabla \cdot (\chi \nabla \phi). \]  

(19)

A volumetric molar condensation rate is defined as

\[ Q = \frac{c D_{O2, Air}}{\delta} \left( \frac{A}{V} \ln \frac{1-x_{H2O}^{sat}}{1-x_{H2O}} \right) = c \gamma \ln \frac{1-x_{H2O}^{sat}}{1-x_{H2O}}, \]  

(20)

where \( c \) is the total molar concentration, \( \delta \) is a film thickness, \( A/V \) is the liquid/gas interfacial area per unit volume, \( x_{H2O} \) is the water vapor mole fraction in the gas phase, and \( x_{H2O}^{sat} \) is the saturation mole fraction. The logarithmic expression on the right hand side of Eq. (20) is obtained if the idealized problem is considered in which a condensable vapor is diffusing at steady state through a stagnant film of a noncondensable gas to a cold flat surface where the vapor condenses [19]. A condensation rate constant is defined as \( \gamma = (A/V)(D_{O2, Air} / \delta) \). In Eq. (20), the driving force for finite-rate phase change is the deviation of the local thermodynamic state from the equilibrium state. For increasing
condensation rates, the local thermodynamic state approaches the equilibrium state. The saturation pressure is correlated according to [26]

\[
\log_{10}(p_{\text{H}_2\text{O}}^{\text{sat}} 10^{-5}) = -2.1794 + 0.02953(T - 273.15) \\
-9.1837 \times 10^{-5}(T - 273.15)^2 \\
+1.4454 \times 10^{-7}(T - 273.15)^3
\]  

(21)

and it is related to the saturation mole fraction by

\[
p_{\text{H}_2\text{O}}^{\text{sat}} = x_{\text{H}_2\text{O}}^{\text{sat}} cRT.
\]  

(22)

Effective binary diffusivities

\[
D_{i,j} = f(\epsilon) g(s) D_{i,j,0}
\]

(23)

are defined in terms of binary diffusivities \(D_{i,j,0}\), a porosity function \(f(\epsilon)\), and a liquid saturation function \(g(s)\) [17,20]. The binary diffusivities are obtained from Chapman-Enskog kinetic theory [19],

\[
D_{i,f,0} = 5.9543 \times 10^{-4} \sqrt{\frac{T_h}{\Omega_{i,j}} \left( M_i^{-1} + M_j^{-1} \right)} \\
cRT(\sigma_{i,j}^2 \Omega_{i,j}),
\]  

(24)

that is written in terms of SI units. The Bruggeman correction is used for the porosity function [17,27],

\[
f(\epsilon) = \epsilon^{1.5},
\]

(25)

and a quadratic behavior is used for the saturation function [17],

\[
g(s) = (1-s)^2.
\]

(26)
4.2.2. Boundary conditions

The catalyst layer is assumed to be sufficiently thin such that it can be treated as a boundary condition. The local transfer current density at the reaction boundary \((z = 0)\) can be written as [28]

\[
j(y) = i \alpha \exp \left( \frac{\alpha F}{RT(y, z = 0)} \phi(y, z = 0) \right),
\]

where \(i\) is the exchange current density, \(\alpha\) is the transfer coefficient, \(F\) is the Faraday constant, \(R\) is the universal gas constant, and \(\phi\) is the solid phase potential that substitutes the cathode overpotential. Note that the electrolyte phase potential is assumed to be zero (i.e., uniform) at \(z = 0\) [6]. Three-dimensional models [29] show that this is a reasonable assumption, since in the catalyst layer, the gradient of the electrolyte phase potential along the \(z\) direction is much larger than the gradient along the \(y\) direction. At the reaction boundary, the local molar fluxes of oxygen and water vapor are coupled to the local transfer current density as

\[
\begin{align*}
\mathbf{e}_z \cdot \mathbf{N}_{\text{O}_2}(y, z = 0) &= -\frac{j(y)}{a_{\text{O}_2} F}, \\
\mathbf{e}_z \cdot \mathbf{N}_{\text{H}_2\text{O}}(y, z = 0) &= \frac{j(y)}{a_{\text{H}_2\text{O}} F},
\end{align*}
\]

respectively, where \(a_{\text{O}_2} = 4\) and \(a_{\text{H}_2\text{O}} = 2\) are the stoichiometric coefficients of the cathode reaction, and \(\mathbf{e}_z\) is a unit vector normal to the reaction boundary (see Fig. 4.1). Electro-osmotic drag in the membrane causes liquid water to be transported from the anode side to the cathode side. Back-diffusion of liquid water in the membrane can also be an important transport mechanism. A net liquid water flux is defined at the reaction boundary, given by

\[
\frac{\rho_l \kappa \mathbf{v}_l}{M_l} \frac{\partial \mathbf{S}(y, z = 0)}{\partial z} = -n_3 \frac{j(y)}{F},
\]
that takes into account both mechanisms. Herein, an effective drag coefficient $n_d = 1/2$ is used [17], which means that 1/2 molecule H$_2$O per one proton is transported through the membrane from the anode side to the cathode side. The heat flux at the reaction boundary can be written as

$$k \frac{\partial T(y, z = 0)}{\partial z} = -j(y)\phi(y, z = 0) - j(y) \frac{T(y, z = 0)(-\Delta s)}{a_{o2}F},$$

where the first and second term on the right hand side of Eq. (31) account for the irreversible and reversible reaction heat [30], respectively. Note that $\Delta s$ is the reaction entropy of the cathode half-cell reaction [31], and the solid phase potential $\phi$ substitutes the cathode overpotential. It is assumed that heat fluxes induced by other heat sources in the fuel cell are not subject to cross the cathode reaction boundary. Such an assumption regarding the thermal management of the entire cell is required, since only the cathode side is modeled. At the reaction boundary ($z = 0$), the electric potential field $\phi$ governing the transport of electrons in the porous diffusion layer is coupled to the transfer current density as

$$\chi \frac{\partial \phi(y, z = 0)}{\partial z} = j(y).$$

At the channel boundary ($-h/2 \leq y \leq 0, z = L$), Dirichlet boundary conditions are used for the oxygen mole fraction, the water vapor mole fraction, and the reduced liquid water saturation, given by

$$x_{o2} (-h/2 \leq y \leq 0, z = L) = x_{o2}^h, \quad \text{(33)}$$

$$x_{H2O} (-h/2 \leq y \leq 0, z = L) = x_{H2O}^h, \quad \text{(34)}$$

and

$$S (-h/2 \leq y \leq 0, z = L) = S_h. \quad \text{(35)}$$

Zero flux boundary conditions are employed for the temperature and the electric potential, given by

$$e_z \cdot \nabla T(-h/2 \leq y \leq 0, z = L) = 0 \quad \text{(36)}$$

103
and
\[ \mathbf{e}_z \cdot \nabla \phi (-h/2 \leq y \leq 0, z = L) = 0. \]  (37)

At the current collector boundary \((-b/2 \leq y \leq -h/2, z = L)\), Dirichlet boundary conditions are used for the temperature and the electric potential, given by
\[ T(-b/2 \leq y \leq -h/2, z = L) = T_b \]  (38)
and
\[ \phi(-b/2 \leq y \leq -h/2, z = L) = \phi_b, \]  (39)
where zero flux boundary conditions are used for the remaining quantities, given by
\[ \mathbf{e}_z \cdot \nabla x_{O_2}(-b/2 \leq y \leq -h/2, z = L) = 0, \]  (40)
\[ \mathbf{e}_z \cdot \nabla x_{H_2O}(-b/2 \leq y \leq -h/2, z = L) = 0, \]  (41)
and
\[ \mathbf{e}_z \cdot \nabla S(-b/2 \leq y \leq -h/2, z = L) = 0. \]  (42)

In fuel cell stacks with cooling flow patterns between adjacent current collector plates [32], the generated heat is mainly removed by the coolant and not by the fuel cell feed gases, in order to provide a uniform cell temperature. Since the thermal conductivity of the current collector material is several orders of magnitude higher than the thermal conductivity of the feed gas, the heat flux between the diffusion medium and the cooling flow pattern is mainly directed through the current collector rib. The convective heat transfer coefficient between the bulk fluid flow in the channel and the channel boundary is given as \( \beta_c = (k_F / h) \cdot Nu \), where \( k_F \) is the fluid thermal conductivity and \( Nu \) is the Nusselt number. In the current collector material, a corresponding heat transfer coefficient may be defined as \( \beta_s = k_s / h \), where \( k_s \) is the solid thermal conductivity. Using properties of the fluid, the solid material, and typical Nusselt numbers for convective heat transfer in fully developed channel flows, \( \beta_s / \beta_c = Nu^{-1} k_s / k_F \equiv 10^3 \) is obtained, hence justifying in this case the adiabatic condition at
the channel boundary. At the left and right symmetry boundaries, given by \( y = -b/2 \) and \( y = 0 \), respectively, zero flux boundary conditions are employed for all quantities.

The average current density \( j_{\text{avg}} \) is defined as the length-average of the local transfer current density \( j(y) \), given by

\[
j_{\text{avg}} = \frac{1}{b/2} \int_{-b/2}^{0} j(y) \, dy.
\]  

(43)

An additional current density is defined as

\[
j_0 = j_0 \exp \left( \frac{\alpha F}{RT_h} \phi_h \right),
\]

(44)

which represents a maximum current density that could be obtained for infinitely large transport properties (such as mass diffusivities, electrical and thermal conductivities) or for infinitely small length scales. We define a local performance number, given by

\[
\Pi = j(y) / j_0,
\]

(45)

and an average performance number, given by

\[
\Pi_{\text{avg}} = j_{\text{avg}} / j_0,
\]

(46)

that quantify performance losses \((1 - \Pi)\) attributed to the finite size of the diffusion layer. Note that \( \Pi \) is a measure for how close we are to the “ideal” case.

4.3. Nondimensional mathematical formulation

The governing equations and boundary conditions are nondimensionalized to generalize the results. The diffusion layer width \( b \) is used as a length scale, the current collector temperature \( T_h \) is used as a temperature scale, and the electric potential \( \phi_h \) of the current collector is used as an electric potential scale, leading to scaled quantities given by

\[
\tilde{y} = y / b, \quad \tilde{z} = z / b, \quad \tilde{T} = T / T_h, \quad \tilde{\phi} = \phi / \phi_h,
\]

(47)
where tilde indicates nondimensionalized quantities. Note that \( \tilde{h} = h / b \) is the scaled channel width and \( \tilde{L} = L / b \) is the scaled diffusion layer thickness. In Appendix A, the governing equations from the previous section are written in nondimensional form. The scaled boundary conditions are listed in Appendix B and two different sets of scaling parameters are given in Appendix C. It can be seen from Appendix C, that the problem to be solved depends on a set of nineteen parameters \( \tilde{K}_1, \tilde{K}_2, \tilde{K}_3, \ldots, \tilde{K}_{19} \) or alternatively on a set of nineteen parameters \( \tilde{x}_1, \tilde{x}_2, \tilde{x}_3, \ldots, \tilde{x}_{19} \) in which the current collector width \( b \) appears only in \( \tilde{x}_9 \). The problem further depends on the functional forms of \( f(\varepsilon), g(s), J(S), \) and \( \kappa_{\|}(S) \).

4.4. Numerical solution

The governing equations were discretized based on the finite volume method [33] on a structured grid using a second order scheme with linear interpolation functions between grid points. Grid refinement with four different grids was performed to ensure that the numerical solutions are grid independent. In the standard case, grids consisting of 40x10, 80x20, 160x40, and 320x80 control volumes were used. When comparing contours of \( x_{O_2}, x_{H_2O}, S, T - T_h, \) and \( \tilde{\phi} \), the two finer grids yield practically indistinguishable results. The average current density \( j_{avg} / j_0 \) obtained from the 80x20 grid is 0.26% higher than the average current density obtained from the 40x10 grid. The average current density obtained from the 160x40 grid is 0.13% higher than the average current density obtained from the 80x20 grid. The average current density obtained from the 320x80 grid is 0.068% higher than the average current density obtained from the 160x40 grid. The algorithm was implemented in Fortran.

4.5. Results and discussion

In this section, a standard case is investigated that is based on the parameters listed in Table 4.1. Several transport and geometry parameters are varied and discussed in more detail.

Fig. 4.2 shows the distribution of the oxygen mole fraction \( x_{O_2} \), the water vapor mole fraction \( x_{H_2O} \), the liquid water saturation \( S \), the temperature difference \( T - T_h \), and the electric potential \( \tilde{\phi} \) for the standard case. It is seen from Fig. 4.2(a) that the oxygen mole fraction underneath the current collector rib is substantially reduced compared to the oxygen mole fraction underneath the channel. In contrast, the water vapor mole fraction exhibits a much
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total width ( b ) (mm)</td>
<td>2.0 (^d)</td>
</tr>
<tr>
<td>Channel width ( h ) (mm)</td>
<td>1.0 (^d)</td>
</tr>
<tr>
<td>Diffusion layer thickness ( L ) (mm)</td>
<td>0.25 (^d)</td>
</tr>
<tr>
<td>Condensation rate constant ( \gamma ) (s(^{-1}))</td>
<td>900 (^a)</td>
</tr>
<tr>
<td>Molecular weight of water ( M_w ) (kg mol(^{-1}))</td>
<td>0.018</td>
</tr>
<tr>
<td>Viscosity of liquid water ( \mu ) (Pa s)</td>
<td>0.000404 (^b)</td>
</tr>
<tr>
<td>Absolute permeability ( \kappa ) (m(^2))</td>
<td>2.55x10(^{-13}) (^a)</td>
</tr>
<tr>
<td>Porosity ( \varepsilon )</td>
<td>0.5 (^a)</td>
</tr>
<tr>
<td>Total molar concentration ( c ) (mol m(^{-3}))</td>
<td>35.1 (^c)</td>
</tr>
<tr>
<td>Density of liquid water ( \rho ) (kg m(^{-3}))</td>
<td>978 (^b)</td>
</tr>
<tr>
<td>Surface tension ( \sigma ) (N m(^{-1}))</td>
<td>0.0645 (^b)</td>
</tr>
<tr>
<td>Contact angle ( \theta ) (deg)</td>
<td>100.0 (^d)</td>
</tr>
<tr>
<td>Effective electrical conductivity ( \chi ) (Ω m(^{-1}))</td>
<td>1000.0 (^d)</td>
</tr>
<tr>
<td>Effective thermal conductivity ( k ) (W m(^{-1}) K(^{-1}))</td>
<td>4 (^a)</td>
</tr>
<tr>
<td>Latent heat of condensation ( h_{fg} ) (J mol(^{-1}))</td>
<td>42,034 (^b)</td>
</tr>
<tr>
<td>Tafel constant ( \alpha )</td>
<td>0.5 (^c)</td>
</tr>
<tr>
<td>Exchange current density ( i ) (A m(^{-2}))</td>
<td>0.21 (^e)</td>
</tr>
<tr>
<td>Stoichiometric coefficient ( a_{\text{O}_2} )</td>
<td>4</td>
</tr>
<tr>
<td>Stoichiometric coefficient ( a_{\text{H}_2\text{O}} )</td>
<td>2</td>
</tr>
<tr>
<td>Effective drag coefficient ( n_d )</td>
<td>0.5 (^a)</td>
</tr>
<tr>
<td>Oxygen mole fraction in the channel ( x_{\text{O}_2} )</td>
<td>0.146 (^f)</td>
</tr>
<tr>
<td>Water vapor mole fraction in the channel ( x_{\text{H}_2\text{O}} )</td>
<td>0.305 (^f)</td>
</tr>
<tr>
<td>Channel saturation ( S_h )</td>
<td>0.1 (^d)</td>
</tr>
<tr>
<td>Immobile saturation ( S_{im} )</td>
<td>0.0 (^g)</td>
</tr>
<tr>
<td>Current collector temperature ( T_h ) (K)</td>
<td>343 (^a)</td>
</tr>
<tr>
<td>Current collector potential ( \phi_h ) (V)</td>
<td>0.8 (^d)</td>
</tr>
</tbody>
</table>

\(^a\) Reference [17].
\(^b\) Reference [35].
Note that \( c = p / (RT_0^e) \), where \( p = 1 \text{ bar} \).

Assumed.

Reference [36].

Corresponding to 100% relative humidity of air at \( T_0 \) [i.e., \( x_{\text{H}_2\text{O}}^0 = x_{\text{H}_2\text{O}}^* (T_0) \) ]

In this study, \( s_m = 0 \) is assumed.
Fig. 4.2. Standard case. (a) Oxygen mole fraction $x_{O_2}$. (b) Water vapor mole fraction $x_{H_2O}$. (c) Liquid water saturation $S$. (d) Temperature difference $T_\phi - T_b$ ($= T - T_b$) (K). (e) Electric potential $\phi$. 
more uniform distribution [see Fig. 4.2(b)]. The highest liquid water saturation is found at the reaction boundary underneath the middle of the current collector rib \((y = \pm 1/2)\) [see Fig. 4.2(c)]. The point with the highest temperature is located at the reaction boundary underneath the middle of the channel \((y = 0)\) [see Fig. 4.2(d)], whereas the lowest temperature within the domain is found at the current collector boundary. Note that in Fig. 4.2(d) the difference between the local temperature \(T\) and the current collector temperature \(T_h\) is plotted. The maximum temperature difference within the diffusion layer is about 2.5 K. The electric potential varies only slightly [see Fig. 4.2(e)] and the highest potential difference exists between the current collector and the origin of the frame. It should be noted that the results in this study are based on the functional forms of \(f(\varepsilon), g(s), J(S),\) and \(k_{\text{el}}(S)\). It is worth noting that, although the methodology presented herein is general, the accuracy of these functions with respect to specific types of porous diffusion media for PEM fuel cells affects the modeling predictions. Microscopic pore-level modeling and experiments with respect to specific diffusion layer media are currently needed to obtain medium-specific and accurate functional forms [34], aiding the macroscopic modeling.

![Fig. 4.3](image)

**Fig. 4.3.** Standard case. (a) Volumetric condensation heat source \(\tilde{Q}K_{\delta}\). (b) Volumetric Joule heat source \(\tilde{K}_J(\nabla \theta)^2 \times 10^4\).

Fig. 4.3(a) shows the distribution of the volumetric heat source \(\tilde{Q}K_{\delta}\) due to phase change. It is seen that in the present case not only condensation (positive sign) can occur in the diffusion layer, but also evaporation (negative sign). Evaporation occurs in a half-circular area adjacent to the channel. Note that the water vapor mole fraction at the channel boundary
equals the saturation mole fraction at temperature $T_h$ (see Table 4.1). The reason for the fact that evaporation can occur is that the temperature at the channel boundary exceeds the current collector temperature $T_h$ [see Fig. 4.2(d)], such that the local saturation pressure is higher than the partial pressure of water vapor. Fig. 4.3(b) reveals a strongly non-uniform distribution of the volumetric Joule heat source $\tilde{K}_5 \left( \tilde{\nabla} \tilde{\phi} \right)^2$, with two local maxima at the edges of the current collector ribs. Note that the nondimensional quantities $\tilde{Q} \tilde{K}_6$ and $\tilde{K}_5 \left( \tilde{\nabla} \tilde{\phi} \right)^2$ need to be multiplied by $kT_h/b^2$ to obtain the respective dimensional quantities $Qh_b$ and $\chi (\nabla \phi)^2$. In the standard case, $kT_h/b^2 = 343 \text{ W/cm}^3$ applies. Integration of the volumetric condensation heat source $\tilde{Q} \tilde{K}_6$ over the rectangular diffusion layer area $(-1/2 \leq \tilde{y} \leq 1/2, 0 \leq \tilde{z} \leq 1)$ gives a length-specific heat source of $1.2 \times 10^{-3}$ (1.6 W/m). If the absolute quantity $|\tilde{Q} \tilde{K}_6|$ is integrated accordingly, a value of $4.7 \times 10^{-3}$ (6.5 W/m) is obtained, implying that the heat source due to condensation is $2.95 \times 10^{-3}$ (4.1 W/m) and the heat sink due to evaporation is $1.75 \times 10^{-3}$ (2.4 W/m). The same integration applied to the volumetric Joule heat source $\tilde{K}_5 \left( \tilde{\nabla} \tilde{\phi} \right)^2$ leads to a length-specific Joule heat source of $1.2 \times 10^{-4}$ (0.16 W/m). Integration of the irreversible reaction heat flux $\tilde{K}_{13} \tilde{\phi}$ along the reaction boundary $(-1/2 \leq \tilde{y} \leq 1/2)$ gives a length-specific heat flux of $1.3 \times 10^{-2}$ (18 W/m). Integration of the reversible reaction heat flux $\tilde{K}_{14} \tilde{T}$ along the reaction boundary gives a length-specific heat flux of $2.5 \times 10^{-3}$ (3.4 W/m). Dividing by the current collector width $b$ provides a membrane-area-specific condensation heat source (0.080 W/cm²), joule heat source (8.2 $\times 10^{-3}$ W/cm²), irreversible reaction heat flux (0.92 W/cm²), and reversible reaction heat flux (0.17 W/cm²).

Fig. 4.4 shows the distribution of the absolute values of the oxygen flux $\tilde{N}_{\text{O}_2}$, the water vapor flux $\tilde{N}_{\text{H}_2\text{O}}$, and the liquid water flux $\tilde{N}_{\text{L}}$. Strong non-uniformities of the magnitudes of the different fluxes exist. The highest oxygen fluxes are obtained near the edges of the current collector ribs (see Fig. 4.4). It can be seen that the oxygen flux near the edges at channel boundary is considerably larger than in the middle of the channel boundary, since oxygen must be provided to the parts of the reaction boundary underneath the current collector ribs. In contrast, the highest water vapor fluxes result in the middle of the channel boundary as well as at the reaction boundary approximately a quarter left and right from the symmetry axis. It is
Fig. 4.4. Standard case. Absolute values of molar fluxes. (a) $|\vec{N}_{O_2}| = \sqrt{(e_y \vec{N}_{O_2})^2 + (e_z \vec{N}_{O_2})^2}$.  
(b) $|\vec{N}_{H_2O}| = \sqrt{(e_y \vec{N}_{H_2O})^2 + (e_z \vec{N}_{H_2O})^2}$.  
(c) $10^4 |\vec{N}_L| = 10^4 \sqrt{(e_y \vec{N}_L)^2 + (e_z \vec{N}_L)^2}$.  


Fig. 4.5. Standard case with different effective electrical conductivities i.e., \( \chi = (62.5, 125, 250, 500, 1000, 2000, 4000, 8000) \Omega^{-1} \text{m}^{-1} \). Distributions at the reaction boundary \( z = 0 \). (a) Current density \( j(y)/j_0 \). (b) Irreversible reaction heat fluxes \( -\tilde{K}_{13} \tilde{j} \phi \) (solid lines) and reversible reaction heat fluxes \( -\tilde{K}_{14} \tilde{j} T \) (dashed lines). (c) Liquid water saturation \( S(y/b) \).
Fig. 4.6. Standard case with different contact angles [i.e., $\theta = (95, 100, 110, 120, 130, 140, 150, 160, 170)$ deg]. Note that the curves also represent the standard case with different absolute permeabilities [i.e., $\kappa = (0.077, 0.31, 1.2, 2.6, 4.2, 6.0, 7.6, 9.0, 9.9) \times 10^{-13}$ m$^2$, respectively]. Distributions at the reaction boundary $\bar{z} = 0$. (a) Current density $j(y)/j_0$. (b) Liquid water saturation $S(y/b)$.
Fig. 4.7. Standard case with different drag coefficients \([i.e., n_d = (0.5, 1.0, 1.5, 2.0, 2.5)]\).

Distributions at the reaction boundary \(z = 0\). (a) Current density \(j(y)/j_0\). (b) Liquid water saturation \(S(y/b)\).
Fig. 4.8. Standard case with different condensation rate constants \( \{i.e., \gamma = (90, 9000) \text{ s}^{-1}\}\). (a) Water vapor mole fraction \( x_{\text{H}_2\text{O}} \) \( (\gamma = 90 \text{ s}^{-1}) \). (b) Liquid water saturation \( S \) \( (\gamma = 90 \text{ s}^{-1}) \). (c) Condensation heat source \( \tilde{Q}_\text{K}_6 \) \( (\gamma = 90 \text{ s}^{-1}) \). (d) Water vapor mole fraction \( x_{\text{H}_2\text{O}} \) \( (\gamma = 9000 \text{ s}^{-1}) \). (e) Liquid water saturation \( S(y/b) \) \( (\gamma = 9000 \text{ s}^{-1}) \). (f) Condensation heat source \( \tilde{Q}_\text{K}_6 \) \( (\gamma = 9000 \text{ s}^{-1}) \).
interesting to note that the water vapor flux first decreases along the symmetry axis in the positive z direction due to condensation, then reaches a local minimum in the middle of the diffusion layer, and finally increases again near the channel boundary due to evaporation. The highest liquid water fluxes are found near the edges of the current collector ribs. Along the symmetry axis in the positive z direction, the liquid water flux first increases due to condensation and then gradually decreases when approaching the channel boundary due to the onset of evaporation, reflecting the opposite behavior of the water vapor flux. These results along with the results of the previous paragraph reveal that it is imperative that heat transfer be included in two-phase models for PEM fuel cells in order to be able to accurately predict liquid water fluxes as well as heat and mass sources due to phase change. Indeed, an isothermal model would not predict evaporation here and therefore could also not reflect a decreasing liquid water flux near the channel boundary. In order to mimic isothermal conditions for comparison purposes, the standard case with a very high effective thermal conductivity has been evaluated (not shown here for brevity). The characteristic distribution of the water vapor flux, the liquid water flux, and the heat and mass sources due to phase change are affected substantially, and a 6% higher average current density is obtained in the isothermal case compared to the nonisothermal standard case. The strong two-dimensionality of the transport phenomena in the diffusion layer further suggests that a one-dimensional treatment of the two-phase transport mechanisms along the direction perpendicular to the membrane can be an oversimplified approach.

In Fig. 4.5(a), the distribution of the scaled local current density \( j(y)/j_0 \) [i.e., the local performance number \( \Pi(y) \)] at the reaction boundary is plotted for different effective electrical conductivities \( \chi \) of the diffusion medium. For low conductivities \( \chi \), a minimum is found in the middle underneath the channel and two maxima are located underneath the edges of the current collector ribs. For high conductivities \( \chi \), a maximum exists in the middle underneath the channel and two minima are located in the middle underneath the current collector rib. In the former case, ohmic and mass transfer resistances are dominant whereas in the latter case only mass transfer resistances are dominant. If the electrical conductivity \( \chi \) is increased, the two maxima of the current density profile are shifted towards the symmetry axis converging in one single maximum underneath the middle of the channel. Note that in this graph the local performance number \( \Pi = j(y)/j_0 \) is plotted, in which the local current density \( j(y) \) is scaled with the maximum current density \( j_0 \). It is seen that the local
performance number ranges between 21% and 63%, which means that performance losses attributed to the finite length scales of the device range between 79% and 37%. In Fig. 4.5(b), the corresponding distributions of the irreversible reaction heat fluxes $-\bar{K}_{13}\bar{j}\phi$ (solid lines) and the reversible reaction heat fluxes $-\bar{K}_{14}\bar{j}T$ (dashed lines) at the reaction boundary are plotted. Similar characteristic distributions are obtained as for the current density distributions. Fig. 4.5(c) shows the distribution of the liquid water saturation $S$ at the reaction boundary. Although the transfer current density at the reaction boundary underneath the channel can be larger than underneath the current collector ribs, the liquid water saturation $S$ at the reaction boundary has always a maximum underneath the middle of the current collector rib (i.e., at $\bar{y} = \pm 1/2$) and a minimum underneath the middle of the channel (i.e., at $\bar{y} = 0$). The higher the effective electrical conductivity $\chi$ of the diffusion medium, the higher the local transfer current densities and water production rates from electrochemical reactions are, resulting in enhanced liquid water saturations [see Fig. 4.5(c)].

In Fig. 4.6, the effect of the contact angle $\theta$ (indicative of the wetting of the diffusion layer material by water) on the distribution of the local current density $j(y)/j_0$ and liquid water saturation $S$ at the reaction boundary is investigated. Figs. 4.6(a) and (b) show that the higher the contact angle $\theta$ (less wetting), the lower the local liquid water saturation $S$ at the reaction boundary is and the higher the local current density $j(y)/j_0$ is. It is seen that the contact angle $\theta$ has a major influence on the liquid water saturation level. It should be noted that the nondimensional formulation of the governing equations further allows for a more general interpretation of the results in Fig. 4.6. The set of curves essentially corresponds to a variation of the scaling parameter $\xi_s$ (see Appendix C), such that the results of Figs. 4.6(a) and (b) can also be understood as a variation of the absolute permeability $\kappa$. Higher contact angles $\theta$ and higher absolute permeabilities $\kappa$ provide reduced liquid water saturations. In Fig. 4.7, the effective drag coefficient $n_d$ for water transport across the membrane is varied. A rather large variation of the effective drag coefficient is required to obtain a significant change in the liquid water saturation distribution and the current density distribution at the reaction boundary.

In Fig. 4.8, the distributions of the water vapor mole fraction $x_{H_2O}$, the liquid water saturation $S$, and the condensation heat source $\bar{Q}\bar{K}_6$ are presented for two different condensation rate constants [i.e., $\gamma = (90, 9000) \text{s}^{-1}$]. Note that $\gamma = (A/V)(D_{CO2, Air}/\delta)$ applies,
such that the condensation rate constant is the product of a liquid/gas interfacial area per unit volume and a mass transfer coefficient. Figs. 4.2(b), 4.2(c), and 4.3(a) are the corresponding graphs that represent the standard case with $\gamma = 900s^{-1}$. The distribution of the water vapor mole fraction $x_{\text{H}_2\text{O}}$ is shown in Figs. 4.8(a), 4.2(b), and 4.8(d) for $\gamma$ values of 90, 900, and 9000 s$^{-1}$, respectively. The higher the condensation rate constant is, the lower the difference between the maximum and the minimum water vapor mole fraction within the diffusion layer. If the condensation rate constant is increased, a relative humidity of unity is approached within the diffusion medium. The characteristic distribution of the water vapor mole fraction changes drastically if the condensation rate constant is increased, which means that the shape of the contour lines transforms from featuring a minimum to featuring a maximum at the centerline. The distribution of the liquid water saturation $S$ is shown in Figs. 4.8(b), 4.2(c), and 4.8(e) for $\gamma$ values of 90, 900, and 9000s$^{-1}$, respectively. It is seen that the characteristic distribution of the liquid water saturation remains similar for the different values. The maximum liquid water saturation slightly increases if the condensation rate constant is increased. The distribution of the condensation heat source $\tilde{Q}\tilde{K}_6$ is shown in Figs. 4.8(c), 4.3(a), and 4.8(f) for $\gamma$ values of 90, 900, and 9000s$^{-1}$, respectively. The condensation heat source is positive in regions of the diffusion medium where condensation occurs, that is, next to the reaction boundary, and it is negative where evaporation occurs, that is, next to the channel boundary. The characteristic distribution of the condensation heat source is dramatically changed if the condensation rate constant increases. At high condensation rate constants, water vapor mainly condenses close to the reaction boundary and also mainly evaporates close to the channel boundary, whereas low condensation rates result in a spatially more gradual transition between condensation and evaporation.

Fig. 4.9(a) shows the distribution of the local current density $j(y)/j_0$ at the reaction boundary for different current collector potentials $\phi_6$. At low potentials $\phi_6$, the current density distribution is quite uniform. The higher the current collector potential $\phi_6$, the more non-uniform the current density distribution $j(y)$ at the reaction boundary is and the lower the local performance numbers $\Pi = j(y)/j_0$ are. In Fig. 4.9(b), the liquid water saturation distributions $S$ at the reaction boundary are plotted. The higher the current collector potential, the higher the local liquid water saturation level is, due to enhanced transfer current densities. Maximum liquid water saturations exist underneath the middle of the current collector ribs.
(i.e., at $\tilde{y} = \pm 1/2$) whereas minimum saturations exist underneath the middle of the channel (i.e., at $\tilde{y} = 0$). It is seen that the saturation distribution at the reaction boundary exhibits a U-

![Graph](image)

**Fig. 4.9.** Standard case with different electric potentials [i.e., $\phi_h = (0.6, 0.7, 0.8, 0.9, 1.0) \text{ V}$]. Distributions at the reaction boundary $\tilde{z} = 0$. (a) Current density $j(y) / j_0$. (b) Liquid water saturation $S(y/b)$.

![Graph](image)

**Fig. 4.10.** Standard case with different saturation functions $g(s)$. Current density distributions $j(y) / j_0$ at the reaction boundary $\tilde{z} = 0$. 

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Fig. 4.11. Standard case with different electrode widths $b$ [i.e., $b = (2.0, 1.0, 0.5)$ mm] and electrode thicknesses $L$ [i.e., $L = (1/32, 2/32, 3/32, 4/32, 5/32, 6/32, 7/32, 8/32)$]. Distributions at the reaction boundary $z = 0$. (a) Current density $j(y)/j_0$ ($b = 2.0$ mm). (b) Liquid water saturation $S(y/b)$ ($b = 2.0$ mm). (c) Current density $j(y)/j_0$ ($b = 1.0$ mm). (d) Liquid water saturation $S(y/b)$ ($b = 1.0$ mm). (e) Current density $j(y)/j_0$ ($b = 0.5$ mm). (f) Liquid water saturation $S(y/b)$ ($b = 0.5$ mm).
shape. If $\phi_b < 0.6\,\text{V}$, the distribution is almost uniform. For values near $\phi_b = 0.8\,\text{V}$, the strongest non-uniformity is found. At higher potentials $\phi_b$, the distribution becomes more uniform again, due to oxygen depletion underneath the current collector rib. Fig. 4.10 shows the influence of the saturation function $g(s)$ on the local current density distribution $j(y)/j_0$ at the reaction boundary. The presence of liquid water considerably reduces the current density due to reduced effective mass diffusivities. This effect is most important underneath the middle of the current collector ribs (i.e., at $\tilde{y} = \pm 1/2$) where the highest liquid water saturation exists.

In Fig. 4.11, the effect of downscaling of the channel width $b$, the current collector width $b$, and the diffusion layer thickness $L$ on the distribution of the transfer current density $j(y)/j_0$ and the liquid water saturation $S$ at the reaction boundary is investigated. In Figs. 4.11(a) and (b), the effect of the variation of the diffusion layer thickness on the current density and liquid water saturation distribution is investigated. Herein, the channel and rib widths are kept constant and their values correspond to the ones of the standard case. Fig. 4.11(a) shows that for small diffusion layer thicknesses, the transfer current density distribution at the reaction boundary has two maxima underneath the edges of the current collector ribs (i.e., near $\tilde{y} = \pm 1/4$). If the diffusion layer thickness is increased, the two maxima combine into one single maximum located underneath the middle of the channel. The larger the diffusion layer thickness, the more uniform the current density distribution is, that is, the smaller the difference between the maximum and the minimum local transfer current density is. From Fig. 4.11(b) it can be seen that the maximum liquid water saturation is always found underneath the middle of the current collector rib (i.e., at $\tilde{y} = \pm 1/2$) and that the minimum liquid water saturation always exists underneath the middle of the channel (i.e., at $\tilde{y} = 0$). The smaller the diffusion layer thickness is, the larger the maximum liquid water saturation, and the larger the difference between the maximum and the minimum liquid water saturation. In Figs. 4.11(c) and (d), the channel width and the current collector rib widths are scaled down by a factor of two. Since the same nondimensional set of diffusion layer thicknesses is investigated as before, this implies that the dimensional diffusion layer thicknesses are divided by two. As an example, a diffusion layer thickness of $1/32$ in Figs. 4.11(a) and (b) is identical to a diffusion layer thickness of $2/32$ in Figs. 4.11(c) and (d). It is seen that a variation of the diffusion layer thickness leads to similar characteristic current density and liquid water saturation distributions at the reaction boundary as before. However,
the current density distributions are shifted upwards, whereas the liquid water saturation profiles are shifted downwards in the graph. Hence, higher local current densities and lower local liquid water saturations can be obtained at decreasing length scales. It should be noted that the graphs reveal substantial local current density improvements. In Figs. 4.11(e) and (f), the channel width and the current collector rib width are scaled down again by a factor of two, leading to identical conclusions as before. Substantial local current density improvements can still be achieved.

![Graph showing current density distributions](image)

**Fig. 4.12. Standard case with different electrode thicknesses \( \bar{L} \) [i.e., \( 1/32 \leq \bar{L} \leq 8/32 \)] and electrode widths \( b \) [i.e., \( b = (2.0, 1.0, 0.5) \text{ mm} \), subject to \( h = b/2 \). Average current densities \( j_{\text{avg}} / j_0 \) for \( b = 2 \text{ mm} \) (bottom curve), \( b = 1 \text{ mm} \) (middle curve), and \( b = 0.5 \text{ mm} \) (upper curve).]

In Fig. 4.12, the corresponding average densities \( j_{\text{avg}} / j_0 \) (i.e., the performance numbers \( \Pi \)) are plotted. It can be seen, that for all three channel widths, there exists an optimum diffusion layer thickness that provides a maximum average current density. He et al. [12] and Natarajan and Nguyen [11] already predicted the existence of an optimum diffusion layer thickness. However, they did not account for electron transport and heat transfer in their studies [11,12]. This paper shows that both electron transport and multicomponent nonisothermal two-phase transport in the diffusion layer need to be considered in optimizing the diffusion layer thickness. The smaller the channel width, the smaller the optimum diffusion layer thickness is. For channel widths \( h \) of 1.0, 0.5, and 0.25 mm and \( h = b/2 \), maximum performance numbers of 0.51, 0.66, and 0.78 are obtained at optimum diffusion layer thicknesses \( \bar{L} \) (\( L \)) of 0.084 (168\( \mu \)m), 0.088 (88\( \mu \)m), and 0.093 (46\( \mu \)m), respectively.
This study therefore makes a rather strong claim: based on the standard case, downscaling of the channel and rib width by a factor of 2 allows for a 29% (0.66/0.51) performance improvement, downscaling by a factor of 4 allows for a 53% (0.78/0.51) performance improvement, and infinite downscaling allows for a theoretical maximum performance improvement of 96% (1.0/0.51). It is important to note that downscaling of the channel width also requires downscaling of the diffusion layer thickness to achieve maximum average current densities. If the channel width is scaled down while maintaining a constant diffusion layer thickness, the average current density improvement can be smaller, although Fig. 4.12 suggests that the gain is still substantial. These results reveal that substantial current density improvements can be obtained at decreasing length scales, e.g., within double-staircase PEM fuel cells.

In Fig. 4.13, the effect of the variation of the channel width $\tilde{h}$ on the average density $j_{\text{avg}} / j_0$ (i.e., the performance number $\Pi$) is investigated. An optimum channel width exists that provides a maximum average current density. In the standard case, an optimum channel width $\tilde{h}$ of 0.70 is found. If the effective electrical conductivity $\chi$ of the diffusion medium is reduced by 50%, a smaller optimum channel width $\tilde{h}$ of 0.63 results. The smaller the effective electrical conductivity $\chi$ is, the smaller the optimum channel width $\tilde{h}$. If $\chi$ is increased towards infinity, the optimum channel width approaches asymptotically 1.0. As a result, it should be noted that optimum channel widths can only be predicted if an electric
potential field governing the transport of electrons is included in the model. Combining the results of Figs. 4.12 and 4.13, it follows that for a given width $b$, there exists an optimum pair $(L, h)$ of diffusion layer thickness and channel width that provides a maximum average current density.

4.6. Conclusions

In this study, a thorough model for the porous diffusion layers of a PEM fuel cell was presented in which all the governing macroscopic transport phenomena, including multicomponent diffusion, transport of liquid water, electronic current transfer, and heat transfer are considered. A nondimensional mathematical formulation of the model was introduced to generalize the results. The model was applied to the cathode diffusion layer. A performance number was introduced to quantify losses in the diffusion layer attributed to mass transfer, the presence of liquid water, charge transfer, and heat transfer. The results show a strong two-dimensionality and coupling of the two-phase transport phenomena in the diffusion layer, and therefore also imply that a one-dimensional treatment of the transport mechanisms along the direction perpendicular to the membrane can be an oversimplified approach.

Based on this two-phase model, the effect of downscaling of channel width, current collector rib width, and diffusion layer thickness on the performance of PEM fuel cells was systematically investigated and optimum length ratios (i.e., optimum diffusion layer thicknesses, optimum channel and rib width) were identified at decreasing length scales. It was also shown that the optimum diffusion layer thickness scales down as the channel width is scaled down. In other words, for smaller channel and current collector widths, the optimum diffusion layer thickness is also smaller. The results of this study reveal the great potential of downscaled PEM fuel cells in achieving enhanced power densities.
Appendix A. Nondimensional governing equations

\[ 0 = -\vec{\nabla} \cdot \vec{N}_{o_2} \] (A.1)

\[ 0 = -\vec{\nabla} \cdot \vec{N}_{H_2O} - \vec{Q} \vec{K}_3 \] (A.2)

\[ 0 = -\vec{\nabla} \cdot \vec{N}_l + \vec{Q} \vec{K}_4 \] (A.3)

\[ 0 = \vec{\nabla} \cdot (\vec{\nabla} \vec{T}) + \vec{K}_5 (\vec{\nabla} \vec{\phi})^2 + \vec{Q} \vec{K}_6 \] (A.4)

\[ 0 = \vec{\nabla} \cdot (\vec{\nabla} \vec{\phi}) \] (A.5)

\[ \vec{N}_{o_2} = \frac{-(\vec{\nabla} x_{H_2O} + \vec{\nabla} x_{o_2}) x_{o_2} + \vec{K}_1 \vec{\nabla} x_{o_2} (-1 + x_{o_2} + x_{H_2O})}{(-1 + x_{o_2} + x_{H_2O}) \vec{K} x_{H_2O} - x_{o_2} + \vec{K}_1 (-1 + x_{o_2} + x_{H_2O})} f(\vec{e}) g(s) \] (A.6)

\[ \vec{N}_{H_2O} = \frac{-(\vec{\nabla} x_{H_2O} + \vec{\nabla} x_{o_2}) x_{H_2O} + \vec{K}_1 \vec{\nabla} x_{H_2O} (-1 + x_{o_2} + x_{H_2O})}{(-1 + x_{o_2} + x_{H_2O}) \vec{K} x_{H_2O} - x_{o_2} + \vec{K}_1 (-1 + x_{o_2} + x_{H_2O})} f(\vec{e}) g(s) \] (A.7)

\[ \vec{N}_l = -\kappa_l \frac{dJ}{dS} \vec{\nabla} S \] (A.8)

\[ \vec{Q} = \ln \frac{1 - x_{H_2O}^{\text{sat}}}{1 - x_{H_2O}} \] (A.9)

\[ x_{H_2O}^{\text{sat}} = \frac{p_{H_2O}^{\text{sat}} (K_7 \vec{T})}{K_8 \vec{T}} \] (A.10)
\[
\begin{align*}
\tilde{N}_{O_2} &= \frac{b}{cD_{O_2,N_2,0}} N_{O_2} \\
\tilde{N}_{H_2O} &= \frac{b}{cD_{H_2O,N_2,0}} N_{H_2O} \\
\tilde{N}_L &= \frac{b M_L \mu_L (\kappa' / \epsilon)^{1/2}}{\rho_L \kappa \sigma \cos \theta} N_L \\
(\tilde{Q} &= Q / (c \gamma))
\end{align*}
\]
Appendix B. Nondimensional boundary conditions

B.1. Reaction boundary  $\bar{z} = 0$

\[ \bar{j} = j / i = x_{o2} \exp \left( \frac{\bar{K}_0 \bar{\theta}}{\bar{I}} \right) \]  \hspace{1cm} (B.1)

\[ \bar{j}_0 = x_{o2}^h \exp (\bar{K}_0), \quad \bar{j}_0 = j_0 / i \]  \hspace{1cm} (B.2)

\[ \bar{j}_{\text{avg}} = \int_{-1/2}^{1/2} \bar{j}(\bar{y}) \, d\bar{y}, \quad \bar{j}_{\text{avg}} = j_{\text{avg}} / i \]  \hspace{1cm} (B.3)

\[ e_\tau \cdot \bar{N}_{o2} = -\bar{K}_{10} \bar{j} \]  \hspace{1cm} (B.4)

\[ e_\tau \cdot \bar{N}_{H2O} = \bar{K}_{11} \bar{j} \]  \hspace{1cm} (B.5)

\[ \kappa_{il} \frac{d\bar{j}}{dS} \frac{\partial S}{\partial \bar{z}} = -\bar{K}_{12} \bar{j} \]  \hspace{1cm} (B.6)

\[ \frac{\partial \bar{I}}{\partial \bar{z}} = -\bar{K}_{13} \bar{j} \bar{\phi} - \bar{K}_{14} \bar{j} \bar{\bar{I}} \]  \hspace{1cm} (B.7)

\[ \frac{\partial \bar{\phi}}{\partial \bar{z}} = \bar{j} \frac{\bar{K}_{15}}{\bar{K}_5} \]  \hspace{1cm} (B.8)

B.2. Other boundaries

\[ x_{o2} \left( -\bar{h}/2 \leq \bar{y} \leq 0, \bar{z} = \bar{L} \right) = \bar{K}_{15} \]  \hspace{1cm} (B.9)

\[ x_{H2O} \left( -\bar{h}/2 \leq \bar{y} \leq 0, \bar{z} = \bar{L} \right) = \bar{K}_{16} \]  \hspace{1cm} (B.10)

\[ S \left( -\bar{h}/2 \leq \bar{y} \leq 0, \bar{z} = \bar{L} \right) = \bar{K}_{17} \]  \hspace{1cm} (B.11)
\( \tilde{r}( -\frac{1}{2} \leq \tilde{y} \leq -\frac{h}{2}, \tilde{z} = \tilde{L} ) = 1 \) \hfill \text{(B.12)}

\( \tilde{\phi}( -\frac{1}{2} \leq \tilde{y} \leq -\frac{h}{2}, \tilde{z} = \tilde{L} ) = 1 \) \hfill \text{(B.13)}
Appendix C. Scaling parameters

\[ \tilde{K}_1 = \frac{D_{O_2,H_2O,0}}{D_{H_2O,N2,0}} = \xi_1 \]  
(C.1)

\[ \tilde{K}_2 = \frac{D_{O_2,N2,0}}{D_{H_2O,N2,0}} = \xi_2 \]  
(C.2)

\[ \tilde{K}_3 = \frac{\gamma}{D_{H_2O,N2,0}} = \xi_2 \xi_9 \xi_{10} \]  
(C.3)

\[ \tilde{K}_4 = \frac{M_i \mu_i b^2 (\kappa / \epsilon)^{1/2} c \gamma}{\rho_i k \sigma |\cos \theta|} = \xi_7 \xi_8 \xi_{10} \xi_{11} \]  
(C.4)

\[ \tilde{K}_5 = \chi \phi_0^2 / (k T_h) = \xi_5 \xi_6 \xi_7 \xi_{14} \]  
(C.5)

\[ \tilde{K}_6 = h_0 b^2 c \gamma / (k T_h) = \xi_5 \xi_7 \xi_{15} \xi_{16} \]  
(C.6)

\[ K_7 = T_h = \xi_6 \]  
(C.7)

\[ K_8 = cRT_h = \xi_7 \]  
(C.8)

\[ \tilde{K}_9 = \alpha F \phi_h / (RT_h) = \xi_8 \]  
(C.9)

\[ \tilde{K}_{10} = bi / (a_{O_2} FcD_{O_2,N2,0}) = \xi_9 \]  
(C.10)

\[ \tilde{K}_{11} = bi / (a_{H_2O} FcD_{H_2O,N2,0}) = \xi_9 \xi_{10} \xi_{11} \]  
(C.11)

\[ \tilde{K}_{12} = \frac{n_i M_i \mu_i i (\kappa / \epsilon)^{1/2} b}{F \rho_i k \sigma |\cos \theta|} = \xi_7 \xi_8 \xi_{10} \xi_{11} \]  
(C.12)

\[ \tilde{K}_{13} = i \phi_h b / (k T_h) = \xi_5 \xi_7 \xi_{12} \]  
(C.13)
\[ \tilde{K}_{14} = i(-\Delta s) b / (k a_{o_2} F) = \tilde{\xi}_{14} \tilde{\xi}_{13}^{-1} \tilde{\xi}_{12} \tilde{\xi}_{11} \] (C.14)

\[ \tilde{K}_{15} = x_{o_2}^b = \tilde{\xi}_{15} \] (C.15)

\[ \tilde{K}_{16} = x_{H_2O}^b = \tilde{\xi}_{16} \] (C.16)

\[ \tilde{K}_{17} = S_h = \tilde{\xi}_{17} \] (C.17)

\[ \tilde{K}_{18} = \tilde{h} = \tilde{\xi}_{18} \] (C.18)

\[ \tilde{K}_{19} = \tilde{L} = \tilde{\xi}_{19} \] (C.19)

\[ \tilde{\xi}_{3} = \left( a_{o_2}^2 F^2 / i^2 \right) c^2 D_{O_2,N_2,0} \gamma \] (C.20)

\[ \tilde{\xi}_{4} = \frac{M_1 \mu_h (\kappa'/\epsilon)^{1/2} c D_{H_2O,N_2,0}}{\rho_h \kappa \sigma | \cos \theta |} \] (C.21)

\[ \tilde{\xi}_{5} = k T_h / \left( c D_{H_2O,N_2,0} h_g \right) \] (C.22)

\[ \tilde{\xi}_{10} = a_{o_2} / a_{H_2O} \] (C.23)

\[ \tilde{\xi}_{11} = n_a a_{o_2} \] (C.24)

\[ \tilde{\xi}_{12} = a_{o_2} R T_h / (\alpha h_g) \] (C.25)

\[ \tilde{\xi}_{13} = (-\Delta s) T_h / h_g \] (C.26)
\[ \varrho_{s_{14}} = \frac{\chi R^2 T_h^2}{\alpha^2 F^2 h_{e} c D_{H_2O,N2,0}} \] (C.27)
References


Abstract

In this paper, a novel multistage polymer electrolyte fuel cell (PEFC) concept is introduced according to which the cell potential is subject to a variation along the channel direction. A commonly used condition in which the cell potential is uniformly distributed along the flow direction is replaced herein by a generalized condition in which the cell potential is nonuniformly distributed along the flow direction. It is shown that the proposed multistage fuel cell concept involving nonuniform cell potential distribution functions allows to simultaneously generate electric power at various cell potentials without a reduction of the maximum electric cell power density. The proposed multistage fuel cell concept further allows for enhanced maximum electric cell power densities compared to the traditional concept involving a uniform cell potential distribution. An analytical model is used to perform quantitative calculations based on this concept. A conjugate gradient algorithm is implemented to optimize the cell potential distribution function along the flow direction.

Nomenclature

Latin symbols

\( b \) catalyst layer width, m
\( C \) constant
\( c \) molar concentration, mol m\(^{-3}\)
\( D \) diffusion coefficient, m\(^2\) s\(^{-1}\)
\( E \) cell potential, V
\( F \) Faraday constant, 96485 C mol\(^{-1}\)

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\(^c\) This chapter is published in:
List of Symbols

Latin Symbols

- \( h \) channel height and width, m
- \( i_{ex} \) volumetric exchange current density, A m\(^{-3}\)
- \( j \) average current density, A m\(^{-2}\)
- \( k \) index
- \( L \) total channel length, m
- \( Le \) Lewis number
- \( l \) thickness, m
- \( m \) number of discontinuities
- \( Nu \) Nusselt number
- \( n \) number of stages
- \( P \) electric power, W
- \( Pr \) Prandtl number
- \( R \) universal gas constant, 8.314 J K\(^{-1}\) mol\(^{-1}\)
- \( Sh \) Sherwood number
- \( T \) cell temperature, K
- \( U \) open circuit potential, V
- \( v \) inlet flow velocity, m s\(^{-1}\)
- \( z \) number of electrons

Greek Symbols

- \( \alpha \) transfer coefficient
- \( \beta \) dimensionless parameter
- \( \gamma \) dimensionless parameter
- \( \kappa \) mass transfer coefficient, m s\(^{-1}\)
- \( \lambda \) length of a single stage, m
- \( \lambda_c \) characteristic length of oxygen consumption, m
- \( \lambda_o \) characteristic length of diffusion losses, m
- \( \eta \) cathode overpotential, V
- \( \xi \) inlet mole fraction of oxygen
- \( \phi \) overpotential vector
- \( \theta \) parameter vector
- \( \Psi \) performance parameter
5.1. Introduction

Polymer electrolyte fuel cells have the potential to be established as novel energy conversion devices due to potentially high efficiencies and high power densities. In portable applications, the available volume for the fuel cell and fuel storage is limited. Miniaturization and the increase in electric power demand of portable applications require that fuel cells be continuously optimized with respect to maximum electric power densities and efficiencies. This can be achieved for example by optimization of the geometric structure and the operating conditions of the fuel cell.

Several studies have been published addressing geometric optimization of the flow structure and the diffusion zone [1-10]. Cha et al. [4] investigated the effect of channel width on the performance of polymer electrolyte fuel cells. Earlier contributions addressing geometric optimization issues are due to He et al. [1] and Natarajan et al. [3]. Porous materials as fluid distributors in polymer electrolyte fuel cells have been investigated in [5] based on a three-dimensional single-phase model. Improved electric power densities are predicted compared to traditional channeled systems due to reduced effective lengths at which the transport phenomena occur. Multi-scale tree network channels as fluid distributors constructing double-staircase polymer electrolyte fuel cells [9] and pyramidal direct methanol fuel cells [7] have been recently introduced. Such multi-scale flow structures obey more favorable scaling laws than existing fuel cell flow structures. A net power density has been
introduced [7, 9] that is defined as the difference between the electric power density and the pumping power density required for fluid circulation. In these studies [7, 9], it is recognized that it is imperative that fluid flow irreversibilities be considered in constraint optimization of polymer electrolyte fuel cells. A common method of these studies is to investigate fuel cell designs in which the transport phenomena occur at reduced effective lengths compared to the existing traditional counterparts, since irreversibilities caused by the various transport processes are due to the finite size of the energy conversion device. The aim of the present study is not on the geometric optimization aspects but rather on the optimization of the operating conditions of the fuel cell. Polymer electrolyte fuel cells are generally operated under a constant cell potential distribution along the channel [11-17]. Existing fuel cell models are usually solved based on this assumption [11-17].

In this paper, a novel multistage polymer electrolyte fuel cell concept is introduced according to which the cell potential is subject to a stepwise or continuous variation along the channel direction. A common boundary condition in which the cell potential is uniformly distributed along the flow direction is replaced herein by a boundary condition in which the cell potential is nonuniformly distributed along the flow direction. An analytical model is used to perform quantitative calculations based on this concept. A conjugate gradient algorithm is implemented to optimize the cell potential distribution function along the flow direction targeting at maximizing the electric cell power density.

5.2. The multistage fuel cell concept

In Fig. 5.1, the proposed multistage fuel cell concept is shown. The fuel cell has a length $L$ and it is separated along the channel direction into $n$ independent stages of length $\lambda$, given by

$$\lambda = L/(m+1) = L/n,$$

where $m$ is the number of discontinuities of the cell potential distribution function. Each stage has its own cell potential $E_k$. It is assumed that no physical or chemical interactions can occur between different stages. The proposed concept could be realized using segmented current collector plates that were originally developed to perform locally resolved current density measurements [18]. Such current collector plates are divided into electrically isolated
segments allowing applying individual cell potentials to each segment. The concept could also be realized by simply feeding the reactant gases through a sequence of single fuel cells or stacks that are operated at different cell potentials. Hydrogen and oxygen are consumed along each stage, where the composition of the fluid mixtures in the anode and cathode channels at the end of stage \( k \) are identical to the composition of the fluid mixtures at the beginning of stage \( k + 1 \). The cell potential remains constant along a certain stage such that the cell potential distribution function along the entire channel includes a maximum of \( m \) discontinuities or steps. The cell potentials \( E_k \) are optimized with respect to maximum electric power densities of the entire channel. If \( n \) is finite, the cell potential distribution function along the channel is a discrete function, and it becomes a continuous function if \( n \) tends to infinity. In contrast to the existing traditional single-stage fuel cell concepts with one cell potential optimization parameter \( E_1 \), the proposed multistage concept has \( n \) optimization parameters \( E_1, E_2, \ldots, E_n \).

![Fig. 5.1. Schematic drawing of the proposed multistage polymer electrolyte fuel cell concept including a channel that consists of \( n \) separated stages. Along-the-channel cross-section showing the segmented cathode current collector (SCC), the cathode channel (CC), the membrane-electrode-assembly (MEA), and the anode channel (AC). Instead of applying a single cell potential along the entire channel as in traditional concepts, the fuel cell is divided into \( n \) stages where each stage has its own cell potential \( E_k \).](image)
5.3. Mathematical formulation

In this study, an analytical model originally proposed and experimentally validated by Kulikovsky and co-workers [16, 19] is used. This model was extended and generalized by Senn and Poulikakos [9] to describe the transport phenomena in double-staircase polymer electrolyte fuel cells with tree network channels as fluid distributors. Three-dimensional computational fluid dynamics modeling was performed to derive mass transfer correlations for oxygen between the bulk fluid flow in the cathode channel and the cathode catalyst layer, with respect to different channel and current collector rib widths. The generalized model [9] is employed in this paper to investigate the effect of the variation of the cell potential along a single channel. The model is based on first principles and allows for a closed analytical solution. It takes into account oxygen mass transfer between the cathode channel and the cathode catalyst layer, oxygen consumption along the cathode channel, and activation overpotentials in the cathode catalyst layer. Ohmic overpotentials due to electron transfer in the diffusion and catalyst layers are neglected. The anode is considered as an ideal source of protons. The anode overpotential is therefore neglected along with mass transfer resistances on the anode side. A thin membrane is considered and ohmic losses due to proton transfer in the electrolyte phase of the catalyst layers and the membrane are neglected.

Models of different sophistication levels were developed in the past [20]. Three-dimensional or quasi three-dimensional models provide the most comprehensive insight into the transport phenomena occurring inside the cell. However, they still require substantial computational time and resources to be solved numerically with respect to entire cells. Multiparametric optimization becomes even more expensive or impossible, especially if the number of optimization parameters within a certain objective function is large. In contrast, simple models can be solved very fast and therefore open the possibility to address multiparametric optimization issues.

5.3.1. Governing equations

The mean current density of the \( k \)th stage can be written as [16]

\[
J_k = J^* k \left[ 1 - \exp \left( -\frac{\lambda}{\lambda_{\text{act},k} + \lambda_{\text{diff}}} \right) \right],
\]
where \( j_k^* \) is the stoichiometric current density of the \( k \)th stage, \( \lambda \) is the length of a single stage, \( \lambda_{C,k} \) is the characteristic length of oxygen consumption related to the \( k \)th stage, and \( \lambda_D \) is the characteristic length of diffusion losses related to the \( k \)th stage. The stoichiometric current density of the \( k \)th stage can be written as [9, 16]

\[
j_k^* = zFh^2vb^{-1}c_{O_2,h,k}, \quad (3)
\]

where \( z \) is the number of electrons involved in the cathode reaction, \( F \) is the Faraday constant, \( h \) is the width of the square cross-sectional channel, \( b \) is the catalyst layer width, \( v \) is the bulk fluid velocity in the cathode channel, and \( c_{O_2,h,k} \) is the oxygen concentration at the beginning of the channel of the \( k \)th stage. The characteristic length of oxygen consumption related to the \( k \)th stage is given by [16]

\[
\lambda_{C,k} = \frac{zh^2c_{\text{ref}}}{bl_{cex}}\exp\left(-\frac{\alpha F}{RT}\eta_k\right), \quad (4)
\]

where \( c_{\text{ref}} \) is the reference concentration, \( l_c \) is the cathode catalyst layer thickness, \( l_{cex} \) is the exchange current density, \( \alpha \) is the transfer coefficient, \( R \) is the universal gas constant, \( T \) is the cell temperature, and \( \eta_k \) is the cathode overpotential at the \( k \)th stage. The characteristic length of diffusion losses can be written as [9, 16]

\[
\lambda_D = h^2vb^{-1}n^*, \quad (5)
\]

where \( n^* \) is the overall mass transfer coefficient between the bulk fluid flow in the cathode channel and the cathode catalyst layer. Equations (2)-(5) were derived by Kulikovsky (see Ref. [16]). The overall mass transfer coefficient can be written as [9]

\[
\kappa = \left(\kappa_{n}^{-1} + \kappa_{h}^{-1}\right)^{-1}, \quad (6)
\]

where \( \kappa_{n} \) is the oxygen mass transfer coefficient between the bulk fluid flow in the cathode channel and the cathode channel/diffusion layer interface, and \( \kappa_{h} \) is the oxygen mass transfer coefficient between the cathode channel/diffusion layer interface and the cathode catalyst layer. For laminar fully developed flow in a square duct with three adiabatic walls and a wall
with a uniform heat flux, the Nusselt number $Nu$ is constant, that is, $Nu = 2.712$ (see Ref. [21]). The Sherwood number $Sh$ can be related to the Nusselt number $Nu$ according to the Reynolds analogy [22, 23], $Sh = NuLe$, where $Le = Sc/Pr$ is the Lewis number, $Sc$ is the Schmidt number, and $Pr$ is the Prandtl number. For the fluid properties in this study, $Le = 1$, and the Sherwood number for mass transfer between the bulk fluid flow in the channel and the channel/diffusion layer interface is given by [9]

$$Sh_h = 2.7.$$  \hspace{1cm} (7)

The corresponding mass transfer coefficient reads [9]

$$\kappa_h = Sh_h D_h / h,$$  \hspace{1cm} (8)

where $D_h$ denotes the oxygen diffusion coefficient in the cathode channel. The Sherwood number for mass transfer between the channel/diffusion layer interface and the catalyst layer shall be defined as [9]

$$Sh_b = \left[ 1 + \frac{(b - h)}{(4l_b)} \right]^{-1}.$$  \hspace{1cm} (9)

The corresponding mass transfer coefficient reads [9]

$$\kappa_b = Sh_b D_b / l_b = \frac{D_b}{\frac{1}{2} \left[ l_b + \left[ l_b + \frac{(b - h)}{2} \right] \right]},$$  \hspace{1cm} (10)

where $D_b$ is the effective oxygen diffusion coefficient in the cathode diffusion layer. The effective diffusion length in Eq. (10), denoted by the denominator on the right hand side, is defined as the mean value between a minimum diffusion length $l_b$ and a maximum diffusion length $l_b + (b - h)/2$ between the channel/diffusion layer interface and the catalyst layer. Equations (9) and (10) were derived in a previous study [9] based on three-dimensional numerical solutions of the Navier-Stokes and species conservation equations. The Bruggeman correction [24, 25] is used to relate the free-stream diffusion coefficient $D_h$ to the effective diffusion coefficient $D_b$ using the diffusion layer porosity $\varepsilon$, according to
\begin{align}
D_b &= D_a \varepsilon^{3/2}, \quad (11)
\end{align}

with a tortuosity factor of \(3/2\). The oxygen concentration at the beginning of the channel of the \(k\)th stage reads \([9]\)

\begin{align}
c_{O_2, h, k} &= \xi c \left[ \exp\left( \frac{\lambda}{\lambda_{c,0} + \lambda_{D}} \right) \right] \prod_{i=1}^{k} \exp\left( -\frac{\lambda}{\lambda_{c,i-1} + \lambda_{D}} \right), \quad (12)
\end{align}

where \(\xi\) is the molar fraction of oxygen at the inlet of the first stage, and \(c\) is the total molar concentration. Note that \(\lambda_{c,0}\) is obtained from Eq. (4) with \(k = 0\). Neglecting the anode overpotential and ohmic overpotentials in the electrodes and the electrolyte phase of the catalyst layers and the membrane, the cell potential of the \(k\)th stage \(E_k\) is given as

\begin{align}
E_k &= U - \eta_k, \quad (13)
\end{align}

where \(U\) is the open circuit potential and \(\eta_k\) is the cathode overpotential of the \(k\)th stage. The electric power generated at the \(k\)th stage reads

\begin{align}
P_k &= j_k \lambda b E_k, \quad (14)
\end{align}

and the electric power obtained from all stages is written as

\begin{align}
P &= \sum_{k=1}^{n} P_k. \quad (15)
\end{align}

5.3.2. Nondimensional governing equations

The governing equations are written in nondimensional form to generalize the results. The mean current density \(j_k\) is scaled with a standard stoichiometric current density \(j_{st}\), given by

\begin{align}
j_{st} &= zFh^2v_0b^{-1}L^{-1} \xi c, \quad (16)
\end{align}
such that the nondimensional current density reads $\tilde{j}_k = j_k / j_a$. The electric power generated at the $k$th stage $P_k$ and the total electric power $P$ are scaled with a standard electric power, given by

$$P_{st} = j_a L b U = z F h^2 \eta \xi c U,$$

such that the nondimensional forms read $\tilde{P}_k = P_k / P_{st}$ and $\tilde{P} = P / P_{st}$. The cathode overpotentials are scaled with the open circuit potential $U$, given by $\tilde{\eta}_k = \eta_k / U$, and the cell potential of the $k$th stage reads $\tilde{E}_k = 1 - \tilde{\eta}_k$. The channel length $L$ is used as a length scale such that $\tilde{\lambda} = \lambda / L$, $\tilde{\lambda}_{c,k} = \lambda_{c,k} / L$, and $\tilde{\lambda}_D = \lambda_D / L$ applies.

The mean current density of the $k$th stage can be written in nondimensional form as

$$\tilde{j}_k = n \tilde{\beta}_j \left[ \exp \left( \frac{1}{n} \right) \right] \left[ \prod_{i=0}^{n-1} \exp \left( - \frac{1}{n} \tilde{\lambda}_{c,i+1} + \tilde{\lambda}_D \right) \right] \left[ 1 - \exp \left( - \frac{1}{n} \tilde{\lambda}_{c,k} + \tilde{\lambda}_D \right) \right],$$

the scaled electric power generated at the $k$th stage reads

$$\tilde{P}_k = \tilde{\beta}_D \tilde{\eta}_k (1 - \tilde{\eta}_k),$$

and the scaled electric power obtained from all stages is written as

$$\tilde{P} = \sum_{k=1}^{n} \tilde{P}_k.$$

The scaled characteristic length of oxygen consumption related to the $k$th stage is given as

$$\tilde{\lambda}_{c,k} = \tilde{\beta}_j \exp \left( - \tilde{\beta}_j \tilde{\eta}_k \right)$$

and the characteristic length of diffusion losses reads
The mean current density of the $k$th stage $\tilde{j}_k$ depends on the four nondimensional parameters $\tilde{\beta}_1$, $\tilde{\beta}_2$, $\tilde{\beta}_3$, and $\tilde{\beta}_5$. The scaled electric power $\tilde{P}$ obtained from all stages depends on the four nondimensional parameters $\tilde{\beta}_1$, $\tilde{\beta}_2$, $\tilde{\beta}_3$, and $\tilde{\beta}_4$. The parameter set $\tilde{\beta}_1$, $\tilde{\beta}_2$, $\tilde{\beta}_3$, and $\tilde{\beta}_4$, and $\tilde{\beta}_5$ can also be written in terms of a parameter set $\tilde{\gamma}_1$, $\tilde{\gamma}_2$, $\tilde{\gamma}_3$, $\tilde{\gamma}_4$, and $\tilde{\gamma}_5$, in which the velocity $v$ appears only in $\tilde{\gamma}_1$. The two sets are given as

$$\tilde{\beta}_1 = zFh^2v_{\text{ref}} (bLl_{\text{ex}})^{-1} = \tilde{\gamma}_1, \quad (23)$$

$$\tilde{\beta}_2 = \alphaF U (RT)^{-1} = \tilde{\gamma}_2, \quad (24)$$

$$\tilde{\beta}_3 = h^2v(bL\kappa)^{-1} = \tilde{\gamma}_3, \quad (25)$$

$$\tilde{\beta}_4 = zFh^2v\xi cUP_{\text{sti}}^{-1} = \tilde{\gamma}_4, \quad (26)$$

$$\tilde{\beta}_5 = zFh^2v(bL)^{-1} \xi c_{\text{ref}}^{-1} = \tilde{\gamma}_5, \quad (27)$$

$$\tilde{\gamma}_1 = l_{\text{ex}} (zFc_{\text{ref}} \kappa)^{-1}, \quad (28)$$

$$\tilde{\gamma}_2 = \xi cUblLl_{\text{ex}}c_{\text{ref}}^{-1}P_{\text{sti}}^{-1}, \quad (29)$$

and

$$\tilde{\gamma}_5 = \xi c_{\text{ref}}l_{\text{ex}}c_{\text{ref}}^{-1}f_{\text{sti}}^{-1}. \quad (30)$$

With Eqs. (18), (19), and (21)-(30), the electric power of the $k$th stage $\tilde{P}_k$ can be written in terms of the parameter set $\tilde{\gamma}_1$, $\tilde{\gamma}_2$, $\tilde{\gamma}_3$, and $\tilde{\gamma}_4$, given by
Using Eqs. (20) and (31), the total electric power $\tilde{P}$ is given as

$$
\tilde{P} = \sum_{k=1}^{n} \left[ \tilde{y}_1 \tilde{y}_3 (1 - \tilde{h}_k) \left[ \exp \left( \frac{1}{n} \tilde{y}_1 \exp \left( -\tilde{y}_2 \tilde{h}_k \right) + \tilde{y}_3 \right) \right] \prod_{i=1}^{k} \exp \left( -\frac{1}{n} \tilde{y}_1 \exp \left( -\tilde{y}_2 \tilde{h}_{i-1} \right) + \tilde{y}_3 \right) \right] \times \left[ 1 - \exp \left( -\frac{1}{n} \tilde{y}_1 \exp \left( -\tilde{y}_2 \tilde{h}_k \right) + \tilde{y}_3 \right) \right].
$$

The total electric power $\tilde{P}$ is a function of the number of stages $n$, the cathode overpotentials $\tilde{h}_1, \tilde{h}_2, \tilde{h}_3, \ldots, \tilde{h}_n$, and the parameters $\tilde{y}_1, \tilde{y}_2, \tilde{y}_3$, and $\tilde{y}_4$. It may be written as

$$
\tilde{P} = f\left( n, \phi_n, \tilde{\phi} \right), \quad \phi_n = (\tilde{h}_1, \tilde{h}_2, \tilde{h}_3, \ldots, \tilde{h}_n)^T \quad \text{and} \quad \tilde{\phi} = (\tilde{y}_1, \tilde{y}_2, \tilde{y}_3, \tilde{y}_4)^T.
$$

Note that $\tilde{h}_k = 1 - \tilde{E}_k$ applies such that $\tilde{h}_k$ may be substituted by $1 - \tilde{E}_k$ in the above formulations.

5.4. Optimization

The total electric power $\tilde{P} = f\left( n, \phi_n, \tilde{\phi} \right)$ shall then be maximized with respect to $\phi_n$ in order to optimize the cell potential distribution along the channel. The optimization statement shall be formulated as: Find a vector $\phi_{n,\text{max}} \in \mathbb{R}^{n \times 1}$ such that

$$
f\left( n, \phi_{n,\text{max}}, \tilde{\phi} \right) \geq f\left( n, \phi_n, \tilde{\phi} \right), \quad \forall \phi_n \in \mathbb{R}^{n \times 1},
$$

where $0 \leq \tilde{h}_k \leq 1$. A performance number $\Psi$ is defined that relates the maximum electric power of a $n$-stage concept to the maximum electric power of a traditional single-stage concept, given by
A conjugate gradient algorithm [26] is implemented to minimize \( f(n, \phi_n, \theta) \equiv C - f(n, \phi_n, \theta) \) with respect to \( \phi_n \). An initial vector \( \phi_{n,0} = (\tilde{\eta}_{1,0}, \tilde{\eta}_{2,0}, \tilde{\eta}_{3,0}, \ldots, \tilde{\eta}_{n,0}, \ldots) \) is set at the beginning of the iteration procedure. A gradient vector is calculated at each iteration step, given by

\[
\dot{g}_i = \left( \frac{\partial f(n, \phi_{n,i}, \theta)}{\partial \tilde{\eta}_{1,i}}, \frac{\partial f(n, \phi_{n,i}, \theta)}{\partial \tilde{\eta}_{2,i}}, \frac{\partial f(n, \phi_{n,i}, \theta)}{\partial \tilde{\eta}_{3,i}}, \ldots, \frac{\partial f(n, \phi_{n,i}, \theta)}{\partial \tilde{\eta}_{n,i}} \right)^T.
\]

The direction vector is updated according to

\[
\tilde{p}_i = -\dot{g}_i + \sigma_i \tilde{p}_{i-1},
\]

where

\[
\sigma_i = \begin{cases} 0, & \text{if } i = 0 \\ \frac{\overline{g}_i^\top \dot{g}_i}{\overline{g}_{i-1}^\top \dot{g}_{i-1}}, & \text{if } i \geq 1 \end{cases}
\]

The function \( \hat{f}(n, \phi_{n,i} + \delta \tilde{p}_i, \theta) \) is minimized with respect to \( \delta_i \) such that

\[
\frac{\partial \hat{f}(n, \phi_{n,i} + \delta \tilde{p}_i, \theta)}{\partial \delta_i} = 0.
\]

With the resulting \( \delta_i \), the updated overpotential vector is given by \( \phi_{n,i+1} = \phi_{n,i} + \delta_i \tilde{p}_i \).

5.5. Results and discussion

A standard case is considered that is based on the parameters given in Table 1. The standard case is defined by the parameters \( \tilde{y}_{1,sl}, \tilde{y}_{2,sl}, \tilde{y}_{3,sl}, \) and \( \tilde{y}_{4,sl} \) which are also listed in

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Table 1. These parameters are obtained through Eqs. (23), (24), (28), and (29), using the values of Table 1, where \( v \) is replaced by the cathode inlet velocity \( v_{st} \) of the standard case.

The effect of the number of stages \( n \) on the maximum electric power \( \hat{P} \) will be discussed. In addition, the effect of the variation of the parameters \( \tilde{y}_1 \) and \( \tilde{y}_2 \) on the maximum electric power \( \hat{P} \) will be investigated. A variation of the parameter \( \tilde{y}_1 \) represents a variation of the cathode inlet velocity \( v \), since \( v \propto \tilde{y}_1 \), and a variation of the parameter \( \tilde{y}_2 \) represents a variation of the transfer coefficient \( \alpha \), since \( \alpha \propto \tilde{y}_2 \). Figure 5.2 illustrates the course of the optimization of the cathode overpotentials \( \tilde{f}_{jk} = 1 - \tilde{E}_k \) for \( n = 21 \) stages and different initial conditions, based on an inlet flow rate \( \tilde{y}_1 = \tilde{y}_{1,\text{st}} / 160 \).

Figure 5.3 shows the distribution of optimized cathode overpotentials \( \tilde{f}_{jk} = 1 - \tilde{E}_k \) for different numbers of stages \( n \) and different inlet flow rates \( \tilde{y}_1 \). Note that the optimum cell potential distribution can also be extracted from Fig. 5.3, since \( \tilde{E}_k = 1 - \tilde{f}_k \). It can be seen that the values of the optimized cathode overpotentials \( \tilde{f}_{jk} = 1 - \tilde{E}_k \) monotonically increase along the flow direction, i.e., with increasing index \( k \). This implies that the optimized cell potentials \( \tilde{E}_k = 1 - \tilde{f}_k \) monotonically decrease along the flow direction. The overpotential difference between consecutive stages, given by \( \tilde{f}_{k+1} - \tilde{f}_k \), increases along the flow direction, i.e., with increasing index \( k \). The cell potential difference between consecutive stages, given by \( \left| \tilde{E}_{k+1} - \tilde{E}_k \right| \), decreases along the flow direction, i.e., with increasing index \( k \). The maximum overpotential difference along the channel is given by \( \tilde{f}_n - \tilde{f}_1 \), that is, the maximum overpotential is obtained at the last stage with the lowest inlet oxygen concentration and the minimum overpotential results at the first stage with the highest inlet oxygen concentration. The maximum cell potential difference along the channel is given by \( \tilde{E}_n - \tilde{E}_1 \), that is, the minimum cell potential is obtained at the last stage with the lowest inlet oxygen concentration and the maximum cell potential results at the first stage with the highest inlet oxygen concentration. The higher the number of stages \( n \), the larger the maximum overpotential difference \( \tilde{f}_n - \tilde{f}_1 \) and maximum cell potential difference \( \tilde{E}_n - \tilde{E}_1 \) along the channel, approaching asymptotically constant values as \( n \) tends to infinity. If the inlet flow rate \( \tilde{y}_1 \) tends to infinity, the oxygen concentration tends to remain constant along the channel.

In such a case, the optimized cathode overpotentials \( \tilde{f}_{jk} = 1 - \tilde{E}_k \) also tend to remain constant
along the channel and the performance parameter $\Psi$ tends to unity. If the inlet flow rate is decreased, the variation of the optimized cathode overpotentials $\tilde{\eta}_k = 1 - \tilde{E}_k$ along the channel becomes more pronounced. Figure 5.3 shows that this variation can be significant. It should be noted that the optimum individual current densities $\tilde{j}_k$ (corresponding to Fig. 5.3) are subject to decrease along the flow direction. The same holds for the optimum individual electric power densities $\tilde{P}_k/(\lambda/L)$.

In Fig. 5.4, the performance parameter $\Psi$ is plotted for two different values of the parameter $\tilde{y}_2$. The performance parameter $\Psi$ relates the electric power obtained from a multistage channel (with optimized cathode overpotentials $\tilde{\eta}_k$) to the electric power obtained from a traditional single-stage channel (with optimized cathode overpotential $\tilde{\eta}_1$). The performance parameter $\Psi$ tends to unity as the inlet flow rate $\tilde{y}_1$ tends to infinity. If the inlet flow rate $\tilde{y}_1$ is decreased, the performance number $\Psi$ increases and reaches a maximum in the range $10^3 < \tilde{y}_1 < 10^4$. If the number of stages $n$ is increased, the performance parameter $\Psi$ also increases and asymptotically approaches a maximum as the number of stages $n$ tends to infinity. Figure 5.4 shows that based on the multistage concept, electric power can be generated at significantly different cell potentials along a channel without any loss in electric power. The results also indicate that higher electric power densities can be achieved based on the proposed multistage concept with nonuniform cell potential distributions along the channel. This concept can be applied to micro- and macroscale applications that require electric power at various cell potentials.

5.6. Conclusions

A novel multistage fuel cell concept was introduced according to which the cell potential is allowed to vary along the channel direction. It was shown that the proposed concept allows to simultaneously generate electric power at various cell potentials without a reduction of the maximum electric cell power density. The multistage concept further allows for enhanced maximum electric cell power densities compared to the traditional concept involving uniform cell potential distributions along the channel. In practical applications, the proposed concept could be realized using segmented current collector plates which were originally developed to perform locally resolved current density measurements.
Table 5.1. Geometry and operating condition parameters.
Values are taken from Ref. [9].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of electrons $z$</td>
<td>4</td>
</tr>
<tr>
<td>Transfer coefficient $\alpha$</td>
<td>0.5</td>
</tr>
<tr>
<td>Cell temperature $T$ (K)</td>
<td>363</td>
</tr>
<tr>
<td>Open circuit potential $U$ (V)</td>
<td>1.2</td>
</tr>
<tr>
<td>Reference molar concentration of oxygen $c_{\text{ref}}$ (mol/cm$^3$)</td>
<td>$3.31 \times 10^{-5}$</td>
</tr>
<tr>
<td>Volumetric exchange current density $i_{\text{ex}}$ (A/cm$^3$)</td>
<td>$3.5 \times 10^{-3}$</td>
</tr>
<tr>
<td>Diffusion coefficient of O$_2$ in the gas channel $D_h$ (cm$^2$/s)</td>
<td>0.356</td>
</tr>
<tr>
<td>Diffusion coefficient of O$_2$ in the diffusion layer $D_b$ (cm$^2$/s)</td>
<td>0.0318</td>
</tr>
<tr>
<td>Diffusion layer wet porosity $\varepsilon$</td>
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</tr>
<tr>
<td>Oxygen molar fraction at the inlet $\zeta$</td>
<td>0.0627</td>
</tr>
<tr>
<td>Total molar concentration of the gas mixture $c$ (mol/cm$^3$)</td>
<td>$3.31 \times 10^{-5}$</td>
</tr>
<tr>
<td>Channel height and width $h$ (cm)</td>
<td>0.1</td>
</tr>
<tr>
<td>Catalyst layer width $b$ (cm)</td>
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</tr>
<tr>
<td>Diffusion layer thickness $l_b$ (cm)</td>
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</tr>
<tr>
<td>Catalyst layer thickness $l_c$ (cm)</td>
<td>0.006</td>
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<tr>
<td>Channel length $L$ (cm)</td>
<td>10</td>
</tr>
<tr>
<td>Inlet flow velocity in the standard case $v_{\text{st}}$ (m/s)</td>
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</tr>
<tr>
<td>$\tilde{\gamma}_{1,\text{st}}$</td>
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</tr>
<tr>
<td>$\tilde{\gamma}_{2,\text{st}}$</td>
<td>19.2</td>
</tr>
<tr>
<td>$\tilde{\gamma}_{3,\text{st}}$</td>
<td>$2.34 \times 10^{-6}$</td>
</tr>
<tr>
<td>$\tilde{\gamma}_{4,\text{st}}$</td>
<td>$3.29 \times 10^{-7}$</td>
</tr>
<tr>
<td>$\tilde{\gamma}_{5,\text{st}}$</td>
<td>$3.29 \times 10^{-7}$</td>
</tr>
</tbody>
</table>
Fig. 5.2. Optimization of $\tilde{\eta}_k = 1 - \bar{E}_k$ for different initial values $\tilde{\eta}_{k, (m)}$, where $n = 21$, $\tilde{\gamma}_1 = \tilde{\gamma}_{1, st} / 160$, $\tilde{\gamma}_2 = \tilde{\gamma}_{2, st}$, $\tilde{\gamma}_3 = \tilde{\gamma}_{3, st}$, and $\tilde{\gamma}_4 = \tilde{\gamma}_{4, st}$. Arrows indicate the direction of increasing $k$. (a) $\tilde{\eta}_{k, (m)} = 0.8$, $\forall k, 1 \leq k \leq n$. (b) $\tilde{\eta}_{k, (m)} = 0.7$, $\forall k, 1 \leq k \leq n$. 

Fig. 5.3. Optimized $\tilde{\eta}_n = 1 - \tilde{E}_n$ for different number of stages $n$ and different inlet flow rates $\tilde{y}_i$, where $\tilde{y}_2 = \tilde{y}_{2,\text{st}}$, $\tilde{y}_3 = \tilde{y}_{3,\text{st}}$, and $\tilde{y}_4 = \tilde{y}_{4,\text{st}}$. (a) $\tilde{y}_1 = \tilde{y}_{1,\text{st}}/10$. (b) $\tilde{y}_1 = \tilde{y}_{1,\text{st}}/20$. (c) $\tilde{y}_1 = \tilde{y}_{1,\text{st}}/40$. (d) $\tilde{y}_1 = \tilde{y}_{1,\text{st}}/80$. 
Fig. 5.4. Performance parameter $\Psi$ as a function of $n$ and $\tilde{\gamma}_1$. The arrows indicate the direction of increasing $n$, where $n = 1, 2, 3, \ldots, 11$. (a) $\tilde{\gamma}_2 = \tilde{\gamma}_{2,\text{st}}$. (b) $\tilde{\gamma}_2 = 4\tilde{\gamma}_{2,\text{st}}/5$. 
References


6. Laminar mixing, heat transfer and pressure drop in tree-like microchannel nets

Abstract

The laminar convective heat transfer and pressure drop characteristics in tree-like microchannel nets are numerically investigated and compared to the corresponding characteristics in traditional serpentine flow patterns, by solving the Navier-Stokes and energy equation for an incompressible fluid with constant properties in three dimensions. A constant heat flux is applied to the walls of the square cross-sectional channels. The intrinsic advantage of tree-like nets with respect to both heat transfer and pressure drop is demonstrated. In addition, secondary flow motions initiated at bifurcations and their important role on thermal mixing are identified and discussed. Thermal management issues in polymer electrolyte fuel cells are addressed and in this context, the future employment of tree nets is recommended.

Nomenclature

Latin letters

\( a \) distance (m)

\( Br \) Brinkman number (-)

\( c_p \) specific heat capacity (J kg\(^{-1}\) K\(^{-1}\))

\( d \) channel diameter (m)

\( Ec \) Eckert number (-)

\( f \) Moody (or Darcy) friction factor (-)

\( h \) heat transfer coefficient (W m\(^{-2}\) K\(^{-1}\))

\( k \) branching level (-)

\( L \) channel length (m)

\(^f\) This chapter is published in:
\( \textit{m} \) total number of branching levels (-)
\( \dot{\textit{m}} \) mass flow rate (kg s\(^{-1}\))
\( \textit{n} \) parameter (-)
\( \text{Nu} \) Nusselt number (-)
\( \textit{p} \) pressure (Pa)
\( \text{Pr} \) Prandtl number (-)
\( \dot{q} \) wall heat flux (W m\(^{-2}\))
\( \textit{r} \) length ratio (-)
\( \text{Re} \) Reynolds number (-)
\( \text{S} \) surface area (m\(^2\))
\( \text{t} \) time (s)
\( \text{i} \) temperature (K)
\( \text{v} \) velocity (m s\(^{-1}\))
\( \textit{x, y, z} \) coordinates (m)

Greek letters
\( \beta \) channel diameter ratio (-)
\( \gamma \) channel length ratio (-)
\( \lambda \) thermal conductivity (W m\(^{-1}\) K\(^{-1}\))
\( \mu \) dynamic viscosity (Pa s)
\( \rho \) density (kg m\(^{-3}\))
\( \xi, \eta, \zeta \) coordinates (m)

Subscripts
\( \textit{0} \) zeroth branching level
\( \textit{i, j} \) indices (Einstein summation convention)
\( \text{in} \) inlet
\( \textit{k} \) branching level
\( \text{m} \) mean
\( \text{max} \) maximum
\( \text{min} \) minimum
\( \text{ref} \) reference
6.1. Introduction

Effective thermal and water management in polymer electrolyte fuel cells is key to ensure high cell performance and efficiency. The irreversibility of electrochemical reactions and joule heating are the most important factors causing heat generation inside PEM fuel cells. The temperature distribution in the cell has a strong impact on the cell performance since it influences the water distribution by means of condensation and affects the multicomponent gas diffusion transport characteristics through thermocapillary forces and thermal buoyancy. Also, the kinetics of electrochemical reactions directly depends on temperature. Excessive global or local cell temperature due to insufficient or non-effective cell cooling may cause membrane dehydration, shrinking or even rupture. Membrane hydration is important to ensure high proton conductivity and thus cell performance. Hence, thermal and water management issues are strongly coupled and they have a direct impact on cell performance. Thermal management includes the removal of the generated heat from inside the cell to the outside. Further, a temporally and spatially uniform temperature distribution must be provided, hot spots need to be avoided, and pumping power required for the coolant circulation has to be minimized in order to ensure high overall cell efficiency. Therefore, pressure drop must be minimized while maximizing the heat transfer capability at the same time.

For thermal management in PEM fuel cell stacks, usually serpentine or meander cooling patterns are used, having only one or a few inlets and outlets, for liquid or gas coolant, depending on the system design and the cell size. For overall stack functionality reasons, the number of fluid inlets and outlets must be small, making parallel cooling patterns usually inappropriate. These circumstances call for a flow geometry with minimum flow resistance between a volume and one point, i.e. between the inside of the cell and the inlet or outlet. In this paper, the use of deterministic tree networks of Bejan and co-workers [1,2], also termed as fractal networks of branching tubes [3], is suggested for this purpose. Bejan and Errera [4] discussed a deterministic tree network for fluid flow with minimum flow resistance between a
volume and a point, subjected to two constraints: fixed total volume and fixed channel volume. Bejan [5] showed that the total heat convected by a double tree is proportional to the total volume raised to power 3/4. Chen and Cheng [6], following the principles put forth by Bejan and co-workers [1,2,5], presented an analytical study on the heat transfer and pressure drop characteristics in fractal tree-like microchannel nets in which a comparison is made between fractal nets and traditional parallel channels. After simplifying assumptions including neglecting the effect of bifurcation on pressure drop and heat transfer they found that the considered fractal nets provide higher heat transfer capability and cause less pressure drop.

In the course of electronics miniaturization during the last decade, denser component packing led to higher energy dissipation rates and necessitated the demand for high-performance micro heat exchangers consisting of microchannel systems being based on gas or liquid convective heat transfer in single or two-phase flow regimes [7-9]. Compared to large diameter channels, the large surface to volume ratio of small diameter channels provides a better heat transfer capability and therefore makes microchannel systems attractive for dealing with high heat fluxes. However, a penalty is paid due to the higher pressure drop, caused again by the increased surface to volume ratio. In the literature, microchannels are generally defined as channels having a hydraulic diameter smaller than 1 mm and larger than 1 μm [7].

A substantial research effort has been focused on the experimental [10-17,19,21] and numerical [18-24] investigation of single phase flow in such microchannels. Most of this work described in literature is concerned with two parameters, the friction factor and the heat transfer coefficient, regarding channels with diameters between 1μm and 1mm. Experimental results show agreement but also substantial deviation from classical theory developed for larger channels. Possible reasons for the measured deviations are discussed and investigated in the literature [25-33]: measurement inaccuracy at the micro-scales, high relative surface roughness at the channel walls, the electric double-layer (EDL) effect, viscous heating, and slip-flow for gases at high Knudsen numbers. Due to the large surface to volume ratio, surface related phenomena become important or rather dominant at the micro-scales and they might not be neglected, as at the larger scales. However, the literature is not conclusive with respect to the dependence of the above mentioned two parameters on the hydraulic diameter in the submicron-scales. A key property of a tree net is that there is not an intrinsic length-scale, defined in an ad-hoc manner. Such scales are reduced from one branching level to the next higher one, such that the relative importance of different phenomena depends on the branching level.
Fig. 6.1. Thermal management in polymer electrolyte fuel cell stacks. (a) Traditional serpentine or meander cooling patterns without a separation layer between the bipolar plates. (b) Superimposed tree nets. One net is imposed on the back side of the anode bipolar plate and another net is imposed on the back side of the cathode bipolar plate. The two nets are separated by a separation layer. Vertical holes in this layer connect the ends of the highest branching levels to each other.

In this paper, a numerical analysis of the fundamental heat transfer and pressure drop characteristics in tree-like microchannel nets as shown in Figs. 6.1 and 6.2 is presented. The future application of tree nets for thermal management in PEM fuel cells is suggested and discussed, among other application areas. In the analytical work by Chen and Cheng [6], the effect of bifurcation on heat transfer and pressure drop is neglected and it is assumed for simplicity, that the laminar flow is fully developed both thermally and hydrodynamically. Such assumptions are appropriate if for the flow channels, the length to diameter ratio is very high and the Reynolds number is rather small, such that the hydrodynamic and thermal development lengths can be neglected compared to the channel lengths. The present computational study is not based on such assumptions and it takes into account important hydrodynamic and thermal effects from bifurcations, such as secondary flow motions and convective thermal mixing. The Navier-Stokes equations and the energy equation are numerically solved in three dimensions in conjunction with a constant heat flux boundary...
condition at the channel walls. The characteristic variations of the Nusselt number and the friction factor along the tree net are discussed and compared to the ones of a serpentine flow pattern having the same heat transfer surface area.

![Diagram of tree net](image)

**Fig. 6.2.** Tree net with six branching levels \( m = 6 \), \( \beta = \frac{d_{k+1}}{d_k} = 2^{-1/3} \), \( \gamma = \frac{L_{k+1}}{L_k} = 2^{-1/2} \), \( L_0 / d_0 = 10 \), \( r = 0.95 \), and \( \Delta d_k = a_k \). (a) Three-dimensional view. (b) Top view. (c) Schematic of the geometric structure of the tree net. (d) Computational domain with inlet and outlet mass flow rates.

### 6.2. Mathematical model

In the following mathematical model, an incompressible fluid is assumed with constant viscosity \( \mu \), constant heat capacity \( c_p \), and constant thermal conductivity \( \lambda \). Using the Einstein summation convention, continuity reads

\[
\frac{\partial v_j}{\partial x_j} = 0, \tag{1}
\]

momentum conservation is written as
\[ \frac{\partial}{\partial t} (\rho v_i) + \frac{\partial}{\partial x_j} (\rho v_i v_j) = -\frac{\partial p}{\partial x_i} + \frac{\partial}{\partial x_j} \left( \mu \frac{\partial v_i}{\partial x_j} \right), \quad i = 1, 2, 3 \]  

(2)

and the energy equation including the viscous dissipation term is given by

\[ \frac{\partial}{\partial t} (\rho T) + \frac{\partial}{\partial x_j} (\rho v_i T) = \frac{\partial}{\partial x_j} \left( \frac{\lambda}{c_p} \frac{\partial T}{\partial x_j} \right) + \mu \left( \frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right) \frac{\partial v_i}{\partial x_j}. \]  

(3)

For a non-dimensional representation of the problem, the hydraulic channel diameter \( d_0 \) of the zeroth branching level is used as a length-scale, the inlet velocity \( v_{in} \) is used as a velocity scale, the inlet temperature \( T_{in} \) and a maximum temperature \( T_{max} \) are used for temperature scaling, and pressure is scaled through a reference pressure \( p_{ref} \):

\[ \tilde{x}_j \equiv \frac{x_j}{d_0}, \quad \tilde{t} \equiv \frac{t v_{in}}{d_0}, \quad \tilde{v}_j \equiv \frac{v_j}{v_{in}}, \quad \tilde{T} \equiv \frac{T - T_{in}}{T_{max} - T_{in}}, \quad \tilde{p} \equiv \frac{p - p_{ref}}{\rho v_{in}^2}. \]  

(4)

The maximum temperature is defined as \( T_{max} = q^* S / (m_{w,0} c_p) + T_{in} \), where \( q^* \) is the constant wall heat flux and \( S \) represents the corresponding heated surface area. Based on these scalings and the definition of non-dimensional numbers,

\[ \text{Re} \equiv \rho v_{in} d_0 / \mu, \quad \text{Pr} \equiv c_p \mu / \lambda, \quad \text{Br} \equiv \mu v_{in}^2 / \lambda (T_{max} - T_{in}), \quad (Ec \equiv \text{Br/Pr}), \]  

(5)

the conservation equations (1) to (3) can be written in non-dimensional form as

\[ \frac{\partial \tilde{v}_i}{\partial \tilde{x}_j} = 0, \]  

(6)

\[ \frac{\partial}{\partial \tilde{t}} \tilde{v}_i + \frac{\partial}{\partial \tilde{x}_j} (\tilde{v}_i \tilde{v}_j) = -\frac{\partial \tilde{p}}{\partial \tilde{x}_i} + \frac{1}{\text{Re}} \frac{\partial^2 \tilde{v}_i}{\partial \tilde{x}_j \partial \tilde{x}_j}, \quad i = 1, 2, 3 \]  

(7)

and

\[ \frac{\partial}{\partial \tilde{t}} \tilde{T} + \frac{\partial}{\partial \tilde{x}_j} (\tilde{v}_j \tilde{T}) = \frac{1}{\text{Re Pr}} \frac{\partial^2 \tilde{T}}{\partial \tilde{x}_j \partial \tilde{x}_j} + \frac{\text{Br}}{\text{Re Pr}} \left( \frac{\partial \tilde{T}}{\partial \tilde{x}_j} + \frac{\partial \tilde{T}}{\partial \tilde{x}_j} \right) \frac{\partial \tilde{T}}{\partial \tilde{x}_j}. \]  

(8)
6.3. Numerical solution

6.3.1. Models and boundary conditions

Based on the above mathematical formulation, the fluid mechanics and heat transfer in a tree-like net consisting of channels with square cross sections, as shown in Fig. 6.2, is computed. The fractal geometry considered here is fixed if the following independent parameters are given: the number of branching levels $m$, the ratio of the channel diameters $\beta = d_{k+1} / d_k$ between two consecutive branching levels, the corresponding channel length ratio $\gamma = L_{k+1} / L_k$, the length to diameter ratio $I_0 / d_0$ at the zeroth branching level, the ratio $r$ of the straight channel length and the entire channel length $L_k$ including the length of the converging duct, and the length $I_0$ or the diameter $d_0$ at the zeroth branching level. In this study, a fractal geometry with $m = 6$, $\beta = 2^{-1/3}$, $\gamma = 2^{-1/2}$, $I_0 / d_0 = 10$, $r = 0.95$, and $d_0 = 1$ mm is investigated. Optimization of a single plane construct consisting of a T-shaped junction with respect to minimum flow resistance by fixing the total tube volume yields the optimal diameter ratio $\beta = d_{k+1} / d_k = 2^{-1/3}$, known as Murray’s law [34,35], which is independent of the length ratio $\gamma = L_{k+1} / L_k$ and geometry. If the space allocated to the construct is further fixed, i.e. $2L_{k+1}I_k = \text{const.}$, a second minimization of the flow resistance [5] yields the optimal length ratio $\gamma = L_{k+1} / L_k = 2^{-1/3}$. However, this length ratio creates the practical problem of channel overlapping for a right angled plane construct with $m > 4$. To circumvent this, $\gamma = 2^{-1/2}$ is chosen in this study. Such a tree net has one fluid inlet at the zeroth branching level and a number of $2^m$ fluid outlets at the highest branching level, where $m$ represents the total number of branching levels. A traditional heat removal concept for PEM fuel cells is shown in Fig. 6.1(a) in which a serpentine or meander flow pattern is manufactured into one of the bipolar plates.

An alternative concept utilizing the tree network of channels requires that on top of the first net, a second net of identical geometry is superimposed and the ends of the highest branching levels of each net are then vertically connected in order to build up a closed fractal tree, having one fluid inlet at the zeroth branching level of the first net and one fluid outlet at the zeroth branching level of the second net. A novel concept for thermal management in PEM fuel cell stacks which is based on this principle is presented in Fig. 6.1(b): A tree-like flow pattern (first tree net) is imposed on the back side of the anode bipolar plate and another net (second tree net) is imposed on the back side of the adjacent cathode bipolar plate, such
that each bipolar plate contains a flow pattern for reactant and product gas on the one side and a tree-like flow pattern for thermal management on the other side. Adjacent bipolar plates are separated by a separation layer including vertical holes which connect the ends of the highest branching levels of each net. In this manner, the anode side is cooled with colder coolant whereas the cathode side is cooled with preheated, warmer coolant providing a higher temperature level on the cathode side than on the anode side. Higher temperatures on the cathode side enhance electrochemical reaction rates and increase the saturation pressure of water vapor leading to a reduced amount of condensation which in turn reduces mass transport limitations at high current densities. On the cathode side, the large electrode overpotential and the condensation of water vapor are main performance-limiting factors which are addressed with the proposed concept. Half (or part) of the tree net may be manufactured on the bipolar plate and the other half on the separation layer. Alternatively, the entire tree net may be manufactured on the bipolar plate only. Such manufacturing issues, although mentioned in passing to indicate possible solutions, are not the main theme of this work which focuses on the basic thermofluidic aspects of the problem. Heat conduction taking place in the solid material between the flow channels (clearly also tractable numerically) is not considered in this work opting for the simple constant heat flux condition on the wall, and only the first net is modeled according to Figs. 6.2(a)-6.2(c), since the main focus is to demonstrate the power of the tree channel concept leaving further quantification tied to specific applications for future parametric studies.

This net is symmetric with respect to the planes \( y = 0 \) and \( z = 0 \). Therefore, for the computational domain drawn in Fig. 6.2(d), symmetry boundary conditions are applied at \( y = 0 \) and \( z = 0 \). A constant velocity profile is applied to the inlet boundary condition. The tree net is cut at the left end of the second and the consequent branching levels and constant mass flow outlet boundary conditions are used to reduce the number of degrees of freedom of the computational model, cf. Fig. 6.2(d). This configuration of outlet boundary conditions implicitly incorporates the assumption, that at a bifurcation, half of the mass flow is directed to the left and the other half to the right. By modeling an entire tree net with \( m = 4 \) for a wide range of inlet Reynolds numbers, it was found that this is a very good assumption indeed, even if for the flow it is not possible to hydrodynamically fully develop before bifurcating. At the highest branching levels, fixed pressure outlet boundary conditions, \( p_{\text{ref}} = 0 \), together with zero flux thermal boundary conditions are applied. For heat transfer, a constant fluid
inlet temperature profile is set and at the walls of the tree net, a constant heat flux $q''$ and non-slip boundary conditions are applied.

The serpentine geometry as shown in Fig. 6.3 has exactly the same heat transfer surface area as the complete fractal geometry with an identical wall heat flux $q''$. Its square cross-sectional channels are of constant diameter $d_0$ which equals to the largest channel diameter in the tree net. The entire serpentine flow pattern covers the same rectangular area as the tree net.

![Fig. 6.3. Serpentine flow pattern with the same heat transfer surface area as the tree net and covering the same rectangular area.](image)

### 6.3.2. Solution method, grid independence

The set of partial differential equations (6) to (8) with the boundary conditions described above is numerically solved with a finite-volume central scheme on a structured grid using the licensed solver CFD-ACE distributed by CFD Research Corporation of Huntsville, USA. Algebraic multigrid solver is used in conjunction with a convergence criterion of $1 \times 10^{-10}$.

The computational grid of the three-dimensional fractal geometry consists of 1,816,800 cells. By increasing the cell number to 2,721,705, practically indistinguishable temperature contours and velocity contours of all three components are obtained when comparing to the results obtained from the coarser grid. By decreasing the cell number to 790,425, small discrepancies are obtained for temperature and velocity contours. The grid resolution of the serpentine flow geometry is consistent with the one of the fractal geometry and it contains 1,063,200 cells.
6.4. Validation

The numerical results are validated with analytical and numerical solutions from literature. For incompressible, laminar and fully developed steady flow of constant viscosity in a square duct, an exact analytical solution [18] can be obtained for the mass and momentum equations (6) and (7). Within this framework, the exact Moody (or Darcy) friction factor \( f \) [18] is given as

\[
f \frac{Re}{24} = 1 - 192 \pi^{-5} \sum_{n=1,3,5} n^{-5} \tanh \left( \frac{n \pi}{2} \right) \equiv 56.908.
\]

Iqbal et al. [36] analyzed the H2 boundary condition [18] of rectangular ducts with all four walls heated for a thermally and hydrodynamically fully developed flow with constant fluid properties and neglecting viscous dissipation. For a square duct, they obtained \( \text{Nu} = 3.091 \) by means of a variational approach. Chandrupatla and Sastri [37] obtained \( \text{Nu} = 3.095 \) which is in agreement. Their finite difference solutions were computed by using the iterative extrapolated Liebmann method.

For \( \text{Re}_{\infty} = 20 \), the flow becomes fully developed both thermally and hydrodynamically in the first channel of the serpentine flow pattern. The present numerical solution of Eqs. (6)-(8), neglecting viscous dissipation in the energy equation like in the references mentioned earlier to facilitate the comparison, yields \( f \frac{Re}{56.976 (+0.118\% \text{ compared to Ref. [18]})} \) and \( \text{Nu} = 3.096 (+0.162\% \text{ and } +0.0323\% \text{ compared to Refs. [36] and [37], respectively}) \), which is in very good agreement with the previously mentioned results.

6.5. Nusselt number and friction factor

In order to investigate the heat transfer and pressure drop characteristics of the tree net and the serpentine flow pattern, the local Nusselt number and local friction factor are determined at each discrete channel cross-section along the flow direction. The local Nusselt number then depends on the position \( \zeta_k \) as indicated in Figs. 6.2(c) and 6.3, i.e.

\[
\text{Nu}_k (\zeta_k) = h_k (\zeta_k) d / \lambda
\]

where the subscript \( k \) indicates the branching level in the case of the tree net. With the constant wall heat flux \( q^* \), the local heat transfer coefficient reads
\[ h_k (\xi_k) = q^* \left[ T_{w,m,k} (\xi_k) - T_{m,k} (\xi_k) \right] \]  

(11)

where the mean fluid temperature is given as

\[ T_{m,k} (\xi_k) = \frac{1}{\int_0^{\xi_{k,max}} \int_{\eta_{k,min}}^{\eta_{k,max}} v_{\xi,k} (\xi_k, \eta_k, \xi_k) \left( \frac{\partial}{\partial \xi_k} \right) \eta_k d\xi_k d\xi_k}{\int_0^{\xi_{k,max}} \int_{\eta_{k,min}}^{\eta_{k,max}} v_{\xi,k} (\xi_k, \eta_k, \xi_k) \eta_k d\xi_k d\xi_k} \]  

(12)

and the peripherally averaged wall temperature reads

\[ T_{w,m,k} (\xi_k) = \frac{1}{d_k/2} \int_0^{\xi_{k,max}} \int_{\eta_{k,min}}^{\eta_{k,max}} T_{w,k} (\xi_k, \eta_k, \xi_k) \eta_k d\xi_k d\xi_k \]  

(13)

Herein, \( v_{\xi,k} \) is the velocity component in \( \xi_k \)-direction at the \( k \)th branching level. The Reynolds number at the \( k \)th branching level,

\[ \text{Re}_k = \rho v_{\xi,m,k} d_k / \mu \]  

(14)

with the mean velocity

\[ v_{\xi,m,k} = \frac{1}{d_k/2} \int_0^{\xi_{k,max}} \int_{\eta_{k,min}}^{\eta_{k,max}} v_{\xi,k} (\xi_k, \eta_k, \xi_k) \eta_k d\xi_k d\xi_k = 2^{-k} \beta^{-k} v_{in} \]  

(15)

and the definition of the friction factor,

\[ f_k (\xi_k) = -\frac{\partial p_{m,k}}{\partial \xi_k} \frac{2d_k}{\rho v_{\xi,m,k}^2} \]  

(16)

are used to compute the local \( f_k \text{Re}_k (\xi_k) \) which depends on the position along the flow direction. The cross-sectional average of the static pressure
\[ p_{m,k} (\xi_k) = \frac{\int_{\xi_k}^{\xi_{k,min}} \int_{\eta_k}^{\eta_{k,min}} p_k (\xi_k, \eta_k, \zeta_k) \, d\eta_k \, d\xi_k}{\int_{\xi_k}^{\xi_{k,min}} \int_{\eta_k}^{\eta_{k,min}} d\eta_k \, d\xi_k} \]  

(17)

is used to determine the pressure gradient in Eq. (16).

<table>
<thead>
<tr>
<th>Table 6.1. Properties of liquid water at 1 bar and 75 °C [38]. Boundary conditions and geometry parameters.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Density ( \rho ) (kg m(^{-3}))</strong></td>
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<tr>
<td><strong>Dynamic viscosity ( \mu ) (Pa s)</strong></td>
</tr>
<tr>
<td><strong>Thermal conductivity ( \lambda ) (W m(^{-1}) K(^{-1}))</strong></td>
</tr>
<tr>
<td><strong>Specific heat capacity ( c_p ) (J kg(^{-1}) K(^{-1}))</strong></td>
</tr>
<tr>
<td><strong>Inlet velocity ( v_0 ) for ( Re_k=0 ) = 20 (cm s(^{-1}))</strong></td>
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<tr>
<td><strong>Inlet velocity ( v_0 ) for ( Re_k=0 ) = 200 (cm s(^{-1}))</strong></td>
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<tr>
<td><strong>Wall heat flux ( q^w ) for ( Re_k=0 ) = 20 (W m(^{-2}) K(^{-1}))</strong></td>
</tr>
<tr>
<td><strong>Wall heat flux ( q^w ) for ( Re_k=0 ) = 200 (W m(^{-2}) K(^{-1}))</strong></td>
</tr>
<tr>
<td><strong>Channel diameter ( d_0 ) at the zeroth branching level (mm)</strong></td>
</tr>
<tr>
<td><strong>Surface area ( S ) (m(^2))</strong></td>
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</tbody>
</table>

6.6. Numerical results and discussion

The equations governing fluid flow and heat transfer, Eqs. (6)-(8), are numerically solved with respect to the tree and serpentine channel patterns. For each configuration, two cases are considered: The first case is based on \( Re_k=0 \) = 20 and \( Pr = 2.39 \) whereas the second case is based on \( Re_k=0 \) = 200 and \( Pr = 2.39 \). This Prandtl number represents the properties of liquid water at 1 bar and 75 °C [38]. The operating temperature range for PEM fuel cells is usually between 65 °C and 100 °C. For a channel diameter of \( d_0 = 1 \) mm at the zeroth branching level, these Reynolds numbers then imply a mean liquid water inlet velocity of 0.774 cm/s and 7.74 cm/s, respectively. In this section, laminar mixing, pressure drop, and heat transfer characteristics in the fractal and serpentine flow pattern are discussed and
compared to each other. Dimensional results are based on the parameters given in Table 6.1. Characteristics are plotted for the right-sided branches, cf. Fig. 6.2(d).

Fig. 6.4. Laminar mixing at the first bifurcation in the tree net at $Re_{x=0} = 200$. (a) Streamlines in top view: Transverse vortices with their axis transverse to the flow causing recirculation and longitudinal vortices with their axis along the flow in the streamwise direction. (b) Temperature (K) contours showing hot spots in the recirculation area at $z = 0$.

6.6.1. Laminar mixing

As the flow passes through bifurcations, secondary flow motions are initiated as shown in Fig. 6.4(a). The higher the flow Reynolds number, the larger their relative magnitude is. Transverse vortices with their axis transverse to the flow in the streamwise direction generate recirculation near the inner corners of the bifurcations, where the fluid velocity is much slower than at the outer wall, leading to hot spots in this area, cf. Fig. 6.4(b). Further, two longitudinal vortices of opposite orientation with their axis along the flow in the streamwise direction are generated, as seen in Fig. 6.5. Thereby, cold fluid is moved from the outer to the inner wall and finally to the channel core as the strength of the vortices decays with increasing distance from the bifurcation, cf. Fig. 6.5. With increasing branching level $k$, the flow Reynolds number becomes smaller and thereby the initial strength of longitudinal vortices is reduced such that cold fluid is not anymore subject to establish a closed ring with warmer fluid inside this ring.
For the tree net, the distance $d_k$ as indicated in Fig. 6.2(c) has been varied to investigate the dependence of the vortex structures on different geometric configurations of the converging passages. Identical longitudinal vortex structures of varying strength are found for different values of $d_k$. Herein, the following parameter set has been investigated for the higher Reynolds number level ($Re_{k=0} = 200$): $d_k \in (-2a_k, -a_k, 0, a_k, 2a_k)$ with $a_k = (d_k - d_{k+1}) / 2$ where the geometry with $\Delta d_k = a_k$ represents the case being mainly discussed in this study. The strength of the longitudinal vortices increases for larger values of $d_k$, increasing thereby the peak local Nusselt number $Nu_{k=1,\text{max}}$ according to 10.2, 10.9, 12.7, 15.1, and 17.0. However, the pressure drop in the entire tree net increases at the same time according to 50.2, 52.1, 56.1, 65.0, and 87.3 Pa, respectively. Therefore, the effect of thermal mixing can be intensified with increasing values of $d_k$ at the cost of additional pressure drop and vice versa. The channel cross sectional area at the interface of two consecutive branching levels $k$ and $k+1$, i.e. $(d_k - 2d_k)d_{k+1}$, is reduced with increasing $d_k$. Therefore, the flow is locally accelerated before entering the higher branching level which causes higher strengths for longitudinal vortices and therefore enhanced thermal mixing. More detailed optimization of the bifurcation geometry at the different branching levels and inlet Reynolds number with respect to both aspects is left to algorithmic optimization studies considering also complexly curved walls. Fluid mixing could also be intensified by different passive methods, e.g. by placing ridges on the floor of the channels at an oblique angle [39] or by inserting C-shaped repeating units in the streamwise direction [40].
Fig. 6.5. (a) Temperature (K) contours at four consecutive cross-sections in the first, second, and third branching level of the tree net at $Re_{k=0} = 200$. (b) Vorticity ($s^{-1}$) and pressure (Pa) contours at two consecutive cross-sections in the first branching level $k = 1$ of the tree net at $Re_{k=0} = 200$. 
6.6.2. Pressure drop

In the tree net, the flow is subject to develop hydrodynamically and thermally in the entrance region of the zeroth branching level due to the constant velocity and temperature profiles at the inlet. At bifurcations, the flow is disturbed and secondary flow motions are initiated which then decay along the next following straight channel portions, such that the flow tends to develop again before reaching the next bifurcation. In the serpentine channels, the flow is subject to develop in the straight channels whereas it is disturbed again at each turn.

Fig. 6.6. Friction factor. (a) Tree net with $Re_{k=0} = 20$. (b) Serpentine pattern with $Re_{k=0} = 20$. (c) Tree net with $Re_{k=0} = 200$. (d) Serpentine pattern with $Re_{k=0} = 200$. 
For $Re_k=20$, the hydrodynamic development lengths are small compared to the length of the corresponding straight channels. This is seen in Figs. 6.6(a) and 6.6(b) from the course of the friction factor which evens out at a certain level when the flow becomes fully developed. In the tree net, the pressure drop across the first bifurcation (0.145 Pa) is 16.2% of the pressure drop between $\xi_k=0,\min$ and $\xi_k=0,\max$ in the straight channel of the zeroth branching level (0.898 Pa), cf. Fig. 6.7(a). Herein, the cross-sectional average of the static pressure at $\xi_k,\max$ is subtracted from the corresponding value at $\xi_k+1,\min$ to evaluate the pressure drop across a bifurcation. The pressure drop across the sixth bifurcation (0.114 Pa) is 28.3% of the pressure drop in the straight channel of the fifth branching level (0.404 Pa). Consequently, at the higher branching levels, the contribution of the pressure drop obtained across bifurcations becomes more important compared to the pressure drop in the straight channels, as seen from Fig. 6.7(a).

![Fig. 6.7. Pressure drop in the straight channels between $\xi_k=0,\min$ and $\xi_k=0,\max$ (x). Pressure drop across bifurcations between $\xi_k,\max$ and $\xi_k+1,\min$ (+). (a) Tree net with $Re_k=20$. (b) Tree net with $Re_k=200$.](image)

This fact is due to the growing ratio between the channel diameter and the channel length when going to higher branching levels, i.e. $d_{k+1}/L_{k+1} = (\beta/\gamma)d_k/L_k \approx 1.12d_k/L_k$. Therefore, analytical approaches [6] where the laminar flow is assumed to be hydrodynamically fully developed everywhere and where the effect of bifurcation on pressure drop is neglected, are only adequate if the hydrodynamic development lengths are very small compared to the
length of the straight channels, i.e. for low Reynolds numbers, high $L_k/d_k$ ratios and for the lower branching levels. For the entire tree net, the resulting overall pressure drop (4.88 Pa) is only 56.9% of the pressure drop obtained from the corresponding serpentine flow pattern (8.57 Pa) having exactly the same surface area $S$. As a further comparison, the pressure drop in a single square cross-sectional straight channel with diameter $d_0$ and surface area $S$ can be obtained analytically from Eqs. (16) and (9) by assuming fully developed flow. A value of 8.48 Pa is found for such a straight channel flow which is only slightly below the pressure drop in the serpentine flow pattern but at the same time almost double the pressure drop in the tree net.

Table 6.2. Total pressure drop in the tree network and serpentine channel system for different inlet Reynolds numbers.

<table>
<thead>
<tr>
<th>$Re_{x=0}$</th>
<th>Tree network</th>
<th>Serpentine</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>4.88 Pa</td>
<td>8.57 Pa</td>
</tr>
<tr>
<td>200</td>
<td>65 Pa</td>
<td>118 Pa</td>
</tr>
</tbody>
</table>

For $Re_{x=0} = 200$, the flow does not fully develop any more at the lower branching levels $k = 0, 1, 2$ of the tree net, as seen from Fig. 6.6(c). In the serpentine pattern, the flow develops in the long straight channels, $k = 0, 2, 4$, such that the friction factor variations in the shorter channels $k = 1$ and $k = 3$ are similar to each other, cf. Fig. 6.6(d). The pressure drop across the first bifurcation in the tree net (4.03 Pa) is 31.5% of the pressure drop in the straight channel of the zeroth branching level (12.8 Pa), cf. Fig. 6.7(b). The pressure drop across the fifth bifurcation (1.29 Pa) is 25.4% of the pressure drop in the straight channel of the fourth branching level (5.09 Pa). Here, the relative importance of the bifurcation pressure drop does not monotonically increase with increasing branching levels, since the flow does not develop fully at the lower branching levels leading to a higher relative pressure drop from bifurcations at these branching levels. For $k = 0$ to $k = 5$, these ratios are 31.5%, 26.9%, 24.8%, 24.5%, 25.4%, and 27.1%, respectively. As expected, the ratios increase again after the third branching level where the flow tends to develop more approaching fully developed state before bifurcating. The overall pressure drop resulting from the entire tree net (65.0 Pa) is only 55.1% of the pressure drop obtained from the corresponding serpentine flow pattern.
When comparing the overall pressure drop of the tree net at $Re_{k=0} = 20$ (4.88 Pa) to the one at $Re_{k=0} = 200$ (65.0 Pa), an increase by a factor of 13.3 is identified. For fully developed flow and neglecting effects from bifurcations, a factor of 10 would be expected. When considering again a single straight channel with fully developed flow, a pressure drop of 84.8 Pa is found analytically, which is substantially below the pressure drop in the serpentine flow pattern and at the same time also substantially above the pressure drop in the tree net. The total pressure drop of the tree network and serpentine channel system is summarized in Table 6.2. for different inlet Reynolds numbers.

![Nusselt Number](image_url)

*Fig. 6.8. Nusselt Number. (a) Tree net with $Re_{k=0} = 20$. (b) Serpentine pattern with $Re_{k=0} = 20$. (c) Tree net with $Re_{k=0} = 200$. (d) Serpentine pattern with $Re_{k=0} = 200*.}
In conclusion, the relative effect of pressure drop from bifurcations becomes more dominant at the higher branching levels. In spite of the large number of bifurcations in the tree net compared to a much lower number of turns in the serpentine flow pattern, the tree net proves significantly beneficial in terms of pressure drop.

6.6.3. Heat transfer

In the tree net, the flow becomes thermally fully developed at each branching level for $Re_{k=0} = 20$. This is seen in Fig. 6.8(a) from the variation of the Nusselt number which evens out at a certain level when the flow is subject to develop. The same applies to the serpentine flow pattern, cf. Fig. 6.8(b). As expected, the heat transfer coefficient $h_k$ in the thermally fully developed region scales with $h_k \propto 1/d_k$ which implies that in the highest level of the tree net a more than four times higher heat transfer coefficient can be obtained than in the serpentine flow pattern, as seen from Figs. 6.9(a) and 6.9(b). Therefore, a smaller temperature difference is needed to transfer the same heat flux from the channel walls to the bulk fluid at the higher branching levels of the tree net. Due to the constant wall heat flux boundary condition used in this study and since the channel diameter gets smaller when going to higher branching levels, the length-specific heat transfer rate to the fluid decreases from one branching level to the next higher one, i.e. by the factor $\beta \equiv 0.794$. The heat transfer rate to a single channel of the branching level $k+1$ is $\gamma \beta \equiv 0.561$ times smaller than the heat transfer rate to a single channel of the branching level $k$. However, the heat transfer rate to all the channels of the branching level $k+1$ is $2\gamma \beta \equiv 1.12$ times larger than the heat transfer rate to all the channels of the branching level $k$. Only for large $L_k/d_k$ ratios and low Reynolds numbers or if the thermal development length can be neglected with respect to the channel length $L_k$, the assumption of constant Nusselt number to compute the heat transfer capability of the tree net is adequate.

For a ten times higher inlet Reynolds number to the tree net, i.e. $Re_{k=0} = 200$, the flow does not thermally develop any more, except at the highest branching levels, as seen from Fig. 6.8(c). When the flow passes through the bifurcation, secondary flow motions are initiated that degenerate the thermal boundary layer. This effect causes high-temperature fluid, which is captivated near the walls in the fully developed region, to mix with low-temperature fluid from the channel core, as illustrated in Fig. 6.5. This convective thermal mixing effect provides a smaller difference between the mean wall temperature $T_{w,m,k}$ and the mean fluid
temperature $T_{m,k}$ and, due to the constant wall heat flux, leads to an increase of the local Nusselt number $\text{Nu}_k$ in the straight channels right after bifurcations, cf. Fig. 6.8(c). The effect of thermal mixing caused by secondary flow motions and reinitiated at each bifurcation becomes dominant at this inlet Reynolds number level and the Nusselt number reaches a peak value of $\text{Nu}_{k=1} = 15.1$ at a distance $\xi_{k=1}/\xi_{k=1,\text{max}} = 0.106$ after bifurcating. This value is almost five times larger than the Nusselt number of a thermally and hydrodynamically fully developed flow. For higher branching levels, the peak Nusselt number decreases from one level to the next higher. The effectiveness of thermal mixing initiated at bifurcations depends on the Reynolds number. It is improved for increasing Reynolds numbers and vice versa. Since the Reynolds number decreases from one branching level to the next higher one, i.e. according to $\text{Re}_{k=1}/\text{Re}_k = 1/(2\beta) \approx 0.630$, thermal mixing becomes less effective at the higher branching levels which manifests itself in the above mentioned decrease of the peak Nusselt number from one level to the next higher one. The local heat transfer coefficient increases from one branching level to the next higher with high local peaks due to thermal mixing, cf. Fig. 6.9(c). In many applications, e.g. fuel cell cooling and electronics cooling, a thermofluidic design for thermal management is subject to the constraint of a maximum temperature difference within the considered system. Therefore, when attempting to transfer larger heat fluxes under such a constraint, higher heat transfer coefficients are required since they allow a certain heat flux to be transferred at a smaller temperature difference. In this respect, the tree net proves significantly beneficial, as shown in Figs. 6.9(a)-6.9(d).
Fig. 6.9. Heat transfer coefficient. (a) Tree net with Re$_{\infty}$ = 20. (b) Serpentine pattern with Re$_{\infty}$ = 20. (c) Tree net with Re$_{\infty}$ = 200. (d) Serpentine pattern with Re$_{\infty}$ = 200.
Fig. 6.10. Mean fluid temperature, mean wall temperature, and maximum wall temperature. (a) Tree net with \( \text{Re}_{W}=20, \quad q'' = 776.8 \text{ W m}^{-2} \text{ K}^{-1} \). (b) Serpentine pattern with \( \text{Re}_{W}=20, \quad q'' = 776.8 \text{ W m}^{-2} \text{ K}^{-1} \). (c) Tree net with \( \text{Re}_{W}=200, \quad q'' = 7768 \text{ W m}^{-2} \text{ K}^{-1} \). (d) Serpentine pattern with \( \text{Re}_{W}=200, \quad q'' = 7768 \text{ W m}^{-2} \text{ K}^{-1} \).
The higher the branching level, the more beneficial it proves. Hence, when considering a single tree net, a higher maximum heat rate could be transferred than with the serpentine flow pattern, if a certain maximum temperature difference is imposed on the two systems, as seen from Figs. 6.10(a)-6.10(d). On the other hand, reduced temperature differences needed to transfer a constant wall heat flux at the higher branching levels imply a reduced maximum temperature difference within the entire system. At $Re_{\text{w}0} = 200$, a maximum temperature difference between $T_{w,max}$ and $T_{m,min}$ of 12.0 K is obtained from the tree net, compared to the corresponding value of 16.0 K from the serpentine flow pattern. For $Re_{\text{w}0} = 20$ and with a ten times lower wall heat flux than in the higher Reynolds number case, these two values are closer together, as seen from Figs. 6.10(a)-6.10(d). The higher the wall heat flux and the larger the total number of branching levels, the more advantageous the single tree net with respect to small temperature differences. Providing a uniform temperature distribution is one of the previously mentioned important requirements for effective thermal management in polymer electrolyte fuel cells.

For a double tree net, this argumentation no longer holds. The same maximum temperature difference will be obtained from a double tree net and from a serpentine flow pattern of identical surface area and with identical constant wall heat flux. However, it is still thermodynamically desirable to transfer a certain heat flux with a small temperature difference because of smaller corresponding entropy generation. In addition, there is room for the transfer of higher heat fluxes if needed, by increasing the temperature difference. As an example, a substantially higher overall heat transfer rate could be obtained from the single or double tree net compared to the serpentine flow pattern of the same surface area, if instead of the constant wall heat flux a constant temperature difference, $T_{w,m,k} - T_{m,k} = \text{const.}$, could be maintained along the entire channel system. This can be seen from the variation of the mean wall temperature and the mean fluid temperature in Figs. 6.10(a) and 6.10(b): In the fully developed regions of the tree net, the difference between the mean wall temperature and the mean fluid temperature decreases from one branching level to the next higher whereas in the serpentine pattern this difference remains constant. Enforcing such a constant temperature difference in all the branching levels of the tree net would imply larger heat fluxes at the higher branching levels and therefore the curves indicating the variation of the mean fluid temperature would get steeper from one branching level to the next higher. Hence, under such conditions, a higher mean fluid temperature would be obtained at the end of the three net than at the end of the serpentine pattern. Alternatively, in trying to get the same mean fluid
temperature at the end of both configurations, a tree net with a smaller number of branching levels would be necessary which would further reduce the amount of pressure drop in the tree net.

Finally, it is worth mentioning that the effect of viscous dissipation can be safely neglected in the cases considered so far, as seen from the local Brinkman numbers, which are in the order of $1 \times 10^{-6}$. This was also numerically verified by simply dropping the viscous dissipation term out of the energy equation and then comparing with the former results.

6.7. Conclusions

A thorough three-dimensional forced convection model was presented for two geometrical channel configurations with constant wall heat flux: a tree-like net and a serpentine flow pattern having the same surface area. The tree network configuration represents the main novel concept of this paper for cooling systems in applications such as fuel cells and electronic devices. The serpentine configuration is typical in the cooling of PEM fuel cells and provides a basis of comparison.

It is found that the tree net with six branching levels generates almost half the pressure drop than the corresponding serpentine flow pattern having the same surface area and inlet Reynolds number. The effect of pressure drop from bifurcations and turns is substantial and should not be neglected for simplicity by using fully developed flow friction factors in the considered cases. Although the number of bifurcations in the tree net is larger than the number of turns in the serpentine flow pattern, from which one would expect a lower pressure drop from the serpentine flow pattern, the tree net proves to be markedly beneficial in terms of pressure drop.

In addition to hydrodynamic advantages, the tree net further provides a larger heat transfer capability than the serpentine pattern. Laminar mixing by secondary flow motions initiated at bifurcations causes substantially improved local Nusselt numbers. Much higher heat transfer coefficients are obtained for the tree net which implies that at the higher branch levels, a certain heat flux can be transferred with a smaller temperature difference. A much higher heat transfer rate could be obtained for the tree net by increasing this temperature difference. If for the water temperature it is possible to reach the boiling temperature, i.e. if the cell would be operated above this temperature level, evaporation can occur, leading to different regimes of two-phase flow in the cooling channels. This case was not investigated in the present study which focused on the single-phase flow regime.
Due to their intrinsic advantage with respect to both heat transfer and pressure drop, tree-like nets have the potential to significantly aid the thermal management in polymer electrolyte fuel cells at different length scales as well as in other thermal systems.

References


Summary

In this thesis, the focus is on computational modeling of polymer electrolyte fuel cells and direct methanol fuel cells, the investigation of the fundamental multiphase transport phenomena in the fuel cell, and the development of novel multi-scale flow structures, aiming at achieving higher power densities and efficiencies. Double-staircase-shaped and pyramidal-shaped tree network channel systems are introduced as novel multi-scale flow structures for high-performance polymer electrolyte fuel cells and direct methanol fuel cells. In addition, porous materials as fluid distributors in polymer electrolyte fuel cells are investigated. In this thesis it is recognized the first time that it is imperative that fluid flow irreversibilities be considered if the power density of a fuel cell is to be maximized. Constrained multiparametric genetic optimization of the entire geometric structure and operating conditions of the fuel cell is performed the first time. It is shown that downscaling of the channel width and the current collector rib width provides higher electric power densities since the transport phenomena occur at reduced effective lengths. Optimum geometric aspect ratios are identified at decreasing length scales.

The models that are developed and used in this dissertation to describe transport in porous media are macroscopic models, implying that the governing equations are averaged over a representative elementary volume. The latter has a characteristic diameter that is much larger than the characteristic pore diameter but at the same time also much smaller than the characteristic length scale of the domain. This means that the transport phenomena are not resolved for at the pore level. Instead, effective transport properties, such as effective mass diffusivities, effective electrical conductivities, and effective thermal conductivities are employed in order to account for specific porous structures. Such effective properties are usually correlated in terms of the porosity and the liquid water saturation, involving material-specific functional forms. Concerning liquid water transport, diffusion mass transfer, electric
current transfer, and heat transfer, more accurate and material-specific functional forms are required to improve computational modeling. Such functional forms may be extracted from microscopic pore-scale modeling, in which the governing transport phenomena are solved for at the pore level within a geometrically accurately reconstructed computational domain, or from detailed experiments. Models are currently validated using global or locally resolved current density measurements. In view of the large number of different transport phenomena, such validation procedures are questionable. In the future, experiments must provide spatially- and time-resolved information about all the relevant governing transport phenomena within the different domains, in order to improve the modeling capabilities.
Curriculum vitae

Stephan Martin Senn
Born on September 24th, 1977.
Citizen of Boniswil AG, Switzerland.

Education
1984 – 1989 Primarschule, Möriken, Switzerland.
1997 – 2002 Studies at the Department of Mechanical and Process Engineering at the Swiss Federal Institute of Technology (ETH Zurich).
03/2002 Diploma in Mechanical Engineering, ETH Zurich.
04/2002 – 04/2005 Ph. D. candidate, research and teaching assistant. Laboratory of Thermodynamics in Emerging Technologies, Institute of Energy Technology, Department of Mechanical and Process Engineering, Swiss Federal Institute of Technology (ETH Zurich).
Advisor: Prof. Dr. Dimos Poulakakos.

Professional experience
06/1993 – 10/2001 Assistant, Urs Senn Steuer- und Unternehmungsberatung, Aarau.
03/1999 – 07/1999 Hilfsassistent, Mechanics I, ETH Zurich.


04/2002 – 05/2005 *Supervisor* of 2 diploma theses and 2 semester theses, ETHZ.


A. Refereed journal articles


**B. Refereed conference articles**


**C. Conference and symposium proceedings**


D. Research reports


