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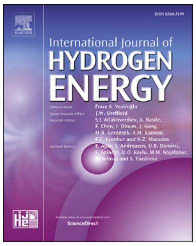

Effect of membrane electrode assembly design on the cold start process of proton exchange membrane fuel cells

Zirong Yang, Qing Du[**]*, Sen Huo, Kui Jiao*[*]

State Key Laboratory of Engines, Tianjin University, 135 Yaguan Road, Tianjin, 300350, China

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ABSTRACT

A transient multiphase model for cold start process is developed considering micro-porous layer (MPL), super-cooled water freezing mechanism and ice formation in cathode channel. The effect of MPL's hydrophobicity on the output performance and ice/water distribution is investigated under various startup temperatures, structural properties, membrane thicknesses and surrounding heat transfer coefficients. Under the maximum power startup mode, it is found that the hydrophobicity disparity of MPL has negligible influences when started from −15 °C, but it strongly affects the overall performance when started from −10 °C, especially after the cell survives the cold start. Decreasing the MPL's hydrophobicity leads to higher current density, meanwhile, it facilitates the super-cooled water's removal, which in turn reduces the ice formation in catalyst layer. However, excessive water accumulation happens if the generated water is hindered from getting into gas diffusion layer (GDL) due to the significant hydrophobicity gap. Weakening the GDL's hydrophobicity contributes to the water removal since the generated water is easier to diffuse out. A thinner membrane benefits the cold start owing to the reduction of ohmic loss and improvement of membrane hydration, and is more sensitive to the hydrophobicity of MPL. Ice formation in cathode channel is identified under various surrounding heat transfer coefficients.

Introduction

Proton exchange membrane fuel cell (PEMFC) is widely recognized as one of the most promising energy sources for automobile applications in the future, owing to its high power density, high electric efficiency and zero emission. Despite those brilliant advantages, there are some problems remained to be solved before its successful commercialization such as cold start, which means startup from subzero temperatures.

During a cold start process, water generated through electrochemical reaction freezes to ice/frost, leading to severe blockage of effective reaction sites and transport passages through the porous layers, thereby, hindering the occurrence of oxygen reduction reaction (ORR) and transport of gas reactants. Moreover, when water turns into ice, its volume expands, and this could irreversibly damage the microscopic structure of component layers, resulting in performance degradation [1,2]. In general, cold start process is the competition between ice formation and heat generation. If the cell's

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[*] *Corresponding author.*
[**] *Corresponding author.*

E-mail addresses: duqing@tju.edu.cn (Q. Du), kjiao@tju.edu.cn (K. Jiao).

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Nomenclature

a	water activity
A	cell geometric area, m^2
ASR	area specific resistance, Ω cm^2
c	mole concentration, mol m^{-3}
C_p	specific heat, J kg^{-1} K^{-1}
D	mass diffusivity, m^2 s^{-1}
EW	equivalent weight of membrane, 1.1 kg mol^{-1}
F	Faraday's constant, 96487 C mol^{-1}
h	surrounding 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}
K	permeability, m^2
M	molecular weight, kg mol^{-1}
n_d	electro-osmotic drag coefficient
p	pressure, Pa
P	power, W
$\dot{Q}$	heat transfer rate, W
R	universal gas constant, 8.314 J mol^{-1} K^{-1}
r	pore radius, m
s	volume fraction
S	source terms, entropy, J mol^{-1} K^{-1}
t	time, s
Δt	time step size, s
T	temperature, K
T^0	standard temperature, 298 K
V	voltage, V

Greek letters

α	transfer coefficient
ε	porosity
ζ	water transfer rate, s^{-1}
κ	electric conductivity, S m^{-1}
λ	water content
ξ	stoichiometry ratio
μ	dynamic viscosity, kg m^{-1} s^{-1}
ρ	density, kg m^{-3}
ω	volume fraction of ionomer
σ	surface tension, N m^{-1}
δ	thickness, m

Subscripts and superscripts

a	anode
act	activation
atm	atmosphere
BP	bipolar plate
c	cathode, capillary
CH	flow channel
CL	catalyst layer
conc	concentration
eff	effective
ele	electronic
eq	equilibrium
f	frozen
fl	fluid phase
FPD	freezing point depression
fmw	frozen membrane water
g	gas phase
GDL	gas diffusion layer
H_2O	water
ice	ice
ion	ionic
l	liquid phase
lq	liquid water
mem	membrane
MPL	micro-porous layer
N	normal condition
nerest	Nerest
nf	non-frozen
nmw	non-frozen membrane water
ohmic	ohmic
out	output
per	permeation
react	reaction
ref	reference state
sat	saturation
sl	solid phase
suplq	super-cooled water
surr	surroundings
T	energy (for source term)
vp	water vapor
n-f	non-frozen membrane water to frozen membrane water
n-suplq	non-frozen membrane water to super-cooled water
n-v	non-frozen membrane water to water vapor
suplq-i	super-cooled water to ice
v-l	water vapor to liquid water
v-suplq	water vapor to super-cooled/liquid water

temperature rises above 0 °C before the porous layers are fully occupied by ice, the cold start is successful. Thus, water management is of vital significance since it is beneficial to decrease ice formation by expelling the generated water out of porous layers as quickly as possible, meanwhile, it is necessary to maintain the membrane hydration for good proton conductivity.

In the past decades, both experimental and modeling studies have been carried out to investigate the cold start process. Experimental studies have mainly focused on the effects of operating conditions [3–7], structure designs [8–11] and visualization of ice formation [12–18]. To cast more sights on the freezing process inside fuel cells, technological methods such as electrochemical impedance spectroscopy [4], scanning electron microscopy [11,12,18], infrared radiation imaging [13,14], X-ray and neutron diffraction [15,19], Raman spectroscopic examination [20] have been adopted. In previous visualization studies, the state of super-cooled water was extensively identified. Ishikawa et al. [13,14] developed a system using visible and infrared images to investigate the phenomenon of water freezing at subzero temperatures. The authors pointed out that water was generated in a super-

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