

An innovative method of modeling direct methanol fuel cells

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Abstract

In this paper a computer model of a direct methanol fuel cell (DMFC) was presented. Chemical reactions of methanol oxidation and oxygen reduction were modeled with HYSYS software. Obtained results were used to evaluate the maximum cell voltage and limiting current density for the investigated fuel cell. An equivalent electric circuit was used for computing cell voltage after accounting for ohmic losses and methanol crossover losses. A simulation of a polarization curve for a cell supplied with 0.5 mole/dm³ methanol and pure oxygen operating at 70°C was performed and validated with experimental data. The effects of cathode gas humidification and methanol concentration change in the range of 0.5 mole/dm³–3 mole/dm³ on cell performance were investigated. Difficulties with evaluating methanol oxidation rate and methanol crossover loss numerical values were encountered. Experimental data were used to find these values. This procedure greatly reduced the range of model's applicability. Proposed metho methanol fuel cells had intrinsic challenges. The ways to tackle them were described.

Keywords: modeling, direct methanol fuel cells

1. Introduction

Unique advantages of direct methanol fuel cells have made them an interesting power source for portable power devices and vehicles. Methanol fuel has the high energy density, low cost, facile distribution and storage. In addition to having high specific energy and energy density ensuring longer operation times, one of the main advantages of the DMFC over the rechargeable batteries is that they do not require an external electrical power source for re-charge. The DMFC can be quickly re-fueled which is convenient and greatly enhances the mobility, enabling the use of

electronic devices in remote areas where charging batteries is problematic. This technology is still in a prototype phase due to several obstacles including high manufacturing cost, quick degradation and fuel crossover that prevent from a large scale commercialization. High cost is mainly due to high loadings of precious metal catalysts on both the anode and the cathode side. High catalyst loadings are required because of the sluggish methanol oxidation reaction kinetics in comparison to less complex hydrogen oxidation reaction. The oxygen reduction reaction on the cathode is affected by methanol crossover phenomenon.

Research and development of DMFCs are greatly supported by computer modeling which is used for design and optimization processes. Computer simulations provide better understanding

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of fuel cells working principles. There are several different approaches to direct methanol fuel cells modeling. Most commonly presented approach includes development of interdisciplinary mathematical models based on laws of fluid mechanics and electrochemistry as described in [1–4]. Unknown coefficients in equations are evaluated on the basis of experimental data. Development of computational fluid dynamics (CFD) contributed to development of two- and three dimensional mathematical models based on finite volume method. These models exhibit high accuracy of cell performance simulation. However, the level of complexity of mathematical models made them impractical for power management uses, thus creating a need for simpler models based on an equivalent electrical circuit, as presented in [5–8]. Electrical circuits consist of resistors, capacitors, inductors and diodes. A structure of an equivalent circuit is defined on the basis of a mathematical equations, electrochemical impedance spectroscopy results or other experimental data. The model of a direct methanol fuel cell described in this paper is a hybrid model where electrochemical reactions were modeled with HYSYS software and obtained results were used in an equivalent electrical circuit for computation of cell voltage. This innovative approach was first proposed in [9]. It was applied to Solid Oxide Fuel Cells by one of the authors and now it's functionality for methanol supplied fuel cells was analyzed.

2. DMFC description

The model was developed for a direct methanol fuel cell described and tested by Ge et al [10] due to lack of in-house fuel cell hardware and experimental set-up. Experimental results presented in [10] were used for model validation. The active area of the considered fuel cell was 5 cm^2 . The anode and cathode catalyst loadings were 3 mg/cm^2 Pt-Ru black and 3 mg/cm^2 Pt black respectively. Ruthenium was added to the anode catalyst to improve methanol oxidation reaction kinetics. Membrane was made of Nafion 117. The sample membrane–electrode assembly of a DMFC is shown in Fig. 1.

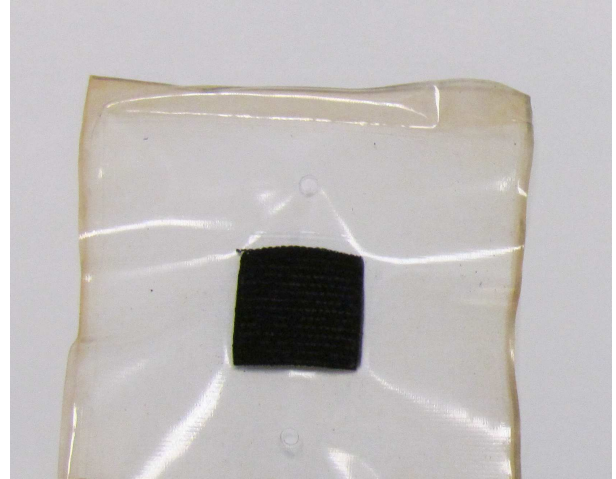


Figure 1: Membrane electrode assembly (MEA) for a direct methanol fuel cell

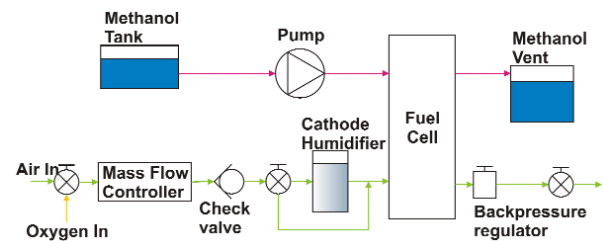


Figure 2: Direct methanol fuel cell experimental setup

The experimental set-up used for fuel cell testing by Ge et al [10] is shown in Fig. 2. Methanol was supplied to a fuel cell from a methanol tank by a pump. Excess methanol, water and reaction products were vented to a waste methanol tank. Oxygen was supplied from a tank at a rate adjusted by a mass flow controller. Oxygen was humidified in a cathode humidifier before entering the fuel cell.

3. Model description

HYSYS software was used to acquire accurate thermodynamic properties prediction for methanol oxidation and oxygen reduction reactions. Two different fluid packages were applied in the model. A Lee-Kesler Plocker Equation of State (EOS) model was used for oxygen reduction reaction computation as a recommended method for non-polar substances behavior modeling. A NRTL activity model was used for methanol oxidation reaction computation. In this approach,

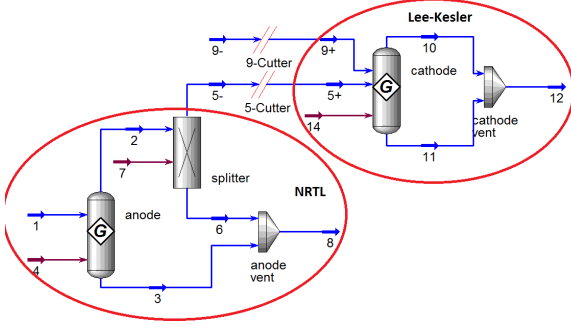
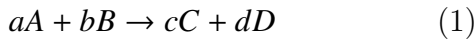


Figure 3: Direct methanol fuel cell model diagram

Table 1: Direct methanol fuel cell working conditions

Parameter	Value	Unit
methanol flow rate	1.2	ml/min/cm ²
methanol concentration	0.5, 1, 2, 3	mol/dm ³
oxygen flow rate	120	ml/min/cm ²
operating temperature	70	°C

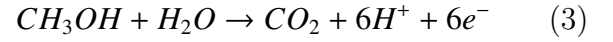
an equation of state was used for predicting the vapor fugacity coefficients and an activity coefficients model was used for the liquid phase behavior simulation. Activity coefficients were determined from total excess Gibbs free energy equation. Equilibrium constants were used for determining amounts of products. A definition of an equilibrium constant for a sample reaction 1, is given by equation 2.



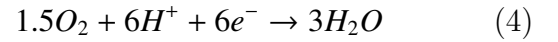
$$K_{eq} = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (2)$$

Activity equals partial pressure in a mixture for gases and molar concentration in a solution for liquids. The equilibrium constant was calculated for all reactions attached to Gibbs reactor. The fuel cell flow diagram in HYSYS software environment, Fig. 3, consisted of two Gibbs reactors that represented the anode and the cathode respectively and a splitter between them.

The anode was supplied with 0.5 mole/dm³ methanol at a rate of 1.2 ml/min/cm². Methanol was oxidized at 70°C according to reaction 3.



Hydrogen, that was a product of methanol oxidation reaction, was extracted from the gas fraction that contained hydrogen, methanol and water vapor in Splitter. Hydrogen was transported to the cathode. The excess methanol, water and other methanol oxidation reaction products were directed to the anode vent. Cathode was supplied with pure oxygen at a rate of 120 ml/min/cm². Oxygen was reduced at 70°C according to reaction 4. Cathode reaction products were directed to the cathode vent. Anode and cathode half-reactions summed up, represented the overall cell reaction, Eq. 5. The reversible voltage for this reaction at 70°C was 1.2 V.



Maximum cell voltage and maximum current density were calculated from Nernst equation, Eq. 6 and Faraday's law, Eq. 7 respectively. The Nernst equation contained hydrogen partial pressures at the anode vent and the cathode vent. Hydrogen was present in both the anode and the cathode, because it was a product of methanol oxidation reaction. Hydrogen appeared also in eq 7, because there were two electrons created per every hydrogen particle in reaction 3.

$$E_{max} = \frac{RT}{2F} \ln \frac{p_{H2 an}}{p_{H2 cat}} \quad (6)$$

$$i_{max} = \frac{2Fn_{H2}}{A} \quad (7)$$

Polarization curves were obtained from an equivalent electrical circuit, Fig. 4. The equivalent electrical circuit was first proposed by one of the authors for SOFCs modeling in Fig. [9]. The approach was applied to methanol fueled fuel cell in this study in order to assess its functionality for a different fuel cell type. According to Fig. [9], E_{max} represented the maximum cell voltage characteristic for an electrochemical reaction. Cell voltage (E) was obtained after accounting for

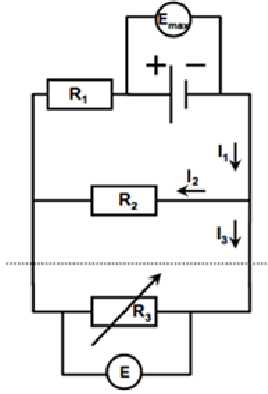


Figure 4: An equivalent electrical circuit of a direct methanol fuel cell [9]

ohmic losses. The total electric current generated in a fuel cell was represented by I_1 . The parasitic electric current due to methanol crossover and other electrical losses was represented by I_2 . Resistors R_1 and R_2 represented cell's ionic and electrical resistance respectively. The load (R_3) was supplied by electric current I_3 .

In order to express cell voltage as a function of current density a dimensionless hydrogen utilization factor was introduced (η_{H_2}). It was changed from zero to one resulting in current density change from zero to i_{\max} . The number of hydrogen particles produced in methanol oxidation reaction was directly proportional to the electrical current according to Faraday's law. Cell voltage (E_{DMFC}) was calculated from Eq. 8. Eq. 8 was derived from equivalent electrical circuit.

$$E_{DMFC} = \frac{E_{\max} - r_1 \cdot \eta_{H_2} \cdot i_{\max}}{\frac{r_1}{r_2} \cdot (1 - \eta_{H_2}) + 1} \quad (8)$$

The presented model was used to establish the polarization curves for methanol concentration range of 0.5–3 mole/dm³. Investigation of oxygen humidification effect on cell performance required model modification. Oxygen was humidified at 70°C in a water tank was introduced before the cathode.

4. Results and discussion

The model was validated with the experimental results presented in [10], as previously mentioned. Simulation of methanol oxidation reaction

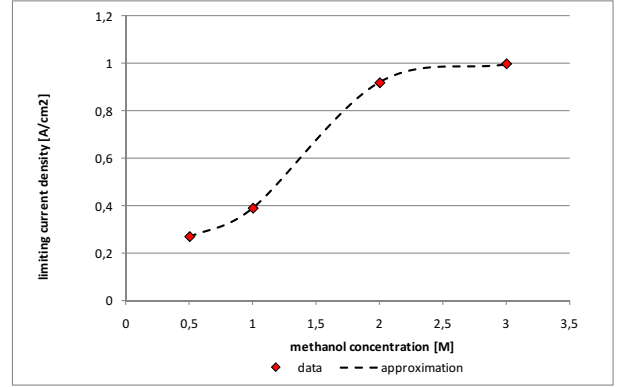


Figure 5: Limiting current density of a direct methanol fuel cell as a function of methanol concentration

for 0.5 mole/dm³ methanol solution with the proposed method was found to be troublesome. Limiting current density was found to be 5.615 A/cm² with 97.68% of methanol undergoing oxidation reaction in equilibrium conditions. These results were not consistent with experimental data where limiting current density was 0.27 A/cm² and only 4.8% of supplied methanol underwent reaction. The conclusion was that reaction rate was significantly influenced by mass transport and catalyst effectiveness. These effects were not possible to be accounted for in proposed modeling methodology, because reactions were calculated on the basis of equilibrium. The limiting current density was set constant. The numerical value was read from experimental data [10]. This movement greatly reduced the model universality. The use of experimental data was also necessary for determining ionic and electrical resistance. Their values were affected by methanol crossover loss which was dependent on temperature, methanol concentration, current density and material properties. The complexity of methanol crossover phenomenon made defining it precisely enough troublesome.

The change in limiting current density value with methanol concentration change caused the need for finding a limiting current density for each methanol concentration, shown in Fig. 5. Symbols represent limiting current densities determined on the basis of experimental data points. An approximating function was found in order to predict the limiting current density for methanol

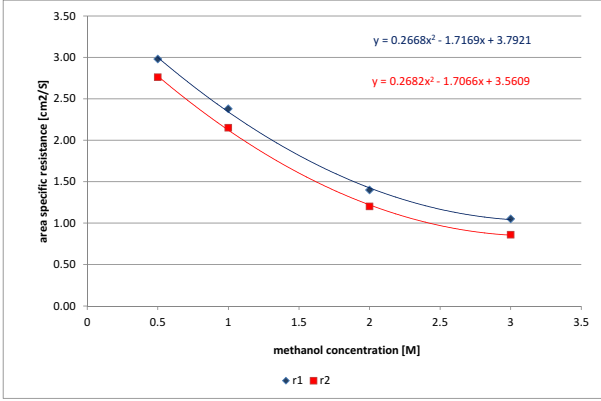


Figure 6: Ionic (r_1) and electrical (r_2) area specific resistances in a function of methanol concentration

Table 2: Limiting current density values and resistance values for different methanol concentrations

c mol/dm ³	r_1 cm ² /S	r_2 cm ² /S	i_{\max} A/cm ²
0.5	2.98	2.76	0.27
1	2.38	2.15	0.39
2	1.40	1.20	0.92
3	1.05	0.86	1

concentration range of 0.5–3 mole/dm³.

To account for change in voltage losses with methanol concentration change, an adjustment of resistance values in the equivalent electrical circuit was needed. The ionic (r_1) and electrical (r_2) area specific resistances for different methanol concentrations were depicted in Fig. 6. Symbols represent resistance values obtained from experimental data points, Fig. 8. In order to assess resistance values for other methanol concentrations within the range of 0.5–3 mole/dm³ approximating functions were found. Limiting current density values and resistance values for different methanol concentrations were summarized in Table 2. Development of approximating functions for unknown parameters, was authors contribution to previously presented modeling approach. It was the only way this modeling method could be applicable to DMFCs.

The polarization curves obtained from the proposed model together with experimental results for 0.5 mole/dm³ methanol solution were depicted in Fig. 7.

Oxygen humidification was found to cause a

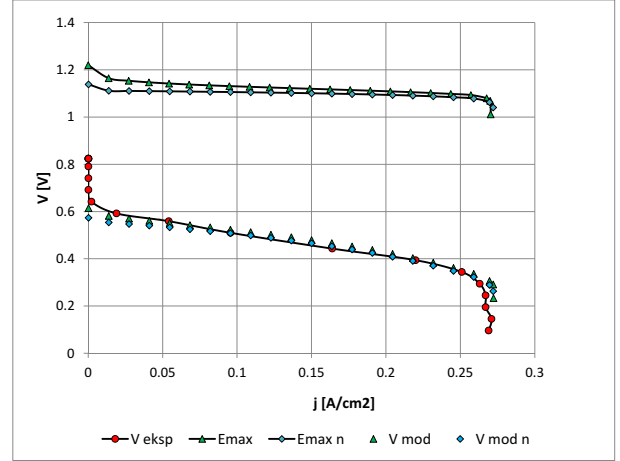


Figure 7: Polarization curves for a DMFC supplied with 0.5 mol/dm³ methanol and pure oxygen at 70°C, dry oxygen and humidified oxygen

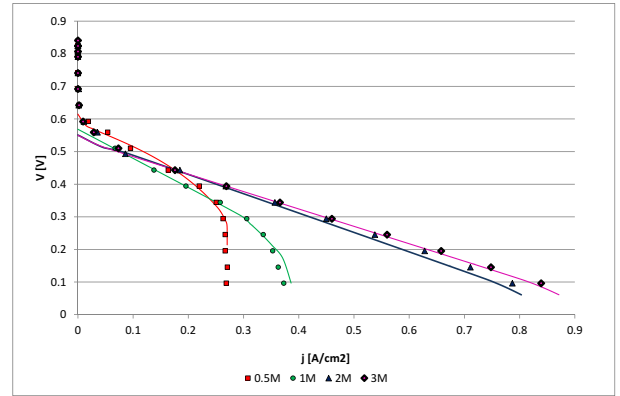


Figure 8: Polarization curves for methanol concentration 0.5–3 mole/dm³ and 6 ml/min flow rate, cell temperature 70°C, cathode: pure oxygen, 600 sccm

maximum cell voltage decrease due to change of hydrogen partial pressure. It's effect on the polarization curve was negligible, Fig. 7. It can be justified with high membrane water content which did not change significantly with the introduction of oxygen humidification. Large amounts of water supplied to the anode side ensured membrane saturation and good ionic conductivity. Obtained characteristics were in good accordance with the experimental data.

The influence of methanol concentration change on polarization curves, Fig. 8, was found to be profound. Experimental data were represented by symbols, respective simulation results were shown with solid lines.

The increase in methanol concentration from

0.5 mole/dm³ to 2 mole/dm³ improved the cell performance. A further increase in concentration had a negligible effect on current density-voltage curve. For lower methanol concentrations an increase in methanol concentration improved the oxidation reaction kinetics, thus resulting in an increase of limiting current density and enhancement of the overall performance. However, an increase in methanol concentration caused a concomitant increase of methanol crossover, which was oxidized on the cathode surface. At some point this phenomenon started limiting the oxygen reduction reaction rate. Oxygen was consumed in methanol oxidation reaction at the cathode. In some cases this phenomenon not only offset the performance enhancement, but even deteriorated it, as presented in [10].

Polarization curves obtained from the presented model (Fig. 8, solid lines) were in good accordance with the experimental data for the investigated cell at chosen operating conditions. The range of model applicability was, however, very restricted for the proposed method due to complexity of DMFCs working principles.

5. Conclusions

A modeling method developed by one of the authors and designated for SOFCs, was proposed for direct methanol fuel cells modeling. The chemical reactions were modeled with HYSYS software and cell voltage was computed from an equivalent electrical circuit. Presented approach, previously proved by one of the authors successful in high temperature fuel cells modeling, was found not to be very practical in DMFCs modeling. It is a common practice to omit the activation losses and mass transport losses in SOFCs modeling. This approach turned out not to be suitable for DMFCs modeling. It was difficult to evaluate methanol oxidation and oxygen reduction reaction rates due to their high dependence on mass transport and catalyst effectiveness. The limiting current density had to be defined with the use of experimental data. The resistors in the equivalent electrical circuit which represented cell's losses also had to be determined with the use

of experimental data due to difficulties with defining methanol crossover loss. Simulation results were in good accordance with the experimental current density-voltage characteristics over a narrow range of operating parameters after developing mathematical approximating functions for unknown parameters. In order to extend the model's functionality additional approximating functions for limiting current density and cell losses should be derived.

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Nomenclature

[A], [B], [C], [D]	activity of chemical species
η_{H_2}	hydrogen utilization factor
A	active area, cm ²

A, B, C, D	chemical species
a, b, c, d	stoichiometric coefficients
E_{\max}	maximum cell voltage, V
E_{DMFC}	cell voltage, V
F	Faraday's constant, C/mol
i_{\max}	maximum current density, A/cm ²
K_{eq}	chemical equilibrium constant
n_{H2}	hydrogen molar flow, mole/s
$p_{H2\ an}$	hydrogen partial pressure at an- ode's vent, bar
$p_{H2\ cat}$	hydrogen partial pressure at cathode's vent, bar
R	universal gas constant, J/mol/K
r_1	area specific ionic resistance, cm ² /S
r_2	area specific electrical resistance, cm ² /S
T	temperature, K