



A novel method for analysis and prediction of methanol mass transfer in direct methanol fuel cell

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ABSTRACT

Two-phase gas/liquid flows coupled with electrochemical reactions in the anode of direct methanol fuel cell (DMFC) are quite complicated transport phenomena. The methanol transport is a key factor influencing the performance as well as fuel utilization efficiency. In this paper, a dimensionless correlation of methanol mass transfer in DMFC anode is proposed. Firstly, a method for detecting methanol concentration in catalyst layer was developed, which is the key parameter to obtain the mass transfer coefficient. Then, the influences of the various factors on the mass transfer coefficient, including physical properties of fluid, structures of the electrode, cell configuration and cell operation conditions, were investigated. And a correlation between four dimensionless groups, i.e., Sh , Re , Sc and Π (ratio of consumption and feeding rate of methanol), was deduced using the dimensional analysis. Finally, MEA optimization and fuel utilization efficiency evaluation based on the above analysis is performed. A maximum power density of 178 mW cm^{-2} at 80°C and atomistic air is achieved, 40% higher than that of commercial one made by Johnson Matthey.

1. Introduction

Direct methanol fuel cell (DMFC) have been attracting extensive attention as portable power sources because of the high energy density and convenient fuel storage/refilling [1–4]. The performance of DMFCs is strongly influenced by the coupled kinetics and mass transport processes in the anode. As far as mass transport in the anode is concerned, the thin porous electrode (20–50 μm) make it difficult to observe the dynamic behavior of two-phase mass transfer process.

It is not an easy task to elucidate the mass transfer phenomena occurring in the anode of DMFC. There are several mass transfer mechanisms proposed for gas evolving electrode, i.e., (1) bubble-induced microconvection; (2) two-phase forced convection; (3) two-phase free convection; (4) single-phase free convection and (5) diffusion [5]. Various mathematical models have been developed to describe the mass transfer process in DMFC [6–11], however the physical descriptions of the two-phase gas/liquid flow coupled with electrochemical reactions are still unclear. Until now, an accurate macroscopic correlation for predicting the mass transfer coefficient is critical to provide insight into cell design, as well as to optimize the operation conditions.

The issue of various factors on methanol mass transfer coefficient is quite complicated by the nature of multi-scale electrode structure coupled with electrochemical reaction. To the best of our knowledge,

no relationship has been reported to describe the mass transfer coefficient of methanol under various operation conditions of DMFCs, since it is of great challenge to measure the methanol concentration in the thin catalyst layer ($\approx 30 \mu\text{m}$) under realistic conditions. It is not an easy task to fabricate and mount micro methanol concentration sensor in the micro-scale catalyst layer. Up to now, the mass transfer coefficient measurement is limited to the off-line and abnormal situation where the concentration in the catalyst layer approaches zero. Under such situation, the methanol electrooxidation in the anode of DMFCs reaches a limiting current. And the mass transfer coefficient can be determined from the limiting current [12–15]. However, DMFC system never work at limiting current condition and the methanol transfer coefficient calculated doesn't reflect the carbon dioxide gas evolution and flow at different current densities.

In the present work, the methanol concentration is derived from the flux of methanol crossover with a proposed one-dimension methanol transfer model, thus the mass transfer coefficient could be obtained from an expression which gives the relationship between the coefficient and the flux of methanol crossover. The influence of cell temperature, methanol concentration and feeding rate, type of gas diffusion layer on the mass transfer coefficient are explored. Then, the dimensional analysis is applied to obtain an equation in terms of Sherwood number, Reynolds number, Schmidt number and Π (ratio of consumption and

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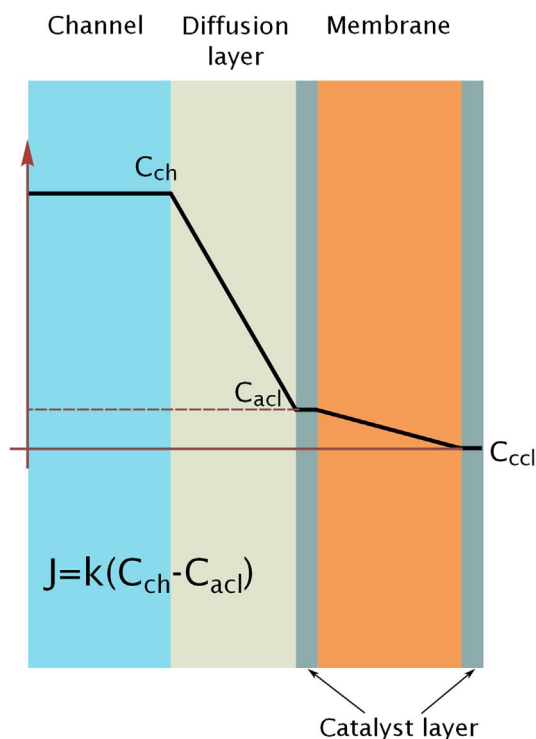


Fig. 1. Methanol concentration profile in direct methanol fuel cell.

feed rate). Furthermore, the results are compared with the values predicted by the classical Sherwood relation. The relation derived could provide insight into cell design, as well as optimal operation conditions.

2. Analysis

A simple one-dimension model is proposed to calculate the current dependent mass transfer coefficient in the DMFC anode, illustrated by Fig. 1. The flux of methanol (J) transport from the channel to the catalyst layer is proportional to the mass-transport coefficient k :

$$J = k_m(C_{ch} - C_{acl}) \quad (1)$$

where C_{acl} is the methanol concentration in the anode catalyst layer (the concentration is assumed to be constant since the catalyst layer is very thin), C_{ch} is the mean concentration between the channel inlet and outlet, i.e.

$$C_{ch} = \frac{C_{in} + C_{out}}{2} = \frac{C_{in} + C_{in} - \frac{JA}{u}}{2} = C_{in} - \frac{JA}{2u} \quad (2)$$

where A is the active area of the electrode and u is the flow rate of methanol solution ($\text{m}^3 \text{s}^{-1}$). The flux of methanol is proportional to the cell current density, therefore, we have

$$J = \frac{j + j_{xover}}{nF} \quad (3)$$

where j is the discharging current density, and j_{xover} is the equivalent crossover current density induced by the methanol crossover, it can be written as

$$j_{xover} = nFJ_{MeOH}^{xover} \quad (4)$$

As long as we know the C_{acl} , the mass transfer coefficient can be calculated according to Eq. (1). Although it is hard to measure the methanol concentration in anode catalyst layer directly, it is easy to derive the C_{acl} from the flux of methanol crossover since the measurement of the methanol crossover is convenient [16,17].

The crossover methanol consists of the methanol permeating by diffusion and the transporting by electro-osmotic drag [18]:

$$J_{MeOH}^{xover} = J_{MeOH}^{diff} + J_{MeOH}^{drag} = D_{MeOH}^{pem} \frac{C_{acl} - C_{ccl}}{h_{pem}} + n_{drag} \frac{j}{F} \frac{C_{acl}}{C_{H_2O}} \quad (5)$$

here, D_{MeOH}^{pem} is the methanol diffusion coefficient in the proton exchange membrane, h_{pem} is the thickness of membrane, C_{H_2O} is the concentration of water in mole, n_{drag} is the electroosmotic drag coefficient (the number of molecules of methanol-water mixture transported by one proton, it is assumed that the proton does not distinguish methanol from water molecules, hence the methanol dragged by proton is proportional to the methanol concentration). Assuming the crossover methanol is completely oxidation in the cathode, the methanol concentration in cathode catalyst layer C_{ccl} is zero. Then

$$C_{acl} = J_{MeOH}^{xover} / \left(\frac{D_{MeOH}^{pem}}{h_{pem}} + n_{drag} \frac{j}{F} \frac{1}{C_{H_2O}} \right) \quad (6)$$

Now the determination of mass transfer coefficient can be determined by the amount of methanol crossover.

3. Material and methods

3.1. Membrane electrode assembly (MEA) preparation

To investigate the influence of the type of gas diffusion layer on the mass transfer coefficient, two porous material, carbon paper (TGP 060) and carbon cloth (ELAT) with a microporous layer, was used as the anode gas diffusion layers. The electrodes were prepared using a screen printing method. PtRu black (Johnson Matthey Inc., Hispec 6000) and Pt/C (Johnson Matthey Inc., Hispec 9100, 60 wt.% Pt) were used as the catalyst for anode and cathode, respectively. The metal loading for anode was 4 mg cm^{-2} and for cathode was 2.5 mg cm^{-2} . The MEA with an active area of $2 \text{ cm} \times 2 \text{ cm}$ were prepared by hot pressing the anode and cathode on either side of a Nafion® 115 membrane. Two single cells, Cell I and Cell II, were used in our tests. The only difference between Cell I and Cell II is the anode gas diffusion layer: Cell I uses carbon paper while Cell II uses carbon cloth.

Two types of MEAs were taken into consideration for optimization, One is a commercial MEA (carbon paper, TGP 060) made by Johnson Matthey. Another is homemade MEA (carbon cloth, CeTech WOS1002) with their electrodes prepared using a brush painting method. Both of them have an active area of $2 \text{ cm} \times 2 \text{ cm}$.

3.2. Measurement of methanol crossover

The method described here is similar to that reported by Dohle et al. [16]. Methanol and CO_2 crossover was determined by measuring the concentration of CO_2 in the cathode exhaust using a Vaisala GMP222 sensor. In the early experimental model for methanol crossover, the CO_2 flux measured at the cathode is completely attributed to the oxidation of crossover methanol. Recent works have shown that the permeated amount of CO_2 generated at anode through the membrane to cathode cannot be neglected [16,17,19,20]. Thus, the flux of methanol crossover is calculated as the CO_2 flux of the cathode exhausted gas in the fuel cell mode minus that in the driven mode.

$$J_{MeOH}^{perm} = J_{CO_2}^{FC} - J_{CO_2}^{driven} \quad (7)$$

Measurement in a fuel cell mode: the cell was discharged at a constant current density for 30 min and the CO_2 concentrations in the cathode exhaust were recorded. The anode was fed with 0.5 M or 1 M aqueous methanol solution at a flow rate of $0.26\text{--}1.78 \text{ mL min}^{-1}$ (corresponding to a equivalent current of $300\text{--}2400 \text{ mA cm}^{-2}$); cathode was fed with nonhumidified O_2 at a flow rate of 80 mL min^{-1} . In this mode, the measured CO_2 amount is a sum of CO_2 resulting from the oxidation of crossover methanol and CO_2 permeated from anode to cathode, as shown in Fig. 2a.

Measurement in a driven mode testing: the cell was operated in a

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