Numerical analysis of a high-temperature proton exchange membrane fuel cell under humidified operation with stepwise reactant supply

Hyung Soon Kim [a], Seung Won Jeon [b], Dowon Cha [a], Yongchan Kim [a,*]

[a] Department of Mechanical Engineering, Korea University, Anam-Dong, Sungbuk-Ku, Seoul 136-713, Republic of Korea
[b] Korea Institute of Civil Engineering and Building Technology, Baekgok-ri, Mado-myeon, Hwaseong-si, Gyeonggi-do, 18544, Republic of Korea

ARTICLE INFO

ABSTRACT

Dynamic response is a very important issue in a vehicle powered by a proton exchange membrane fuel cell (PEMFC) due to its frequent load change. In this study, three-dimensional transient simulation was conducted to investigate the dynamic response of a high temperature PEMFC. A stepwise change in the cell voltage was conducted to simulate the sudden load change during vehicle operation. After the load change, the oxygen concentration, ionic conductivity, and local current density were analyzed, and the water transport through the membrane electrode assembly (MEA) was also evaluated to determine the characteristics of overshoot and settling time. The result showed that the overshoot was mainly due to the pre-existing excessive oxygen. At the humidified condition, the overshoot increased with increasing relative humidity due to higher ionic conductivity and electrochemical reaction rate. In addition, a stepwise mass flow control strategy for the reactants decreased the overshoot and settling time by decreasing the amount of oversupplied oxygen immediately after the load change. The settling time for the stepwise mass flow control was approximately 30% lower than that for the constant mass flow rate control.

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Introduction

Proton exchange membrane fuel cells (PEMFCs) have been widely used in various applications because of their advantages of eco-friendliness, high power density, high efficiency, and rapid start-up. Especially, transportation is the most promising application of the PEMFC, as a substitute to the internal combustion engine. Dynamic response is a very important issue during the operation of a fuel cell powered vehicle, due to its frequent load change. In a fuel cell operated vehicle, overshoot or undershoot occurs during the sudden change of cell voltage or current density. The overshoot (or undershoot) means the cell voltage (or current density) difference between the peak (or bottom) value and the steady state value during the load change. Generally, an overshoot or undershoot is generated from the time delay between the load change and oxygen concentration [1—3]. Furthermore, the electrochemical reaction rate increases or decreases in an instant due to the excess or lack of oxygen concentration. Peng et al. [2] and Sousa et al. [4] discovered that increasing the charge double layer reduces the magnitude of the overshoot.

Nomenclature

A	electrocatalytic surface area per unit volume, m^{-1}
c_i	molar concentration of species i, $kmol\ m^{-3}$
CL	catalyst layer
$D_{i,j}$	binary diffusion coefficient, $m^2\ s^{-1}$
$D_{i,j}^{eff}$	effective binary diffusion coefficient, $m^2\ s^{-1}$
DL	phosphoric acid doping level
E_A	activation energy, $J\ mol^{-1}$
F	faraday constant, $9.64853 \times 10^4\ C\ mol^{-1}$
h_i	enthalpy of species i, $kJ\ kg^{-1}$
i_m	ionic current density, $A\ m^{-2}$
i^{ref}	reference exchange current density, $A\ m^{-2}$
i_0^{ref}	reference exchange current density at reference temperature, $A\ m^{-2}$
j	volumetric transfer current, $A\ m^{-3}$
J_i	diffusion flux of species i, $kg\ m^{-2}\ s^{-1}$
K	permeability
k^{eff}	effective thermal conductivity, $W\ m^{-1}\ K^{-1}$
k_f	thermal conductivity of fluid, $W\ m^{-1}\ K^{-1}$
k_s	thermal conductivity of solid, $W\ m^{-1}\ K^{-1}$
$\dot{m}$	mass flow rate, $kg\ s^{-1}$
M_i	molecular weight of species i, $kg\ kmol^{-1}$
p	pressure, $N\ m^{-2}$
p_{abs}	absolute pressure, $N\ m^{-2}$
R	universal gas constant, $8.314\ J\ mol^{-1}\ K^{-1}$
RH	relative humidity
S_h	source term of energy conservation, $kJ\ m^{-3}\ s^{-1}$
S_k	source term of species conservation, $kg\ m^{-3}\ s^{-1}$
S_m	source term of mass conservation, $kg\ m^{-3}\ s^{-1}$
S_u	momentum source in porous medium, $N\ m^{-3}$
S_ϕ	source term of charge conservation, $A\ m^{-3}$
t	time, s
T	temperature, K
u_i	velocity, $m\ s^{-1}$
V_{OC}	open circuit voltage, V
Y_i	mass fraction of species i

Greek letters

α	transfer coefficient
ΔS	entropy change for the oxygen reduction reaction, $J\ kmol^{-1}\ K^{-1}$
ε	porosity
ζ	stoichiometric ratio
η	overpotential, V
κ_m	ionic conductivity, $S\ m^{-1}$
κ_s	electrical conductivity, $S\ m^{-1}$
μ	viscosity, $N\ m^{-2}\ s^{-1}$
ρ	density, $kg\ m^{-3}$
σ_{ij}	arithmetic mean of Lennard-Jones parameter, Å
ϕ	potential, V
Ω_D	diffusion collision integral

Subscripts

a	anode
c	cathode
m	membrane phase
s	solid phase

Park and Min [3] reported that the transient response of voltage strongly depended on the cell temperature because the activation and ohmic over-voltages were affected by the MEA temperature. Since the overshoot and undershoot are attributed to the time delay of the oxygen concentration, the stoichiometric ratio significantly influences the characteristics of the overshoot and undershoot [2,5,6].

The relative humidity of a reactant has a significant effect on the dynamic response of a PEMFC. Both the hydration of the membrane and the oxygen concentration are greatly influenced by the relative humidity of the reactant. Wang and Wang [7], Wang and Wang [8], and Kim et al. [5] explained the effect of membrane water transport on the overshoot and undershoot. Wang and Wang [8] reported that the membrane water accumulation was responsible for the dynamic behavior of a PEMFC under low humidity operation, while the oxygen transport dictated the dynamic response under high humidity operation. Kim et al. [5] showed that the reduced relative humidity led to a decrease in the initial membrane hydration and an increase in the voltage undershoot. However, most previous studies investigated the humidity dependence on the overshoot (or undershoot) at low temperature conditions using Nafion as a membrane. The influence of the relative humidity on the dynamic response of a PEMFC significantly differs between low temperature and high temperature operations. A Nafion membrane cannot be used at a high temperature operation due to its vulnerability to heat. The oxygen concentration decreases dramatically due to an exponentially increased

saturation water vapor pressure at high temperature. While a high temperature PEMFC with a polybenzimidazole (PBI)-based membrane can operate under a dry condition, the ionic conductivity of the PBI-based membrane also increases in the humidified condition due to the higher proton diffusion rate [9−12]. Therefore, it is necessary to evaluate the effect of the relative humidity on the dynamic response of a PEMFC under high temperature operation.

In this study, three-dimensional transient simulation was conducted to investigate the dynamic response of a high temperature PEMFC. During the stepwise change of the voltage, the effects of the relative humidity on the overshoot and settling time were examined. The variations of oxygen concentration, ionic conductivity, and local current density were observed to analyze the characteristics of the overshoot and settling time. The water transport was also investigated through the membrane electrode assembly (MEA) at the dry and humidified conditions. In addition, a simple control strategy was suggested to reduce the overshoot and settling time by adjusting the mass flow rate of the reactants.

Numerical analysis and model validation

Computational model

Three-dimensional transient simulation was conducted using Fluent 14 to simulate the electrochemical reaction of a PEMFC