DECHEMA FORSCHUNGSINSTITUT

Chemical Technology

DMFC model with COMSOL

J.-F. Drillet
e-mail: drillet@dechema.de
Funded by: BMWi via AiF
Period: 01.12.2013 - 30.11.2016

Gefördert durch: Bundesministerium für Wirtschaft und Energie aufgrund eines Beschlusses des Deutschen Bundestages

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 is presented below.

Function principle of DMFC

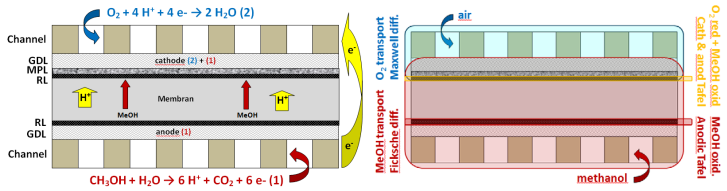


Fig. 1: (Left) Schematic illustration of DMFC with Flow Fields Channels, Gas Diffusion Layers (GDL), Microporous Layer (MPL), Reaction Layers (RL), Polymer Exchange Membrane as well as anodic and cathodic electrochemical reactions. (Right) Domains repartition of methanol and oxygen species transport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

Assumptions: isothermal conditions and no methanol crossover at $GDL_{cath.}$/$channel_{cath.}$ 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

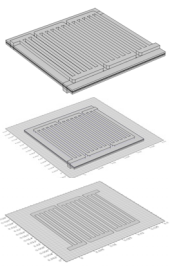


Fig. 2: DMFC geometry building-up starting from the bottom.

Mesh

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

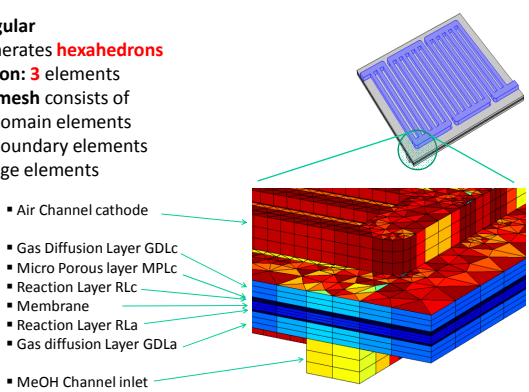


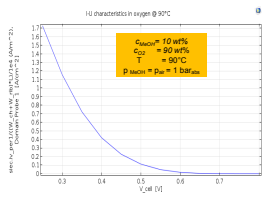
Fig. 3: Mesh structure of DMFC.

Physics

Electronic/Ionic charge balance	Ohm's law	$I = \sigma \Delta \cdot V$
Charge transfer kinetics for η <<	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 η >>	Tafel	$i_{loc} = i_0\, 10^{\eta/A_a}$, $i_{loc} = -i_0\, 10^{\eta/A_c}$
Concentration dependency of i_0		$i_0 = i_{0\_MORa} * (rfc s.c\_wMeOH_g / c_{MeOH,ref})$
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	$-\nabla \cdot [-\rho \omega_i \sum_{j=1}^{N} D_{ij} \left(\frac{M}{M_j}\right)(\nabla \omega_j + \omega_j \frac{\nabla M}{M}) + (x_j - \omega_j \frac{\nabla p}{p})] + \omega_i \rho u] = 0$

Table 1: List of equations used in DMFC model.

Results



Test	V_{cell} V	w_{O2_in} wt%	$E_{0,MORa}$ V	$E_{0,MORc}$ V	$E_{0,ORRc}$ V	I_{max} A cm^{-2}
04.07.2016	0.8	0.9	0.45	0.6	1	0.39
12.07.2016	0.8	0.9	0.35	0.6	1.1	1.85
10.08.2016	0.8	0.9	0.35	0.6	1.23	div
16.08.2016	0.8	0.9	0.35	0.6	1.2	1.75
22.08.2016	0.8	0.9	0.25	0.6	1.2	3.3
05.09.2016	0.8	0.9	0.3	0.55	1.2	div.
07.09.2016	0.8	0.9	0.25	0.55	1.2	div.
12.09.2016	0.8	0.9	0.35	0.6	1.15	1.85
19.09.2016	0.8	0.9	0.35	0.55	1.1	1.2
23.09.2016	0.8	0.2	0.35	0.55	1.1	0.015
29.09.2016	0.8	0.2	0.35	0.55	1.15	div.
04.10.2016	0.8	0.2	0.35	0.6	1.15	0.040

Fig. 4: U-I characteristic (left) in 90wt% O_2 and (right) I_{max} in function of c_{O2} and E_0.

- Modeled fuel cell performance is strongly depending on E_0 values.
- It is still not clear, why calculation with 20wt% O_2 led to very low I_{max} values.

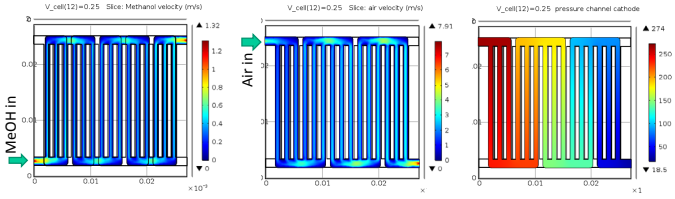


Fig. 5: Velocity of (left) MeOH & (middle) air as well as pressure profiles in channels.

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

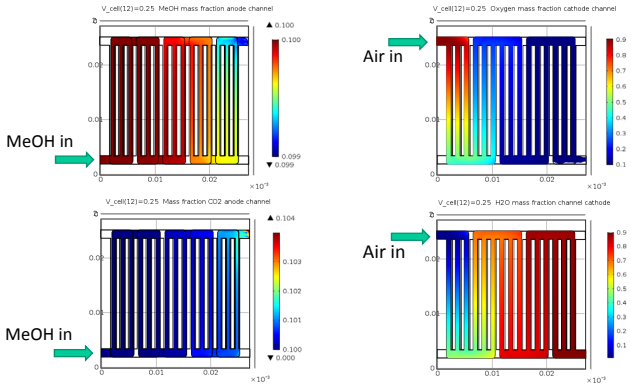


Fig. 6: Mass fraction profile of (top) educts & (bottom) products in channels at 90°C.

- No MeOH mass transport limitation in flow fields channels.
- Impressive increase of H_2O concentration from 0.023 up to 0.9 wt% at the cathode

Summary, outlook & acknowledgements

- Simplified DMFC model with Comsol with MeOH crossover through PEM membrane has been developed for 90wt% O_2.
- Next step will focus on air modus, implementation of electro-osmotic drag & model validation.

BMWi, project partners from ZSW Ulm and ICVT Stuttgart as well as members of industrial committee and finally COMSOL team are greatly acknowledged for financial support (17955 BG/3), excellent cooperation and technical support, respectively.