Energy 98 (2016) 204–214

Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

An experimental study on the effect of membrane thickness and PTFE (polytetrafluoroethylene) loading on methanol crossover in direct methanol fuel cell

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ARTICLE INFO

Article history:
Received 2 April 2015
Received in revised form
14 December 2015
Accepted 16 December 2015
Available online 6 February 2016

Keywords:
Methanol crossover
PTFE loading
Membrane thickness
Peak power density
Limiting current density
Fuel cell efficiency

ABSTRACT

Methanol crossover from anode to cathode is a process which adversely affects the performance of a DMFC (direct methanol fuel cell). Increasing the electrolyte membrane thickness and addition of a MPL (microporous layer) using PTFE (polytetrafluoroethylene) loading are two techniques used to reduce methanol crossover by increasing the mass transfer resistance. This paper reports experiments carried out to study the effect of membrane thickness and PTFE loading in anode MPL on methanol crossover in a 25 cm^2 DMFC. The rate of methanol crossover is indirectly measured by measuring the CO_2 concentration at the cathode exit. The influence of PTFE content (0–20%) and membrane thickness (183 μm and 254 μm) on limiting current density, peak power density and cell efficiency are reported. The experimental results show that the methanol crossover current density is reduced by 24% using thicker membrane compared to MEA (membrane electrode assembly) with thin membrane. This leads to enhanced peak power density of 22 mW/cm^2 with cell efficiency of 10%. About 20% of methanol crossover current density is reduced by 10% PTFE loading in anode MPL, which helps in improving peak power density from 13 to 24 mW/cm^2 with cell efficiency of 8% compared to membrane as mass transfer resistance layer.

1. Introduction

DMFC (direct methanol fuel cell) is a potential power source in low to medium power applications such as mobile phones, laptops and other portable applications due to its advantages such as good efficiency, low environmental emission and simple structure. Methanol is a fuel which makes DMFC attractive due to its unique features such as high energy density, low cost and easy handling. However, major challenges for large scale use of DMFC are methanol crossover from anode to cathode and slow reaction kinetics. In the cell, methanol is consumed in the anode catalyst layer through an electrochemical reaction and excess methanol diffuses through the membrane to the cathode and this phenomenon is called “methanol crossover”. This causes fuel loss and the cell performance is affected by the mixed potential which reduces the FUE (fuel utilisation efficiency). Methanol crossover can be reduced by (i) operating the cell at low methanol concentration and low temperature; (ii) increasing the diffusion layer thickness or reducing its porosity by PTFE (polytetrafluoroethylene) loading, which adversely affects limiting current density and power density due to the uneven porous structure and leads to high mass transfer resistance (iii) introducing an additional mass transfer resistance in the form of a MPL (microporous layer) or increasing electrolyte membrane thickness. The latter method not only reduces methanol crossover but also enhances cell efficiency with high power density.

1.1. State of the art

Ge and Liu [1] and Eccarius et al. [2] carried out experiments to study the effects of cell temperature, methanol concentration, MFR (methanol flow rate) and AFR (air flow rate) on methanol crossover. They reported that the membrane thickness was increased from 90 to 180 μm to reduce methanol crossover. The effect of cell temperature on reaction kinetics is more significant at low cell voltage. The cell performance is high between 1 and 2 M. There is no significant impact on the polarisation curve after a certain limit of MFR (7 ml/min) due to increased methanol crossover. Han and Liu [3] and Casalegno et al. [4] measured methanol crossover rate in

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http://dx.doi.org/10.1016/j.energy.2015.12.101
0360-5442/

Nomenclature

A	Active area/cm^2
D^{eff}	Effective diffusion coefficient of methanol/cm^2 s^{-1}
F	Faraday's constant/C mol^{-1}
G	Gibbs free energy/kJ mol^{-1}
H	Enthalpy of reaction/kJ mol^{-1}
i	cell current density/mA cm^{-2}
i_c	methanol crossover current density/mA cm^{-2}
M	molecular weight/kg mol^{-1}
N	methanol flux/mol cm^{-2} s^{-1}
P_{max}	Peak power density/mW cm^{-2}
p	pressure/N m^{-2}
Q	air flow rate/ml min^{-1}
R	gas constant (8.314)/J mol^{-1} K^{-1}
T	temperature/K
X	Volume percentage of CO_2
V	Cell Voltage/V
η	Efficiency

Subscripts

cons	consumption
DSFF	Double Serpentine Flow Field
FUE	Fuel Utilisation Efficiency
IFF	Interdigitated Serpentine Flow Field
MCO, c	Methanol crossover
m	methanol
mpl	microporous layer
SSFF	Single Serpentine Flow Field
th	theoretical
o	overall
rev	Reversible

DMFC by measuring the CO_2 concentration at the cathode exit by varying operating conditions and the optimal operating conditions were found. Seo and Lee [5] measured methanol crossover under varying operating conditions such as cell temperature, methanol concentration, cathode back pressure and reactant flow rates. The efficiency of the cell was improved to 23% at 1 M due to lower ohmic and activation losses.

Nakagawa et al. [6] used porous plates as a mass transfer resistance medium to reduce methanol crossover. Porous plate used is 1–2 mm thick with a porosity of 0.41–0.45. The methanol diffusion distance through the porous plate reduces methanol flux through the membrane. The methanol crossover flux is controlled upto 8 M. Shao et al. [7] studied the influence of anode supporting layer and its compositions such as carbon, Nafion and PTFE content. The diffusion layer (carbon cloth) made of Black Pearl 2000 carbon gives the best cell performance and further enhanced by introducing a supporting layer between diffusion layer and catalyst layer. Xu et al. [8] also investigated the effect of anode backing layer with different CP (carbon paper) thickness and PTFE loading on DMFC cell performance. The cell with thin CP results in lower cell voltage for the entire current density region due to weaker under-rib convection and the thick CP leads to lower limiting current density due to through-plane mass transfer resistance. The carbon paper with PTFE loading is tested for 1–4 M concentration and it is found that CP without PTFE gives a high cell performance. The change in cell performance is low for 2 M and is negligible at 4 M. Olivera et al. [9] studied the DMFC cell performance by varying commercial MEA (membrane electrode assembly). The high cell performance is obtained using a tailored MEA of thin membrane with CP at anode and CC (carbon cloth) at the cathode. The pore size of the CP is low (50 μm) compared to carbon cloth (broad pore size distribution of 5–100 μm) which acts as the resistance layer to reduce methanol crossover. The CC at the cathode removes water and can access oxygen for oxygen reduction reaction.

Zhang et al. [10] analysed the influence of anode gas diffusion layer on mass transport and CO_2 removal. They found that the wettability of anode GDL (gas diffusion layer) decreased with increase in PTFE loading. The MEAs with hydrophilic ionomer in anode GDL gives a high cell performance compared to PTFE in anode GDL due to low mass transfer resistance. Adding PTFE to the anode GDL results in CO_2 gas bubbles, which obstruct methanol diffusion. Lin et al. [11] used spraying and scraping methods to prepare MPL and the experimental results show that MPL prepared by spraying method gives high performance due to high mass transfer rate of oxygen (due to increased porosity). More cracks and voids are observed on conventional MPL, which lowers the cell performance. Casalegno et al. [12] experimentally analysed the influence of operating conditions on methanol crossover rate and the characterisation of DMFC with different MEA. They reported that the MPL in cathode leads to 15% methanol crossover reduction at low current density and that of 45% by MPL on both anode and cathode. The cell efficiency is 15% for MEA without MPL and increased to 17% for MEA with MPL on anode and cathode at peak power density. Krishnamurthy and Deepalochani [13] carried out experiments to study the effect of PTFE loading in diffusion layer and MPL and found that PTFE content in cathode MPL plays an important role in platinum utilisation. Xu et al. [14] conducted experiments to determine methanol crossover, water crossover and fuel utilisation efficiency. Two additional layers of MPL coated on CC at the cathode worked as the water management layer. Methanol and water crossover are reduced, which results in high fuel utilisation efficiency of 50%. Yang et al. [15] studied the effect of hydrophobic carbon cloth (10% PTFE) and MPL coated CC on cell performance. They found that MPL coated CC gives 50 mW/cm^2 at 2 M. Hydrophobic CC with 10% PTFE results in lower limiting current density due to high mass transfer resistance and ohmic losses. The experimental studies [1–17] on the effect of diffusion layer, MPL and membrane thickness on cell performance are given in Table 1.

Ahmed and Dincer [18] reviewed the four categories of membranes such as modified Nafion membranes, copolymer membranes, blend membranes and composite membranes. They reported that the methanol permeability is reduced up to two orders of magnitude, which helps in reducing methanol crossover. Hybrid membrane and integrated composite membrane were tested by Meenakshi et al. [19] and Wan et al. [20]. They found that the peak power density is increased due to reduced methanol permeability through membrane with enhanced proton conductivity.

In summary, there appears to be quite a bit of uncertainty and difference of opinion regarding the effects of mass transfer resistance layers on DMFC performance. Diffusivity of methanol through the membrane is reduced by providing mass transfer resistance on anode before it reaches the membrane. Based on the literature review, this research work focus on two different methods used to reduce methanol crossover. These are (i) using different anode MPLs and (ii) different membrane thicknesses. Performance of the cell with different methanol crossover reduction methods are analysed and compared. Methanol crossover is estimated by measuring CO_2 concentration at the cathode exit for varying PTFE loading in anode MPL and electrolyte membrane thickness.