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Modeling of assisted cold start processes with anode catalytic hydrogen–oxygen reaction in proton exchange membrane fuel cell

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ABSTRACT

Catalytic hydrogen–oxygen reaction is a potentially effective way to help start up proton exchange membrane fuel cells (PEMFCs) from sub-zero temperatures. In this study, the anode hydrogen–oxygen catalytic reaction is implemented in a three-dimensional multiphase cold start model. It is found that successful cold start from −20 °C can be achieved with the assist of the catalytic reaction in galvanostatic mode. With anode catalytic reaction, the start-up current density must be moderate, because a high current density lowers the assisted heating effect, and a low current density slows down the start-up process. The temperature difference between the anode and cathode catalyst layers (CLs) is negligible, which indicates that the heating location in the electrodes for the catalytic reaction makes no significant difference. The humidification of anode due to the catalytic reaction also reduces the ohmic resistance of the membrane, leading to enhanced performance during the start-up processes.

1. Introduction

Proton exchange membrane fuel cell (PEMFC) has the advantages of zero/low emission and high energy conversion efficiency [1,2]. However, its adaptability to different environmental conditions is weaker than some other energy conservation devices such as internal combustion engines. One of the major issues is the start-up ability from sub-zero temperatures, especially for transportation applications expected to endure wide temperature rage.

Modeling [3–12] and experimental [13–20] studies have been conducted to investigate the cold start processes in PEMFCs. Some modeling studies focused on identifying the key parameters influencing the cold start performance and improving the start-up ability [3–7]. Several studies among them analyzed the lower limit of the successful self-start temperatures. Without any assisting strategy, Jiao and Li [3] found that it is possible to start a PEMFC at −3 °C, and Hishinuma [4] reported that it is impossible to start up at the temperatures lower than −5 °C. Analytical and numerical models were also developed to analyze the related design and operating parameters and the start-up mechanisms [5–12]. Furthermore, experimental studies mainly concentrated on the visualization of the ice formation processes [13–15], and the measurement of output performance during the cold start processes of PEMFC [16–20].

For practical applications, PEMFCs need to be able to start up quickly and efficiently from extremely low temperatures

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Nomenclature

A	geometric area, m^2
c	molar concentration, mol m^{-3}
C_p	specific heat, J kg^{-1} K^{-1}
D	mass diffusivity, m^2 s^{-1}
E	activation energy, kJ mol^{-1}
EW	equivalent weight of membrane, 1100 kg $kmol^{-1}$
F	Faraday's constant, 96,487 C mol^{-1}
h	Enthalpy, J mol^{-1}; heat transfer coefficient, W m^{-2} K^{-1}
I	current density, A cm^{-2}
j	reaction rate, A m^{-3}
k	thermal conductivity, W m^{-1} K^{-1}; pre exponential factor
K	permeability, m^2
$\dot{m}$	mass flow/transfer rate, kg s^{-1}
M	molecular weight, kg $kmol^{-1}$
p	pressure, Pa
R_{ca}	reaction rate, mol m^{-3} s^{-1}
RH	relative humidity
s	volume fraction
S	source terms, entropy, J $kmol^{-1}$ K^{-1}
t	time, s
T	temperature, K or °C
$\vec{u}$	velocity, m s^{-1}
Y	mass fraction

Greek letters

ε	porosity
η	over potential, V
ι	interfacial drag coefficient
κ	electrical conductivity, S m^{-1}
λ	water content in ionomer
μ	dynamic viscosity, kg m^{-1} s^{-1}
ξ	stoichiometry ratio
ρ	density, kg m^{-3}
φ	electrical potential, V
ω	volume fraction of ionomer in catalyst layer

Subscripts and superscripts

a	anode
act	activation
BP	bi-polar plate
c	cathode
ca	catalytic reaction
$cell$	cell property
CL	catalyst layer
ec	electrochemistry reaction
eff	effective
ele	electronic
EOD	electro-osmotic drag
f	frozen
fl	fluid phase
fmw	frozen membrane water
g	gas phase
GDL	gas diffusion layer
H_2	hydrogen
i	the ith components or the ith cell in a stack
ice	ice
in	inlet
$init$	initial condition
ion	ionic
lq	liquid water
m	mass (for source term)
mem	membrane
nf	non-frozen
nmw	non-frozen membrane water
O_2	oxygen
out	outlet
pc	phase change
ref	reference state
sl	solid phase
$surr$	surroundings
T	energy (for source term)
u	momentum (for source term)
vp	water vapor
$wall$	surrounding wall of the single cell or stacks
0	intrinsic value
$l-i$	liquid water to ice (vice versa)
$n-f$	non-frozen membrane water to frozen membrane water (vice versa)
$n-i$	non-frozen membrane water to ice
$n-v$	non-frozen membrane water to vapor (vice versa)
$v-i$	vapor to ice
$v-l$	vapor to water liquid (vice versa)

(e.g. −30 °C), and various assisting strategies [21–24] were therefore developed to improve the cold start performance. Pesaran et al. [25] reviewed and summarized 36 patents of assisted PEMFC cold start strategies. It was also concluded that although the isolation method is efficient for reducing the energy consumption, it increases the weight; and the electrical heating methods are energy demanding and require complex system design [26]. Some other assisting strategies like the external hydrogen burning method reported by Ahluwalia and Wang [27] needs special microchannel design to control the burning process of hydrogen, and potentially has explosion risk.

By comparing with other assisting strategies for PEMFC cold start, the catalytic reaction method has advantages such as simple system design, easy implementation and high heating efficiency. This method provides extra air (or oxygen) in hydrogen-rich anode, or extra hydrogen in air-rich cathode, and the hydrogen–oxygen reaction in anode or cathode catalyst layer (CL) releases heat. This heating method also has little negative influence on the normal performance of PEMFC [28,29]. Sun et al. [29] also reported that the hydrogen–oxygen catalytic reaction in PEMFC is safe even when the concentration of hydrogen is in the explosion limits.

This method can be used before the start-up processes for preheating [28,29] or during the start-up processes. For PEMFC in automotive applications, quick and efficient start-up is needed, and utilizing the hydrogen–oxygen catalytic reaction simultaneously during the cold start processes is favorable because it shortens the start-up period.