Numerical simulation of methanol crossover in a

Flowing Electrolyte Direct Methanol Fuel Cell

By

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Abstract

Direct methanol fuel cells with proton exchange membranes (PEM-DMFCs) provide compact power supplies with high energy density for applications such as portable electronic equipment. However, the efficiency is significantly reduced by methanol crossover, causing reduced cell voltage and redundant fuel dissipation. The simple concept of flowing electrolyte direct methanol fuel cells (FE-DMFCs) solves this problem. In this design, any methanol penetrating the anode-membrane interface is effectively removed by the flowing electrolyte, thus hindering its arrival at the cathode.

A computational fluid dynamics (CFD) model is created to analyze methanol transport in the FE-DMFC by numerically solving the 3D convection-diffusion equation. Average methanol flux at anode and cathode (crossover) is simulated and compared to the equivalent PEM-DMFCs without flowing electrolyte, verifying that the rate of methanol crossover can be drastically reduced. Diffusion is found to be the dominate means of crossover, although the electro-osmosis contribution increases with current density. Performance of the FE-DMFC at different operating conditions is analyzed, and it is concluded that thin electrolyte channels with high flow rates is the optimum choice to reduce methanol crossover while maintaining good proton transfer characteristics.
This thesis is based on the following journal papers:


To my parents, for their endless support
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1 Introduction

1.1 Background

A fuel cell is an electrochemical device that converts a fuel to electrical power. The core of the fuel cell is its membrane electrode assembly (MEA) that contains two porous electrodes, anode and cathode, separated by an ion conducting electrolyte as shown in Fig. 1.

![Figure 1: Schematic of a conventional fuel cell MEA with proton conducting electrolyte.](image)

Most fuel cells use hydrogen as fuel and oxygen in the ambient air as oxidant, to produce water and electric current. The sides of the MEA are in contact with the fuel and oxidant channels, which provide reactants for the electrochemical reactions at the electrodes. All these components are supported by a metallic backing layer enclosing the single cell. The fuel is oxidized at the anode catalyst sites, producing electrons that move through an external load to the cathode, thus generating electrical power. The current-voltage characteristics, also called the polarization curve, are determined by the reaction rates and internal losses of the fuel cell.
Although invented back in the 19th century, fuel cells are still considered a new technology. The main dilemma is the need for expensive novel materials and advanced manufacturing processes, making them outscored by competing technologies such as the internal combustion engine. Utilization of fuel cells has therefore been limited to applications that appreciate other advantages like high power density and reliability, and where cost competitiveness is not the primary target. Alkaline fuel cells were an important part of the US space program in the 1960s, supplying electrical power and pure drinking water by low-weight systems in an environment where cost is secondary. The other main existing market-ready application is secure backup power systems. Phosphoric acid fuel cells, a medium-temperature fuel cell with acid electrolyte, have been tested and evaluated for this purpose for many years and are often considered among the most reliable backup power systems on the market.

High efficiency and low emissions combined with an extremely simple mechanism without any moving parts make fuel cells very competitive for a variety of other applications, if the cost targets can be accomplished. Several new fuel cell designs are emerging, such as the low-temperature hydrogen fuelled proton exchange membrane fuel cell (PEMFC) and the high-temperature solid oxide fuel cell (SOFC) that handles various fuels like natural gas. Applications range from micro scale fuel cells for portable electronic equipment to large scale fuel cell power plants for combined heat and power generation. Portable computers and cellular phones are likely to become the first fuel cell powered products ready for the mass market. For such appliances, low-temperature fuel
cells with proton exchange membranes (PEM) as electrolytes are being adopted. Liquid fuels are preferred because of simple storage and handling, although the anode fuel oxidation process is more complex. One of the best available liquid fuels in terms of system overall efficiency (also called well-to-wheel efficiency) is methanol [1], that can be utilized directly in a direct methanol fuel cell (DMFC). For medium-scale applications such as transportation, the DMFC cannot yet compete with the PEMFC, mostly due to its comparatively low cell efficiency and expensive catalysts [2]. On the other hand, for systems where size and weight are more important, it exhibits high potential. The power densities and energy densities of DMFCs are superior, even compared to newly developed lithium ion batteries [2]. The current obstacles are low cell efficiency and high cost, factors that must be improved to enable mass market penetration.

1.2 Methanol crossover

The cell reactions of a DMFC are:

$$\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6e^- \quad \text{Anode}$$

$$\frac{3}{2}\text{O}_2 + 6\text{H}^+ + 6e^- \rightarrow 3\text{H}_2\text{O} \quad \text{Cathode}$$

$$\text{CH}_3\text{OH} + \frac{3}{2}\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{CO}_2 \quad \text{Overall cell reaction}$$

Aqueous methanol and oxygen enters the cell, in which carbon dioxide and water is produced. The MEA is similar to the PEMFC equivalent, except for the anode catalysts used to oxidize methanol. Protons generated at the anode diffuse through the membrane to the cathode compartment, where they react with oxygen to form water. The function of
the membrane is to physically separate the electrodes, transfer protons from anode to cathode and act as an insulator to electric current. A good electrolyte has high proton conductivity, low methanol permeation and low electronic conductivity, and should also be as thin as possible. Polymer materials such as Nafion® are commonly adopted as proton exchange membranes, with sulphuric acid side groups attached to its polymer backbone structure. If the membrane is fully hydrated, its properties are similar to those of a dilute acid electrolyte. Protons are relatively loosely bound to the sulphuric acid side groups and can easily be transferred across the membrane when the fuel cell is in operation.

Methanol is water soluble and thus mobile in a hydrated membrane. Investigations of the most common polymer membrane material, Nafion®, have identified that methanol can penetrate sulphonic acid membranes [3]. This transfer of methanol to the cathode, called methanol crossover, leads to a significant loss in oxygen reduction performance at the cathode. A mixed potential arises when methanol is oxidized at the cathodic catalyst sites, thus reducing cell voltage. Apart from that, crossover is a substantial loss of fuel that produces no current whatsoever. Therefore, overall cell potential as well as fuel efficiency is reduced by this effect. Important strategies to reduce methanol crossover include anode fuel feed control and utilization of effective methanol oxidizing anode catalysts. There is much ongoing work in this field, and several advanced methods of minimizing crossover have been presented. For instance, the electrolyte material can be replaced with other high-performance materials [4, 5] or be modified chemically [6, 7] to achieve lower methanol permeation. Shim et al. [8] suggest the use of a methanol
impermeable barrier material wedged inside the membrane, allowing protons to pass but preventing methanol molecules from reaching the cathode catalyst layer. However, many of these materials show reduced proton conductivity.

### 1.3 Flowing electrolyte direct methanol fuel cells

Another method to reduce methanol crossover is also available, based on a membrane electrode assembly concept invented by Kordesch et al. [9, 10], where the membrane is partially replaced by a flowing electrolyte (dilute sulphuric acid). A schematic of the FE-DMFC is presented in Fig. 2.

![Simplified 2D cross-section of the FE-DMFC](image)

**Fig. 2: Simplified 2D cross-section of the FE-DMFC (not to scale).**

This novel design efficiently removes methanol from the electrolyte compartment by simple convection, and hinders its arrival at the cathode. The thin membrane layers that separate the different channels of the cell may be considered optional or be replaced by a thinner and cheaper material. Experimental data reveal that power density and efficiency
are significantly improved by the flowing electrolyte system [13]. The methanol in the electrolyte can be separated externally in the methanol clean-up system as presented in Fig. 3, thus obtaining high fuel efficiency [10]. Many numerical as well as mathematical models of the conventional DMFC can be found in the literature [11, 12], but to make the FE-DMFC competitive much more work is needed. A mathematical model of the FE-DMFC has been developed by Golriz et al. [13], which can be extended by support of numerical simulations.

![Diagram of a FE-DMFC system](image)

**Fig. 3:** One possible FE-DMFC system including a methanol clean-up system in the electrolyte loop.

The objective of this thesis is to numerically simulate methanol crossover characteristics for the FE-DMFC. The work includes a parametric study of methanol transport in the FE-DMFC by diffusion that numerically simulates methanol crossover for different operating conditions [14]. Fuel feed concentration, electrolyte channel thickness, electrolyte flow rate and channel orientation are studied. A more advanced model is also presented, that captures methanol crossover by diffusion as well as electro-osmosis [15], reinforcing the
results of the previous investigation. The new analysis includes simulations at various cell current densities and coefficients of electro-osmosis, and evaluates the possibilities to use enhanced electrolyte flow rates. Simulations of the conventional PEM-DMFC are also performed and compared to the results of the FE-DMFC study. The model is intended to indicate suitable operating conditions and to provide performance data for a future optimization study. The material presented here is a summary of the main findings of the two scientific papers by Kjeang et al. [14, 15]. The interested reader is encouraged to read the complete papers, provided in the appendix. The work has been performed at Carleton University in Ottawa, Canada, in collaboration with Calgary based Energy Visions Inc.
2 Method

To simulate methanol crossover for different operating conditions one needs to focus on the interior parts of the membrane electrode assembly. A good way to simplify the system is to ignore the effects of the complex fuel and oxidant channels and instead assume a constant methanol concentration at the electrode surfaces. The geometry of the domain for methanol transport is thus reduced to the parts shown in the sketch of Fig. 4. The domain consists of the anode side membrane next to the surface of the anode catalyst layer, the flowing electrolyte (FE) channel and the cathode side membrane attached to the cathode catalyst layer surface.

![Fig. 4: Domain for the methanol crossover analysis in the FE-DMFC (not to scale).](image)

2.1 Electrolyte channel flow

To determine the rate of methanol crossover in a FE-DMFC, the first step is to calculate the electrolyte velocity field in the FE channel. The steady-state velocity profile is
calculated based on conservation of mass and momentum in three dimensions. Momentum conservation is described by the 3D Navier-Stokes equation for incompressible fluids in an Eulerian frame with no source term and ignored gravity

$$\rho(v \cdot \nabla)v = -\nabla P + \mu v \nabla^2 v$$ \hspace{1cm} (1)

For the particular geometry of the FE channel (main flow in longitudinal direction \((x)\) from inlet to outlet, channel width \((L_z)\) much larger than the transverse thickness between the membranes \((L_y)\), see Fig. 4) the flow in the middle of the channel can be modeled as a two-dimensional steady-state flow between two flat plates caused by a pressure gradient in the longitudinal direction (Poiseuille flow). The analytical solution of Eq. (1) with no-slip boundary conditions is a linear pressure gradient \((\Pi)\) along the electrolyte flow, and

$$v_x(y) = \frac{\Pi}{2 \mu_y} y(L_y - y)$$ \hspace{1cm} (2)

This laminar fully developed parabolic velocity profile has zero velocity at the top and bottom membrane surfaces and a maximum in the center of the channel. It is assumed to be representative for the bulk of the flow, except near the channel edges at \(z = 0\) and \(z = L_z\). There is also a small fluid flow in the transverse direction from anode to cathode \((v_y)\) due to electro-osmosis, whose origin is described with the species transfer in the next chapter.
2.2 Species transfer in the MEA

Species movement normally occurs because of gradients in chemical potential. The most common way to move a body of fluid is to apply a pressure gradient, like in the main electrolyte flow. The pressure gradient in the transverse direction between the electrodes is assumed to be zero everywhere, and water flux by diffusion is expected to be negligible. For dilute methanol in water, the obvious concentration gradient between the electrodes causes methanol transport by diffusion.

The flow of electric or ionic current cause fluid flow by a phenomenon described as the electron wind [16]. In electrochemical devices like fuel cells, this force is called electro-osmosis. It leaves the polymer structure of the membranes intact, but induces water transport along the direction of proton flow towards the cathode [17], determined by

\[
J_{H_2O} = \frac{i}{F} \lambda
\]  

The coefficient of electro-osmosis (\(\lambda\)) is equivalent to the number of water molecules dragged by each proton. Assuming uniform proton flux equal to the cell current density (\(i\)), the previously discussed transverse water velocity can now be calculated by

\[
v_y = \frac{iM_{H_2O}}{F \rho_{H_2O}} \lambda
\]
Methanol transport follows by convection, in the same manner as in the bulk electrolyte flow. For a dilute species like methanol in this case, chemical potential is assumed to equal solute concentration \( (c) \). Conservation of species in a 3D Eulerian frame is described by the convection-diffusion equation for time dependent solute diffusion as

\[
\frac{\partial c}{\partial t} + \mathbf{v} \cdot \nabla c + \nabla (D \nabla c) = 0
\]  

(5)

The first term represents the change in time, the second one is the convective term and the third one is the diffusive term. \( D \) denotes the diffusivity of the solute species in the particular solvent. Methanol transport by convection as well as diffusion is solved simultaneously by applying this equation to the fuel cell MEA domain. For this purpose, a locally developed CFD code called SimManTec that solves the equation by a 3D transient nonlinear space-time method is utilized. A continuous Galerkin method in space and a discontinuous method in time are used to discretize the domain. Dirichlet boundary conditions are applied to the anode and cathode surfaces facing the membranes. A fixed methanol concentration in the range of 0-4 M is applied at the anode surface, assuming that the methanol concentration along the anode surface facing the anode side membrane is the same everywhere. In reality, anode surface concentration depends on cell current density, as reported by Jeng and Chen [18]. At the cathode catalyst sites, most or all methanol that arrives is expected to oxidize or evaporate instantly, and the methanol concentration is assumed to be zero.
3 Results and discussion

3.1 Model validation

The model is validated by applying the 3D advection-diffusion equation to a simple 1D PEM domain consisting of four equally sized elements and five nodes. The numerical results at high current density are compared to the 1D analytical solution in Fig. 5. The methanol concentration distribution is shown to be very accurate. The analytical result for zero current density is added as reference case, and the effect of electro-osmosis can clearly be seen. At zero current density, there is only diffusion and the curve is completely linear. Electro-osmosis appears for nonzero current densities and the curve gets bent towards the cathode side. The numerical results for methanol flux at anode and cathode deviate about 1% compared to the analytical solution.

![Graph showing methanol concentration distribution](image)

Fig. 5: Methanol concentration distribution for the 4 element 1D PEM test case compared to the analytical solution.

Conditions: \( c_{CH_{3}OH}^{a} = 1 \text{ M}, i = 0.5 \text{ A cm}^{-2}, \lambda = 2.5 \)
3.2 3D simulations

Simulations of methanol transport from anode to cathode are performed on the entire 3D domain shown in Fig. 4. Aspect ratios in the electrolyte channel are large (length $L_x = 50$ mm, width $L_z = 50$ mm and thickness $0 < L_y < 2$ mm), which implies that the behavior along the channel width direction is fairly constant. The magnitude of methanol transport only differs near the $z$-edges, where viscous effects exist. The thickness of these viscous edge effects is shown to be negligible compared to the channel width, which is verified by comparing 3D and 2D results [14].

3.3 Parametric study

For the purpose of this study, to simulate methanol crossover for various operating conditions and determine the influence of different variables, a complete 3D model is extensive. In fact, a more accurate parametric study can be performed using single slice geometries, basically in 2D, which ignore the viscous edge effects and focus on performance in the bulk of the electrolyte channel flow. Fig. 6 presents an illustration of the results attained with the single slice model in the FE channel inlet region. Methanol entering through the anode membrane is effectively removed by the flowing electrolyte and its arrival at the cathode is hindered. However, methanol concentration in the electrolyte increases towards the channel outlet and methanol crossover cannot be stopped completely.
Methanol flux at the anode and cathode (crossover) is analyzed as a function of anode surface methanol concentration. All fluxes are shown to be proportional to the anode surface concentration, which is valid for all current densities and other parameter settings. A reference anode surface concentration of $c_{\text{an}, \text{ref}} = 1 \text{ M}$ is therefore used in the study.

Proportional methanol fluxes also imply that the methanol crossover reduction for the FE-DMFC compared to the PEM-DMFC is independent of anode surface concentration. This is an important result valid at both electrodes, assuming that the concentration drop from the fuel feed stream to the anode surface is equal for both designs. One can thereby use a fixed anode surface concentration for further investigations.

The remaining variables cannot be extracted and analyzed separately. Instead, simulations are run for various combinations of settings. First of all, anode and cathode methanol flux is simulated at zero current density as a function of electrolyte flow rate.
and channel thickness. Methanol crossover reduction achieved with the FE-DMFC compared to the PEM-DMFC at zero current density and constant anode surface concentration is demonstrated in Fig. 7. The reduction obviously increases with electrolyte flow rate and channel thickness. For a 1.8 mm thick channel at high flow rates, methanol crossover reduction is approaching 100%. The drawback with thick channels is that the proton resistance is proportional to the channel thickness, which is likely to reduce cell voltage. To maintain high flow rates, additional pumping power is required. A complete crossover reduction is therefore not entirely an asset, and one should particularly avoid unnecessarily thick channels.

![Graph showing reduction of methanol crossover](image)

**Fig. 7:** Reduction of methanol crossover compared to the PEM-DMFC for various FE channel thicknesses and volumetric flow rates, at zero current density.

For the results of Fig. 7, methanol transport takes place by pure diffusion. Electro-osmosis appears in addition to diffusion at nonzero current densities, when the fuel cell is switched on. Methanol crossover as well as anode methanol flux thus increases with current density. Anode methanol flux also increases with flow rate and decreases with...
channel thickness. Enhanced anode flux improves methanol transfer from the fuel channel to the anode catalyst layer, which in turn may improve anode reaction rates. The unused fuel captured by the flowing electrolyte must however be recovered to maintain high fuel efficiency.

![Graph of anode methanol flux reduction](image1)

![Graph of methanol crossover reduction](image2)

**Fig. 8:** Anode methanol flux reduction (a) and methanol crossover reduction (b) compared to the PEM-DMFC as a function of electrolyte flow rate. The numbers indicate channel thickness.

*Conditions: \( i = 0.3 \text{ A cm}^{-2}, \lambda = 2.5 \)*
The most likely mode of operation is at peak power current density, which for the FE-DMFC is near 0.3 A/cm² [19]. Methanol crossover reduction at this current density is therefore analyzed in detail for a selection of thin electrolyte channels, as presented in Fig. 8. The coefficient of electro-osmosis ($\lambda$) is set to 2.5, as suggested by Mazumder [20]. Anode methanol flux appears to be in the same range as for the PEM-DMFC.

Negative reduction, as for the 0.15 mm and 0.30 mm channels, means that anode flux is greater than for the PEM-DMFC, which might be beneficial from a system point of view. Methanol crossover is significantly reduced for all channels at nonzero flow rates. If one wants to achieve 75% reduction, it is sufficient with a 0.15 mm channel at high flow rate (0.04 cm³ s⁻¹) or a 0.3 mm channel at low flow rate (0.02 cm³ s⁻¹). For 85% reduction, a 0.3 mm channel at high flow rate or a 0.6 mm channel at low flow rate is recommended.

### 3.4 Electro-osmosis

As mentioned, crossover appears as pure diffusion at zero current density. If the total flux is measured for nonzero current densities, one can let the increase in crossover be equal to the electro-osmosis contribution. Fig. 9a shows typical results achieved with this strategy at constant anode surface concentration. Diffusion is the dominating methanol crossover component even for current densities in the high range. For all cases investigated, the electro-osmosis fraction of the total methanol crossover is less than 50%. In a real operating scenario, the methanol concentration drops when oxidation takes place at the anode catalyst layer, reducing both components at high current densities.
Fig. 9: Typical diffusion and electro-osmosis methanol crossover contributions for the FE-DMFC at various cell current densities.

**Conditions:**

(a) Constant $c_{CH_3OH}^{a}$ = 1 M, $L_y$ = 0.6 mm, $\dot{V}$ = 0.02 cm$^3$ s$^{-1}$, $\lambda$ = 2.5

(b) Variable $c_{CH_3OH}^{a}$ [18], $L_y$ = 0.6 mm, $\dot{V}$ = 0.02 cm$^3$ s$^{-1}$, $\lambda$ = 2.5

The plot of Fig. 9b has the same parameter settings as Fig. 9a except for the anode surface concentration, which in (b) decreases with cell current density according to the values given by Jeng and Chen [18] for a PEM-DMFC. The magnitude of both methanol
crossover contributions drops considerably with current density. However, the diffusion and electro-osmosis fractions remain the same as in Fig. 9a. For further investigation, the entire anode compartment and its concentration drop must be included in the FE-DMFC model.

3.5 Channel orientation

Methanol concentration in the fuel feed channel has its maximum at the inlet and decreases gradually towards the outlet. If one assume that the fuel feed channel is straight, the anode surface concentration thus becomes linear along the fuel flow direction. There are three options of electrolyte and fuel channel orientations: parallel flow, counter flow and cross flow. To reduce methanol crossover, counter flow is revealed as the superior choice. Fig. 10 shows the improvements achieved with counter flow orientation compared to parallel flow and cross flow.

![Graph showing methanol crossover reduction](image_url)

**Fig. 10: Reduction of methanol crossover for counter flow compared to parallel flow and cross flow.**

*Conditions: $L_y = 0.6$ mm, $i = 0$*
3.6 Nonzero inlet methanol concentration

If the FE channel outlet methanol concentration is kept low or if some of the methanol is recovered externally, it is possible to re-circulate the electrolyte to the inlet and use it again. Results for various inlet methanol concentrations are presented in Fig. 11 for two randomly selected sets of operating conditions, case 1 and case 2. The performance of the FE-DMFC decreases linearly with inlet concentration for both cases. At an inlet concentration of 50% of the anode surface concentration, average methanol flux is equal at both electrodes. The system can still be considered to run at inlet concentrations below 20%, with its performance somewhat reduced.

![Graph showing methanol crossover reduction at nonzero inlet concentrations for case 1 and 2.](image)

**Fig. 11: Methanol crossover reduction at nonzero inlet concentrations for case 1 and 2.**

**Case 1:** $c_{CH_3OH} = 1$ M, $L_y = 0.15$ mm, $\dot{V} = 0.04$ cm$^3$ s$^{-1}$, $i = 0.3$ A cm$^{-2}$, $\lambda = 2.5$

**Case 2:** $c_{CH_3OH} = 1$ M, $L_y = 0.6$ mm, $\dot{V} = 0.02$ cm$^3$ s$^{-1}$, $i = 0.1$ A cm$^{-2}$, $\lambda = 2.5$
3.7 Pumping power

The pumping power required to maintain the electrolyte flow is calculated analytically for the laminar velocity profile described by Eq. (2). Thin channels and high flow rates cause large pressure drops and high pumping power requirements. Among all the cases in the parametric study, the 0.15 mm thick channel with high flow rate has the highest pumping power, 1.8 µW. As a comparison, the maximum power output of a FE-DMFC single cell is determined from experimental data [19]. For a 50 x 50 mm$^2$ cell, it is approximately 1.7 W near 0.3 A cm$^{-2}$. Obviously, the electrolyte pumping power is negligible compared to the fuel cell power output, which approves utilization of high flow rates to reduce methanol crossover. If the unused fuel removed by the electrolyte is recovered externally, thin electrolyte channels with high flow rates thus provide very efficient FE-DMFC systems with substantially reduced methanol crossover.

4 Conclusions

1. Methanol crossover can be significantly reduced by the flowing electrolyte of the FE-DMFC design compared to the equivalent PEM-DMFC, thus improving efficiency.

2. Diffusion is the dominate means of methanol transport for all current densities, although the electro-osmosis component increases with current density.

3. Methanol crossover reduction for the FE-DMFC compared to the PEM-DMFC is independent of anode surface concentration. Counter flow is the superior choice of orientation for the fuel and electrolyte channels. Electrolyte
channel inlet methanol concentrations up to 20% can be allowed. Methanol
crossover is minimized for thick electrolyte channels with high flow rates, but
its proton resistance is proportional to the channel thickness.

4. Anode methanol transfer is maximized for thin electrolyte channels with high
flow rates, which could improve anode reaction rates.

5. The electrolyte pumping power is negligible compared to the fuel cell power
output, even at high flow rates. The FE-DMFC system efficiency could thus
be improved by using thin electrolyte channels with enhanced flow rates,
given that the unused fuel is recovered externally.

Nomenclature

\( c \) Concentration \([\text{mole m}^{-3}]\)

\( D \) Solute diffusivity \([\text{m}^2 \text{s}^{-1}]\)

\( F \) Faraday’s constant \([\text{C mole}^{-1}]\)

\( i \) Cell current density \([\text{A m}^{-2}]\)

\( J \) Species molar flux \([\text{mole s}^{-1} \text{m}^{-2}]\)

\( L_x \) Length of MEA and FE channel in longitudinal direction \([\text{m}]\)

\( L_y \) Thickness of FE channel in axial direction \([\text{m}]\)

\( L_z \) Width of MEA and FE channel in transverse direction \([\text{m}]\)

\( M \) Molar mass \([\text{kg mole}^{-1}]\)

\( P \) Pressure \([\text{Pa}]\)

\( t \) Time \([\text{s}]\)
\( \dot{V} \) Volumetric flow rate [m\(^3\) s\(^{-1}\)]

\( v \) Fluid velocity [m s\(^{-1}\)]

\( x \) Direction of FE flow (longitudinal) [-]

\( y \) Direction across FE channel (axial) [-]

\( z \) Direction of FE channel width (transverse) [-]

**Greek symbols**

\( \lambda \) Coefficient of electro-osmosis (number of methanol molecules dragged by each proton) [-]

\( \mu_v \) Kinematic viscosity [kg m\(^{-1}\) s\(^{-1}\)]

\( \Pi \) Pressure gradient [Pa m\(^{-1}\)]

\( \rho \) Density [kg m\(^{-3}\)]

**Sub- and superscripts**

\( a \) Anode surface location

\( CH_3OH \) Methanol

\( H_2O \) Water

\( ref \) Reference value
References


A Parametric Study of Methanol Crossover in a Flowing Electrolyte Direct Methanol Fuel Cell

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\textbf{Abstract}

Direct methanol fuel cells (DMFCs) have significant potential to become a leading technology for energy conversion in a variety of applications. However, problems such as methanol crossover reduce the efficiency and open circuit voltage of the cells. The novel design of flowing electrolyte direct methanol fuel cells (FE-DMFCs) addresses this issue. Methanol molecules are effectively removed from the membrane electrode assembly by the flowing electrolyte, and the unused fuel can be utilized externally.
In this paper, a general 3D numerical CFD model is established to simulate methanol crossover by convection-diffusion in the FE-DMFC. Illustrations of methanol concentration distribution and methanol molar flux densities are presented, and the performance is compared to conventional DMFCs. The results indicate that methanol crossover can be reduced significantly. A parameter study is performed where the influences of anode fuel feed concentration, electrolyte channel thickness and electrolyte volumetric flow rate on methanol crossover are evaluated. In addition, effects of various electrolyte channel orientations are determined. According to the simulations, counter flow is the superior choice of channel orientations to minimize crossover.

**Keywords:** Direct methanol fuel cell (DMFC); methanol crossover; numerical modeling; simulation; flowing electrolyte; proton exchange membrane (PEM)

## 1 Introduction

The research efforts and interests in fuel cell technology and development are increasing rapidly. Governments, companies and universities worldwide are gradually adapting to this new technology. Due to high efficiency and low emissions, fuel cells display a great variety of potential applications. The absence of moving parts and an extremely simple mechanism make fuel cells very competitive for small-scale applications. For such applications, low-temperature fuel cells with proton exchange membranes (PEM) are being adopted. Currently, efficient hydrogen PEM fuel cells dominate the market, but the problems with hydrogen storage and distribution are severe. Liquid fuels are much easier to handle although the conversion in fuel cells is more complex. One of the best available
liquid fuels in terms of system overall efficiency (also called well to wheel efficiency) is methanol [1], that can be utilized directly in a direct methanol fuel cell (DMFC). However, the DMFC cannot yet compete with hydrogen fuel cells for transportation purposes, mostly due to its comparatively low cell efficiency and expensive catalysts [2]. On the other hand, for systems where size and weight are more important, it exhibits high potential. The power densities and energy densities of DMFCs are superior, even when compared to newly developed lithium ion batteries [2]. The current obstacles are low cell efficiency and high cost, factors that must be improved to enable commercialization.

The efficiency of direct methanol fuel cells is reduced by two main bottlenecks, slow anode reaction kinetics and methanol crossover. Methanol crossover can be particularly severe in DMFCs with polymer electrolytes. Investigations of the most common solid polymer electrolyte material, Nafion®, have identified that methanol can penetrate sulfonic acid membranes [3]. It has also been shown that methanol crossover leads to a significant loss in oxygen reduction performance at the cathode due to a mixed potential. Apart from that, crossover is a substantial loss of fuel that produces no current whatsoever. Therefore, overall cell potential as well as fuel efficiency is limited by this effect. Control of anode fuel feed concentration and flow rate as well as utilization of effective methanol oxidizing anode catalysts are important strategies to minimize methanol crossover. There is much ongoing work in this field, and several more advanced methods of reducing crossover have been presented. For instance, the electrolyte material can be replaced [4, 5] or be modified chemically [6, 7] to achieve lower methanol permeation. Shim et al. [8] suggest the use of a methanol impermeable barrier between the electrodes, allowing protons to pass but preventing methanol
molecules from reaching the cathode catalyst layer. A method has already been introduced based on a membrane electrode assembly concept invented by Kordesch et al. [9, 10] where the membrane is replaced by a flowing electrolyte. This novel design efficiently removes methanol from the electrolyte department by simple convection. The methanol in the electrolyte can be separated e.g. by membrane methods and consumed or a small amount may be used up in a loaded control sensing cell which then automatically adjusts the methanol feed to the system [10]. Many numerical as well as mathematical models of the conventional DMFC can be found in the literature [11, 12], but to make the FE-DMFC competitive much more work is needed. A mathematical model of the FE-DMFC has been developed by Golriz et al. [13], which can be extended by support of numerical simulations.

The objective of this paper is to model the electrolyte channel of a flowing electrolyte DMFC and numerically simulate the effect of methanol crossover for different operating conditions. Parameters such as electrolyte flow rate, electrolyte channel thickness, fuel concentration and channel orientation will be studied in detail. Simulations of the conventional PEM-DMFC will also be performed and compared to the results of the FE-DMFC study. The model is intended to improve the knowledge of flowing electrolyte fuel cell performance and to serve as a vital part of a future optimization study.

2 Flowing Electrolyte Direct Methanol Fuel Cells

A general direct methanol fuel cell basically consists of a membrane electrode assembly (MEA) supported by gas diffusion layers and bipolar plates. The MEA contains two
porous electrodes (anode and cathode) immersed in an proton-conducting electrolyte. Fuel (aqueous methanol) is supplied to the anode compartment and oxidizes at the catalyst layer to form carbon dioxide, protons and electrons. The protons diffuse through the electrolyte to the cathode compartment, where they react with oxygen to produce water as the end product. The cell reactions are:

\[
\begin{align*}
\text{CH}_3\text{OH} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \quad \text{Anode} \\
3/2\text{O}_2 + 6\text{H}^+ + 6\text{e}^- & \rightarrow 3\text{H}_2\text{O} \quad \text{Cathode} \\
\text{CH}_3\text{OH} + 3/2\text{O}_2 & \rightarrow 2\text{H}_2\text{O} + \text{CO}_2 \quad \text{Overall cell reaction}
\end{align*}
\]

The electrons generated at the anode flow through an external load before arriving at the cathode, thus providing useful electrical power. A schematic of a general DMFC with proton exchange membrane (PEM) is presented in figure 1. The function of the membrane is to physically separate the electrodes, transfer protons from anode to cathode and act as an insulator to electric current. A good electrolyte shall have high proton conductivity, low methanol permeation and low electronic conductivity, and shall also be as thin as possible. Nafion® is the commonly used material, and very thin films can be produced. However, the problem of methanol permeation in these membranes leads to reduced cell voltage and low efficiency. The new concept of flowing electrolyte direct methanol fuel cells (FE-DMFCs) addresses this issue. Here, in one configuration, an electrolyte channel is immersed between two thin PEM layers as in figure 2. The flowing electrolyte (dilute sulfuric acid) effectively removes methanol from the MEA by convection, and hinder its arrival at the cathode. The MEA of the second generation FE-DMFC, with a 50 X 50 mm$^2$ surface area, still contains two thin layers of PEM (50 µm
thick) attached to the electrodes. However, the main function of these layers is to physically separate the different channels of the cell. The PEM-layers could be considered optional and may be removed or replaced by a thinner and cheaper material. The electrolyte channel width is a target for optimization. Other advantages of a circulating electrolyte system are simple thermal and water management; the possibility to remove side reaction products and impurities such as aldehyde residues, carboxylic acids or other intermediates produced during the oxidation of methanol; and the option to adjust the electrolyte flow rate relative to current density or fuel concentration to minimize fuel crossover. Moreover, methanol transport from the fuel channel to the anode catalyst layer is enhanced by the flowing electrolyte, which has been shown to improve performance at high current densities [14].

3 Method

As mentioned in the introduction, the objective of this work is to create a numerical model of the electrolyte compartment of the FE-DMFC and to simulate methanol crossover for various operating conditions. All parts of the fuel cell MEA between the catalyst layer of the anode and the catalyst layer of the cathode are included in the domain. The catalyst layers of the electrodes are assumed to be infinitely thin. The structure of the electrolyte department in a FE-DMFC is displayed in figure 2. Notice that it consists of two proton exchange membranes with a flowing electrolyte channel in between. A three-dimensional model is necessary due to the geometry of the fuel cell in general and the electrolyte channel fluid flow in particular. For this purpose, a computational fluid dynamics (CFD) model is an obvious choice.
Methanol crossover in direct methanol fuel cells occurs due to the driving forces of chemical potential gradients, pressure gradients and electro-osmosis [15]. For solutes, the chemical potential gradient equals the concentration gradient. If the solute diffusivity is assumed to be independent of concentration, the steady state methanol molar flux density across the membrane of a PEM-DMFC is described by

\[ \hat{n}_{\text{MeOH}} = \frac{D}{L_{\text{PEM}}} \Delta c - \frac{c_2 K}{L_{\text{PEM}}} \Delta P + \frac{\lambda}{nF} i = k_c \Delta c + k_p \Delta P + k_i i \]  

(1)

According to Wang et al [12], the flux due to the pressure gradient in this equation is small compared to the other fluxes and can therefore be neglected. At low current densities, the diffusion flux dominates and electro-osmosis flux is small. However, at high current densities both fluxes are significant. In a FE-DMFC, with a fluid flow present and an Eulerian formulation, diffusion is replaced by convection-diffusion. The process is more complex than pure diffusion, but the dominant effect is a suction mechanism that enhances mass transfer. In this context, especially at low current densities, the contribution of electro-osmosis may also be neglected. The flux in the membrane is thus simplified to

\[ \hat{n}_{\text{MeOH}} = -\frac{D}{L_{\text{PEM}}} \Delta c \]  

(2)
In this paper, only the convection-diffusion contribution is being analyzed. The diffusivity then becomes a crucial parameter for the quality of the results.

For the FE-DMFC, the temperature dependence of the diffusivity of methanol in Nafion®, \( D_{\text{MeOH/PEM}} \), as well as methanol in water, \( D_{\text{MeOH/H}_2\text{O}} \), must be determined (except for its high proton conductivity, dilute sulphuric acid is assumed to have the same properties as water). In general, diffusivity exhibits exponential temperature dependence such as

\[
D(T) = D_{\text{ref}} \exp \left( \frac{\Delta E}{R} \left[ \frac{1}{T_{\text{ref}}} - \frac{1}{T} \right] \right) \tag{3}
\]

Scott et al. [16] suggest \( D_{\text{MeOH/PEM}} = 4.9 \times 10^{-10} \text{m}^2 \text{s}^{-1} \) at 333K and \( D_{\text{MeOH/H}_2\text{O}} = 2.8 \times 10^{-9} \text{m}^2 \text{s}^{-1} \) at 363K as reference values for the relationship in Eq. (3), and \( \Delta E / R = 2436\text{K} \)

However, several other functions can be found. Kulikovsky [17] recommends the reference value of methanol diffusivity in water in void pores to be \( D_{\text{ref}} = 1.58 \times 10^{-9} \text{m}^2 \text{s}^{-1} \) at \( T_{\text{ref}} = 298\text{K} \), and use the temperature dependence

\[
D_{\text{MeOH/H}_2\text{O}}(T) = D_{\text{ref}} \exp \left( 0.026236(T - T_{\text{ref}}) \right) \tag{4}
\]
This is in agreement with the reference value for methanol in water given by Physics Handbook [18], \( D_{\text{MeOH} / \text{H}_2\text{O}} = 1.4 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1} \) at 291K, although both differs significantly from the value used by Scott et al. [16]. For methanol in Nafion®, Kulikovsky [17] uses

\[
D_{\text{MeOH} / \text{PEM}}(T) = 4.012 \cdot 10^{-13} \exp(0.024312T)
\]  

(5)

This function is also different than the function given by Scott et al. [16]. For this work, the diffusivities given by Scott et al. [16] are chosen, mainly because the operating temperature of the FE-DMFC is in the same range as their reference values. Note that the uncertainty of these values can be considered high.

The steady-state velocity profile in the FE channel is calculated based on conservation of mass and momentum in three dimensions. Conservation of mass for incompressible fluids can be described by the 3D continuity equation

\[
\nabla \cdot \n \n = 0
\]  

(6)

No-slip boundary conditions and the Reynolds number flow imply that \( v_y = 0 \) and \( v_z = 0 \) in the entire channel. Thus, assuming that the flux of methanol and water across the anode side membrane is small compared to the electrolyte flow, fluid flow takes place in the \( x \)-direction only. Momentum conservation is described by the 3D Navier-Stokes equation for incompressible fluids.
\[
\rho \frac{\partial \bar{v}}{\partial t} + \rho (\bar{v} \cdot \nabla) \bar{v} = -\nabla P + \rho \bar{g} + \mu_s \nabla^2 \bar{v}
\]  

(7)

If gravity is ignored, the steady-state equation can be written as

\[
\rho (\bar{v} \cdot \nabla) \bar{v} = -\nabla P + \mu_s \nabla^2 \bar{v}
\]  

(8)

For the particular geometry of the FE channel (main flow in \(x\)-direction from inlet to outlet, channel width much larger left to right (\(z\)) than between the top and bottom membranes (\(y\)) the flow in the middle of the channel can be modeled as a two-dimensional steady-state flow between two plates caused by a pressure gradient in the \(x\)-direction (Poiseuille flow). The solution of Eq. (8) with no-slip boundary conditions is a linear pressure gradient, \(\Pi\), along the electrolyte flow direction, and

\[
v_x(y) = \frac{\Pi}{2\mu} y(L_y - y)
\]  

(9)

This fully developed parabolic velocity profile has zero velocities at the top and bottom membrane surfaces and a maximum in the center of the channel. It is assumed to be representative for the bulk of the flow, except near the left and right channel edges at \(z = 0\) and \(z = L_z\). The thickness of these edge effects is assumed to be of the same order of magnitude as the channel thickness between the membranes. The velocity profile is assumed to have a parabolic shape where edge effects are present, with zero velocity at the edge increasing gradually to the free stream velocity as one moves away from the
edge. The free stream velocity is determined by Eq. (9) independently of the \( z \)-coordinate. The volumetric flow rate and mean velocity are obtained by surface integration. The Reynolds number is calculated by

\[
Re = \frac{\rho v_{\max} L}{\mu}
\]  

The characteristic length of the FE channel is its thickness, \( L_y \). Due to low velocities and thin channels, the electrolyte flow is expected to be laminar.

To solve the mass transfer problem in the presence of a velocity field, convection as well as diffusion must be considered. Conservation of species gives the convection-diffusion equation for time dependent solute diffusion in 3D as

\[
\frac{\partial \mu}{\partial t} + \vec{v} \cdot \nabla \mu + \nabla (\nabla \mu) = S
\]  

For the case with no internal chemical reactions or sources, Eq. (11) is simplified to

\[
\frac{\partial \mu}{\partial t} + \vec{v} \cdot \nabla \mu + \nabla (\nabla \mu) = 0
\]  

For a dilute species in a liquid solvent one can assume that the chemical potential equals solute concentration. Thus, one finally obtains Fickian advection-diffusion
\[
\frac{\partial c}{\partial t} + \vec{v} \cdot \nabla c + \nabla (-D \nabla c) = 0
\]  

(13)

The time dependent solute convection-diffusion equation in the presence of a velocity field, Eq. (13), applied to the fuel cell MEA domain, is solved using an in-house CFD software called SimManTec Framework. In this software code, the solute convection-diffusion equation is solved using a 3D transient nonlinear space-time method. The method treats time dependent problems like stationary problems using space-time meshes that discretize space and time independently. Usually, finite element methods use a semi-discrete algorithm, i.e., discretizes space using FEM and use what can be considered a finite difference method such as Crank-Nicholson in time. In problems where the domain undergoes deformations in time, the classical finite difference approach may become difficult to use. The space-time domain can be considered a four dimensional continuum, where time is treated as the fourth dimension space variable. But since information is transferred from earlier to later times, the standard stepwise approach from finite differences is preserved. A continuous Galerkin method in space and a discontinuous method in time are used for the discretization.

The methanol crossover model of the FE-DMFC is incorporated as a time dependent problem with constant velocity. Initially, the concentration is assumed to be linear across the MEA with zero velocity in the FE channel. The solver is then run with the Poiseuille velocity field until the steady-state solution is obtained. Here, steady-state is defined at the time step where the difference of integrated crossover compared to the previous step
is less than 0.2%. Time step size is chosen according to the accuracy criterion $0.1 < F_0 < 10$, based on the dimensionless Fourier number

$$F_0 = \frac{D \Delta t}{\Delta y^2}$$  \hspace{1cm} (14)

For the solute convection-diffusion problem, $\Delta y$ represents the mesh element size in the anode-to-cathode direction across the FE channel. The operating temperature is set to 60°C. Dirichlet boundary conditions are applied to the anode and cathode surfaces facing the membranes. Either constant or linear methanol concentration in the range of 1-4 M is applied at the anode surface, and zero concentration at the cathode surface. These settings assume that the methanol concentration along the anode membrane side surface is the same as the fuel feed concentration. Also, zero concentration at the cathode indicates that all methanol molecules reaching the cathode surface are being oxidized instantly at the catalyst sites. Neumann boundary conditions with zero molar flux density are applied to all other surfaces.

4 Results and discussion

4.1 Mesh convergence analysis and model validation

To get accurate results using the convection-diffusion solver it appears to be crucial to employ elements that are not too distorted or elongated. If the aspect ratio of the element blocks becomes too large, the solution may not converge. For the geometry of the MEA, which has thin membrane films of aspect ratios up to 1,000, this is particularly important. When meshing the MEA, this implies that the number of elements becomes very large.
Therefore, the mesh convergence analysis is carried out using a simplified geometry. The electrolyte flow rate, FE channel thickness and concentrations used as reference case are
\[ \dot{V} = 4 \cdot 10^{-8} \text{ m}^3 \text{ s}^{-1}, \ L_y = 0.6 \text{ mm}, \ c_a = 4 \text{ M} \text{ and } c_c = 0 \text{ M}, \text{ respectively.} \]

It is convenient to determine the necessary number of elements in the \( y \)-direction, which is of micron-scale, at first. For quality purposes on one hand and computational time on the other, 8 elements of eight-node bricks across the electrolyte channel is found to be the best choice. One element is enough across the thickness of the membranes where there is no fluid velocity present. The mesh convergence results are computed based on a single slice in the \( z \)-direction, which enables square element projections on the \( yz \)-plane. The element size in the \( x \)-direction is extended to test the accuracy of the results for different aspect ratios. The aspect ratio equal to 5 gives an error of about 0.2 % compared to the ideal case with perfectly cubic elements (aspect ratio 1). This can be considered a reasonable upper limit. 200 elements in the \( x \)-direction are suitable for the model, which corresponds to aspect ratio 3.33. Each \( z \)-slice thus consists of 2,000 elements and 4,422 nodes.

The model is validated for the case with zero FE velocity, which is a straightforward analytical calculation using Eq. (13). With zero velocity, the steady-state solution is

\[ \dot{n} = -D \nabla c = -D \frac{\Delta c}{L_y} \quad (15) \]
This constant methanol molar flux implies a linear concentration distribution across the membranes and the stationary electrolyte. The gradient is higher in the membrane material (low diffusivity) than in the flowing electrolyte (high diffusivity) and

\[ c_a - c_e = \Delta c_{PEM} + \Delta c_{FE} \]  \hspace{1cm} (16)

In this equation, \( \Delta c_{PEM} \) represents the sum of the concentration drops across both membranes in the MEA of the FE-DMFC. A simulation of the model is run for a single slice in the z-direction. The development of the expected concentration profile with time is monitored and steady-state is verified. Total methanol molar flux is determined by post-processing surface integration applied to the membrane parts. The average molar flux across the anode side PEM membrane is computed by

\[ \hat{n}_{ave} = \frac{1}{A_{PEM}} \int_A \hat{n}dA \]  \hspace{1cm} (17)

This gives \( \hat{n}_{ave} = 0.00671 \text{mole s}^{-1} \text{m}^{-2} \), which is constant throughout all parts when the electrolyte is immobile. The deviation from the analytical result is 0.03%. Also, the resulting concentration distribution is clearly linear as expected.

### 4.2 3D simulations

As a result of the mesh convergence analysis, 3D simulations of the entire domain from anode to cathode with cubic elements become computationally expensive. To be able to
run full 3D simulations of the 50 mm wide channel, the aspect ratio is increased from 3.33 to 5 and the number of elements in the $y$-direction reduced to 6. Also, a symmetry plane in the middle of the FE channel ($z = 25$ mm) is identified, cutting the MEA into two equivalent parts. With these modifications, the number of elements is reduced to 40,000. It is a trade-off in accuracy to reduce the number of elements but for simulations for illustrative purposes the precision is still acceptable.

Methanol crossover 3D simulations of the MEA part of the FE-DMFC is performed for the case with electrolyte flow rate $\dot{V} = 0.02$ cm$^3$ s$^{-1}$, FE channel thickness $L_y = 0.6$ mm and constant anode concentration $c_a = 4$ M. The time step size is chosen to have a Fourier number in the range $0.1 < Fo < 10$, and a time dependent simulation is run until steady-state is reached. Element Courant numbers are determined by

$$Co = \frac{v_{\text{max}} \Delta t}{\Delta x}$$

(18)

For the time step size chosen, $Co = 20$. The physical ratio of convection to diffusion is determined by the Peclet number for the problem

$$Pe = \frac{L_s v_{\text{ave}}}{D} = 3 \cdot 10^4$$

(19)

Apparently, convection is much stronger than diffusion. The results obtained consist of a velocity profile, methanol concentration distribution and molar flux density at all nodes.
As described, the velocity has a fully developed parabolic Poiseuille profile across the thickness of the FE channel. In the $z$-direction, the bulk of the flow is uniform except near the edges, where it is parabolic due to edge effects. For this velocity profile, the volumetric flow rate must be determined by surface integration applied to the channel intersection

$$\dot{V} = \int_A v_z dA$$  \hspace{1cm} (20)

The total volumetric flow rate becomes $\dot{V} = 1.81 \cdot 10^{-8} \text{ m}^3 \text{ s}^{-1}$, which is slightly lower than for the single slice model because of the edge effects in $z$. Edge effects can also be seen in the concentration distribution. Near the very edge, where the velocity approaches zero, the concentration is linear across the FE channel. This is not the case in the bulk of the fluid flow, where the flowing electrolyte efficiently removes most of the methanol penetrating the anode side membrane. A contour plot of methanol concentration in the middle of the FE channel is presented in figure 3. The figure clearly shows the build-up of a concentration edge effect in the $z$-direction, which appears to have the same thickness as for the velocity. The contours indicate that the bulk of the flow has uniform concentration distribution along the $z$-axis. In the case with zero fluid velocity, the concentration in the bulk would be equal to the concentration at the edge (pure diffusion). Obviously, convection is the dominate means of mass transfer in the electrolyte channel.

Methanol molar flux density across the anode and cathode surfaces is shown in figure 4. Methanol crossover (cathode flux) is significantly higher near the outlet of the channel
than close to the inlet. On the other hand, molar flux across the anode has its maximum at the channel inlet, and decreases along the flow direction. At the edge ($z = 0$), the flux across the anode is the same as the flux across the cathode (except near the inlet). That means, where the fluid velocity is zero no species are removed by convection and the only transport mechanism is pure diffusion. Further away from the edge, convection dominates. At a short distance from the edge, the flux is approximately the same as in the middle of the channel ($z = 25$ mm). Note that the anode flux is significantly larger than for pure diffusion due to the suction effect at the anode surface. The suction effect may enhance mass transfer in the catalyst layer of the anode and improve reaction-rates and efficiency. Contrarily, more methanol will mix into the flowing electrolyte. It is thus necessary to process or consume this electrolyte and methanol mixture externally. However, it is even more important to keep methanol away from the cathode catalyst layer. For this purpose, the flowing electrolyte shows great promise. Except very near the $z$-edge where the velocity is too small, methanol crossover is reduced to a minimum. The average molar flux density across anode and cathode is calculated by surface integration as in Eq. (17) to $\dot{n}_a = 0.01284$ mole $s^{-1} m^{-2}$ and $\dot{n}_c = 0.001962$ mole $s^{-1} m^{-2}$. In this case, 85% of the fuel penetrating the anode is removed by the flowing electrolyte, which is more than three times better than the case with zero electrolyte velocity.

As a comparison, this model is also run for the PEM-DMFC case, where the flowing electrolyte channel is removed completely. The two membranes are merged to one single membrane of thickness 0.1 mm. For this simple geometry, methanol flux is entirely one-dimensional and all of the species penetrating the anode will arrive at the cathode. The
results for \( c_a = 4 \text{ M} \) and \( c_c = 0 \text{ M} \) are \( \dot{n}_a = \dot{n}_c = 0.0196 \text{ mole s}^{-1}\text{m}^{-2} \). The methanol crossover in the FE-DMFC is reduced by 90% compared to this result.

### 4.3 Parameter study

For the overall performance of the FE-DMFC, a 3D model of at least half the MEA is essential. However, it is excessive for a detailed parameter study. A basically two-dimensional model of one single slice in the middle of the channel \((z = 25 \text{ mm})\), like the one used in the mesh convergence analysis, is instead considered. This slice with only one element in the \( z \)-direction is assumed to be representative for the whole geometry.

From a system point of view, the edge effect should be included. However, since the bulk of the geometry dominates the performance of the electrolyte channel, the single slice model serves the purpose of a parameter study. Simulations on the single slice domain are carried out for a variety of parameter input data. Methanol crossover can be modeled as a function of several variables such as operating temperature, pressure, FE velocity field and flow rate, FE channel dimensions, methanol concentration at anode and cathode, current density, cell voltage, etc. In this preliminary parameter study, focus is on three of these variables; methanol concentration at anode, electrolyte volumetric flow rate and FE channel thickness. The temperature is constant at 60°C, the cathode concentration is assumed to be zero and the methanol flux density is assumed to be independent of the other variables. Thus,

\[
\dot{n} = f(c_a, \dot{V}, L_y)
\]  

(21)
Since the concentration gradient is included in both time-independent terms in the convection-diffusion equation, Eq. (14), the anode concentration is expected to be an independent variable and is therefore treated separately, as in

\[ \dot{n} = f(c_a) \cdot f(\dot{V}, L_y) \]  

(22)

If the flow rate and channel thickness are held constant, one gets a linear concentration dependency

\[ \dot{n} = k_1 \cdot c_a \]  

(23)

Plots of the simulation outcome of methanol molar flux density across anode and cathode as a function of anode concentration are presented in figure 5a. Methanol crossover in the FE-DMFC equals cathode flux. Results for the PEM-DMFC are also shown, and for this type, methanol flux (crossover) is the same at both electrodes. Figure 5b displays three different flux fractions; crossover fraction for FE-DMFC, crossover fraction compared to PEM-DMFC and anode flux fraction compared to PEM-DMFC. These plots clearly show that methanol molar flux is directly proportional to anode surface concentration, which confirms the dependency suggested in Eq. (23). The quantitative results are similar to the results of the complete 3D simulation: methanol flux across the cathode is 87.2% lower than the anode flux, and methanol crossover is reduced by 91.4% compared to the PEM-DMFC. The reductions obtained are independent of anode concentration. Additional tests
are performed for other values of $V$ and $L_y$, and these results also show a linear dependency.

The results obtained for $c_a = 4$ M are also used to evaluate the accuracy of the single slice model. Table 1 shows average values of methanol flux from the single slice model as well as the full 3D model, which is used as the reference case.

As the single slice model ignores the edge effects at the left and right channel edges, it is expected to overestimate the reduction of methanol crossover. This is confirmed by the 14.5% reduction in flux across the cathode compared to the 3D case. In the same manner, anode flux is slightly higher. Moreover, the electrolyte flow rate is 8.8% higher than for the full 3D model that justifies the changes in methanol flux. Considering the fact that the models operate at different flow rates, the results of the single slice model are quite reasonable. In practice, edge effects can be avoided by constructing the electrolyte channel a few millimeters wider than the catalyst surfaces at the electrodes.

Simulations are run for several combinations of the two other variables, FE volumetric flow rate and FE channel thickness. Four different levels of each variable are used, and methanol concentration at the anode surface is constant. Element Courant numbers for the single slice model are in the range $5 < \text{Co} < 50$ and the problem Peclet numbers are between $10^4$ and $10^5$. The results of these tests are summarized in the surface plots in figure 6, which display the average methanol molar flux density as a function of both variables. The anode molar flux increases with flow rate and decreases with channel...
thickness. The methanol suction effect apparently is enhanced by an electrolyte high velocity and a thin channel. However, the appropriateness of inducing methanol suction is a matter for future consideration: it may be preferable to avoid methanol penetration of the anode, thus minimizing anode flux and the need for processing of unused fuel. For this scenario, a wide channel with a low flow rate is favorable. Nevertheless, anode flux in the FE-DMFC is still far below the value of the PEM-DMFC (0.02 mole s⁻¹ m⁻²). Cathode molar flux density (methanol crossover) on the other hand, is most certainly a means of minimization. Figure 7 displays the achieved reduction of crossover compared to the equivalent PEM-DMFC. To reduce crossover, high FE flow rates and wide channels are to be used. The effect of increasing either one of them appears to be of the same magnitude. Notice that except for the cases with zero flow rates, the crossover reduction is more than 65% for all combinations being tested.

It is also obvious that the volumetric flow rate and channel thickness variables cannot be treated independently. The overall output effect of increasing or decreasing one of the variables may be the same independent of the other variable, but the magnitude is likely to vary. For an overview of the effect of changing channel thickness, figure 8 shows results for constant flow rate \( \dot{V} = 0.02 \text{ cm}^3 \text{ s}^{-1} \). For that particular electrolyte flow rate, methanol crossover is kept low for all channel thicknesses analyzed. For \( L_y = 0.3 \text{ mm} \), the crossover is reduced by 80% and for \( L_y = 0.6 \text{ mm} \) the reduction is over 90% compared to the PEM-DMFC. The plots of figure 9 also take the other variable, electrolyte flow rate, into account. All four channel thicknesses are analyzed and compared to the PEM case. The results once again indicate significant removal of
methanol by the flowing electrolyte. Methanol crossover is reduced, even with zero flow rates. However, there is a problem with the insertion of the electrolyte channel. There is always a certain resistance in the electrolyte, not only for methanol, but also for protons. To maintain a high cell voltage, the rate of proton transfer from anode to cathode must be kept high and steady. Cell internal resistance is proportional to channel thickness, and it is important to avoid unnecessary wide channels. From this point of view, it is most likely better to increase the flow rate as a means of reducing crossover. The channel thickness can then be kept at a low value. Therefore, channel thicknesses larger than 0.6 mm are likely to be too wide and will not be analyzed further. Figure 10 displays fractions of methanol crossover for the 0.3 and 0.6 mm thick channels as a function of flow rate. For instance, if a crossover rate less than 20% (80% reduction) compared to the PEM-DMFC is desired, a 0.3 mm wide channel needs a flow rate of 0.02 cm$^3$ s$^{-1}$ whereas for a 0.6 mm channel, 0.01 cm$^3$ s$^{-1}$ is sufficient. For crossover rates below 10%, these flow rates should be doubled. The drawback with an increased electrolyte flow rate is the additional pump work needed. The pumping power must be monitored and included in an optimization study of the fuel cell performance.

To improve the performance of the FE-DMFC, the flowing electrolyte channel orientation is another important parameter. The function of the channel itself is not improved by changing its orientation, but its orientation art to the fuel channel is important. The anode surface concentration obviously depends on fuel channel orientation. Methanol concentration in the fuel feed has its maximum at the inlet and decreases gradually towards the outlet. Unlike the electrolyte channel, the fuel channel
has several bends and a complex geometry. It extends over the anode surface like a maze. For the model, the fuel channel is assumed to be straight, with decreasing methanol concentration along the direction of the flow. This implies a linear anode surface concentration. There are three options of electrolyte and fuel channel orientations: parallel flow, counter flow and cross flow. Simulations of parallel flow and counter flow are performed for a linear anode concentration starting at 4 M and ending at 2 M. Simulation results are compared to the case of constant anode concentration \( c_a = 3 \text{ M} \) in figure 11. Apparently, methanol crossover is lower for counter flow than for parallel flow although the anode flux is enhanced. For parallel flow, the crossover rate is even higher than for constant anode concentration. Figure 12 presents an analysis of the accomplished crossover reduction for counter flow orientation. The results indicate excellent improvements using counter flow. For an electrolyte flow rate of 0.02 cm\(^3\) s\(^{-1}\), the reduction of methanol crossover is 26% and 15% compared to parallel flow and constant anode concentration, respectively.

### 5 Conclusions

A general three-dimensional numerical CFD model of the flowing electrolyte direct methanol fuel cell is used to simulate methanol crossover for a variety of operating conditions. Methanol concentration distribution and methanol molar flux densities are presented for the full geometry of the MEA. Compared to the equivalent Proton Exchange Membrane direct methanol fuel cell, methanol crossover is greatly reduced due to enhanced mass transfer by convection (90% reduction for reference operating conditions). The rate of crossover is shown to be higher in the presence of concentration
edge effects near the outer edges of the electrolyte channel than in the bulk of the electrolyte flow. It is also more severe near the outlet than at the inlet part of the channel. For a thorough study of various parameters and operating conditions, the general model has to be simplified based on a slice in the middle of the electrolyte channel, which ignores the edge effects. This study focuses on the effect of anode surface methanol concentration, flowing electrolyte channel thickness and volumetric flow rate. The average methanol molar flux density across the cathode surface (average methanol crossover) is shown to be directly proportional to the anode surface concentration. Combined analyses confirm that methanol crossover is inversely proportional to both channel thickness and flow rate. Thus, wide channels and high flow rates are needed to minimize it. Due to the amplified internal cell resistance arising for wide channels, it might be a better strategy to increase the flow rate than the channel thickness. But with increased flow rate, it is important to monitor the pump work needed and make sure it does not substantially reduce the system efficiency.

The convection mechanism also affects methanol flux across the anode surface. High flow rates and low channel thicknesses lead to enhanced anode methanol suction. This improves mass transfer in the anode catalyst layer, which may also improve the reaction rate. However, more fuel will be mixed in the electrolyte, which calls for external processing to maintain fuel efficiency. The anode flux is nevertheless significantly lower than for the PEM-DMFC.

For the case of linearly decreasing anode fuel concentration from inlet to outlet of the fuel channel, different electrolyte channel orientations are considered. Parallel flow and
counter flow are both compared to the general case of constant anode concentration. To reduce fuel crossover, counter flow is shown to be the superior channel orientation.

Overall, the results of this model are in relatively good agreement with experimental data [19]. The model can be improved further by adding the contributions of electro-osmosis and pressure gradients to the rate of methanol crossover, which is an ongoing work. More accurate values of the diffusivity of methanol in Nafion® and water also need to be determined. Further work includes modeling polarization characteristics and determining the internal cell resistance of the electrolyte. The overall objective is to optimize the flowing electrolyte channel by comparing gain in voltage by reduction of methanol crossover to ohmic losses and electrolyte pump work. Additional experiments and measurements of methanol crossover in the FE-DMFC would also be desired.

**Nomenclature**

- \( A \) Area \([m^2]\)
- \( c \) Concentration of methanol \([\text{mole m}^{-3}]\)
- \( c_v \) Specific heat at constant volume \([\text{J kg}^{-1} \text{K}^{-1}]\)
- \( c_2 \) Concentration of methanol at the cathode side of the PEM \([\text{mole m}^{-3}]\)
- \( D \) Solute diffusivity \([\text{m}^2 \text{s}^{-1}]\)
- \( \Delta E \) Activation energy \([\text{J mole}^{-1}]\)
- \( Fo \) Fourier number \([-\] \)
- \( i \) Cell current density \([\text{A m}^{-2}]\)
- \( k_1 \) Constant of linearity \([-\] \)
$k_c$  Constant [-]

$k_p$  Constant [-]

$k_i$  Constant [-]

$K$  Constant related to effective hydraulic permeability \([m^2 \ \text{s}^{-1} \ \text{atm}^{-1}]\)

$L_{PEM}$  Thickness of membrane [m]

$L_x$  Length of MEA in FE flow direction [m]

$L_y$  Thickness of FE channel [m]

$L_z$  Width of MEA transverse to FE flow direction [m]

$\dot{n}$  Methanol molar flux density \([\text{mole s}^{-1} \ \text{m}^{-2}]\)

$P$  Pressure [atm]

$\dot{q}$  Internal heat source \([\text{W m}^{-3}]\)

$R$  Universal gas constant \([\text{J mole}^{-1} \ \text{K}^{-1}]\)

$S$  Source of species \([\text{mole s}^{-1}]\)

$T$  Temperature [K]

$t$  Time [s]

$\dot{V}$  Volumetric flow rate \([\text{m}^3 \ \text{s}^{-1}]\)

$v$  Fluid velocity \([\text{m s}^{-1}]\)

$x$  Direction of FE flow [-]

$y$  Direction across FE channel [-]

$z$  Direction of FE channel width [-]
Greek symbols

\( \alpha \)  Thermal diffusivity \( [m^2 \ s^{-1}] \)

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

\( \lambda \)  Coefficient of electro-osmosis (number of methanol molecules dragged by each proton) \([-]\)

\( \mu \)  Chemical potential \( [J \ mole^{-1}] \)

\( \mu_v \)  Kinematic viscosity \( [kg \ m^{-1} \ s^{-1}] \)

\( \rho \)  Density \( [kg \ m^3] \)

Subscripts

\( a \)  Anode

\( ave \)  Average value

\( c \)  Cathode

\( FE \)  Flowing Electrolyte

\( max \)  Maximum value

\( PEM \)  Proton Exchange Membrane

References


Table 1. Comparison of the results obtained with the single slice model and the full 3D model.

<table>
<thead>
<tr>
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<th>Single slice model</th>
<th>Full 3D model</th>
<th>Diff.</th>
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<tr>
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<tr>
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<td>0.0197</td>
<td>0.0181</td>
<td>+8.8%</td>
</tr>
</tbody>
</table>
Figure captions

Fig. 1.  2D cut plane of a typical DMFC module with proton exchange membrane.

Fig. 2.  2D cut plane of the corresponding FE-DMFC with flowing electrolyte (simplified geometry, not to scale).

Fig. 3.  Methanol concentration (shaded) in the center of the FE channel ($L_y = 0.3$ mm). Fluid flow is in the $x$-direction. The contours represent constant concentration.

Fig. 4.  Anode (a) and cathode (b) methanol molar flux density along the direction of fluid flow ($x$) for various distances from the edge ($z$).

Fig. 5.  (a) Average methanol molar flux density across anode and cathode versus anode surface concentration for FE-DMFC and PEM-DMFC. (b) Methanol molar flux density fractions. Conditions: Volumetric flow rate $0.02 \text{cm}^3 \text{s}^{-1}$ and channel thickness 0.6mm

Fig. 6.  Surface plots of average methanol molar flux density across (a) the anode surface and (b) the cathode surface (crossover), for different electrolyte flow rates and FE channel thickness. Anode fuel feed concentration is kept constant at 4M.

Fig. 7.  Reduction of methanol crossover compared to the PEM-DMFC for various FE channel thicknesses and volumetric flow rates.

Fig. 8.  (a) Average methanol molar flux density vs. FE channel thickness. (b) Molar flux density fractions. FE volumetric flow rate $0.02 \text{ cm}^3 \text{s}^{-1}$ and anode surface concentration 4 M are kept constant.

Fig. 9.  Average methanol molar flux density vs. FE volumetric flow rate for different channel thickness. Anode surface concentration is constant at 4 M.
Fig. 10. Fractions of methanol molar flux at anode and cathode vs. electrolyte flow rate for channel thickness 0.3 and 0.6 mm. Anode surface concentration is 4 M.

Fig. 11. Average anode (a) and cathode (b) methanol molar flux for the cases with constant anode concentration 3M, parallel flow and counter flow with linear anode concentration from 4 M to 2 M. Conditions: FE channel thickness 0.6mm

Fig. 12. Reduction of methanol crossover for counter flow compared to parallel flow and constant anode concentration. Conditions: FE channel thickness 0.6 mm
Figure 1
Figure 2
Figure 4
Figure 5
Figure 6
Figure 7
Figure 8
Figure 9
Figure 10
Electrolyte flow rate [cm$^3$ s$^{-1}$]

Methanol flux [mole s$^{-1}$ m$^{-2}$]

Constant 3 M
Counter flow 2-4 M
Parallel flow 4-2 M

Figure 11
Figure 12
Paper II:

Modeling methanol crossover by diffusion and electro-osmosis in a Flowing Electrolyte Direct Methanol Fuel Cell

Submitted to Fuel Cells
Modeling Methanol Crossover
by Diffusion and Electro-Osmosis
in a Flowing Electrolyte Direct Methanol Fuel Cell

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Abstract

A CFD model is created to analyze methanol transport in the flowing electrolyte direct methanol fuel cell (FE-DMFC) by solving the 3D advection-diffusion equation, with consideration of electro-osmosis. Average methanol flux at the anode and cathode surfaces is simulated and compared to equivalent direct methanol fuel cells. Methanol crossover is defined as methanol flux at the cathode surface, and the results reveal that methanol crossover can be drastically reduced by the flowing electrolyte. Performance of
the FE-DMFC at peak power current density is evaluated, and diffusion is shown to be the dominant contribution although electro-osmosis increases with current density. The power consumption of the electrolyte pump is shown to be negligible compared to the cell power output. This indicates that thin electrolyte channels with high flow rates could further improve the efficiency.

**Keywords:** Direct methanol fuel cell; methanol crossover; electro-osmosis; numerical modeling; flowing electrolyte

1 **Introduction**

Fuel cells display a great variety of potential applications for generation of electric power. High efficiency and low emissions combined with an extremely simple mechanism without any moving parts make fuel cells very competitive. Micro scale fuel cells for applications such as portable computers and cellular phones are likely to become the first products ready for the mass market. For such applications, low-temperature fuel cells with proton exchange membranes (PEM) are being adopted. Liquid fuels are preferred because of simple storage and handling, although the conversion in fuel cells is more complex. One of the best available liquid fuels in terms of system overall efficiency (also called well-to-wheel efficiency) is methanol [1], that can be utilized directly in a direct methanol fuel cell (DMFC). For medium-scale applications such as transportation, the DMFC cannot yet compete with hydrogen fuel cells, mostly due to its comparatively low cell efficiency and expensive catalysts [2]. On the other hand, for systems where size and weight are more important, it exhibits high potential. The power densities and energy
densities of DMFCs are superior, even when compared to newly developed lithium ion batteries [2]. The current obstacles are low cell efficiency and high cost, factors that must be improved to enable mass market penetration.

The performance of DMFCs is reduced by two main bottlenecks, slow anode reaction kinetics and methanol crossover. Investigations of the most common solid polymer electrolyte material, Nafion®, have identified that methanol can penetrate sulphonic acid membranes [3]. It has also been shown that methanol crossover leads to a significant loss in oxygen reduction performance at the cathode due to a mixed potential. Apart from that, crossover is a substantial loss of fuel that produces no current whatsoever. Therefore, overall cell potential as well as fuel efficiency is reduced by this effect. Important strategies to reduce methanol crossover include anode fuel feed control and utilization of effective methanol oxidizing anode catalysts. There is much ongoing work in this field and several advanced methods of minimizing crossover have been presented. For instance, the electrolyte material can be replaced [4, 5] or be modified chemically [6, 7] to achieve lower methanol permeation. Shim et al. [8] suggest the use of a methanol impermeable barrier between the electrodes, allowing protons to pass but preventing methanol molecules from reaching the cathode catalyst layer.

Another method has already been introduced, based on a membrane electrode assembly concept invented by Kordesch et al. [9, 10], where the membrane is replaced by a flowing electrolyte. This novel design efficiently removes methanol from the electrolyte compartment by simple convection. The methanol in the electrolyte can be separated by
membrane methods or other techniques. It can be productively consumed, and a small amount may be used up in a loaded control sensing cell which then automatically adjusts the methanol feed to the system [10]. Many numerical as well as mathematical models of the conventional PEM-DMFC can be found in the literature [11, 12], but to make the flowing electrolyte direct methanol fuel cell (FE-DMFC) competitive much more work is needed. A mathematical model of the FE-DMFC has been developed by Golriz et al. [13], which can be extended by support of numerical simulations. In our previous work [14], a parametric study of methanol transport by diffusion that numerically simulates methanol crossover for different operating conditions has also been performed. Key parameters for a methanol crossover study were identified as FE channel thickness, electrolyte volumetric flow rate, anode surface methanol concentration and channel orientation. It was concluded that a thin electrolyte channel is beneficial, preferably with counter flow orientation. A weakness of the previous model is that it neglects the methanol crossover contribution of electro-osmosis.

The objective of this paper is to develop a new model that captures methanol crossover by diffusion as well as electro-osmosis. The model is intended to indicate suitable operating conditions to improve cell efficiency and to provide performance data for a future optimization study.

2 Flowing Electrolyte Direct Methanol Fuel Cells

A direct methanol fuel cell basically consists of a membrane electrode assembly (MEA) supported by diffusion layers adjacent to the fuel and oxidant channels and bipolar plates.
The MEA contains two porous electrode catalyst layers (anode and cathode) immersed in a proton-conducting electrolyte. The most common electrolyte configuration is the polymer matrix of a proton exchange membrane, as in the regular PEM-DMFC. The function of the membrane is to physically separate the electrodes, transfer protons from anode to cathode and act as an insulator to electric current. A good electrolyte should high proton conductivity, low methanol permeation and low electronic conductivity, and should also be as thin as possible. However, the problem of methanol permeation in thin membranes leads to reduced cell voltage and low overall efficiency. The new concept of flowing electrolyte direct methanol fuel cells addresses this issue. In one configuration, an electrolyte channel is immersed between two thin PEM layers as shown in figure 1. Other possible designs are shown in references [9, 10, and 13]. The flowing electrolyte (dilute sulphuric acid) effectively removes methanol from the MEA by convection, and hinders its arrival at the cathode. The MEA of the second generation FE-DMFC, with a $50 \times 50 \text{ mm}^2$ surface area, still contains two thin layers of PEM (50 µm thick) attached to the electrodes. However, the main function of these layers is to physically separate the different channels of the cell. The PEM-layers could be considered optional and may be removed or replaced by a thinner and cheaper material. The electrolyte channel thickness is a target for optimization. Other advantages of a flowing electrolyte system are simple thermal and water management; the possibility to remove side reaction products and impurities such as aldehyde residues, carboxylic acids or other intermediates produced during the oxidation of methanol; and the option to adjust the electrolyte flow rate relative to current density or fuel concentration to minimize fuel crossover. Moreover,
methanol transport from the fuel channel to the anode catalyst layer is enhanced, which has been shown to improve performance at high current densities [15].

3 Method

To model methanol crossover in a flowing electrolyte direct methanol fuel cell, species transfer within a single cell is to be evaluated. As seen in Fig. 1, the fuel cell contains three different flow channels and several other layers and materials. It is a complex system which is hard to describe by a simple model. The 2D cross-section is itself a considerable simplification that ignores the 3D nature of most of the fuel cell geometry. For instance, the fuel channel is in reality not straight as in the figure, it is constructed like a maze of several parallel channels covering the whole anode diffusion layer surface. To calculate methanol crossover for different operating conditions one needs to focus on the interior parts of the membrane electrode assembly. A good way to simplify the system is to ignore the effects of the complex fuel and oxidant channels and instead assume a constant methanol concentration at the electrode surfaces. The geometry of the domain for methanol transport is thus reduced to the parts shown in Fig. 2. The domain consists of the anode side membrane next to the surface of the anode catalyst layer, the flowing electrolyte channel and the cathode side membrane attached to the cathode catalyst layer surface.
3.1 Electrolyte channel flow

To determine the rate of methanol crossover in a FE-DMFC, the first step is to calculate the electrolyte velocity field in the FE channel. The steady-state velocity profile is calculated based on conservation of mass and momentum in three dimensions. Conservation of mass can be described by the 3D continuity equation in an Eulerian frame

\[ \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = S \]  

For incompressible fluids with no source term, this can be simplified to

\[ \nabla \cdot \mathbf{v} = 0 \]  

No-slip boundary conditions and the Reynolds number flow imply that \( v_y \) and \( v_z \) are zero in the entire channel, except for the transverse velocity generated by electro-osmosis. Assuming that the flux of methanol and water in the transverse direction across the membranes is small compared to the electrolyte flow, fluid flow in the longitudinal direction can be treated separately. Momentum conservation is described by the 3D Navier-Stokes equation for incompressible fluids in an Eulerian frame with no source term

\[ \rho \frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \rho = -\nabla P + \rho g + \mu \nabla^2 \mathbf{v} \]
If gravity is ignored, the steady-state equation can be written as

$$\rho(v \cdot \nabla)v = -\nabla P + \mu_v \nabla^2 v$$  \hspace{1cm} (4)$$

For the particular geometry of the FE channel (main flow in longitudinal direction ($x$) from inlet to outlet, channel width ($z$) much larger than the transverse thickness between the membranes ($y$)) the flow in the middle of the channel can be modeled as a two-dimensional steady-state flow between two flat plates caused by a pressure gradient in the longitudinal direction (Poiseuille flow). The solution of Eq. (4) with no-slip boundary conditions is a linear pressure gradient, $\Pi$, along the electrolyte flow, and

$$v_x(y) = \frac{\Pi}{2\mu_v} y(L_y - y)$$  \hspace{1cm} (5)$$

This fully developed parabolic velocity profile has zero velocity at the top and bottom membrane surfaces and a maximum in the center of the channel. It is assumed to be representative for the bulk of the flow, except near the channel width edges at $z = 0$ and $z = L_z$. The thickness of the viscous effects at the edges is assumed to be of the same order of magnitude as the transverse channel thickness, which is verified using numerical methods. With such thin viscous edge effects compared to the 50 mm channel width it is motivated to neglect these edge effects and focus on the behavior in the bulk flow away
from the edge. The free stream velocity is then determined by Eq. (5) independent of the z-coordinate.

Due to the effect of electro-osmosis there will also be a small fluid flow along with the proton transfer between the electrodes in the transverse direction. This transverse fluid velocity is assumed to be constant across the channel and small compared to the bulk longitudinal velocity, \( v_y \ll v_x \), thus retaining the parabolic profile of the main flow. The origin of the transverse velocity is discussed further in the species transfer chapter.

Volumetric flow rate and mean velocity are obtained by surface integration. The Reynolds number is calculated by

\[
Re = \frac{\rho v L}{\mu_v}
\]

The characteristic length of the FE channel equals its thickness, \( L = L_y \). Due to low velocities and thin channels, the electrolyte flow is expected to be laminar. For simplicity, the electrolyte channel inlet velocity profile is assumed to be fully developed. Channel flow frictional head loss is described by the Darcy-Weisbach equation

\[
h_f = f \frac{L}{D_h} \frac{v^2}{2g}
\]

For laminar flows \( f = \frac{64}{Re} \) [16], and the pressure drop becomes

- 9 -
\[ \Delta P = \frac{32\mu L v}{D_h^2} \]  

The rectangular shaped flowing electrolyte channel, with \( L_y \ll L_z \), has a hydraulic diameter equal to two times its thickness, \( D_h = 2L_y \), and \( v_{ave} = \dot{V}/L_y L_z \). The pumping power needed to keep up the electrolyte flow can thus be calculated by

\[ \dot{W}_p = \dot{V} \Delta P = \dot{V}^2 \frac{8\mu L_x}{L_y^2 L_z} \]  

### 3.2 Species transfer in the MEA

The physics behind water and methanol movement between the electrodes of the FE-DMFC and the method to solve this problem will be described in this chapter. In a conventional PEM-DMFC, mass transfer in the membrane is essentially one-dimensional from anode to cathode. The FE-DMFC system is more complex and requires a more thorough analysis.

Water movement normally occurs because of gradients in chemical potential. The most common way to move a body of water is to apply a pressure gradient. This is obviously the driving force of the main electrolyte flow in the FE-DMFC, but in the transverse direction between the fuel and oxidant channels the pressure gradient is assumed to be zero everywhere. In a porous medium or a membrane material where the level of
hydration can change, water molecules will move by diffusion towards the less hydrated region until chemical equilibrium is achieved. Water produced at the cathode is likely to maintain a high level of hydration in the cathode side membrane. The anode reaction on the other hand consumes water in a way that may cause local dehydration. However, considering the fact that the anode is immersed between two channels (fuel feed and flowing electrolyte) with water in abundance, the anode compartment is likely to be fully hydrated as well. Water flux by diffusion should evidently be negligible. For dilute methanol in water, the obvious concentration gradient between the electrodes causes methanol transport by diffusion.

In some electrical and electrochemical devices there exists another driving force for species transport, caused by the flow of electric or ionic current. Shewmon [17] describes this phenomenon as the “electron wind”. The moving electrons in a conductor hit the atoms in activated states and in bouncing off them, transfer momentum that causes the atoms to move in the same direction as the electrons. According to Shewmon [17], this force is much larger than the electrostatic force acting on the charged interstitial atom by the electric field. Most solvents and even the solvent itself will start moving in the same direction as the electrons, although the lattice atoms remain in their original positions. In electrochemical devices like fuel cells, this force is called electro-osmosis. It leaves the polymer structure of the membranes intact, but induces water transport along the direction of proton flow towards the cathode [18]. The water drag is assumed to be proportional to ionic current density and water content of the membrane [19]. Water content in the membranes of the FE-DMFC is lower than in the FE channel, therefore
limiting the drag. As mentioned, the membranes are expected to be fully hydrated everywhere, and the total water flux can be determined by

\[ J_{H_2O} = \frac{i}{F} \lambda \]  

(10)

The coefficient of electro-osmosis (\( \lambda \)) is equivalent to the number of water molecules dragged by each proton, and ionic current density equals cell current density (\( i \)). Different values of this coefficient can be found in the literature, usually between 2.0 and 3.5 for fully hydrated Nafion membranes [20-22]. The most commonly used value is 2.5, while there appears to be a lack of knowledge of the exact value [20]. Assuming uniform proton flux, the previously discussed transverse water velocity can now be calculated by

\[ v_y = \frac{iM_{H_2O}}{FP_{H_2O}} \lambda \]  

(11)

Concentration dependent methanol transfer by electro-osmosis can be calculated in a similar way, but the most straightforward method is to model the flow of solvent (water) and let the solute (methanol) transport follow by advection in the same way as in the bulk FE channel flow. This method is applicable when the solute concentration is small compared to the solvent concentration. To solve the methanol transfer problem in the presence of a velocity field, advection as well as diffusion must therefore be considered. Conservation of species gives the advection-diffusion equation for time dependent solute diffusion in a 3D Eulerian frame as
\[
\frac{\partial \mu}{\partial t} + v \cdot (\nabla \mu) + \nabla \cdot (-D \nabla \mu) = S
\] (12)

For a dilute species in a liquid solvent one can assume that the chemical potential equals solute concentration, in this case the methanol concentration in water. With no internal chemical reactions or sources, one finally obtains the time dependent Fickian advection-diffusion equation

\[
\frac{\partial c}{\partial t} + v \cdot \nabla c + \nabla (-D \nabla c) = 0
\] (13)

A critical parameter in this equation is the temperature dependent solute diffusivity \( D \), whose value will impact the magnitude of methanol transport in the MEA. For the FE-DMFC, the temperature dependence of the diffusivity of methanol in Nafion\(^\circledR\), \( D_{CH,OH}^{PEM} \), as well as methanol in water, \( D_{CH,OH}^{H_2O} \), must be determined. Except for its high proton conductivity, dilute sulphuric acid is assumed to behave like water. In general, diffusivity exhibits exponential temperature dependence such as

\[
D(T) = D^{ref} \exp \left( \frac{\Delta E}{R} \left( \frac{1}{T^{ref}} - \frac{1}{T} \right) \right)
\] (14)

Scott et al. [23] suggest \( D_{CH,OH}^{PEM} = 4.9 \cdot 10^{-10} \text{ m}^2\text{s}^{-1} \) at 333 K and \( D_{CH,OH}^{H_2O} = 2.8 \cdot 10^{-9} \text{ m}^2\text{s}^{-1} \) at 353 K as reference values for the relationship in Eq. (14), and \( \Delta E / R = 2436 \text{ K} \) for
Nafion® 117. However, several other functions can be found in the literature, for instance by Kulikovsky [24]. For this work, the diffusivities given by Scott et al. [23] are chosen, mainly because the operating temperature of the FE-DMFC is in the same range as their reference values.

The time dependent 3D advection-diffusion equation in the presence of a velocity field, Eq. (13), applied to the fuel cell MEA domain, has to be solved using numerical techniques. A CFD code called SimManTec that solves the advection-diffusion equation by a 3D transient nonlinear space-time method is applied. The scheme treats time dependent problems like stationary problems using space-time meshes that discretize space and time independently. Usually, finite element methods use a semi-discrete algorithm, i.e., discretizes space using FEM and use what can be considered a finite difference method such as Crank-Nicholson in time. In problems where the domain undergoes deformations in time, the classical finite difference approach may become difficult to use. The space-time domain can be considered a four dimensional continuum, where time is treated as the fourth dimension space variable. But since information is transferred from earlier to later times, the standard stepwise approach from finite differences is preserved. A continuous Galerkin method in space and a discontinuous method in time are used for the discretization.

The methanol transfer model of the FE-DMFC is integrated as a time dependent problem with constant velocity. Initially, the concentration is assumed to be linear across the MEA with zero velocity in the FE channel. The solver is then run with the Poiseuille velocity
field switched on until the steady-state solution is obtained. Time step size is selected according to the accuracy criterion $0.1 < \text{Fo} < 10$, based on the dimensionless Fourier number

$$Fo = \frac{D\Delta t}{\Delta y^2}$$

(15)

For the Fickian advection-diffusion problem $\Delta y$ represents the mesh element size in the transverse direction between the electrodes. Dirichlet boundary conditions are applied to the anode and cathode surfaces facing the membranes. A fixed methanol concentration in the range of 0-4 M is applied to the anode surface, assuming that the methanol concentration along the anode surface facing the anode side membrane is constant. In reality, anode surface concentration depends on fuel feed concentration, geometry and materials of all channels and layers, reaction rates and cell current density. The mathematical anode model of a PEM-DMFC reported by Jeng and Chen [22] verifies that the anode surface concentration is considerably lower than the fuel feed concentration, and that it depends on current density. The relative anode surface concentration estimates given by this model are summarized in Table 1. Anode surface concentration decreases with current density due to enhanced methanol consumption in the anode catalyst layer. A complete anode methanol concentration distribution model of the FE-DMFC starting at the fuel feed channel would be desirable, but is beyond the scope of this investigation.

At the cathode catalyst sites, most or all methanol that arrives is expected to oxidize or evaporate instantly, and the methanol concentration should be very low. Zero
concentration at the cathode surface, \( c_{CH,OH} = 0 \), is therefore assumed in the model.

Neumann boundary conditions with zero molar flux density are applied to all other surfaces. All material properties are evaluated at a constant operating temperature of 60°C.

For a simplified one-dimensional geometry as in the PEM-DMFC, Eq. (13) can be solved analytically. The steady-state Fickian advection-diffusion equation in 1D with constant diffusivity is simplified to

\[
D \frac{d^2 c}{dy^2} - v \frac{dc}{dy} = 0
\]  

This expression is a homogeneous linear ordinary differential equation of second order with constant coefficients, and its auxiliary equation is

\[
D \alpha^2 - v \alpha = 0
\]  

The roots of this equation, \( \alpha_1 = 0 \) and \( \alpha_2 = \frac{v}{D} \), are real and unequal, and the solution of the ordinary differential equation is

\[
c(y) = \beta_1 \exp(\alpha_1 y) + \beta_2 \exp(\alpha_2 y)
\]
Dirichlet boundary conditions, for instance \( c(0) = 1 \) and \( c(L) = 0 \), are applied to resolve the coefficients \( \beta_1 \) and \( \beta_2 \). In a 1D solute advection-diffusion problem with constant fluid velocity, the solute flux is independent of location and equal to

\[
J = vc - D \frac{dc}{dy}
\]  

(19)

4 Results and discussion

4.1 Model validation

The numerical results of applying the time dependent Fickian advection-diffusion equation to a 1D PEM domain with four equally sized elements and five nodes are analyzed and compared to the 1D analytical solution of Eqs. (18) and (19). Figure 3 presents methanol concentration and methanol flux values at different positions from anode to cathode, at high current density. In the concentration plot, the analytical solution for zero current density is shown as reference case. The numerical concentration values are in good agreement with the analytical solution. The bending of the curve represents the effect of electro-osmosis. With no electro-osmosis present, the curve is a straight line as in the reference case. The flux values at the interior nodes are also in good agreement, but at the end nodes, numerical errors are observed. At the end nodes, no central difference projections are available, and a single projection from the last Gauss point to the nodal value has to be utilized. To circumvent this problem, the mean of the flux
values at the three nodes closest to the end is calculated. The magnitude of the errors is then reduced to about 1%.

A mesh convergence analysis is performed on a simplified 2D geometry, much smaller than the entire fuel cell MEA domain. A good compromise between accuracy and computational time is found, including additional mesh refinements locally in the membranes and near the anode side membrane, where the methanol concentration gradient is high. The resulting mesh is extended throughout the entire domain.

4.2 Parametric study

Advection-diffusion on the three-dimensional FE-DMFC domain presented in Fig. 2 is quite difficult to implement using numerical techniques, mostly because of geometrically large aspect ratios. The 3D domain can however be simplified using a slice with only one element in the z-direction in the interior part of the channel. The viscous effects at the channel edges are negligible in a 50 mm wide channel, and the basically two-dimensional slice is expected to capture the core performance of methanol transport in the FE channel. This simplification is particularly important for a parametric study, where many different geometries and operating conditions are analyzed. Fig. 4 illustrates methanol transport in the slice model at the FE channel inlet region. Only the first 2 mm of the 50 mm long channel is shown. Methanol is entering the domain through the anode surface, and is carried in the transverse direction through the anode side membrane. When it enters the FE channel, it is effectively removed by the bulk longitudinal electrolyte flow. In this region near the channel inlet, none of the methanol reaches the cathode side membrane.
Figure 5 compares the methanol concentration distribution at various longitudinal positions. For the parameter settings of the figure, methanol concentration in the flowing electrolyte gradually increases towards the channel outlet. Methanol crossover measured at the cathode side PEM also increases towards the outlet, as indicated by the slope of the curves. Contrarily, anode methanol flux is largest near the inlet. Average methanol crossover as well as average anode methanol flux is determined by volume integration applied to the cathode and anode side membranes, respectively. Volumetric electrolyte flow rate is also calculated by integration, as it may differ somewhat to the analytical value. The physical ratio of convection to diffusion is determined by the Peclet number for the problem

\[ Pe = \frac{Lv_{\text{ave}}}{D} \]  

(20)

Peclet numbers of the magnitude \(10^4 < Pe < 10^5\) observed for the main FE channel flow, indicate that convection is much stronger than diffusion in the longitudinal direction. In the transverse direction, diffusion is the dominating means of methanol transport, with Peclet numbers in the range \(0 < Pe < 1\). These values depend on channel thickness and electro-osmosis.

The coefficient of electro-osmosis \((\lambda)\) is included in the parameter study only to show the change in methanol flux induced by modifying its value. Figure 6 shows average methanol flux at the FE-DMFC anode and cathode as a function of \(\lambda\). Its values are in the
range $2.0 < \lambda < 3.5$, and all other parameters are fixed. As expected, methanol transfer increases with $\lambda$. The change is about 5-10% when $\lambda$ is increased from 2.5 to 3.0. The methanol crossover reduction achieved with the FE-DMFC compared to the PEM-DMFC is shown to be fairly independent of $\lambda$, although it decreases somewhat. As suggested by Mazunder [20], $\lambda = 2.5$ is chosen as fixed value for the further analysis. The deviations due to the uncertainty of this value should be small.

The effect of anode surface methanol concentration is presented in Fig. 7. The methanol flux is clearly a linear function of anode surface concentration. This linear relationship was previously shown by Kjeang et al. [14] for purely diffusive fluxes, and it is now verified for the general case including electro-osmosis. Methanol flux at any fixed location in the MEA and for any fixed parameter settings can hence be expressed by

$$J_{\text{CH}_3\text{OH}} = J_{\text{CH}_3\text{OH}}^{\text{ref}} \frac{c_{\text{CH}_3\text{OH}}^a}{c_{\text{CH}_3\text{OH}}^{a,\text{ref}}}$$

(21)

For simplicity, the reference methanol concentration at the anode surface is set to $c_{\text{CH}_3\text{OH}}^{a,\text{ref}} = 1$ M. A linear methanol flux for both kinds of fuel cells also implies that the methanol flux reduction for FE-DMFCs compared to PEM-DMFCs is independent of anode surface concentration, as shown in Fig. 7b. This result is valid at both electrodes, assuming that the concentration drop from the fuel feed stream to the anode surface is equal for both designs. It means that the performance analysis of the FE-DMFC as compared to the PEM-DMFC can be carried out without the implementation of a...
sophisticated anode model to determine methanol concentration distribution in the anode layers as a function of cell current density.

The three remaining parameters, FE channel thickness, electrolyte volumetric flow rate and cell current density, cannot be extracted and analyzed separately. Instead, simulations are run for various combinations of parameter settings. Previous work by Kjeang et al. [14] suggests the use of channels with transverse thickness 0.6 mm or less to avoid internal resistance losses. Figure 8 shows average methanol flux as a function of current density and flow rate for the 0.15 mm channel, assuming constant anode surface concentration. 0.3 mm and 0.6 mm channels are also examined, with results similar to those presented by Kjeang et al. [14] neglecting electro-osmosis. Both anode and cathode methanol flux increase with current density for all combinations of flow rate and channel thickness, due to the flux induced by electro-osmosis. Anode methanol flux increases with flow rate and decreases with channel thickness. For the 0.15 mm channel, it becomes even higher than for the PEM-DMFC. Enhanced anode flux improves methanol transfer from the fuel channel to the anode catalyst layer, which in turn may improve the reaction rates, especially at high current densities. The unused fuel captured by the flowing electrolyte must however be recovered to maintain high fuel efficiency.

Methanol crossover (cathode flux) decreases with flow rate and channel thickness. The best results are achieved with thick channels and high flow rates, but the drawbacks are increased internal proton resistance and additional electrolyte pumping power. Internal proton resistance is proportional to the channel thickness, and unnecessarily thick channels must be avoided. It is probably advantageous to find an optimum considering
methanol crossover reductions and cell voltage losses when choosing the appropriate channel thickness. As proton transfer from anode to cathode is expected to be independent of flow rate, it might be a better solution to increase the flow rate.

Note that the results are based on an anode surface methanol concentration of 1 M for all current densities. The magnitude of the average methanol flux is proportional to the anode concentration as previously shown. At high current densities, the anode surface concentration is likely to drop [22], hence reducing methanol flux. The results of average methanol flux presented here are intended to give an overview of the influence of channel thickness, volumetric flow rate and current density at a fixed anode surface concentration. For a realistic performance analysis at various current densities, refer to the illustrations of methanol crossover reduction for FE versus PEM-DMFC given in Fig. 9. The ability of the flowing electrolyte to reduce methanol crossover decreases slightly with current density. Apparently, electro-osmosis has a greater impact on the FE-DMFC than on the PEM-DMFC, but the 0.6 mm channel still reduces crossover by at least 80% for all current densities and non-zero flow rates investigated. As a benchmark for thin channels, the 0.15 mm channel reduces crossover by around 60% at a flow rate of 0.02 cm$^3$ s$^{-1}$.

4.3 Electro-osmosis

In this study, methanol crossover is assumed to have two contributions; diffusion and electro-osmosis. Considering the Fickian advection-diffusion equation, one can expect the diffusive term to describe the diffusion contribution and the convective term to express the electro-osmosis contribution. When the cell current density is zero, there will
be no transverse water velocity and therefore methanol transport by diffusion only. The transverse water velocity is proportional to current density and the convective term in the advection-diffusion equation is in turn proportional to the water velocity. Convection pushes methanol towards the cathode, increasing the methanol concentration locally in the MEA (see Fig. 3a). As a result, the diffusive term in the advection-diffusion equation is also affected by electro-osmosis.

To analyze the impact of electro-osmosis on methanol crossover, it is more straightforward to consider the change in total flux, i.e. the sum of the convective and diffusive terms of the advection-diffusion equation. As mentioned, crossover appears as pure diffusion at zero cell current density. If the total flux is measured for non-zero current densities, one can let the increase in crossover be equal to the electro-osmosis contribution. Figure 10a shows an example of the results achieved with this strategy at constant anode surface concentration. Diffusion is the dominating methanol crossover component even for current densities in the high range. Electro-osmosis accounts for 30% of the crossover flux at peak power current density (0.3 A cm$^{-2}$ [25]) and 44% at maximum current density (0.5 A cm$^{-2}$ [25]) for the conditions of Fig. 10. Furthermore, the results indicate that the electro-osmosis fraction is independent of electrolyte flow rate, although the magnitude of both contributions decreases with flow rate. Anode methanol flux increases due to electro-osmosis, but not as significant as the crossover. For all cases investigated, the electro-osmosis fraction of methanol crossover is less than 50%, which is in agreement with the transverse Peclet numbers (0 < $Pe_x$ < 1). The fraction is largest for thick channels, but the actual magnitude is higher for thinner ones.
The plot of Fig. 10b has the same parameter settings as Fig. 10a except for the anode surface concentration, which in (b) decreases with cell current density according to the values of Table 1. The purpose of this plot is to show the effect of letting anode surface concentration depend on current density, as in a real operating scenario. The magnitude of both methanol crossover contributions drops considerably with current density. However, the diffusion and electro-osmosis fractions remain the same as in Fig. 10a. To generate more accurate results of this kind, the entire anode compartment and its concentration drop should be included in the model.

Once again, the results of the FE-DMFC analysis are compared to the PEM-DMFC. The electro-osmosis crossover fraction for the PEM case is only 13% at peak power current density and 21% at maximum current density. On the other hand, the magnitude of the electro-osmosis crossover component for the PEM case is actually about three times larger than for the FE case. The flowing electrolyte design is obviously an efficient method to capture and reduce methanol crossover by electro-osmosis.

### 4.4 Performance at peak power density

For most engineering purposes the fuel cell should be run at its peak power density. According to measurements performed by James et al. [25] for specific conditions, the FE-DMFC has its peak power density near \( i = 0.3 \) \( \text{A cm}^{-2} \). This optimum current density may however depend on the parameter settings discussed in this work.
Methanol flux reduction at anode and cathode at fixed current density ($i = 0.3 \, \text{A cm}^{-2}$) for the FE-DMFC compared to the PEM-DMFC is displayed in Fig. 11. These results are independent of anode surface concentration. The anode flux is in fact of the same magnitude as in the PEM case for all non-zero flow rates and channel thicknesses. Negative reduction, as for the 0.15 mm and 0.30 mm channels, means enhanced anode flux. Methanol crossover is significantly reduced for all combinations of channel thickness and flow rate. At low flow rate (0.02 cm$^3$ s$^{-1}$), the crossover reduction is at least 60%. An interesting discussion is how much the channel thickness can be reduced to achieve a particular methanol crossover reduction. If one wants to achieve 75% reduction, it is sufficient with a 0.15 mm channel at high flow rate (0.04 cm$^3$ s$^{-1}$) or a 0.3 mm channel at low flow rate. For 85% reduction, a 0.3 mm channel at high flow rate or a 0.6 mm channel at low flow rate is recommended.

### 4.5 Non-zero inlet methanol concentration

In the analysis so far, the electrolyte has been assumed to be pure at the FE channel inlet. If the FE channel outlet methanol concentration is kept low or if some of the methanol is separated, it is possible to circulate the electrolyte back to the inlet and use it again in order to remove methanol from the MEA. An illustration of the influence of non-zero inlet methanol concentration on methanol crossover flux is shown in Fig. 12. The figure presents values of methanol crossover at various longitudinal locations along the electrolyte flow compared to the normal case with zero inlet concentration. The crossover flux is higher at all locations, but gradually moves towards the values at zero inlet.
concentration. It has a local maximum near the inlet due to the high gradient in the cathode side membrane.

Figure 13 shows average methanol flux for this mode of operation at non-zero inlet methanol concentration at two different combinations of parameter settings. Methanol crossover is shown to increase linearly with inlet methanol concentration, while the anode flux is linearly decreasing. In both cases there appears to be a critical inlet concentration that causes the anode and cathode flux curves to meet, that is, a point where no additional methanol is removed by the flowing electrolyte. This point is located at an inlet concentration of approximately 50% of the anode surface concentration.

Methanol crossover reduction as a function of FE channel inlet methanol concentration is presented in Fig. 14 for the two cases. Again, there seems to be a linear relationship. The ability to reduce crossover drops considerably for both cases with inlet concentration. At an inlet concentration above 40% of the anode surface concentration, the performance of the flowing electrolyte approaches that of a stationary electrolyte. The system can still be considered to run at inlet concentrations below 20%. From 0 to 20% inlet concentration, methanol crossover reduction drops from 78% to 58% for case 1 and from 89% to 79% for case 2.

4.6 Pumping power

From an overall cell efficiency point of view it is important to keep track of all energy consuming processes in the fuel cell. The required pumping power to preserve a
continuous electrolyte flow in the FE-DMFC is determined by Eq. (9). It depends on the electrolyte flow rate and FE channel thickness parameter settings. As a guideline, the pumping power needed for a 0.6 mm thick channel with medium flow rate (0.02 cm$^3$ s$^{-1}$) becomes $W_p = 6.9$ nW at $\Delta P = 0.34$ Pa. Thin channels and high flow rates cause large pressure drops and high pumping power requirements. Among all the cases in the parametric study, the 0.15 mm thick channel with high flow rate (0.04 cm$^3$ s$^{-1}$) has the highest pumping power, $W_{p,max} = 1.8$ µW. The maximum power output of a corresponding FE-DMFC single cell is $W_{cell,max} = 1.7$ W near 0.3 A cm$^{-2}$ [25]. As a result, the electrolyte pumping power is negligible compared to the fuel cell power output.

One must also consider the uncertainty of the pressure drop calculations for extremely thin channels. The flow must behave in the same way as a large-scale channel flow for the equations to be valid. This was in fact proved by experiments performed by Kawahara et al. [26] for circular tube micro-channels down to 100 microns in diameter. The pressure drop and pumping power calculations should thereby be valid for the channels in question. It could be beneficial to test channels thinner than 0.15 mm with an increased flow rate, but the flow pattern would become more complex to analyze.

By way of negligible pumping power, the only drawback with high electrolyte flow rates is the increasing need for external processing to recover the unused fuel removed by the electrolyte. If this can be done in a simple/cheap and efficient way, thin electrolyte channels with high flow rates can be utilized to substantially reduce methanol crossover and provide a very efficient DMFC system.
5 Conclusions

Simulations of methanol crossover in the electrolyte compartment of the flowing electrolyte direct methanol fuel cell are performed based on a CFD model that solves the 3D advection-diffusion equation. The diffusion and electro-osmosis contributions are analyzed for various operating conditions. Diffusion is shown to be the dominating means of methanol crossover at all cell current densities, although the electro-osmosis fraction increases with current density. The exact value of the coefficient of electro-osmosis is revealed to be of minor importance. Methanol concentration distribution and average methanol flux at anode and cathode are simulated for the FE-DMFC and compared to the equivalent PEM-DMFC. Extra attention is given to analyze performance at peak power current density, the most likely mode of operation. Assuming that the anode surface methanol concentration is the same for both designs, methanol crossover is greatly reduced due to enhanced mass transfer by convection (60-90% reduction for most settings).

Average methanol crossover is shown to be proportional to the anode surface methanol concentration for both designs, which implies that the FE crossover reduction ability is independent of anode surface concentration. To minimize methanol crossover, the results confirm that thick FE channels and high electrolyte flow rates are preferable. It is however not required to achieve complete methanol removal. In fact, the system is shown to maintain reasonable performance even at non-zero electrolyte inlet methanol concentrations. The drawback with thick channels is increased proton resistance, which should be avoided. High flow rates and thin channels call for additional pumping power,
but a flow pattern analysis reveals that the electrolyte pumping power is negligible compared to the power output of the cell. Methanol flux across the anode is enhanced by thin channels and high flow rates, which is likely to improve fuel transfer to the catalyst sites particularly at high current densities. Thin electrolyte channels with high flow rates can thus provide efficient FE-DMFC systems with low rates of methanol crossover.

Further work includes a complete model of the anode compartment that combined with the existing model enables accurate predictions of fuel utilization. Together with polarization characteristics and internal cell resistance calculations, this model will become subject for an extensive electrolyte channel optimization study. Additional experiments and measurements of methanol crossover in the FE-DMFC would also be desirable.

**Nomenclature**

- \( c \) Concentration [mole m\(^{-3}\)]
- \( D \) Solute diffusivity [m\(^2\) s\(^{-1}\)]
- \( D_h \) Hydraulic diameter [m]
- \( \Delta E \) Activation energy [J mole\(^{-1}\)]
- \( F \) Faraday’s constant [C mole\(^{-1}\)]
- \( Fo \) Fourier number [-]
- \( h_f \) Head loss [m]
- \( f \) Friction factor [-]
\( g \)  Constant of gravity [m s\(^{-2}\)]

\( i \)  Cell current density [A m\(^{-2}\)]

\( J \)  Species molar flux [mole s\(^{-1}\)m\(^{-2}\)]

\( L_x \)  Length of MEA and FE channel in longitudinal direction [m]

\( L_y \)  Thickness of FE channel in transverse direction [m]

\( L_z \)  Width of MEA and FE channel in the z-direction [m]

\( M \)  Molar mass [kg mol\(^{-1}\)]

\( P \)  Pressure [Pa]

\( Pe \)  Peclet number [-]

\( R \)  Universal gas constant [J mole\(^{-1}\) K\(^{-1}\)]

\( Re \)  Reynolds number [-]

\( S \)  Source of species [mole s\(^{-1}\)]

\( T \)  Temperature [K]

\( t \)  Time [s]

\( \dot{V} \)  Volumetric flow rate [m\(^3\) s\(^{-1}\)]

\( v \)  Fluid velocity [m s\(^{-1}\)]

\( \dot{W}_{cell} \)  Fuel cell power output [W]

\( \dot{W}_p \)  Pumping power [W]

\( x \)  Direction of FE flow (longitudinal) [-]

\( y \)  Direction across FE channel (transverse) [-]

\( z \)  Direction of FE channel width [-]
Greek symbols

α Root of auxiliary equation [m⁻¹]

β Arbitrary constant [-]

λ Coefficient of electro-osmosis (number of methanol molecules dragged by each proton) [-]

μ Chemical potential [J mole⁻¹]

μv Kinematic viscosity [kg m⁻¹ s⁻¹]

Π Pressure gradient [Pa m⁻¹]

ρ Density [kg m⁻³]

Sub- and superscripts

a Anode surface location

ave Average value

c Cathode surface location

CH₃OH Methanol

H₂O Water

max Maximum value

PEM Proton Exchange Membrane

ref Reference value
References


Table 1. Anode surface methanol concentration estimates as a function of cell current density for a PEM-DMFC [22].

<table>
<thead>
<tr>
<th>i [A cm(^{-2})]</th>
<th>( \frac{c_{\text{CH}<em>3\text{OH}}^a}{c</em>{\text{CH}_3\text{OH}}^{a,\text{ref}}} ) [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>0.1</td>
<td>0.89</td>
</tr>
<tr>
<td>0.3</td>
<td>0.66</td>
</tr>
<tr>
<td>0.5</td>
<td>0.40</td>
</tr>
</tbody>
</table>
Figure captions

Fig. 1. 2D schematic of the FE-DMFC (not to scale).

Fig. 2. Domain for the methanol crossover analysis in the FE-DMFC (not to scale).

Fig. 3. Methanol concentration (a) and flux (b) distribution for the 4 element 1D PEM test case compared to the analytical solution.

Conditions: $c_{CH_3OH}^a = 1$ M, $i = 0.5$ A cm$^{-2}$, $\lambda = 2.5$

Fig. 4. Normalized methanol flux (arrows) at the FE channel inlet region (2 mm).

Conditions: $L_y = 0.6$ mm, $\dot{V} = 0.04$ cm$^3$ s$^{-1}$, $i = 0.3$ A cm$^{-2}$, $\lambda = 2.5$

Fig. 5. Typical methanol concentration distribution from anode to cathode at different longitudinal locations.

Conditions: $c_{CH_3OH}^a = c^*$, $L_y = 0.15$ mm, $\dot{V} = 0.04$ cm$^3$ s$^{-1}$, $i = 0.5$ A cm$^{-2}$, $\lambda = 2.5$

Fig. 6. Influence of the coefficient of electro-osmosis on methanol transfer.

Conditions: $c_{CH_3OH}^a = 1$ M, $L_y = 0.6$ mm, $\dot{V} = 0.02$ cm$^3$ s$^{-1}$, $i = 0.5$ A cm$^{-2}$

Fig. 7. Influence of anode surface concentration on methanol transfer (a) and on methanol flux reduction compared to the PEM-DMFC (b).

Conditions: $L_y = 0.6$ mm, $\dot{V} = 0.02$ cm$^3$ s$^{-1}$, $i = 0.5$ A cm$^{-2}$, $\lambda = 2.5$

Fig. 8. Anode and cathode methanol transfer as a function of cell current density and electrolyte flow rate for a 0.15 mm FE channel, at constant anode surface concentration. The numbers indicate electrolyte flow rates for the FE-DMFC.

Conditions: $L_y = 0.15$ mm, $c_{CH_3OH}^a = 1$ M, $\lambda = 2.5$
Fig. 9. Methanol crossover reduction compared to the PEM-DMFC as a function of cell current density and electrolyte flow rate, for channel thickness 0.15 mm (a), 0.3 mm (b) and 0.6 mm (c).

Conditions: $\lambda = 2.5$

Fig. 10. Typical diffusion and electro-osmosis methanol crossover contributions for the FE-DMFC at various cell current densities.

Conditions: (a) Constant $c_{CH,OH}^a = 1$ M, $L_y = 0.6$ mm, $\dot{V} = 0.02$ cm$^3$ s$^{-1}$, $\lambda = 2.5$

(b) Variable $c_{CH,OH}^a$ (see Table 1), $L_y = 0.6$ mm, $\dot{V} = 0.02$ cm$^3$ s$^{-1}$, $\lambda = 2.5$

Fig. 11. Anode methanol flux reduction (a) and methanol crossover reduction (b) as a function of electrolyte flow rate. The numbers indicate channel thickness.

Conditions: $i = 0.3$ A cm$^{-2}$, $\lambda = 2.5$

Fig. 12. Methanol flux distribution at the cathode surface (crossover) along the longitudinal direction for the inlet concentrations 0.00 M, 0.08 M and 0.20 M.

Conditions: $c_{CH,OH}^a = 1$ M, $L_y = 0.6$ mm, $\dot{V} = 0.02$ cm$^3$ s$^{-1}$, $i = 0.1$ A cm$^{-2}$, $\lambda = 2.5$

(case 2)

Fig. 13. Methanol transfer as a function of FE channel inlet methanol concentration for case 1 (a) and case 2 (b).

Case 1: $c_{CH,OH}^a = 1$ M, $L_y = 0.15$ mm, $\dot{V} = 0.04$ cm$^3$ s$^{-1}$, $i = 0.3$ A cm$^{-2}$, $\lambda = 2.5$

Case 2: $c_{CH,OH}^a = 1$ M, $L_y = 0.6$ mm, $\dot{V} = 0.02$ cm$^3$ s$^{-1}$, $i = 0.1$ A cm$^{-2}$, $\lambda = 2.5$

Fig. 14. Methanol crossover reduction at non-zero inlet concentrations for case 1 and 2.

Case 1: $c_{CH,OH}^a = 1$ M, $L_y = 0.15$ mm, $\dot{V} = 0.04$ cm$^3$ s$^{-1}$, $i = 0.3$ A cm$^{-2}$, $\lambda = 2.5$

Case 2: $c_{CH,OH}^a = 1$ M, $L_y = 0.6$ mm, $\dot{V} = 0.02$ cm$^3$ s$^{-1}$, $i = 0.1$ A cm$^{-2}$, $\lambda = 2.5$
Figure 1
Figure 2
Figure 3
Figure 4
Figure 5
Coefficient of electro-osmosis [-]

Average methanol flux $\left[10^{-3} \text{ mole s}^{-1} \text{ m}^{-2}\right]$

PEM anode/cathode
FE anode
FE cathode

Figure 6
Figure 7

(a) Average methanol flux [10^{-3} mole s^{-1} m^{-2}]

(b) Methanol flux reduction [%]

Anode surface concentration [M]

Cathode flux (crossover) reduction

Anode flux reduction
Figure 8
Figure 9
Figure 10
Figure 11
Figure 12
Figure 13
Figure 14