

A CFD BASED TWO-FLUID MODEL FOR A DMFC

*Valeri A. Danilov, Jongkoo Lim and Il Moon**
Department of Chemical Engineering, Yonsei University
Seodaemun-gu Shinchon-dong 134, Seoul 120-749, Korea

Kyoung Hwan Choi
Materials & Devices Laboratory,
Samsung Advanced Institute of Technology, Suwon 440-600, Korea

Abstract

This study presents a CFD model for modeling gas evolution and flow patterns in a DMFC. The model is based on two-fluid model with a new method for estimating the gas content without empirical mass transfer coefficients. The new equation for the source term is derived using the equilibrium flash equation for multicomponent gas-liquid stream. The improved two-fluid model allows studying the effect of flow field geometry on gas evolution and fuel cell performance without empirical correlations. As shown, the flow geometry of the anode side has important implication on gas evolution. The developed CFD model is valuable in simulation of DMFC with different flow fields.

Introduction

The fuel cell technology is a key element of next-generation power system due to high efficiency and high power density. Among critical problems for the improvement of the DMFC performance are anode kinetics, methanol crossover and gas management. Gas management greatly influences the performance of fuel cell. On the anode side, carbon dioxide is produced by electrochemical oxidation of methanol. Inefficient removal of CO₂ bubbles may block anode channels and decrease efficiency of the fuel cell due to the limited mass transport and maldistribution of velocity and reactants.

A few papers are devoted to studying the flow field for gas management on the anode side of a DMFC. Geiger et al. (2000) used the neutron radiography for exploring gas evolution patterns in anode flow fields of DMFC. They reported that gas accumulates to a large extent at the inner section of serpentine gas channels and it blocks a considerable part of the active area. To understand the role of model parameters, Mugia et al. (2003) presented experimental validation and parametric study of the one-dimensional model for multicomponent steady-state DMFC model based on phenomenological transport equations for catalyst layer, diffusion layer and membrane. A comprehensive model for two-phase flow, multicomponent transport, and detailed electrochemical reactions is presented by Wang and Wang (2003) for a liquid-feed DMFC under the assumption of one-dimensional flow along channel.

The trial and error method is inefficient and expensive way of flow field design and optimization due to a high cost of a bipolar plate. Model development for a DMFC is important in modeling a new flow field design. This study presents a CFD model for simulating the gas-liquid flow and gas evolution in fuel cell channels. The model is implemented in a computational fluid dynamics (CFD) package to evaluate flow field designs. The CFD simulations are used to visualize and to analyze the flow patterns and to reduce the number of experiments.

Two - fluid model for anode channels

Fluid dynamics and mass transfer processes have a significant impact on the gas management and fuel cell performance. A two-fluid model is widely used for modeling momentum and mass transfer in gas–liquid flows (Sokolichin and Eigenberger,1997; Wang and Wang, 2003). As applied to the anode channels, continuity and momentum equation are written as follows

$$\nabla \cdot (\mathbf{r} \mathbf{u}) = 0 \quad (1)$$

$$\nabla \cdot (\mathbf{r} \mathbf{u} \mathbf{u}) = -\nabla p + \nabla \cdot \mathbf{T} + \mathbf{r} \mathbf{g} \quad (2)$$

Stress tensor is

$$\mathbf{T}_{ij} = \mathbf{m}_{\text{eff}} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3} \mathbf{d}_{ij} \frac{\partial u_n}{\partial x_n} \right) \quad (3)$$

Additional continuity equation for gas phase is

$$\nabla \cdot (\mathbf{e} \mathbf{r}_G \mathbf{u}_G) = \Gamma_G \quad (4)$$

Species conservation in channels is

$$\nabla \cdot (\mathbf{r} \mathbf{u} C^k) = \nabla \cdot (\mathbf{r} D_{\text{eff}}^k \nabla C^k) \quad (5)$$

where $k = CH_3OH, H_2O, CO_2$.

Mixture parameter – in equation (1) - (5), the mixture variables and properties are given by

Density $\mathbf{r} = \mathbf{e} \mathbf{r}_G + (1 - \mathbf{e}) \mathbf{r}_L$

Concentration $\mathbf{r} \mathbf{C} = C_G \mathbf{e} \mathbf{r}_G + C_L (1 - \mathbf{e}) \mathbf{r}_L$

Velocity $\mathbf{r} \mathbf{u} = u_G \mathbf{r}_G + u_L \mathbf{r}_L$

Diffusion $D_{\text{eff}} = D_G \mathbf{e} + D_L (1 - \mathbf{e})$

Viscosity $\mathbf{m}_{\text{eff}} = \mathbf{m}_G \mathbf{e} + \mathbf{m}_L (1 - \mathbf{e})$

This model assumes constant cell temperature.

Homogeneous two-fluid model in diffusion layer

Continuity equation is

$$\nabla \cdot (\mathbf{r} \mathbf{u}) = 0 \quad (6)$$

Momentum conservation is

$$\mathbf{u} = -\frac{k}{\mathbf{m}_L} (\nabla P + \mathbf{r}_k \mathbf{g}) + \frac{n_d M}{\mathbf{r}_L} \frac{I_e}{F} \quad (7)$$

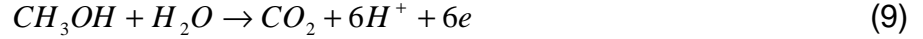
Species conservation is given by

$$\nabla \cdot (\mathbf{g}_c \mathbf{r} \mathbf{u} C^k) = \nabla \cdot (\mathbf{r}_L D_{L,\text{eff}}^k \nabla C_L^k + \mathbf{r}_G D_{G,\text{eff}}^k \nabla C_G^k) - \nabla \cdot ((C_L^k - C_G^k) \mathbf{j}_L) \quad (8)$$

Volume fraction of gas in diffusion layer is characterized by saturation under the assumption of equilibrium in gas - liquid system in porous layer. Details of model variables and mixture properties are described by Wang and Wang, (2003).

Electrokinetics

Fluid flow and mass transfer processes occur in a DMFC in conjunction with electrochemical reactions. These processes have a significant impact on the gas management and fuel cell performance. The current distribution model assumes that (i) the fuel cell is operating under a steady state, (ii) the catalyst layer is isothermal, (iii) isotropic porous media exists in the membrane, diffusion and catalyst layers. The following electrochemical reactions take place at the anode and cathode catalyst layers



Model equations for the current distribution, ohmic losses, and mass diffusion with auxiliary equations and boundary conditions are taken from the original model developed by Mugia et al. (2003) for catalyst layer and membrane and by Wang et al. (2001) for cathode channel.

Boundary conditions

Boundary conditions are required at all boundaries of the computational domains. On all walls the no-slip boundary condition is applied for the momentum equations. At the inlet of anode flow channels the boundary values are prescribed from the stoichiometric flow rate and mass fractions. Oxidation of methanol includes an electrochemical reaction on catalyst layer and multicomponent mass transfer in diffusion layer. Using the condition of fluxes continuity in diffusion layer, we get the next boundary condition for the methanol flux at diffusion layer – catalyst layer interface is

$$N^{MeOH} \Big|_{DL} = -M^{MeOH} \frac{1}{6} \frac{I}{F} \quad (11)$$

The carbon dioxide flux at the interface is

$$N^{CO_2} \Big|_{DL} = M^{CO_2} \frac{1}{6} \frac{I}{F} \quad (12)$$

Gas content in anode channels

The mathematical basis of the homogeneous two-fluid model is given by equations (1) - (5). The homogeneous model assumes that the phases move with the same velocity. The presence of bubbles is reflected by gas content ϵ_G and source term Γ_G . The difficulty in modeling concerns the physical transfer processes taking place across interface such as multicomponent mass transfer.

In accordance with two-fluid model, gas content is found from continuity equation (4). Wang and Wang (2003) used mass transfer equation for estimating the interface mass transfer and the source of mass

$$\Gamma_G = \frac{N_{t,G} C_{G,s} + \mathbf{r}_G \mathbf{b}_G \Delta C_G}{h} \quad (13)$$

where $N_{t,G}$ - total mass flux transferred from liquid to gas phase; \mathbf{b}_G - mass transfer coefficient; ΔC_G - driving force of mass transfer. Gas evaluation with mass transfer coefficients (13) corresponds to a nonequilibrium process of mass transfer between liquid and gas in the anode channel. The empirical correlation was developed for mass transfer from bubble to liquid in Taylor flow in circular capillary tube of monolithic catalyst reactor (Irandous and

Andersen, 1989). The drawback of equation (13) is that mass transfer coefficient from bubbles to liquid is a complicated function of hydrodynamics of gas – liquid flow.

Gas evolution results from interface mass transfer of carbon dioxide produced by chemical reaction in anode catalyst layer. Multicomponent component gas phase is usually assumed to be in equilibrium with liquid phase. Sundmacher and Scott (1999) and Argyropoulos et al. (2000) showed application of equilibrium flash equation for computing the gas content under the assumption of complete mixing in anode channels. For given component molar fractions, the local fractional vaporization g is calculated from solving equilibrium flash equation:

$$\sum_{i=1}^3 \frac{(K_i - 1)C_i \frac{M_{mix}}{M_i}}{(K_i - 1)g + 1} = 0 \quad (14)$$

where K_i - the distribution of the components between the vapor and liquid phases, $K_i = y_i / x_i$; g - the local fractional vaporization, $g = V/(V + L)$. Fractional vaporization is the ratio of evaporated molar gas flow rate to total flow rate. For anode channel stream, the carbon dioxide flux resulting from electrochemical reaction is the main component of gas phase. Gas phase also includes methanol and water components in equilibrium with liquid phase. By definition, source of mass in gas phase in (4) is

$$\Gamma_G = M_G \frac{dG}{dV} \quad (15)$$

For volume dV in anode channel, we define fractional vaporization as follows

$$g = \frac{dG}{L + (N_{anode}^{CO_2} / M^{CO_2})dS} \quad (16)$$

where dG - molar flow rate transferred from liquid to gas phase; L - liquid molar flow rate in channel with volume dV ; dS - area, $dS = dV / h$.

Using equilibrium flash equation (14), we suggest the following equation for estimating the source Γ_G (15)

$$\Gamma_G = M_G g \left(\mathbf{y} + \frac{N_{anode}^{CO_2}}{M^{CO_2} h} \right) \quad (17)$$

where M_G - molecular weight of gas phase; \mathbf{y} - coefficient, $\mathbf{y} = L / dV$. It should be noted that equation (17) corresponds to an equilibrium model of multicomponent mass transfer between liquid and gas in anode channels.

Derivation of the auxiliary equation for coefficient \mathbf{y} is given below. To evaluate the coefficients, we use total mass balance for gas phase in anode channels

$$(G_{out} - G_{in}) = \bar{\Gamma}_G V_{anode} \quad (18)$$

where V_{anode} - volume of anode channels; G_{in} - gas flow rate at inlet section, $G_{in} = 0$; G_{out} - gas flow rate at outlet section, $G_{out} = u_{G,out} \mathbf{r}_G \mathbf{e}_G^{out} S_{out}$; S_{out} - area of the stream outlet section; $u_{G,out}$ - velocity of gas at section S_{out} ; \mathbf{e}_G^{out} - gas content in two-phase stream at section S_{out} .

Mean source of gas is

$$\bar{\Gamma}_G = M_G \bar{g} \left(\bar{\mathbf{y}} + \frac{\bar{N}_{anode}^{CO_2}}{M^{CO_2} h} \right) \quad (19)$$

where $\bar{N}_{anode}^{CO_2}$ - mean carbon dioxide flux at interface; \bar{g} - mean fractional vaporization, $\bar{g} = (g^{in} - g^{out})/2$; g^{in} , g^{out} - fractional vaporization at the inlet and outlet section of anode channels, $g^{in} \approx 0$. Finally, solving (18) and (19) for \bar{y} we have

$$\bar{y} = \frac{G_{out} - G_{in}}{V_{anode} M_G \bar{g}} - \frac{\bar{N}_{anode}^{CO_2}}{M^{CO_2} h} \quad (20)$$

New source term (17) derived without mass transfer coefficients from equilibrium flash equation is in accord with an equilibrium mass transfer process in gas liquid stream.

Case study – 1.4 cm² DMFC

Validity test of the developed model requires experimental data including operating conditions and polarization curve for a DMFC. With this view we use experimental data reported by Wang and Wang (2003) for 1.4 cm² DMFC. They used 1D continuity equation with source term (13) based on empirical mass transfer coefficients for calculating gas content in anode channels. In contrast to Wang and Wang, we use volume averaged homogeneous two-fluid model with new source term (17) without empirical correlations. The coupled nonlinear transport equations (1) – (8) describe the species and gas evolution in a DMFC. The above model equations are coupled closely, so the whole set of equations must be solved simultaneously and iteratively. It should be noted that simulation results in Fig. 1 quantitatively agree with 1D simulation data reported by Wang and Wang (2003) with operating conditions in Table 1

Table 1

Operating conditions of 1.4 cm² DMFC (Wang and Wang, 2003).

Channel height	2.0 mm
Channel width	2.0 mm
Number of channels	1
Cell length	7 cm
Operating temperature	80 C
Cathode channel pressure	1 atm
Anode channel pressure	1 atm
Inlet velocity of anode channel	0.0006 m/s
Inlet methanol concentration	1 M
Inlet velocity of cathode channel	0.2 m/s
Inlet oxygen concentration	21 % mol
Inlet relative humidity at cathode	3.43 %

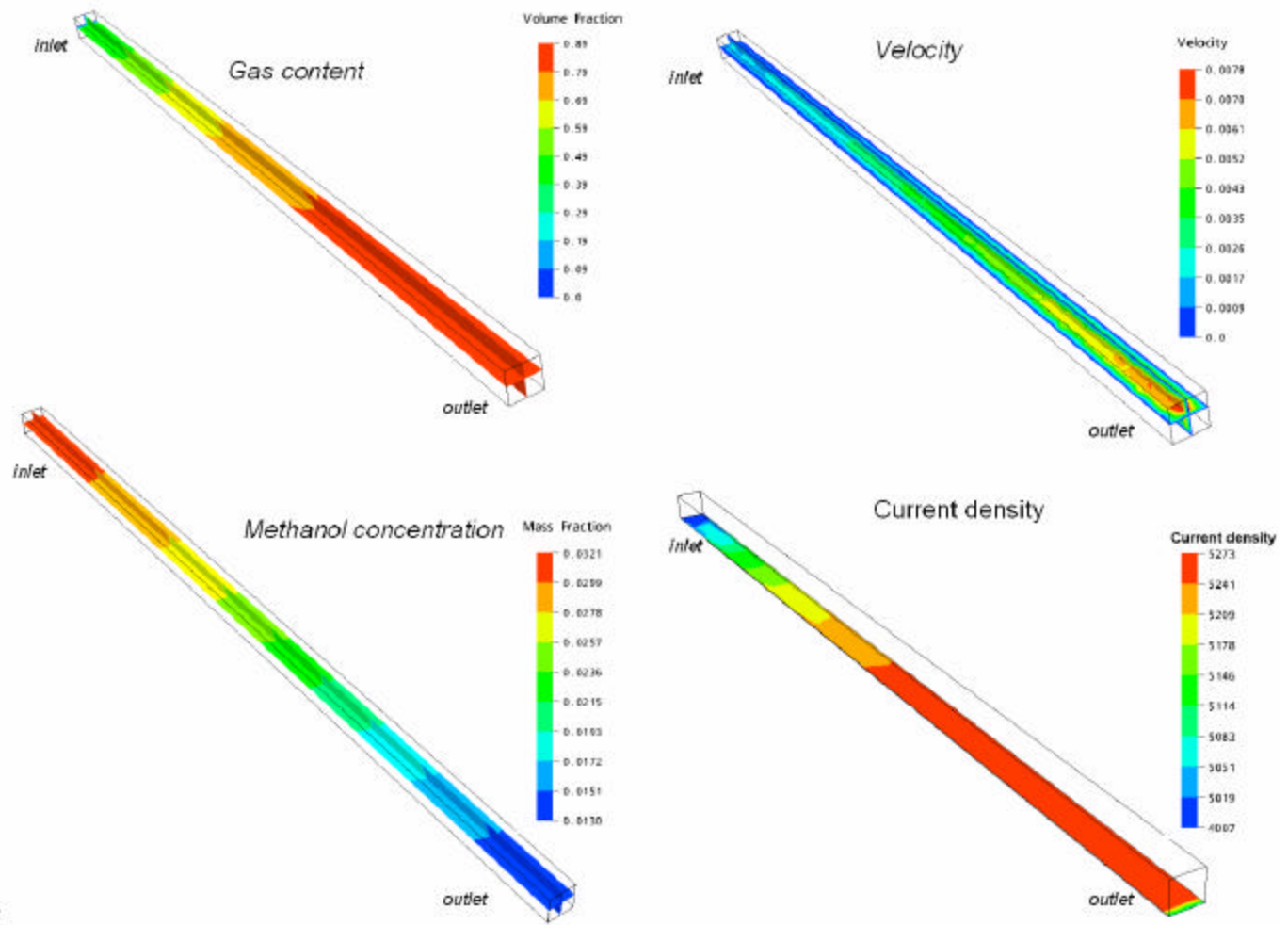


Figure 1. Simulation results for gas content, velocity, methanol concentration and current density in channel of 1.4 cm^2 DMFC with operating conditions from Table 1. Average current density 4500 A/m^2 .

The void fraction in the anode channel increases along the flow direction from 0% at the inlet to 90% at the outlet. The velocity increases along the flow direction due to the volume expansion of the two-phase mixture.

Results and discussion

The main object of gas management is to determine a DMFC design and operating conditions providing uniform distribution of liquid without gas accumulation in channels. Two-fluid model is suitable for simulation of gas management in a DMFC. The using of conventional methods is complicated by the need for empirical correlations for non-equilibrium mass transfer in calculating the gas content (Wang and Wang, 2003). We suggest a new equilibrium mass transfer method for estimating the source term in two-fluid model. In contrast to Wang and Wang (2003), we used two-fluid model with equilibrium multicomponent mass transfer in gas-liquid stream. Physicochemical properties of liquid and gas were calculated from equations cited by Wang and Wang (2003).

This study shows application of the 3D CFD model for exploring gas evolution in DMFC with parallel channels (Fig. 2). The above simulations of different flow field geometries provide a good illustration of the capability of the CFD model. As shown in this paper, the flow geometry of the anode side has an important implication on gas evolution. It should be noted that simulation results and main conclusions qualitatively agree with experimental observations for a transparent DMFC available in literature. The developed 3D CFD model includes all relevant phenomena and factors and it is valuable for gas management in a DMFC design. We have used the developed CFD model for designing a new high-performance DMFC with improved gas management (Lim et al., 2005)

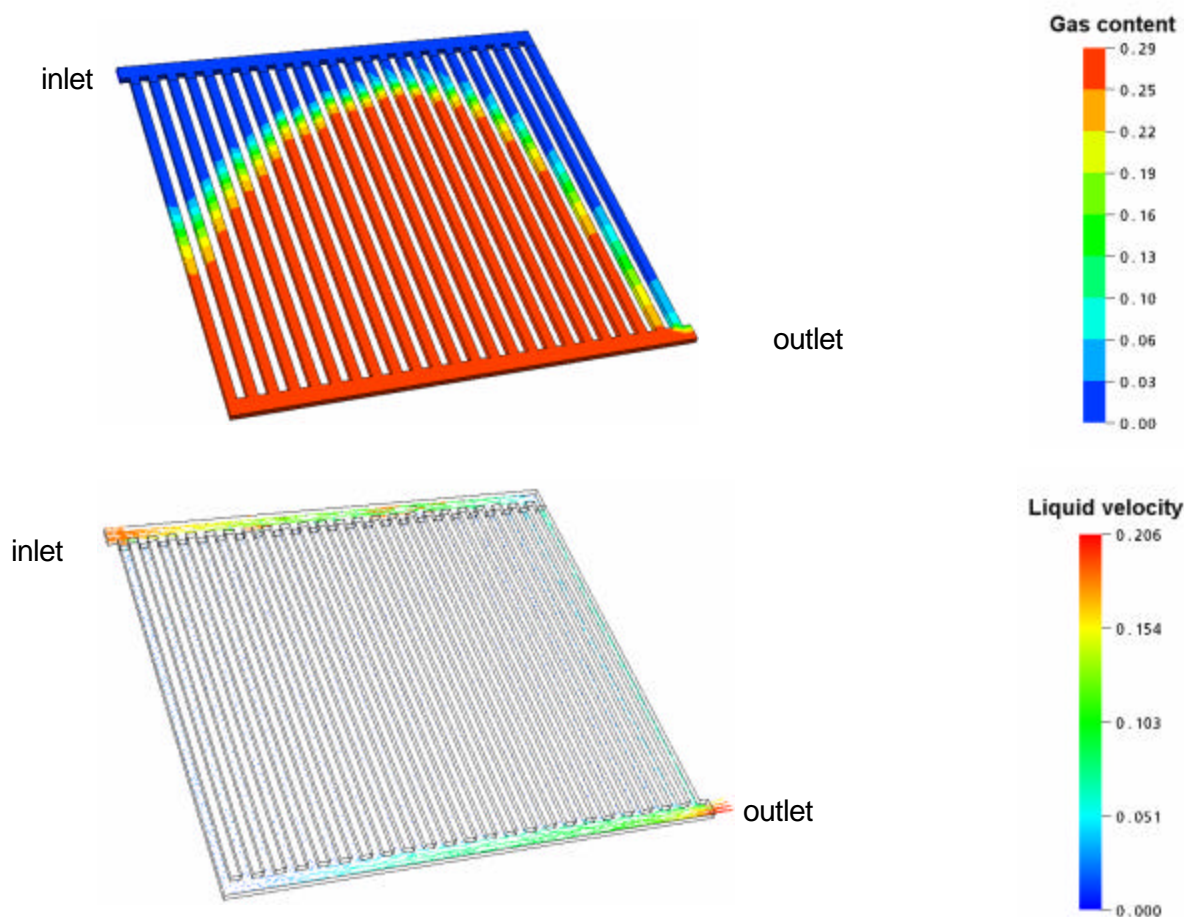


Figure 2. Gas content and velocity distribution in anode channels for DMFC with parallel flow field.

Conclusions

A CFD-based two-fluid model is developed for a DMFC. The improved two-fluid model includes a new method for estimating gas content without empirical correlation for mass transfer between gas and liquid in anode channel. The new equation for the source term is derived using equilibrium flash equation for multicomponent gas-liquid stream. Case study of gas evolution in DMFC with parallel flow field illustrates application of the model. The improved two-fluid model is valuable in CFD-based DMFC design.

Acknowledgements

This work was supported by a grant from Korean Federation of Science and Technology Societies and Korean Science and Engineering Foundation.

Symbols used

C	mass fraction, kg kg^{-1}
D	diffusion, $\text{m}^2 \text{s}^{-1}$
F	Faraday constant, C mol^{-1}
g	acceleration, m s^{-2}
k	permeability of porous material
K	distribution of the components; conductivity of catalyst, $\text{m } \Omega^{-1}$
L	molar flow rate, mol s^{-1}
h	channel height, m
I_e	ionic current density, A m^{-2}
M	molecular weight, kg mol^{-1}
N	mass flux, $\text{kg m}^{-2} \text{s}^{-1}$
n	number of electrons
n_d	electro-osmotic drag coefficient
P	pressure, Pa
r	source term, $\text{kg m}^{-3} \text{s}^{-1}$
s	stoichiometric coefficient
S	area, m^2
T	temperature, K
u	velocity vector, m s^{-1}
V_{anode}	volume of anode channels, m^3
x	molar fraction in liquid phase, mol mol^{-1} ; coordinate, m
y	molar fraction in gas phase, mol mol^{-1} ;
z	coordinate, m
e	porosity, $\text{m}^3 \text{m}^{-3}$
e_G	gas content, $\text{m}^3 \text{m}^{-3}$
g	local fractional vaporization; kinetic factor
g_c	advection correction factor
ρ	density, kg m^{-3}

Γ_G	source of mass in gas phase, $\text{kg m}^{-3} \text{s}^{-1}$
y	coefficient
m	viscosity, Pa s

Subscripts

i	component
in	inlet
out	outlet
L	liquid
G	gas
A	anode
k	component ($MeOH$, CO_2 , H_2O , O_2)
eff	effective
mix	mixture
DL	diffusion layer
t	total
s	interface; solid

References

- J. Lim, V. A. Danilov, Y. Cho, K. Choi, H. Chang, I. Moon. in: Proceeding of PSE ASIA 2005
- A. Geiger, E. Lehmann, P. Vontobel, G.G. Scherer, (Eds.) Scientific Report 2000, Volume V, Switzerland, p.86-87 (<http://www1.psi.ch/>)
- G. Mugia, L. Pisani, A.K. Shukla, K. Scott, J. Electrochem. Soc. **150** (2003) A1231-A1245
- A. Sokolichin, G. Eigenberger, A. Lapin, A. Lübbert, Chem. Eng. Sci. **52** (1997) 611-626
- K. Sundmacher, K. Scott, Chem. Eng. Sci. **54** (1999) 2927-2936
- Z. H. Wang, C. Y. Wang, J. Electrochem. Soc. **150** (2003) A508-A519
- Z.H. Wang, C.Y. Wang, K.S. Chen. Journal of Power Sources, **94** (2001) 40-50
- S. Irandous, B. Andersen, Comput. Chem. Eng. **13** (1989) 519 - 526