DECHEMA FORSCHUNGSINSTITUT

Chemical Technology

Simplified DMFC model with COMSOL

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Introduction

The direct methanol fuel cell (DMFC) is a promising technology for energy supply for portable and stationary applications due to high energy density of methanol, compact design, easy fuel handling and storage. However, poor activity of Pt for methanol oxidation, methanol crossover that results on fuel loss and mixed potential formation at the cathode and low corrosion resistance of Pt/C at high cathodic voltage are technical challenges to overcome. The long-term efficiency of the electrodes is strongly influenced by the nature of the catalyst support that should allow optimal distribution and stabilization of the catalyst nanoparticles, anchorage of functional groups and facile mass transport of reactants and products.
The main task at DFI in this project aims at the development of highly active, methanol-tolerant and corrosion-resistant catalyst for the middle-temperature (120-150°C) DMFC cathode. Another task focus on DMFC modeling with COMSOL multiphysics. Preliminary results about a simplified isothermal model without methanol crossover is presented below.

Function principle of DMFC

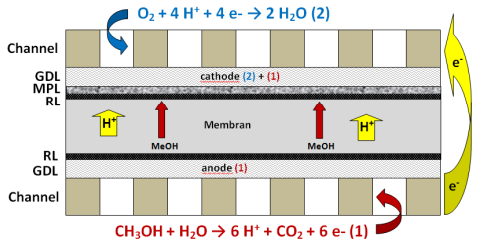

Fig. 1: Schematic illustration of DMFC with Flow Fields Channels, Gas Diffusion Layers (GDL), Microporous Layer (MPL), Reaction Layers (RL) , Polymer Exchange Membrane as well as anodic and cathodic electrochemical reactions.

Assumptions for simplified model: isothermal conditions and no methanol crossover at anode/membrane boundary.

Geometry

In contrast with PEMFC model from Comsol library, this work aims to built a 1:1 laboratory cell (23x23 mm) with an asymmetric geometry due to mirrored channels.

- **WP8 + extrude** opposite direction: H_ch + H_GDLc + H_MPLc + H_RLc + H_M + H_Rla + H_GDLa
- **WP8**: channel cathode
- **WP7 + extrude**: GDL cathode
- **WP6 + extrude**: MPL cathode
- **WP5 + extrude**: RL cathode
- **WP4 + extrude**: Membrane
- **WP3 + extrude**: RL anode
- **WP2 + extrude**: GDL anode
- **WP1 + extrude**: H_ch + H_GDLa + H_Rla + H_M + H_RLc + H_GDLc + H_MPLc
- **WP1**: channel anode

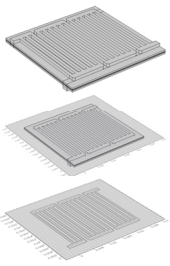

Fig. 2: DMFC geometry building-up starting from the bottom.

Mesh

- **Size:** fine
- **Free Triangular**
- **Swept:** generates **hexahedrons**
  - **Ditribution: 3** elements
- **Complete mesh** consists of
  - **253020** domain elements
  - **172658** boundary elements
  - **32654** edge elements

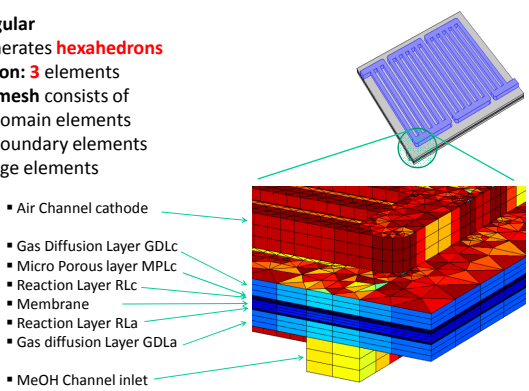

Fig. 3: Mesh structure of DMFC.

Physics

Electronic/Ionic charge balance	Ohm's law	$I = \upsilon \Delta V$
Charge transfer kinetics for $\eta <<$	Butler-Volmer	$i_a = i_0 * (\frac{c_{meoh}}{c_{meoh,ref}}) \exp(\frac{\alpha_{a,a}}{R*T} F * \eta_a)$ with $i_0 = F\, k_0\, c_{ox}^{\alpha}\, c_{red}^{(1-\alpha)}$
Charge transfer kinetics for $\eta >>$	Tafel	$i_{loc} = i_0\, 10^{\eta/Aa}$, $i_{loc} = -i_0\, 10^{\eta/Ac}$
Concentration dependency of i_0		$i_0 = i_{0\_MORa} * (rfcs.c\_wMeOH_g / c_{MeOH,ref})$
Charge transport in electrolyte	Nernst-Planck	$N_i = -D_i \nabla c_i - z_i u_i F c_i \nabla \Phi + c_i u$
Coupled mass transport in free channel and porous electrode	Navier-Stokes	$\rho \frac{\partial u}{\partial t} + \nabla \cdot [-\eta(\nabla u + \nabla u^T) + pI] = -\rho(u \cdot \nabla)u$
	Brinkman	$\frac{\rho}{\varepsilon_p}\frac{\partial u}{\partial t} + \nabla \cdot \left[-\eta \frac{\eta}{\varepsilon_p}(\nabla u + \nabla u^T) + pI\right] = -\frac{\eta}{k} u$
Mass balances in gas phase in gas channels and porous electrodes	Fick	$-\nabla \cdot (-D \cdot \nabla c + c \cdot u) = 0$
	Maxwell-Stefan	$-\nabla \cdot [-\rho \omega_i \sum_{j=1}^{N} D_{ij} \left(\frac{M}{M_j}\left(\nabla \omega_j + \omega_j \frac{\nabla M}{M}\right) + \left(x_j - \omega_j \frac{\nabla p}{p}\right)\right) + \omega_i \rho u] = 0$

Table 1: List of equations used in DMFC model.

Results

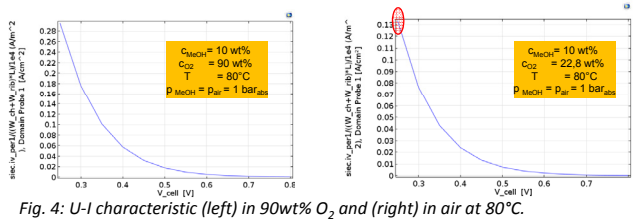

Fig. 4: U-I characteristic (left) in 90wt% O_2 and (right) in air at 80°C.

➢ Fuel cell performance in air is half of that calculated in oxygen-enriched atmosphere; this correlates well with experimental results.

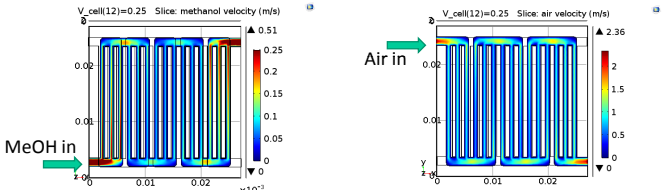

Fig. 5: Velocity profile of (left) methanol and (right) air in channels at 0.25 V & 80°C.

➢ Flow fields geometry should be adapted/optimized for better fuel repartition.

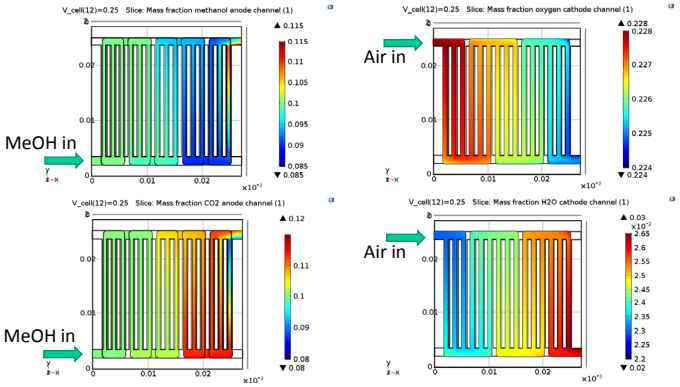

Fig. 6: Mass fraction profile of (top) educts & (bottom) products in channels at 0.25V & 80°C.

➢ No relevant mass transport limitation and water flooding in flow fields channels was calculated at 0.25 V.
➢ Increase in MeOH mass fraction at cell outlet may be due to back diffusion.

Summary, outlook & acknowledgements

➢ First simplified DMFC model with Comsol **without** MeOH crossover through PEM membrane has been successfully developed.
➢ Next step will focus on model extension **with** MeOH crossover & electro-osmotic drag implementation, as well as model validation.

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