

The Direct Methanol Fuel Cell (DMFC): Determination of Model Parameters

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ABSTRACT

This paper is contributed to determining model parameters for DMFCs. Theoretical evaluations are carried out to set up the relationship between the unknown and measurable parameters or variables. A laboratory-scale liquid-feed cell was simulated under different operating conditions. The resulting measurable static performance curves are used as basic information. Some key kinetic and physical parameters can be determined or estimated for a DMFC model.

INTRODUCTION

The DMFC is very promising fuel cell for environmentally-friendly power supply in transportation and resident applications [1-3]. As shown in Fig-1, the DMFC is partitioned with a proton exchange membrane (PEM), a thin polymer film (20-100 μm) with sulfonic acid groups allowing for proton transport and avoiding so-called "chemical short circuits". Compared to the status of other fuel cells, the DMFC still remains to be further developed. In practice, the PEMs are not only good proton conductors, but also permeable to water and methanol. While the permeation of water is usually a minor problem occurring for all types of PEM fuel

cells, the permeation of the anodic methanol to the cathode reaction zone introduces a significant reduction in efficiency of the DMFC. Under open-circuit conditions, the experimental cell voltage is between 0.5 and 0.7 V whereas the thermodynamic value is about 1.2 V. This is mainly due to the methanol cross-over phenomenon, and in addition due to strong adsorption of reaction intermediates at the anode surface [4][5].

Anode:	$\text{CH}_3\text{OH}(\text{l}) + \text{H}_2\text{O}(\text{l}) \xrightarrow{\text{Pt/Ru}} \text{CO}_2(\text{g}) + 6\text{H}^+ + 6\text{e}^-$	$U_{\text{CH}_3\text{OH} \leftrightarrow \text{CO}_2}^{T=25^\circ\text{C}} = 0.02\text{ V}$
Cathode:	$3/2\text{O}_2(\text{g}) + 6\text{H}^+ + 6\text{e}^- \xrightarrow{\text{Pt}} 3\text{H}_2\text{O}(\text{l})$	$U_{\text{O}_2 \leftrightarrow \text{H}_2\text{O}}^{T=25^\circ\text{C}} = 1.23\text{ V}$
Overall:	$\text{CH}_3\text{OH}(\text{l}) + 3/2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	$U_{\text{cell}}^{T=25^\circ\text{C}} = 1.21\text{ V}$

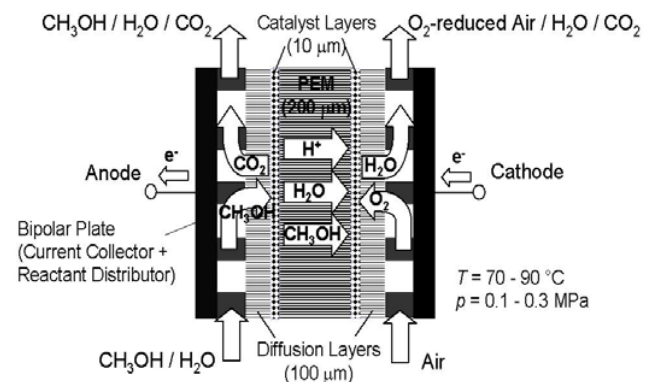


Fig-1 Working principle of a DMFC

The DMFC is composed of its components (anode and cathode compartments, diffusion layers and catalyst layers on both electrodes, PEM) and its dynamical and stationary performances are strongly nonlinear due to electrochemical kinetics. To understand the inter-

system phenomena and optimize the whole performance, proper models for the different cell components are needed. Hence, how the parameters related to a certain nonlinear model can be determined or estimated by using measurable data comes into question. In other words, a successful modeling depends on a successful method for determination of the model parameters. In this paper, a model is proposed to describe the dynamical behavior of a DMFC, based on mass balances, charge balances and electrochemical kinetics. The cell voltage, the cell current density, the methanol feed concentration and the carbon dioxide concentration in the anode compartment are assumed to be measurable. Under different operating conditions (steady states), a method of parameters determination for the proposed model is developed to get some unknown kinetic and physical parameters by using the above mentioned data.

MODELLING OF A DMFC

In general, as shown in Fig-2, modeling of a DMFC system is to set up mathematical equations for describing some behaviors of the DMFC system, such that the difference between measurable outputs of a real DMFC system and corresponding model outputs are small enough in the sense of "good fitting". In this paper, determination of the model parameters is here defined as restoring some model parameters from the measurable inputs and model outputs, generated from the model using the same inputs and given parameters. Hence, in principle, the validation of the proposed method for parameters determination will be limited here to the model proposed.

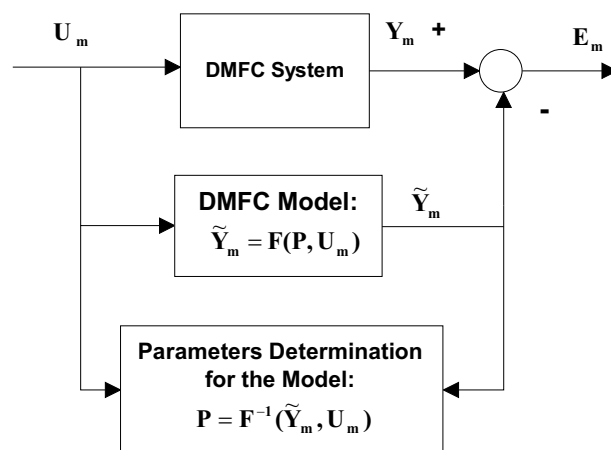


Fig-2 Scheme for the parameters determination for the proposed DMFC model

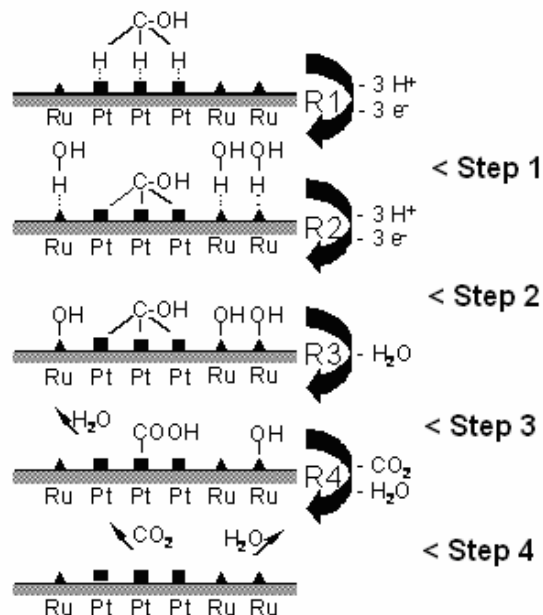


Fig-3 The proposed four-step reaction mechanism in the anode catalyst layer

As well known, electrochemical reactions in the anode catalyst layer play a significant role in the performance of DMFCs. The electro-oxidation of methanol on platinum-ruthenium catalyst is a multi step reaction with six transferred electrons. Several possible reaction mechanisms have been proposed^[6-8], for example, a four-step mechanism^[17], as shown in Fig-3, i.e. two electron transfer reaction steps followed by two chemical reaction steps. Firstly,

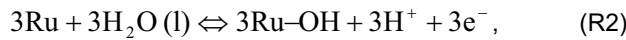
three hydrogen atoms of a methanol at the carbon centre adsorb on active platinum sites and react to release three protons and three electrons, which escape then from the reaction zone. The reaction can be described by



with the reaction rate

$$r_1 = k_1 e^{\frac{\alpha_1 3F}{RT} \eta_a} (\Theta_{\text{Pt}}^3 c_{\text{CH}_3\text{OH}}^{\text{CL}} - e^{-\frac{3F}{RT} \eta_a} \Theta_{\text{Pt}_3\text{-COH}} / K_1). \quad (1)$$

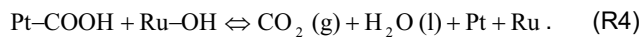
Secondly, three hydrogen atoms of three water molecules adsorb at active ruthenium sites under abstraction of three protons and three electrons, i.e.



with the reaction rate

$$r_2 = k_2 e^{\frac{\alpha_2 3F}{RT} \eta_a} (\Theta_{\text{Ru}}^3 - e^{-\frac{3F}{RT} \eta_a} \Theta_{\text{Ru-OH}}^3 / K_2). \quad (2)$$

Then, the two resulting surface-bound species react in the following steps:



The formed carbon dioxide and water leave the catalyst surface at the corresponding reaction rates

$$r_3 = k_3 (\Theta_{\text{Pt}_3\text{-COH}} \Theta_{\text{Ru-OH}}^2 - \Theta_{\text{Pt}}^2 \Theta_{\text{Ru}}^2 \Theta_{\text{Pt-COOH}} / K_3), \quad (3)$$

$$r_4 = k_4 (\Theta_{\text{Ru-OH}} \Theta_{\text{Pt-COOH}} - c_{\text{CO}_2}^{\text{CL}} \Theta_{\text{Pt}} \Theta_{\text{Ru}} / K_4). \quad (4)$$

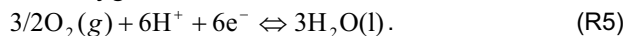
Because all reactions are surface reactions, surface fractions Θ_i are here used as concentration measures. The balances of species on the surface of two catalysts of platinum and ruthenium are given by:

$$\Theta_{\text{Pt}} + \Theta_{\text{Pt}_3\text{-COH}} + \Theta_{\text{Pt-COOH}} = 1, \quad (5)$$

$$\Theta_{\text{Ru}} + \Theta_{\text{Ru-OH}} = 1, \quad (6)$$

that must be obeyed for both stationary and dynamical cases.

The oxygen reduction occurs at the cathode:



The corresponding rate expression is assumed to be of Butler-Volmer type:

$$r_5 = k_5 e^{\frac{\alpha_5 F}{RT} \eta_c} [1 - e^{-\frac{F}{RT} \eta_c} (p_{\text{O}_2} / p^\theta)^{3/2}] \quad (7)$$

with $p_{\text{O}_2} = 0.63 \times 10^5$ Pa and $p^\theta = 10^5$ Pa.

If one of the reaction steps R1-R4 in the anode catalyst layer is assumed as the rate-determining step r_{rds} , characterized as a slow forward and quasi-irreversible reaction, the corresponding rate is approximately the rate at which the methanol CH_3OH is consumed and the carbon dioxide CO_2 produced in the anode catalyst layer. As a possible reaction mechanism, the reaction step R1 is assumed here to be the rate-determining step, hence, the corresponding rate $r_1 = r_{\text{rds}}$ (eq. (1)). Using:

$$\mathbf{X} = [X_1, X_2, X_3, X_4, X_5, X_6]$$

$$= [c_{\text{CH}_3\text{OH}}, c_{\text{CO}_2}, c_{\text{CH}_3\text{OH}}^{\text{CL}}, c_{\text{CO}_2}^{\text{CL}}, \eta_a, \eta_c],$$

$$\mathbf{U} = [U_1, U_2] = [c_{\text{CH}_3\text{OH}}^{\text{F}}, i_{\text{cell}}] \text{ and } Y = U_{\text{cell}}$$

accordingly as the states vector, the inputs vector and the output of the dynamical DMFC system, then, a set of differential equations, governing the mass and charge balances at both electrodes and in the membrane, can be set up as follows:

$$\dot{X}_1 = [\dot{V}_a (U_1 - X_1) - k^{\text{LS}} A^{\text{S}} (X_1 - X_3)] / V_a, \quad (8)$$

$$\dot{X}_2 = [\dot{V}_a (c_{\text{CO}_2}^{\text{F}} - X_2) - k^{\text{LS}} A^{\text{S}} (X_2 - X_4)] / V_a, \quad (9)$$

$$\dot{X}_3 = [k^{\text{LS}} (X_1 - X_3) - n_{\text{CH}_3\text{OH}}^{\text{M}} - r_{\text{rds}}] / d^{\text{CL}}, \quad (10)$$

$$\dot{X}_4 = [k^{\text{LS}} (X_2 - X_4) + r_{\text{rds}}] / d^{\text{CL}}, \quad (11)$$

$$\dot{X}_5 = (U_2 - 6F r_{\text{rds}}) / C_a, \quad (12)$$

$$\dot{X}_6 = [-U_2 - 6F (r_5 + n_{\text{CH}_3\text{OH}}^{\text{M}})] / C_c, \quad (13)$$

$$Y = Y_0 - X_5 + X_6 - (d^{\text{M}} / \kappa^{\text{M}}) U_2 \quad (14)$$

to describe the dynamical behavior of a DMFC cell, where, for the sake of simplicity, the methanol mass flux density $n_{\text{CH}_3\text{OH}}^{\text{M}}$ in the membrane is approximated to be

$$n_{\text{CH}_3\text{OH}}^{\text{M}} = (D_{\text{CH}_3\text{OH}}^{\text{M}} / d^{\text{M}}) X_3 \quad (15)$$

and $Y_0 = U_{\text{cell},0}$ is the theoretical open-circuit voltage of the cell.

The eqs. (8)-(14) can be described in short term with system parameters vector $\mathbf{P}$:

$$\begin{cases} \dot{\mathbf{X}} = \mathbf{f}(\mathbf{X}, \mathbf{U}, \mathbf{P}), \\ \mathbf{Y} = \mathbf{g}(\mathbf{X}, \mathbf{U}, \mathbf{P}), \end{cases} \quad (16)$$

which is a general description for control systems.

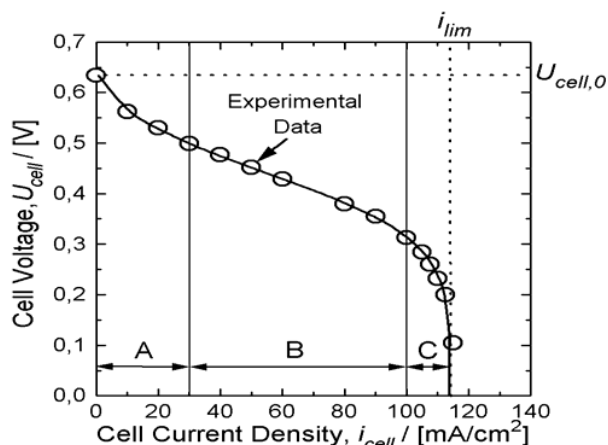


Fig-4 Steady state $i_{cell} - U_{cell}$ curve ($T=70^{\circ}\text{C}$, $c_{\text{CH}_3\text{OH}}^F = 0.5 \text{ mol/l}$, $\dot{v}_a = 1.36 \text{ ml/min}$, $p_a = 0.1 \text{ MPa}$, $p_c = 0.3 \text{ MPa}$)

Typically, the stationary $i_{cell} - U_{cell}$ characteristic shown in Fig-4 can be measured from experiments. There are three distinct regions: at low cell currents (A), the cell voltage is dominated by the electrochemical kinetics of anodic methanol oxidation; by increasing the current load (B), the cell voltage is further decreased due to additional limitations of methanol mass transport to the anode catalyst layer and the growing electrical resistance of the membrane; in the region (C), the system approaches the limiting current i_{lim} , at which the cell voltage breaks down. Another stationary characteristic, i.e. the $c_{\text{CH}_3\text{OH}}^F - U_{cell}$ curve shown in Fig-5, is here proposed to be also measured to get additional information about the cell performance. The information obtained from the $i_{cell} - U_{cell}$ and $c_{\text{CH}_3\text{OH}}^F - U_{cell}$ curves will be applied for determining some kinetic and physical parameters of the above model.

In the following sections, theoretical evaluations are carried out to set up the relationship between the unknown and measurable parameters or variables in order to determine some

unknown parameters, for example, the mass transfer coefficient k^{LS} , the reaction rate expression r_{rds} for the rate-determining step and the value of the product $K_1 K_2 K_3 K_4$, etc.

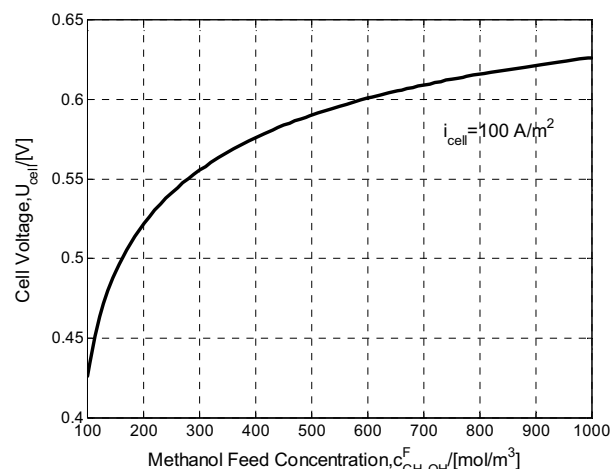


Fig-5 Steady state $c_{\text{CH}_3\text{OH}}^F - U_{cell}$ curve ($T=70^{\circ}\text{C}$, $i_{cell} = 100 \text{ A/m}^2$, $\dot{v}_a = 1.36 \text{ ml/min}$, $p_a = 0.1 \text{ MPa}$, $p_c = 0.3 \text{ MPa}$).

THEORETICAL EVALUATIONS FOR MODEL PARAMETERS DETERMINATION

The data shown in Fig-4 are obtained under the operating points with constant methanol feeding and different current densities, the stationary characteristic shown in Fig-5 with constant current density and different methanol feed concentrations. As well known, the steady states of a process are often selected as its operating points. Frequently, inputs change dynamically around their steady state values after certain control laws to get desired dynamical performance. The parameter setting of a controller depends strongly on the steady states and related system dynamics. In the following, based on the solution of the steady states of the DMFC model, some useful relations between steady states (operating points) and model parameters will be evaluated, in order to get some insight into the relationship between