Modeling the cathode catalyst layer of a Direct Methanol Fuel Cell

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HIGHLIGHTS

- A DMFC model is developed to study the effects of cathode catalyst layer thickness.
- The distribution of methanol concentration in the cathode catalyst layer is considered.
- Modeling results agree well with experimental data for difference CCL thickness.
- Neglecting methanol contamination in the CCL significantly overpredicts fuel cell performance.

ARTICLE INFO

ABSTRACT

A two-dimensional, single phase, multi-component model is developed to study the effects of cathode catalyst layer thickness on DMFC's performance. The simulations consider the effects of mixed potentials as well as the distribution of methanol concentration in the cathode catalyst layer, normally neglected by most DMFC models. In other words, the assumption of zero methanol concentration at the interface between the membrane and cathode catalyst layer (CCL) is not used in this model. COMSOL Multiphysics V4.3, a finite element analysis solver and simulation software, is employed to solve the fully coupled set of equations for electrochemical kinetics, continuity, momentum and species. There is a good agreement between the modeling results and the experimental data. Further modeling results show that neglecting methanol contamination in the CCL, i.e. assuming that methanol concentration goes to zero at the membrane/cathode interface, significantly overpredicts the fuel cell performance.

1. Introduction

Direct Methanol Fuel Cells (DMFCs) are considered a great alternative to lithium-ion batteries for powering the next generation of mobile devices. However, methanol crossover in DMFCs is a serious drawback to the cell performance and any advancement in this type of fuel cells is impeded by such a phenomenon. Two possible ways to mitigate methanol crossover and its effects are: (a) improving the electro-oxidation process in the catalyst layer, and (b) improving the structure of the catalyst and gas diffusion layers.

There are several models in the literature that focus on the effects of mixed potentials in DMFCs. Sundmacher et al. [1] developed a mathematical model that accounts for methanol crossover through the membrane. Wang and Wang [2] employed a two-phase, multicomponent model to investigate the electrochemical kinetics and transport phenomena in DMFCs including the mixed potential effects of methanol oxidation due to methanol crossover.

In their model, the catalyst layers were simplified as planes with no thickness. Liu and Wang [3] studied the mixed potential in DMFCs numerically and provided detailed kinetics of methanol oxidation reaction (MOR) in the cathode. They showed the polarization curves for different cathode catalyst layer (CCL) thicknesses; however, their results do not follow the performance pattern of the experimental ones shown in Ref. [4]. Yin [5] proposed an algebraic model that studies the simultaneous effects of water and methanol crossover. The model treated the catalyst layers as infinitely thin interfaces and assumed that the crossed-over methanol is consumed instantaneously at the membrane/electrode interface. Recently, Kulikovsky [6] considered a direct catalytic reaction between methanol and oxygen in the CCL and compared the result with the assumption of an electrochemical reaction of methanol in the cathode [7].

In a previous experimental work [4], the effects of CCL thickness on the detrimental effect of methanol crossover in a DMFC under various operating conditions were studied. The results showed that when a thicker CCL was used, the fuel cell performance increased significantly. This was attributed to the oxidation of the crossed-over methanol in part of the catalyst layer and leaving the rest of

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Nomenclature

a	specific surface area
ACH	anode channel
ACL	anode catalyst layer
AGDL	anode gas diffusion layer
CCL	cathode catalyst layer
C	methanol concentration
CL	catalyst layer
CO_2	carbon dioxide
D	diffusion coefficient
E	voltage
E^o	equilibrium potential
e^-	electron
ECA	electrochemically active area
EOD	electro osmotic drag
F	Faraday constant
GDL	gas diffusion layer
H^+	proton
H_2	hydrogen
H_2O	water
I	current
i_o^{ref}	reference exchange current density
j	current per unit volume
M	molecular weight
m_{pt}	catalyst loading
MeOH	methanol
MOR	methanol oxidation reaction
N	flux
N_2	nitrogen
O_2	oxygen
ORR	oxygen reduction reaction
P, p	pressure, partial pressure
PEM	proton exchange membrane
R	resistance or gas constant
S	source term
T	temperature
$\mathbf{u}$	velocity
w	mass fraction
x	mole fraction

Greek letters

α	transfer coefficient
γ	reaction order
δ	thickness
ε	porosity
η	activation overpotential
κ	permeability
μ	dynamic viscosity
ρ	density
σ	conductivity
ϕ	potential
ω	a function of methanol concentration

Subscripts

a	anode
c	cathode
ct	charge transfer
m	membrane
mixed	mixed potential
s	solid phase
xover	methanol crossover

Superscripts

eff	effective
M	membrane
ref	reference

the catalyst layer free from methanol contamination, thus leading to mitigations of the effects of mixed potentials. In this paper, a single-phase model was developed to model methanol crossover in DMFCs. The model was used to study the effect of changing the thickness of the CCL on the cell performance. To focus on the effect of the CCL thickness, as shown in the previous experimental results, the effect of liquid water in the CCL was not explicitly studied. The model basically assumesd the effects of liquid water in blocking the active reaction sites for all the three cases with different CCL thicknesses were the same. The simulations considered the effects of mixed potential as well as the distribution of methanol concentration in the CCL that is normally neglected in most of DMFC models. In this modeling, methanol oxidation occurs in the entire CCL unless the local methanol concentration reaches zero.

2. Model description and assumptions

Fig. 1 shows a schematic drawing of a DMFC in the XY plane. The modeling domain consists of the anode and cathode flow channels, gas diffusion layers (GDLs), catalyst layers (CLs), and the Nafion® membrane. In the anode side, the aqueous methanol flows in the channel and then diffuses through the porous GDL until it reaches the catalyst layer, where it is electrochemically oxidized according to the reaction given in Eq. (1). The protons, water and the crossed-over methanol transfer through the membrane. On the cathode side, air flows in the channel and then it is transported to the reaction sites via diffusion and convection, where oxygen reacts with the protons coming from the anode through the membrane and the
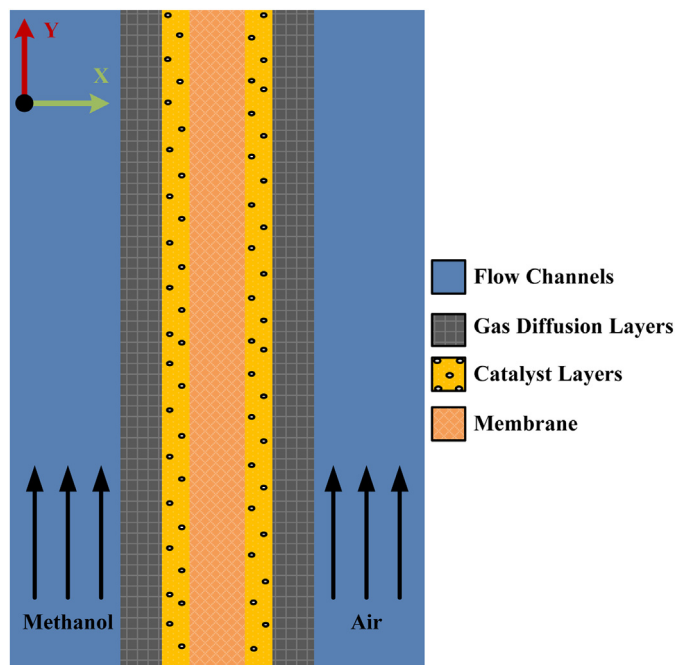

Fig. 1. Schematic of the modeling domain.