# Polarization distribution and theoretical fitting of direct methanol fuel cell

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## ARTICLE INFO

## ABSTRACT

Membrane Electrode Assembly (MEA) is a key component of direct methanol fuel cell. In order to improve the power generation performance of the MEA, it is necessary to reduce polarization losses. The cathode and anode activation polarization, proton exchange membrane ohmic polarization and gas diffusion layer mass transfer polarization were studied under different methanol concentration and operation temperature conditions respectively. A theoretical study of the various polarization fitting and distribution losses was conducted. The polarization distribution results indicated that the activation polarization of cathode and anode are the main over potential contribution and accounted for more than 80%. The ohmic resistance accounted for approximately 10%. By studying the distribution of polarization loss, we got a variety of distribution of polarization losses under different operating conditions, these results provide a theoretical basis for efficient ways to optimize the MEA.

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## Introduction

Direct Methanol Fuel Cell (DMFC) is a power generation device, the chemical energy of methanol can be transformed to electric energy by DMFC directly [1,2]. The DMFC has the characteristics of high energy density, portable fuel, operated under normal temperature and pressure etc. Thus, DMFC can be used as a portable power and has broad application prospects. Membrane Electrode Assembly (MEA) is the critical power generation component of DMFC. The DMFC performance is decided to a large extent by MEA property.

MEA includes gas diffusion layer (GDL), catalyst layer (CL) and proton exchange membrane (PEM). The methanol and product mass transfer and redox reaction comprise the power generation process and the relationship between the current density and the over potential can be expressed by electrochemical Equation [3–5] (1) and (2):

$$U = E_0 + b \log i + iR + f_1 \exp\left(\frac{if_2}{C}\right) \tag{1}$$

$$E_0 = E_r + a \tag{2}$$

In the formula, a represents the Tafel parameter, Er represents the theoretical voltage, E0 is the open circuit voltage, blogi is the activation polarization loss, iR represents the ohmic polarization loss and $f_1 \exp(if_2/c)$ represent the mass transfer polarization loss.

According to the analysis, the DMFC performance can be improved by MEA optimization and decrease in the MEA polarization loss [6–8]. In previous studies that have already been reported were concentrated on the modeling established

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and analysis of mass, thermal, momentum transfer, two-phase flow, methanol crossover, etc. [9]. The DMFC experimental data fitting was also studied [10]. It will provide excellent theoretical modeling for DMFC designed and experimental data fitting. However, in the process of MEA optimization, it is important to know which polarization area optimization can be more efficient to improve the DMFC power generation performance. In this paper, the polarization losses distribution of half-cell and full cell were focused on. It is the significance of the polarization distribution study work in this paper. The DMFC anode side polarization losses were studied by half-cell and feed hydrogen [11,12] to cathode. The DMFC full cell polarization losses were studied by feed air to cathode. In both $CH_3OH-H_2$ and $CH_3OH$-Air system, the anode side is under the same condition. Therefore, the alone cathode side polarization losses can be obtained by data processing and the cathode and anode polarization distributions were obtained respectively. The theoretical direction for further high efficient MEA optimization can be obtained through thorough study of the MEA polarization distribution and the largest polarization loss component under a certain condition.

## Experimental

### Electrochemical measurements

Nafion115 (Dupont®), PtRu black (4 mg/cm$^2$, Johnson Matthey) for anode, 60% Pt/C (3 mg/cm$^2$, Johnson Matthey) for cathode, and GDL (Toray) were used for MEA(6.25 cm$^2$) fabrication. The electrochemical performances of the obtained MEAs were measured on a fuel cell testing system, which comprised methanol solution supply system, temperature and gas (include hydrogen and air) controller, KIKUSUI FC Impedance Meter KFM2150, KIKUSUI FC Scanner KFM2151, KIKUSUI Electronic Load PLZ664WA. The methanol solution concentration was ensured by non-cycle fuel supply. The hydrogen and air for cathode gas supply were switched during the $CH_3OH-H_2$ and $CH_3OH$-Air polarization curves measurement.

### Methanol permeation measurement

The methanol permeation was measured by $BaCO_3$ precipitation method. The cathode and anode outlet product were all fed into excess of BaOH saturated solution during the DMFC test period. The as prepared $BaCO_3$ precipitate containing solution was sealed and conserved for 12 h and then the $BaCO_3$ precipitate was filtered, dried at 100 °C for 12 h and weighed. The $CO_2$ in the air was measured by the same method.

The $N_{CO_2,6}$ of cathode outlet $CO_2$ include the $N_{CO_2,5}$ of the air, MeOH permeation $N_{CO_2,4}$ and $N_{CO_2,3}$ permeated from anode side to cathode side. The $N_{CO_2,2}$ of anode outlet $CO_2$ is the difference between $N_{CO_2,1}$ calculated based on the quantity of electricity supplied and the $N_{CO_2,3}$ permeated from anode side to cathode side. The flux relationship was represented by the formula (3) and (4).

$$N_{MeOH,perm} = N_{CO_2,4} = N_{CO_2,6} - N_{CO_2,3} - N_{CO_2,5} \tag{3}$$

$$N_{CO_2,3} = N_{CO_2,1} - N_{CO_2,2} \tag{4}$$

## Result and discussion

The cathode and anode polarization losses for different methanol concentrations and temperatures were studied. Based on the results, the polarization distribution under the optimized discharge condition was studied in detail.

### Anode polarization

The $CH_3OH-H_2$ system was applied for anode polarization, and 0.5 M, 1 M, 2 M methanol solution concentration were used in the measurement respectively. The temperature was 60 °C, the flow rate of methanol solution was 5 ml/min and hydrogen was 200 ml/min. Equations (1) and (2) were used for polarization curves fitting. The MeOH/$H_2$ polarization curves were shown in Fig. 1 and the values of the fitting parameters were shown in Table 1. As shown in Fig. 1, the symbols were the experimental data and the lines were the fitting curves based on the Equation (1). These results indicated that the resistance won't be effected by methanol concentration obviously.

The $CH_3OH-H_2$ system for anode polarization analysis was also studied under 30 °C, 45 °C, 60°Cand 75 °C respectively and the methanol concentration was 1 M, the flow rate of methanol solution was 5 ml/min and hydrogen was 200 ml/min. The results were shown in Fig. 2. As shown in Fig. 2, the symbols were also the experimental data, the lines were the fitting curves based on the Equation (1) and the values of the fitting parameters were shown in Table 2. The values of parameter a, $f_2$ and R decreased as the temperature increased.

As shown in Table 3, the theoretical potential values for the anode reaction under different methanol concentration and temperature were calculated based on the thermodynamic formula. The Tafel parameter $a$ in Equation (2) can be calculated based on the $E_0$ and $E_r$ data. As shown in Fig. 3, The anode activation polarization loss and mass transfer polarization
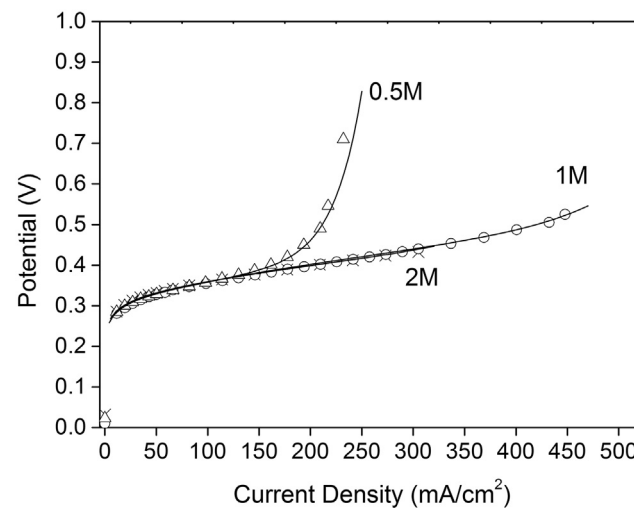


Fig. 1 — Effect of methanol concentration on anode polarization curves.