CHEMICAL ENGINEERING TRANSACTIONS Volume 18, 2009
Editor Jiří Klemeš
Copyright © 2009, AIDIC Servizi S.r.l., ISBN 978-88-95608-04-4 ISSN 1974-9791
DOI: 10.3303/CET0918016

Design and Optimization Of Direct Methanol Fuel Cell (DMFC)

S. Basri, S.K.Kamarudin, W.R.W.Daud
Institute Of Fuel Cell
Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia

Several papers published for the optimization of DMFC considering only the design parameters like feed flow, temperature and methanol crossover. However, this paper present a non liner programming (NLP) optimization with respect to the design and the geometrical parameters of anode and cathode such as methanol concentration, current density, power density, catalyst loading, catalyst layer, over potential, etc. The objective function is to maximize the power output of DMFC. Optimization tool in Matlab and Genetic algorithm (GA) are used to solve the algorithm. The obtained outputs were verified with the experimental results.

1. Introduction

Interest in using direct methanol fuel cells (DMFC) to power portable equipment for commercial application is relatively recent. DMFC can work at room temperature with high energy density compared to other alcohol fuel and the construction is simple. Thereby, it is a good candidate for the use of commercial electronics and micro devices. Having a theoretical energy density of about $6080 Whkg^{-1}$, methanol stores about 10 times more energy than the best lithium-ion batteries.

Several works published in the field of optimization of DMFC. Notable among them are Xu et al. (2005) developed the dynamic optimization for DMFC to provide a constant feeding strategy that achieve the highest power density at given operating condition conditions specified by a set current density. Rao and Rengaswamy (2006) highlighted the presence of local optima and the multi-objective nature of the fuel cell catalyst for design problem using a spherical agglomerate steady state model. Chen et al. (2007) presented an optimization model for annual cost for a given power production level. Secanell et al (2007) formulated a multi variable for optimization of PEM fuel cell in order to maximize the current density at a given electrode voltage with respect to electrode composition parameters using a gradient-based optimization algorithm. Ko et al (2008) study a non-isothermal dynamic optimization model of direct methanol fuel cells (DMFCs) and predicted their performance with an effective optimum-operating strategy. However, all the research concentrated on the optimization of feed flow, power out and current density neglecting the catalyst loading, catalyst layer, and channel layers although this parameters are very significant in determining the cost and performance of

Please cite this article as: Basri S., Kamarudin S.K. and Daud W.R.W., (2009), Design and optimization of direct methanol fuel cell (dmfc), Chemical Engineering Transactions, 18, 111-116 DOI: 10.3303/CET0918016

the cell . Addition to the previous researches, this study will present a non linear optimization with respect to the design and the geometrical parameters of anode and cathode predicting the detail design parameters such as methanol concentration, current density, power density, catalyst loading, catalyst layer, over potential for DMFC for maximum power output. Although NLP approach is computationally more extensive, it has been proven to be more robust and reliable method (Buouerouf & Biegler 1995; Barbosa et al 2000; Itle et al 2004). The NLP problems in the study were solved using optimization tools in MATLAB and genetic algorithm. The validation was done using results from experiment.

2. Design Optimization

The objective function defined as to maximize the power output of DMFC:

$$\text{Maximize} \quad f(x) = P_{output} \tag{1}$$

$$P_{output} = IV \tag{2}$$

$$I = I_{cell} \times Ar \ \text{ and} \tag{3}$$

$$V = V_{cell} = U_O - U_M + \eta_c - \eta_a - \frac{L_m I_{cell}}{\kappa_m} \tag{4}$$

Then, the objective function becomes;

$$\max \quad f(x) = -(x_1 Ar)\left(U_O - U_M + x_2 - x_3 - \frac{L_m x_1}{\kappa_m} \right) \tag{5}$$

Subject to:
Inequality constraints for constraint function

$$0 < P_{opt} \le 0.030 \text{ , or } -P_{opt} < 0 \text{ , } P_{opt} - 0.03 \le 0 \tag{6}$$

$$x_2 < 0 \tag{7}$$

$$0.1 < x_{12} \le 10 \tag{8}$$

$$0.00001 < x_4 \le 0.01 \tag{9}$$

$$0.00001 < x_5 \le 0.01 \tag{10}$$

Equality constraints

$$x_1 - n_M F \sqrt{x_3 D_a^{eff}} \left(\coth\left(\sqrt{x_3 D_a^{eff}}\, x_{14} \right) - \cos\mathrm{ech}\left(\sqrt{x_3 D_a^{eff}}\, x_{14} \right) \right) \left(x_9 + x_{10} \right) = 0 \tag{11}$$

$$x_4 - \frac{x_{16} i_{oM,ref}}{n_M F C_{M,ref}} \exp\left(\frac{\alpha_a x_3 F}{RT} \right) = 0 \tag{12}$$

$$x_5 - \frac{x_{17} i_{oO,ref}}{n_O F C_{Og,ref}} \exp\left(\frac{\alpha_c x_2 F}{RT} \right) = 0 \tag{13}$$

$$x_8 - \frac{-K_{II} x_{10}((k_p \Delta P / L_m) - (\xi x_1 / F))}{1 - \exp((k_p \Delta P / D_m) - (\xi x_1 L_m / D_m F))} = 0 \tag{14}$$

$$x_{10} - \frac{\sqrt{x_4 D_a^{eff}}\,(D_b^{eff} x_{11} / L_b) \cos ech(\sqrt{x_4 / D_a^{eff}}\, x_{14}) /((D_b^{eff} K_I / L_b) + (\sqrt{x_4 D_a^{eff}} \coth(\sqrt{x_4 / D_a^{eff}}\, x_{14}))}{\frac{K_{II}((k_p \Delta P / L_m) \quad (\xi I_{cell} / F)) \exp[-((k_p \Delta P / D_m) - (\xi I_{cell} L_m / D_m F))]}{1 - \exp[\quad ((k_p \Delta P / D_m) \quad (\xi I_{cell} L_m / D_m F))]}} = 0 \tag{15}$$

$$+ \frac{\sqrt{x_4 D_a^{eff}}\,(D_b^{eff} K_1 / L_b) \coth(\sqrt{x_4 / D_a^{eff}}\, x_{14}) + x_4 D_a^{eff}}{(D_b^{eff} K_I / L_b) + \sqrt{x_4 D_a^{eff}} \coth(\sqrt{x_4 / D_a^{eff}}\, x_{14})}$$

$$x_6 - \frac{n_O F((\sqrt{x_5 D_c^{eff}}\, C_{og}) / K_O) \tanh(\sqrt{x_5 / D_c^{eff}}\, L_c)}{1 + (\sqrt{x_5 D_c^{eff}}\, L_d / K_O D_d^{eff}) \tanh(\sqrt{x_5 / D_c^{eff}}\, L_c} = 0 \tag{16}$$

$$x_9 - \frac{\left(D_b^{eff} x_{11} / L_b\right) + \sqrt{x_4 D_a^{eff}} \cos ech\left(\sqrt{x_4 / D_a^{eff}}\, L_a\right) x_{10}}{\left(D_b^{eff} K_I / L_b\right) + \sqrt{x_4 D_a^{eff}} \coth\left(\sqrt{x_4 / D_a^{eff}}\, L_a\right)} = 0 \tag{17}$$

$$x_{14} - \frac{(0.659\, x_{12}/\rho_{Pt}) + (0.341\, x_{12}/\rho_{Ru}) + ((1 - 0.4) x_{12}/0.4\rho_C)}{1 - \varepsilon_a} = 0 \tag{18}$$

$$x_{15} - \frac{(x_{13} / \rho_{Pt}) + ((1 - 0.4) x_{13} / 0.4\rho_C)}{1 - \varepsilon_c} = 0 \tag{19}$$

$$x_{16} - \frac{1}{x_{14}} = 0 \tag{20}$$

$$x_{17} - \frac{1}{x_{15}} = 0 \tag{21}$$

Equality constraints are derive from the shot cut design equation of DMFC model.
Design parameters: D_a, F, $i_{oM,ref}$, $i_{oO,ref}$, I_{leak}, I_O, k_p, K_I, K_{II}, R, R_g.
Design variables: Ar, T, x_i, I_{cell}, U_O, U_M, D_c^{eff}, D_c^{eff}, D_d, D_m, k_p, K_O, C_{H^+}, C_{Og}
Variables x_i were find where i = 1-17
$x_1 = I_{cell}$, $x_2 = \eta_c$, $x_3 = \eta_a$, $x_4 = k$, $x_5 = k_c$, $x_6 = I_O$, $x_7 = I_{leak}$, $x_8 = N_M$
$x_9 = C_a^I$, $x_{10} = C_a^{II}$, $x_{11} = C_b$ $x_{12} = m_{ptru}$, $x_{13} = m_{pt}$, $x_{14} = L_a$, $x_{15} = L_c$,
$x_{16} = a_a$, $x_{17} = a_c$

3. Optimization

The optimization problem formulated above is solved using optimization toolbox in Matlab. It was solved consideration as nonlinear programming (NLP). The estimation of value x_0 obtained from Generic Algorithm (GA) in Matlab. For this study, the optimization tool implemented the Sequential Quadratic Programming (SQP) method assuming as sub-problem of a quadratic programming sub problem that can be solved successively until convergence is achieved for the original problem. The method has an advantage of finding the optimum design from an arbitrary initial design point and typically requires fewer function and gradient evaluations compared to other methods for constrained nonlinear optimization. Table 1 presents the design parameters for this study.

Table 1 Typical value design parameter

Symbol	Value	Unit	Symbol	Value	Unit
D_a	0.503×10^{-4}	($cm^2\ s^{-1}$)	α_A	0.35	
$i_{oM,ref}$	0.763×10^{-7}	($A\ cm^{-2}$)	α_C	0.8	
$i_{oO,ref}$	3.189×10^{-8}	($A\ cm^{-2}$)	ε_a	0.3	
$C_{M,ref}$	0.001	($mol\ cm^{-3}$)	ε_c	0.3	
$C_{Og,ref}$	$0.21/(R_g T)$	($mol\ cm^{-3}$)	ρ_{Ru}	12.37	($g\ cm^{-3}$)
R	8.314	($J\ mol^{-1}\ K^{-1}$)	ρ_{Pt}	21.45	($g\ cm^{-3}$)
R_g	82.06	($atm\ cm^3\ mol^{-1}\ K^{-1}$)	ρ_C	1.9	($g\ cm^{-3}$)
k_p	1.776×10^{-9}	($cm^2\ s^{-1}\ atm^{-1}$)	λ	2.8×10^{-9}	($mol\ m^{-3}$)
F	96500	($Cmol^{-1}$)	κ_m	0.068	($S\ cm^{-1}$)
K_I	1.25		ξ	45	($cm^3\ mol^{-1}$)
K_{II}	0.8		Φ_B	2.26	
n_M	6		n_O	4	

4. Results and Discussion

Table 2 present the results for this study. A case study of power = 9.6 mW was considered in this study. The Design parameters from optimization results were compared with the results from experiment and model. The voltage versus the current density Tafel plot (also known as the polarization curve) was presented in Figure 1. From the graph, clearly shows the model is comparable with experiments. It also observed that the performance of DMFC was improved after the optimization by improving the current density and voltage.

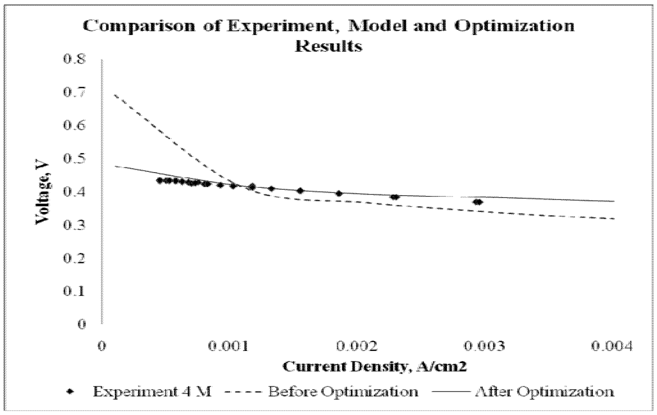

Figure 1 Comparison of Experiment, Model and Optimization for 4 Molar of Methanol Concentration.

5. Conclusion

The main objective of this study, which is to predict the optimum detail design parameters for DMFC were successfully achieved. The complex equations involved have been simplified into matrix forms and solved using Matlab software and genetic algorithm.

Table 2 Comparison of Generic Algorithm and Optimization Tool results.

Parameter	x	Generic Algorithm	Optimization Tool	Unit
Current Density	1	0.3399	0.34	mA cm^{-2}
Cathode Overpotential	2	0.22052	0.221	V
Anode Overpotential	3	0.48109	0.481	V
Rate Constant Methanol Oxidation	4	0.75621	0.756	s^{-1}
Rate Constant Oxygen Reduction	5	0.30655	0.301	s^{-1}
Oxygen Reduction Current Density	6	0.26699	0.267	A cm^{-2}
Crossover Current Density	7	0.76846	0.768	A cm^{-2}
Methanol Flux	8	0.76619	0.766	mol.cm^{-2} s^{-1}
Methanol Concentration at z_1	9	0.66332	0.663	M
Methanol Concentration at z_2	10	0.49114	0.491	M
Methanol Concentration	11	1.65037	1.65	M
Anode Catalyst Loading	12	0.11689	0.117	mg cm^{-2}
Cathode Catalyst Loading	13	0.63584	0.636	mg cm^{-2}
Anode Catalyst Thickness	14	0.93563	0.936	mm
Cathode Catalyst Thickness	15	0.66053	0.661	mm
Specific thickness at anode layer	16	0.96773	0.968	mm^{-1}
Specific thickness at cathode layer	17	0.99937	0.992	mm^{-1}
Power		9.65	9.65	mW

References

Barbosa, J.V.P., Wolf, M.R.M & Maciel, F.R. 2000. Development Of Data reconciliation for dynamic nonlinear system: application the polymerization reactor. Computers & Chem. Eng. 21, 501-506.

Buouerouf, J.S & Biegler, L.T. 1995. Decomposition algorithms for on-line estimation with nonlinear models. Computers & Chem. Eng. 19(10), 1031-1039

Chen, K.I., Winnick, J., Manousiouthakis, V.I. 2006. Global optimization of a simple mathematical model for a proton exchange membrane fuel cell. Computers & Chem. Eng. 30(8):1226-1234.

Garcia, B.L., Sethuraman,V.A., Weidner,J.W., White,R.E, 2004, Mathematical model of direct methanol fuel cell, J. Fuel Cell Sci. & Tech., DOI: 10.1115/1.1782927, 43-48.

Itle, G.C., Salinger, A.G., Pawlowski, R.P., Shadid, J.N. & Biegler, L.T. 2004. A tailored optimization strategy for PDE-based design application to a CVD reactor Computers & Chem. Eng. 28, 291-302.

Ken-Ming Yin, 2007, An algebraic model on the performance of a direct methanol fuel cell with consideration of methanol crossover, J. Power Source, 167, 420–429.

Ko , D.H., Lee, M.J., Jang, W.H., Krewer, U. Non-isothermal dynamic modelling and optimization of a direct methanol fuel cell. Journal Of Power Sourcess, 180, 71-83

Rao, R.M., Rengaswamy, R. 2006. A distributed dynamic model for chronoamperometry, and gas starvation studies in PEM fuel cell cathode Chemical Eng. Sci. 61(22), 7393-7409.

Secanell, M., Karan, K., Suleman, A., Djilali, N. 2007. Multi-variable optimization of PEMFC cathodes using an agglomerate model. Electrochimica Acta, 52(22), 6318-6337.

Xu, C, Follmann, P.M., Biegler, L.T., Jhon, M.S. Numerical simulation and optimization of a direct methanol fuel cell. 2005. Computers & Chem. Eng. 29(88), Pages 1849-1860

Nomenclature

Symbol	
a_a	active area per unit volume in ACL
C_b	Bulk methanol concentration
C_M	methanol concentration
$C_{M,ref}$	reference methanol concentration
C_O	oxygen concentration
C_{Og}	oxygen concentration at CCL
$C_{O,ref}$	reference oxygen concentration
C_a^I	methanol concentration at position z_I
C_a^{II}	methanol concentration at position z_{II}
D_a^{eff}	effective diffusivity of methanol in ACL
D_b^{eff}	effective diffusivity of methanol in ABL
D_c^{eff}	effective oxygen diffusivity in CCL
D_m	methanol diffusivity in membrane
F	Faraday constant
$i_{oM,ref}$	reference methanol oxidation exchange current density
$i_{oO,ref}$	reference oxygen reduction exchange current density
I_{cell}	current density
I_{leak}	cross-over current density
I_O	oxygen reduction current density in cathode catalyst layer
K	potential dependent rate constant of methanol oxidation
k_c	potential dependent rate constant of oxygen reduction

Symbol	
k_p	permeation constant of pressure induced convection
K_I	equilibrium constant of methanol between anode backing layer/anode catalyst layer
K_{II}	equilibrium constant of methanol between ACL/membrane
L_a	ACL thickness
L_b	ABL thickness
L_c	CCL thickness
L_d	cathode gas diffuser thickness
L_m	membrane thickness
M_m	molecular weight of methanol
R	universal gas constant
R_g	Rg universal gas constant
T	absolute temperature
U_M	reference methanol oxidation open circuit voltage
U_O	reference oxygen reduction open circuit voltage
V_{cell}	cell voltage
α_A	anodic transfer coefficient
α_C	cathodic transfer coefficient
η_a	electrode over-potential in anode
η_c	electrode over-potential in cathode
κ_m	proton conductivity in membrane phase
ξ	electro-osmotic drag coefficient
λ	constant in the rate expression