Numerical and experimental investigation on the reactant gas crossover in a PEM fuel cell

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A B S T R A C T

Gas crossover through the membrane is one of the key factors for membrane degradation and performance loss of proton exchange membrane fuel cell (PEMFC). The permeation of hydrogen and oxygen through the membrane are consumed with the generation of heat and water but without the generating of useful work, leading to a fuel inefficiency. On the other hand, hydrogen peroxide (H_2O_2) is most probably formed by the reaction of crossover hydrogen and oxygen at both the anode and cathode side. In addition, the chemical reaction of gas crossover can produce peroxide (HO·) and hydroperoxide (HOO·) radicals, which could accelerate the membrane degradation. In this study, a numerical simulation model has been built using the partial differential equation solver FreeFem++. A steady-state, two-dimensional, single-phase and non-isothermal model of a single PEMFC has been considered to determine the water content distribution, temperature profile, and permeation of gaseous species within the membrane. An in-situ microprobe technique has been also applied to determine the properties of the oxygen crossover with a range of relevant fuel cell operating temperatures and reactant humidity. The numerical results are compared with experimental data of the diffusion coefficient of reactants gases in the membrane, in order to investigate the gaseous species transport characteristics in the membrane at very low current density.

1. Introduction

It is well known that the conventional fossil fuels, primarily gasoline and diesel, are not going to last more than a hundred years in the face of ever-increasing demand in the developed and developing countries [1]. For alternative fuels, there were some potential candidates introduced, such as biofuels, solar, geothermal, hydrogen. Among them, the proton exchange membrane fuel cell (PEMFC) is one of the most promising green power sources for automobile and stationary applications due to its multiple inherent advantages, such as high energy density and efficiency, low operating temperature and emission comparing with internal combustion engine [2]. For those reasons, PEMFCs constitute a promising alternative to powering the next generation of electric vehicles [3]. However, there are two greatest technical barriers, cost and durability, that must be overcome due to hinder the deployment of PEMFCs at large scale. These two barriers are interdependent, as providing more Pt catalyst in the fuel cell system increases

catalyst durability and performance but also significantly increases the fuel cell cost [4]. The US Department of Energy (DOE) has set a durability target 5000 h (equivalent to 150,000 miles of driving) for vehicles and 40,000 h for stationary applications by 2020 with less than 10% loss of performance at full range of operating conditions [5]. The performance degradation and low durability of a PEMFC can be attributed to degradations of their components, such as membrane, catalyst layers, gas diffusion layers [5]. Among these, the degradation of the membrane is one of the most critical issues. There are many factors could degrade the membrane, which including manufacturing/design issues, material characteristics, and operation conditions. These factors result in membrane degradation through physical (including mechanical, thermal degradation) and chemical mechanisms [6].

The physical degradation is caused by time-dependent deformation (creep) under compressive force, changes in temperature, relative humidity (RH). Several reports have shown that flooding phenomena, which causes corrosion of the electrodes, the catalyst layer, the gas diffusion layer (GDL) and the membrane. Furthermore, this flooding prevents the diffusion of the reaction gas in the GDL. In contrast to this, if membrane becomes dehydrated which causes stress concentration of the membrane, leading to membrane pinholes, delamination and cracking, and acceleration

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Nomenclature

a_w	water activity
C	concentration (mol m^{-3})
D	diffusion coefficient (m^2 s^{-1})
E	activation energy for diffusion (J mol^{-1})
F	Faraday constant (C mol^{-1})
i	exchange current density (A m^{-2})
i_{lim}	diffusion-limited current density (A m^{-2})
K	permeability of oxygen in Nafion (mol m^{-1} s^{-1} Pa^{-1})
k	thermal conductivity (W m^{-1} K^{-1})
L	gas channel length (m)
M_m	membrane dry equivalent weight (kg mol^{-1})
N	molar Flux (mol m^{-2} s^{-1})
n_d	drag coefficient
n_{ch}	number of channels
p	pressure (Pa)
Q	gas flow rate (m^3 s^{-1})
R	gas constant (J mol^{-1} K^{-1})
R_{total}	total gas transport resistance (s m^{-1})
S	solubility of oxygen in Nafion (mol m^{-3} Pa^{-1})
T	temperature (K)
V_{cell}	cell voltage (V)
V_{oc}	open circuit potential (V)
W	gas channel width (m)
x	mole fraction

Greek letters

α	transfer coefficient
β	net water flux per proton flux
ΔH	enthalpy of dissolution of oxygen in Nafion (J mol^{-1})
ΔS	entropy change of the anodic/cathodic reaction (J mol^{-1} K^{-1})
δ	thickness (m)
η	overpotential (V)
λ	water content
ρ_{dry}	membrane dry density (kg m^{-3})
σ	membrane proton conductivity (S m^{-1})
ε	porosity

Subscripts

act	activation
ave	average
conc	concentration
i	components H$_2$, O$_2$ and H$_2$O
ohm	ohmic
ref	reference value
w	water in the membrane

Superscripts

ACL	anode catalyst layer
AGC	anode gas channel
CCL	cathode catalyst layer
CGC	cathode gas channel
eff	effective
GC	gas channel
GDL	gas diffusion layer
mem	membrane
sat	saturation

of the chemical degradation [5,6]. Pei et al. [7] also showed flooding and dehydration both had great influence on the lifetime of fuel cells. Therefore, there have been extensively efforts on water and thermal management issue, such as Teranishi et al. [8] used a one-dimensional model along with magnetic resonance imaging experiments to determine the water transfer coefficient and maximum water content in the membrane of PEMFC. They also found the membrane swelling increases with an increasing water content. Sunakawa et al. [9] used a dew point meter (DPM) to measure the amount of water vapor at inlet and outlet of both anode and cathode sides. After that they built a mass transfer model of series resistances by diffusion and transfer of water vapor to define diffusion and electro-osmotic coefficients of water vapor with composite and single membrane. A three-dimensional isothermal single phase model has been developed by Uddin et al. [10] considering the variation of hydration in the membrane that was applied to an actual operating PEMFC. Their model is shown that the water content within membrane increases with increasing relative either humidity or current density.

Chemical degradation of the electrolyte membrane is still a major issue in long-term operation of PEMFCs. That is discussed in terms of peroxide/radical and hydrolysis induced degradation. To realize this, understanding of the mechanism for membrane degradation as well as factors in membrane degradation is absolutely indispensable. Wang et al. [11] have stated that the aforementioned highly exothermal combustion between H$_2$ and O$_2$ can possibly lead to pinholes in the membrane, destroying the membrane electrode assembly (MEA) and causing catastrophic problems. More severely, the chemical reaction on the anode and cathode catalysts can produce peroxide (HO·) and hydroperoxide (HOO·) radicals, which are commonly believed to be responsible for chemical attack on the membrane and catalysts. Further investigation has also revealed that the generation of these radicals as well as the chemical degradation of the membrane is accelerated when the fuel cell is operated under open circuit voltage (OCV) and low humidity conditions [12]. Inaba et al. [13] have reported that fluoride-ion release rate decrease with increasing current density at 80 °C under low humidification. They also have shown that H$_2$O$_2$ is formed at both the anode and cathode, its formation will increase with decreasing current density. In addition, in some literatures also stated that gaseous species transport across the MEA leads to long-term durability problem through H$_2$O$_2$ production [14–16].

In this study, a numerical simulation model has been built using the partial differential equation solver FreeFem++ [17]. This study can help more people in community to access the numerical simulation capability of PEMFC due to FreeFem++'s open source nature, and the FEM based solver facilitates the modeling of possible complex geometry of their target computational domain. A steady-state, two-dimensional, single-phase and non-isothermal model of a single PEMFC has been considered to determine the water content distribution and temperature profile within the MEA, as well as gaseous species transport characteristics in the membrane. The single-phase model used in this work because at very low current density, liquid water generated in the PEMFC is insignificant and can be neglected. The numerical results are compared to experimental data of the diffusion coefficient of reactant gas in the membrane, in order to gain insight on the gaseous species transport characteristics in the membrane.

2. Numerical simulation

2.1. System description

A schematic illustration of the cross section of a typical PEM fuel cell is shown in Fig. 1. A PEMFC consists of a membrane