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MEASUREMENT OF POLARIZATION CURVE AND DEVELOPMENT OF A UNIQUE SEMI-EMPIRICAL MODEL FOR DESCRIPTION OF PEMFC AND DMFC PERFORMANCES

In this study, a single polymer electrolyte membrane fuel cell (PEMFC) in H₂/O₂ form with an effective dimension of 5 cm×5 cm as well as a single direct methanol fuel cell (DMFC) with a dimension of 10 cm×10 cm were fabricated. In an existing test station, the voltage-current density performances of the fabricated PEMFC and DMFC were examined under various operating conditions. As expected, DMFC showed a lower electrical performance which can be attributed to the slower methanol oxidation rate in comparison to the hydrogen oxidation. The results obtained from the cell operation indicated that the temperature has a great effect on the cell performance. At 60 °C, the best power output was obtained for PEMFC. There was a drop in the cell voltage beyond 60 °C, which can be attributed to the reduction of water content inside the membrane. For DMFC, the maximum power output resulted at 64 °C. Increasing oxygen stoichiometry and total cell pressure had a marginal effect on the cell performance. The results also revealed that the cell performance improved by increasing pressure differences between the anode and cathode. A unified semi-empirical thermodynamic based model was developed to describe the cell voltage as a function of current density for both kinds of fuel cells. The model equation parameters were obtained through a nonlinear fit to the experimental data. There was a good agreement between the experimental data and the model predicted cell performance for both types of fuel cells.

Key words: PEMFC; DMFC; semi-empirical model; polarization curve; fuel cell.

The main objectives in fuel cell modeling are to determine the polarization curve and various factors affecting on fuel cell performance in order to obtain maximum power. Therefore, investigation on the fuel cell polarization curve under various operating conditions is essential. Although PEMFC is the first choice for a variety of applications due to its higher electrical performance, the hydration storage and handling still remains a challenge in its development. DMFC is an attractive fuel cell because methanol energy density is much higher than that of hydrogen. Besides, it is an inexpensive liquid and easy to handle, store and transport. However, in practice, DMFC has much lower open circuit voltage (OCV). One of the major reasons for this low performance is methanol crossover through

the proton exchange membrane (PEM), such as Nafion, to reach the cathode side *via* physical diffusion and electro-osmotic drag (by protons). Such crossover not only results in a waste of fuel, but also lowers the cell performance. The effect of methanol crossover in the DMFC has attracted attention worldwide and its impact on cathode operation and system efficiency was extensively investigated [1].

Indeed, rigorous characterization of fuel cells performance considering physical phenomena such as mass and energy transport, electrochemical kinetics, etc., is too complex and cumbersome. The main advantage of thermodynamic based semi-empirical models lies in correlation of cell performance in terms of operating conditions for the practical applications. Most empirical performance models are focused on prediction of polarization curves, which are used to characterize the electrical performance of fuel cells. These models are mainly based on the thermodynamic models, which describe cell performance according to operating conditions such as temperature and

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pressure. In general, the actual fuel cell voltage is lower than its thermodynamic voltage when current is drawn. The voltage losses, usually called overpotential, can be divided into three regions - the active, ohmic and mass-transfer limiting regions [2-4]. It was accepted that in the low current density region, the active overpotential of oxygen reduction at the cathode predominates. In the intermediate region, the cell internal resistance, mainly attributed to the membrane resistance, becomes the major factor resulting in a linear decrease of the discharge curve in this region. In the high current density region, the overall cell reaction rate is limited by depletion of the reactants. Consequently, the mass-transfer overpotential becomes the dominant factor and causes a sharp decay in the power density [5]. Several semi-empirical models have been proposed to describe the fuel cell polarization curve. Srinivasan *et al.* [6] developed an equation that describes the relation between the cell potential and current density in the low and intermediate current density region, where electrode reactions are controlled by the activation and ohmic resistances:

$$E = E_0 - b \log j - R_e j \quad (1)$$

where E_0 is the thermodynamic open-circuit potential. The first two terms of this expression together are a form of the Tafel equation, which accounts for the activation potential, and R_e is the ohmic resistance of the fuel cell components. The $R_e j$ term is the ohmic overpotential [7-9]. Starting from this point, to increase the reliability of the aforementioned equation, Kim *et al.* [10] introduced an additional term that allows fitting of the experimental curves over the whole range of current density. However, they did not find evidence of a link between the introduced parameters and the experimental variables related to mass transport:

$$E = E_0 - b \log j - R_e j - m e^{n j} \quad (2)$$

where m and n are parameters that account for the "mass transport overpotential" as a function of current density. Squadrito [8] used Eq. (3) as a starting point to analyze the different contributions to the mass transport limitation and produced an equation in the following form:

$$E = E_0 - b \log j - R_e j + \alpha j^k \ln(1 - \beta j) \quad (3)$$

Where α , k and β are fixed parameters. The term $\ln(1 - \beta j)$ introduces a limit to the available current density. For $k = 1$, α has the same dimension as R_e and can be interpreted as an additional resistance term due to the overall mass transport limitation [8].

Argyropoulos and his coworkers [11,12] showed the applicability of Kim's and Squadrito's equation [8] for predicting voltage response of the DMFC. This equation focuses on very unfavorable conditions for cell operation, *i.e.*, low methanol solution concentrations and relatively low cell temperatures:

$$E = E_0 - b \log j - R_e j + C_1 \ln(1 - C_2 j) \quad (4)$$

All the models introduced above are semi-empirical. They are based on Srinivasan *et al.*'s model, Eq. (1), and may have serious mathematical defects [6]. When the current density, j , becomes zero, the equation should reduce to the open circuit voltage, E_0 . However, these models do not meet the mathematical boundary condition. The present study proposes a new semi-empirical cell voltage model based on Srinivasan *et al.*'s model with the addition of one extra term to take into account the mass transport overpotential [6]. This term derived from an empirical consideration that accounts the mass transport (diffusion) limitation at high current density region. The resulting equation appeared to be uniquely valid under several experimental conditions for both DMFC and PEMFC on the basis of the experimental data obtained with a 25 cm² PEMFC and a 100 cm² DMFC single cell.

EXPERIMENTAL DETAILS

Polymer electrolyte membrane fuel cell (PEMFC)

Experiments on the fabricated PEMFC with hydrogen feed were performed. The schematic diagram of built fuel cell is shown in Figure 1. The fabricated fuel cell had an effective cross-sectional area of 25 cm². The cell was fitted with single membrane electrode. The assembled cell was sandwiched between two graphite blocks with a flow bed configuration, in the form of parallel channels. The geometry of the channels was rectangular, 1 mm in width and 1 mm in depth, separated by 1 mm pitches. The cell was installed between two copper current collectors, two plastic insulation sheets and two aluminum cover plates. The set was retained with bolts positioned around the cell peripheral. Electrical heaters were placed behind each of the end plates in order to heat the cell to the desired operating temperature. The MEA was purchased from E-TEK, Inc. The catalyst content of the cathode was 0.4 mg Pt cm⁻² and the catalyst content of the anode was 0.2 mg Pt cm⁻² (repeated). Carbon cloth was used as a gas diffusion layer. The membrane was Nafion 112 with total surface area of 64 cm² and effective surface area of 25 cm². The thickness of MEA is 2 mm. Test station was designed to analyze the performance of the fabricated cell. The

fuel cell test station was equipped with a humidifying system for the reactant gases and the cell temperature controller. The humidifying temperature for H₂/O₂ was maintained at 65 °C. The gas flow rates were fixed and checked by electronic mass flow controllers. The cell potential against current density measurements were recorded by a data acquisition unit which is interfaced to a computer. Figure 2 shows a photograph of the experimental apparatus used in this section.

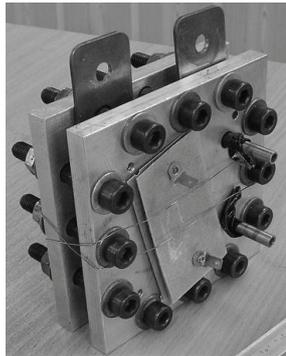


Figure 1. A photograph of the constructed PEM single cell with an effective area of 25 cm².

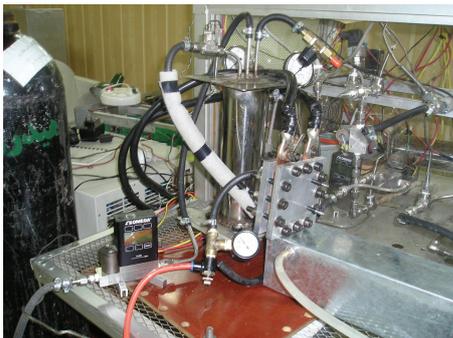


Figure 2. A photograph of apparatus used for PEMFC experiments.

Direct methanol fuel cell (DMFC)

The DMFC used in this study was assembled with Nafion membrane as polymer electrolyte with an effective cross-sectional area of 100 cm². The membrane electrode assembly was purchased from Fuel Cell Store Co. The MEA was sandwiched between two graphite blocks which had a flow bed, in the form of serpentine structure for anode and parallel pattern for cathode. The DMFC with 4 times effective cross-sectional area was similarly fabricated cell as explained above. Tests on the fabricated and assembled DMFC were performed with a cell unit shown in Figure 3. A schematic diagram of facilities used for testing DMFC performance is shown in Figure 4.

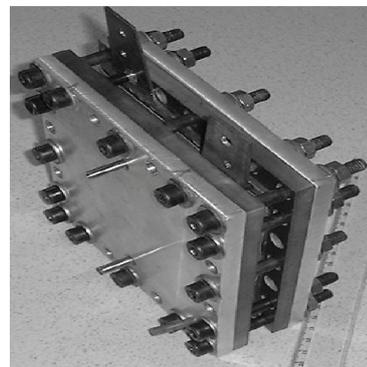


Figure 3. DMFC single cell constructed for experimentation with an effective area of 100 cm².

RESULTS AND DISCUSSION

In this study, an equation derived from a semi-empirical approach is proposed. Through a mechanistic similarity, the basic theory in electrochemistry was used to introduce a simple equation that fits with the experimental data over the entire range of current

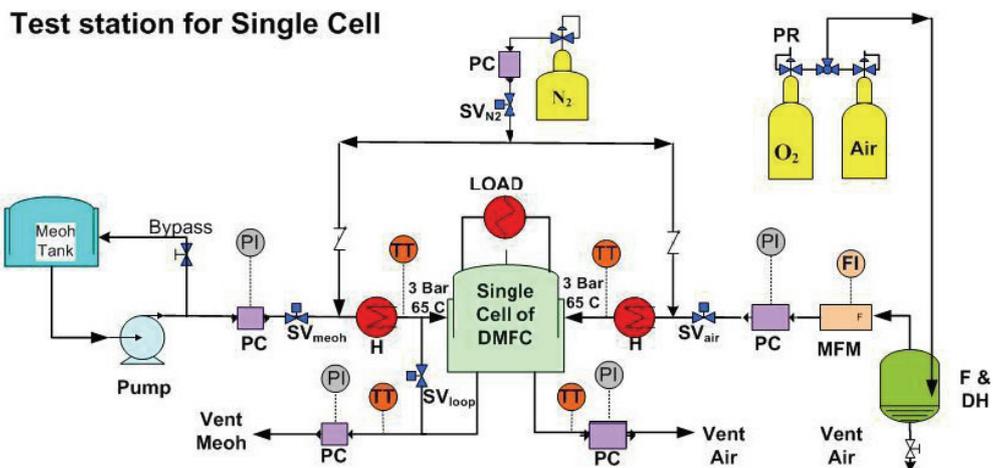


Figure 4. Schematic diagram of the test facilities used for DMFC experiments.

density with high accuracy. The semi-empirical equation is given as follows:

$$E = E_0 - b \log(1 - \alpha j) - R_e j - R_d(1 - \exp(\beta j)) \quad (5)$$

The relationship is similar to equations proposed by the other researchers in the same field. The last term in Eq. (5) describes the potential loss due to the rapid depletion of reactants at high current density which causes a mass transfer resistance leading to a reduction in the fuel cell electrical output. When no current is withdrawn from the cell, no depletion occurs and this term vanishes, while the maximum depletion occurs at limiting current density (j_{limiting} at $E = 0$). It has an advantage of the cell voltage which shifts naturally to its open circuit voltage at zero current density.

In order to calculate each parameter in Eq. (5), two separate sets of experiments were conducted with the fabricated-assembled PEMFC and DMFC single cell. The applicability of the proposed equation was examined under several experimental conditions.

PEMFC with hydrogen feed

To calculate the parameters in Eq. (5), several experiments were conducted with the above constructed hydrogen fuel cell. The experiments were carried out at various temperatures, pressures and cathode flow rates (oxygen stoichiometry). The model parameters were recovered from a nonlinear model

equation to fit the experimental data. The determined model parameters are summarized in Table 1. Equation (5) describes the cell performance at constant temperature and the parameters appearing in this equation were separately recovered from V - j data obtained at different temperatures. The recovered parameters have different values which show their temperature dependency. In this study, since the parameters were empirical, no physically meaningful temperature dependencies were proposed. Therefore, Eq. (5) works at constant temperature and other specified conditions.

Figure 5 compares the computed polarization curves with the measured ones. The calculated curves show good agreement with the experimental data in the investigated temperature range (50–70 °C). It is interesting to mention that among the four sets of experiments at 4 different temperatures (Figure 5), the best overall cell performance was obtained at 60 °C. It was easily understood that the cell performance could be improved by increasing the cell temperature, which results in an increase of internal energy and a decline of activation overpotential. This is because the exchange current density increases with an increase in fuel cell temperature, which reduces the activation losses. However, when the cell temperature was increased up to 70 °C, the performance of the cell was decreased. Even the cell performance at 70

Table 1. Recovered values of semi-empirical model parameters for single PEMFC operated with H_2/O_2

Cell temperature, $t / ^\circ\text{C}$	E_0 / V	b / V	$\alpha / \text{A}^{-1} \text{cm}^2$	$R_e / \Omega \text{cm}^2$	R_d / V	$\beta / \text{A}^{-1} \text{cm}^2$
70	0.981	0.023	0.877	1.527	2.220	-0.039
65	0.910	0.015	0.948	1.321	2.492	-0.046
60	0.902	0.016	1.020	0.936	1.557	-0.051
50	0.901	0.012	0.980	1.051	1.531	-0.051

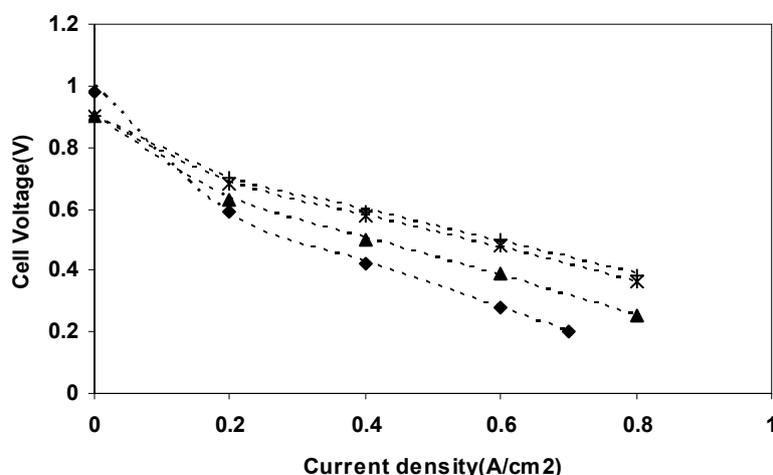


Figure 5. Comparison between experimental data and semi-empirical model prediction (Eq. (5)) for a cell operated with a flow rate of 0.2 slpm for oxygen and hydrogen, pressurized at 1 bar, cell temperatures: 50 (✱); 60 (+); 65 (▲); 70 °C (●).

°C was lower than that of 50 °C. This can be attributed to the low water content inside the cell membrane at high temperatures. In general, water management in PEMFC is very important. The kinetics of oxidation will be accelerated at high temperature. However, the ionic conductivity of Nafion falls at temperatures higher than the humidification temperature due to loss of water, which is necessary for its conductivity, due to evaporation [13-14].

Polarization curves for hydrogen fuel cell with various operating pressures are shown in Figures 6 and 7. In Figure 6, the pressures of anode and cathode sides were kept at the same level. The performance of the fuel cell increases with the increase of the cell operating pressure as shown in Figure 6. An increase of the pressure in both cathode and an-

ode sides increases the reactants concentration in the cell and therefore improves the overall performance. The pressure difference between the cathode and anode sides was also investigated in this study. As it is demonstrated in Figure 7, when the pressure at cathode side was kept higher than that of anode side, cell performance was improved. Figure 8 shows the effect of change in cathode flow rate on the cell performance which indicates that this effect is very marginal. That is due the stoichiometric ratio of H₂:O₂ is 2:1. Since oxygen is a cheap reactant, it is usually used as an excess reactant. In all experiments conducted. In this study, oxygen was used at the ratio higher than stoichiometric ratio. Therefore it had no impact on the cell performance.

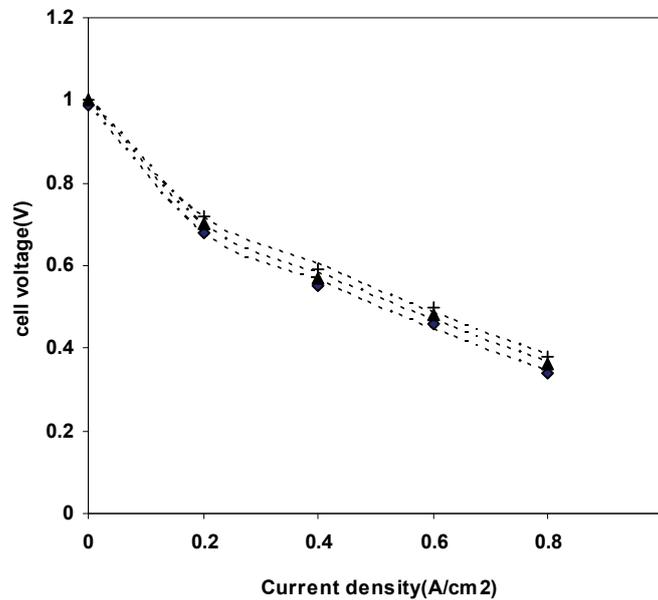


Figure 6. Comparison between experimental data and semi empirical model prediction (Eq. (5)) for a cell operated with a flow rate of 0.2 slpm for oxygen and hydrogen, cell temperature: 60 °C and with the same pressures in cathode and anode: 1.5 (+); 1 (▲); 0.5 bar (●).

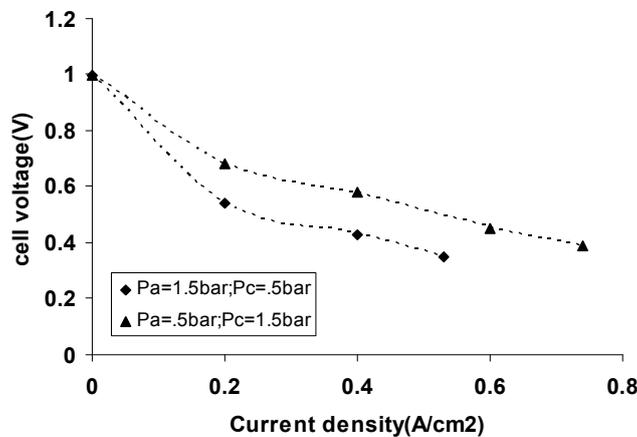


Figure 7. Comparison between experimental data and semi empirical model prediction (Eq. (5)) for a cell operated with a flow rate of 0.2 slpm for oxygen and hydrogen, cell temperature: 60 °C.

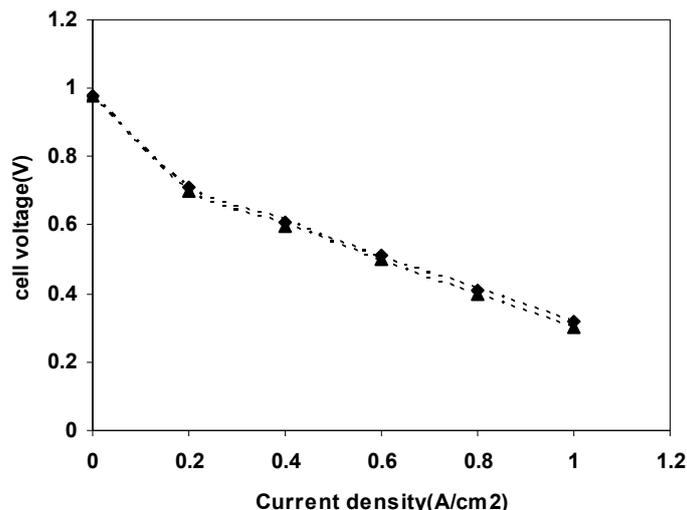


Figure 8. Comparison between experimental data and semi empirical model prediction (Eq. (5)) for a cell operated with a flow rate of 0.2 slpm for hydrogen temperature: 60 °C, pressurized at 1 bar, oxygen flow rates: 0.5 slpm (●); 0.2 slpm (▲).

Direct methanol fuel cell

To evaluate the cell performance, a series of experiments was conducted with the fabricated-assembled direct methanol fuel cell. The experiments were carried out in a wide range of temperatures (40-64 °C) at constant methanol concentration (1 M). In Figure 9, the calculated cell voltages are presented for 1 M methanol solution at three different cell operating temperatures (40, 55 and 64 °C). For this purpose, an experiment was carried out at 62 °C, to study the model predictability in high exchange current density or low cell voltage. The results shown in Figure 10 indicate that the proposed model fitted fairly well with the experimental data. In this study, the advantage of the proposed model is the ability to follow the voltage profile in the limiting current density region or mass

transport limitation region. The parameters for the proposed model are summarized in Table 2.

A quantitative comparison between PEMFC and DMFC was not applicable in terms of the polarization curve. However, it is obvious that oxidation of dilute methanol as the reactant in DMFC is slower than oxidation of hydrogen in PEMFC. Therefore, a qualitative distinction in electrical behavior was performed between them based on the values obtained for the model parameters. Indeed, the major voltage loss was due to ohmic resistance in both fuel cells. However, comparing liquid reactant in DMFC with gaseous reactant in PEMFC, the voltage drop due to mass transfer limitation was stronger in DMFC (comparing the values of R_d and α parameters in Tables 1 and 2).

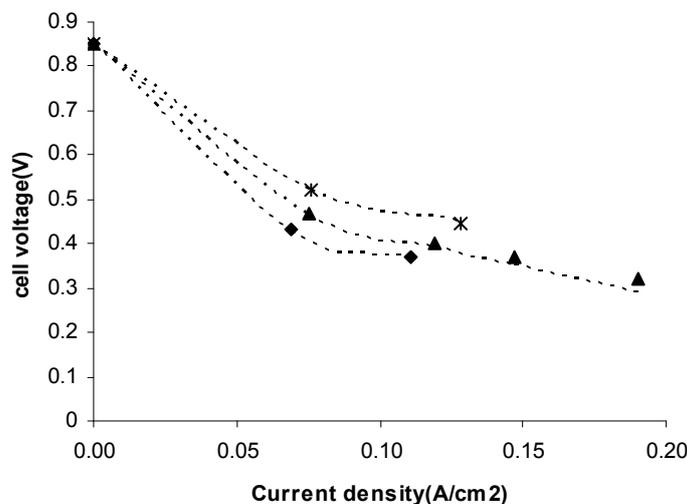


Figure 9. Comparison between experimental data and model prediction based on Eq. (5) (--) for a cell operated with 1 M methanol solution and cell temperatures: 64 °C (*); 55 K (▲); 40 °C (●).

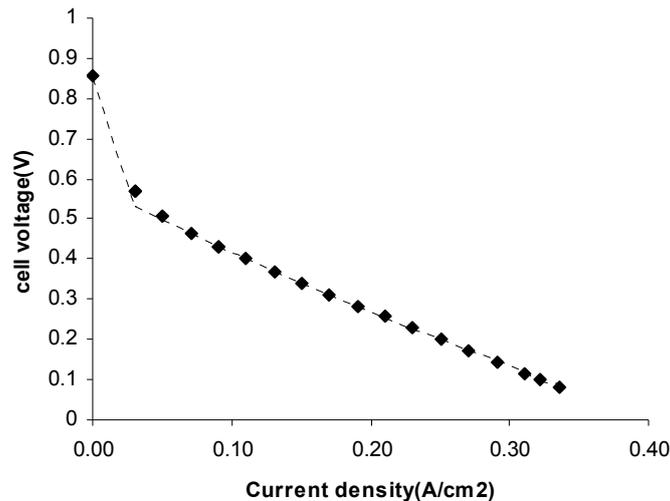


Figure 10 Comparison between experimental data and model prediction based on equation 5 (--) for a cell operated with 1 M methanol solution and cell temperatures 62 °C (◆).

Table 2. Calculated values of the semi-empirical model coefficients for DMFC.

Cell temperature, $t / ^\circ\text{C}$	E_0 / V	b / V	$\alpha / \text{A}^{-1} \text{cm}^2$	$R_e / \Omega \text{cm}^2$	R_d / V	$\beta / \text{A}^{-1} \text{cm}^2$
40	0.850	0.030	3.148	2.923	0.210	-36.436
55	0.851	0.027	2.996	2.364	0.216	-34.902
62	0.853	0.019	2.776	2.026	0.186	-42.112
64	0.853	0.022	3.002	3.002	0.208	-33.616

CONCLUSION

The objective of the present study was to develop a unique semi-empirical model that would simulate the performance of both PEMFC and DMFC without extensive calculations. The advantage of this model is its simplicity and accuracy. A unique semi-empirical model has been developed to describe the voltage-current behavior for both PEMFC and DMFC in which the voltage naturally reduces to OCV when no current is withdrawn from the cell. The model was validated by the experimental data obtained for both types of cells at various operating conditions. To attain these goals, single PEM fuel cell with dimension of 5 cm×5 cm and DMFC with dimension 10 cm×10 cm were constructed and a series of measurements were conducted to characterize the polarization curve. The ultimate goal of the semi-empirical model lies in its ability to predict the cell voltage-current density for the fuel cell systems which are not included in the experimental data. For both types of cells, the results indicated that the model predicts a good agreement between the experimental data and the computed values under different operation conditions. The results of the present study indicate the optimum operating temperature is around 60 °C for both cells and beyond of this temperature the performance of the cell de-

creases due to loss of water content and membrane ion conductivity. Increasing the cell pressure enhanced the cell voltage and increasing the air (oxygen) stoichiometry had no significant influence on the PEMFC performance. The reason was attributed to high oxygen stoichiometry used in this study. On the effect of fitting parameter, it is understood that the major loss in voltage has been due to ohmic loss for both kinds of fuel cells. However, the voltage drop due to mass transfer limitations is more serious for the liquid based reactant in DMFC compared to gas based reactant in PEMFC.

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NAUČNI RAD

ODREĐIVANJE POLARIZACIONE KRIVE I RAZVOJ JEDINSTVENOG SEMI-EMPIRIJSKOG MODELA KOJI OPISUJE PERFORMANSE GORIVNIH ČELIJA SA MEMBRANOM OD POLIMERNOG ELEKTROLITA I SA DIREKTNOM KONVERZIJOM METANOLA

U ovom radu su izrađene gorivna ćelija s protonskom membranom (PEMFC), efektivnih dimenzija 5 cm×5 cm, kao i gorivna ćelija sa direktnom konverzijom metanola (DMFC), dimenzija 10 cm×10 cm. Performanse potencijal-gustina struje za izražene gorive ćelije je ispitan u postojećoj probnoj stanici. Kao što je očekivano, DMFC je pokazala lošije električne performanse, što se može pripisati manjoj brzini oksidacije metanola u odnosu na brzinu oksidacije vodonika. Rezultati dobijeni tokom rada ćelije ukazuju na to da temperatura ima veliki uticaj na njene performanse. Najbolja izlazna snaga za PEMFC je postignuta na 60 °C. Ispod 60 °C je postojao pad napona na ćeliji, koji se može pripisati smanjenju sadržaja vode u membrani. Maksimalna izlazna snaga za DMFC je postignuta na 64 °C. Povećanje količine kiseonika iznad stehiometrijske i ukupnog pritiska ćelije je imao mali efekat na performanse ćelije. Ovaj rezultat je takođe otkrio da se performanse ćelije poboljšavaju povećanjem razlike pritiska između anode i katode. Opšti semi-empirijski, termodinamički zasnovan, model je razvijen da bi se opisao napon na ćeliji u funkciji gustine struje za obe vrste gorivne ćelije. Parametri jednačine modela se izračunate nelinearnom regresijom, koristeći se eksperimentalnim podacima. Za oba tipa gorivne ćelije, postoji dobro slaganje između eksperimentalnih podataka i modela.

Ključne reči: gorivne ćelije sa membranom od polimernog elektrolita; direktne metanolske gorivne ćelije; semi-empirijski model; polarizaciona kriva; gorivna ćelija.