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Modeling of passive alkaline membrane direct methanol fuel cell

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ABSTRACT

In this study, a two-dimensional two-phase model is developed for a passive alkaline anion exchange membrane direct methanol fuel cell (AAEM-DMFC) to understand the role of micro-porous layer (MPL) and the effect of porous media wettability on species transport. The results indicate that different regions of polarization curve exhibit different dependence on the methanol feed concentration. Anode MPL can act as the methanol diffusion barrier to retard the methanol mass transport and thus mitigate the methanol crossover. This effect becomes more significant by increasing anode MPL hydrophobicity, which facilitates the use of highly concentrated methanol fuel. However, the insertion of cathode MPL and changes in the wettability of cathode porous layers show insignificant effects on the methanol crossover. Moreover, the influence of MPL on the water transport depends on the current density. Less water crossover can be achieved by reducing the water diffusion or enhancing the back-diffusion through the membrane. Ultimately, a favorable water distribution and lower methanol crossover might be achieved by designing porous layers with desired properties. The simulation results presented in this study may help guide the optimization of water management and the mitigation of methanol crossover in passive AAEM-DMFC.

1. Introduction

Nowadays, passive direct methanol fuel cell (DMFC) has been regarded as a promising power source candidate for portable electronic devices, owing to its simpler system architecture compared to a conventional active DMFC with air compressor and fuel pump, and increased energy density and efficiency by minimizing or eliminating accessory devices [1,2].

For a passive DMFC, methanol aqueous solution with added alkali and air are passively delivered without any moving component such as pumps and fans (Fig. 1), to minimize the system size and parasitic power loss. However, this system architecture also leads to a lower performance than that of an active DMFC, because the supply of methanol, water and oxygen toward reactive sites only relies on passive transport. Also, the excess methanol and water is difficult to be handled properly, which may cause a severe methanol crossover and cathode flooding [3]. A conventional approach to mitigate methanol crossover is the use of dilute methanol solution, while it requires a larger methanol reservoir and considerably lowers the efficiency of passive DMFC system. Thus, alternative approaches are of particular interest in the ongoing research for lower methanol crossover and better water management. In the previous studies, efforts to this end focused on the new structure design of membrane electrode assembly (MEA) [4–18], modification of conventional proton exchange membranes (PEMs) [19–24] and development of new membranes [25–31].

Proper control of methanol crossover and water transport largely depends on optimized MEA design. In recent studies [6–14], micro-porous layer (MPL), a thin porous media consisting of carbon black powder and hydrophobic agent that is usually applied to the interface between gas diffusion layer (GDL) and catalyst layer (CL) (Fig. 1), has gained increasing attention. In PEM-DMFC literature, it is believed that the insertion of MPL on the anode side can act as liquid diffusion barrier and reduce the mass transport of methanol especially under high current density conditions [6–8]. Less methanol in the anode catalyst layer (ACL) corresponds to lower methanol crossover, which facilitates the use of highly concentrated methanol fuel in the passive DMFC. On the cathode side, hydrophobic MPL aims at directing the liquid water flow back to anode with the buildup of liquid pressure to prevent cathode flooding, to allow a faster water removal from cathode catalyst layer (CCL) and to enhance gas transport toward the catalytic sites [9–11]. Another benefit of MPL is the minimized electric contact

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Nomenclature

a activity
A specific interfacial area (m^{-1})
C molar concentration ($mol\,m^{-3}$); gas constant
D mass diffusivity ($m^2\,s^{-1}$)
E potential (V); effective activation energy ($J\,mol^{-1}$)
EW equivalent weight of the membrane ($kg\,mol^{-1}$)
F Faraday's constant (96,485.0C mol^{-1})
h interfacial transfer rate constant ($m\,s^{-1}$)
i current density ($A\,m^{-2}$)
j reaction rate ($A\,m^{-3}$)
k Henry's constant; relative permeability (m^2); thermal conductivity ($W\,m^{-1}\,K^{-1}$)
K permeability (m^2)
$\dot{m}$ source term of liquid or gas mixture ($kg\,m^{-3}\,s^{-1}$)
M molecular weight ($kg\,mol^{-1}$)
n stoichiometric coefficient of electrons in electrode reaction
n_d electro-osmotic drag coefficient
N flux ($mol\,m^{-2}\,s^{-1}$)
P pressure (Pa)
R universal gas constant ($8.314\,J\,K^{-1}\,mol^{-1}$)
s volume fraction; entropy ($J\,mol^{-1}\,K^{-1}$)
S source term of species ($mol\,m^{-3}\,s^{-1}$)
T temperature (K)
W width (m)
V voltage (V); partial molar volume ($m^3\,mol^{-1}$)
x position or coordinate (m)

Greek letters
α kinetic transfer coefficient
γ water phase change rate (s^{-1})
δ thickness (m)
ε porosity
η voltage loss (V)
θ contact angle ($\circ$)
λ water content in ionomer
μ dynamic viscosity ($kg\,m^{-1}\,s^{-1}$)
ρ density ($kg\,m^{-3}$)
σ conductivity ($S\,m^{-1}$); surface tension coefficient ($N\,m^{-1}$)
ϕ potential (V); average gas relative humidity

Subscripts and superscripts
0 intrinsic value, standard condition, reference
a nanode
aver average
ACL anode catalyst layer
ADL anode diffusion layer
AMPL anode micro-porous layer
c cathode; capillary
cell fuel cell
ch channel
cont contact
cross crossover
cond condensation
CCL cathode catalyst layer
CDL cathode diffusion layer
CL catalyst layer
CMPL cathode micro-porous layer
CO_2 carbon dioxide
DL diffusion layer
e electrolyte
eff effective
evap evaporation
g gas phase
H Henry's law
H_2O water
l liquid phase
m membrane
me methanol
mw membrane water
mv methanol vapor
MPL micro-porous layer
O_2 oxygen
ref reference
rib rib
s solid electrode
sat saturation
tot total
T temperature
w water
wv water vapor
V_s electric potential in the solid electrode
V_m ionic potential in the membrane electrolyte

resistance because it provides a smooth transition from micro CL to macro GDL [12].

To further understand the critical role of MPL, both experimental [8–14] and modeling studies have been carried out [6–18]. Yuan et al. [13] found that adding carbon nanotubes into anode microporous layer (AMPL) improves the contact between AMPL and ACL and is beneficial to efficient mass transport of methanol from reservoir to reaction sites, leading to significant cell performance improvement. Yang et al. [14] concluded that AMPL provides higher catalyst utilization due to the enhanced CO_2 gas removal, thus effectively improves the kinetic of anode methanol oxidation reaction (MOR). Meanwhile, AMPL efficiently decreases the methanol crossover to the cathode side. Yang and Zhao [15] employed a two-phase mass transport model for PEM-DMFC to investigate the effect of MPL on the water transport behavior. Most recently, based on liquid saturation jump theory, Ko et al. [16] developed a one-dimensional two-phase model to investigate the role of MPL on both anode and cathode sides and the effect of ACL contact angle on methanol and water transport.

In addition, efforts have been devoted to the modification of PEMs [19–24] and development of new composite membranes [25–31]. Among these membranes, alkaline anion exchange membrane (AAEM) gains growing interest due to its advantages in suppressing the methanol crossover and optimizing the water management. For an AAEM-DMFC, the charge carrier is hydroxide and its conducting pathway is from cathode to anode, a direction opposite to that in a PEM-DMFC, thus reversed electro-osmotic drag decreases the methanol and water crossover. However, this reversal does not guarantee a successful water management as the cathode water amount is reduced, the complexity remains since water is being consumed in the cathode in an AAEM-DMFC. Thus, further investigation is necessary. Recent experimental results [28,29] confirmed that the methanol permeability of A201 membrane (AAEM produced by Tokuyama, Japan) is about 10–20% of that in Nafion 117 membrane, although its thickness is one-fifth Nafion 117 membrane. With reduced methanol crossover by using AAEMs, it becomes more feasible to use high concentrated methanol solutions in AAEM-DMFCs [30,31].

It is generally accepted that using MPL and AAEM in DMFC can better control methanol crossover and simplify water management, although the role of MPL in AAEM-DMFC is not fully understood because of few studies conducted. Li and Zhao [32] experimentally investigated the effect of insertion of CMPL on