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Three-dimensional non-isothermal modeling of carbon monoxide poisoning in high temperature proton exchange membrane fuel cells with phosphoric acid doped polybenzimidazole membranes

Kui Jiao, Ibrahim E. Alaefour, Xianguo Li *

Department of Mechanical and Mechatronics Engineering, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

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ABSTRACT

The performance of proton exchange membrane fuel cell (PEMFC) degrades when carbon monoxide (*CO*) is present in the supplied fuel, which is referred to as *CO* poisoning. Even though the high temperature PEMFC (HT-PEMFC) with a typical operating temperature range from 100 °C to 200 °C features higher *CO* tolerance than the conventional PEMFC operating at lower than 100 °C, the performance degradation of HT-PEMFC is still significant with high *CO* concentrations (e.g. ⩾0.5% *CO* by volume at 130 °C) in the supplied fuel. In this study, a *CO* poisoning model is developed for HT-PEMFCs with phosphoric acid doped polybenzimidazole (PBI) membranes. The present three-dimensional non-isothermal model compares well with published experimental data at various operating temperatures and *CO* concentrations in the supplied fuel. It is found that the *CO* adsorption/desorption processes follow Langmuir kinetics in HT-PEMFCs instead of the well-known Temkin kinetics in conventional PEMFCs. The results indicate that a HT-PEMFC can operate with sufficiently good performance at 130 °C or higher with hydrogen gas produced by methanol reforming with selective oxidation process, and at 160 °C or higher even without the selective oxidation process. At high current densities, it is also observed that severe performance degradation due to *CO* poisoning only occurs if the volume averaged hydrogen coverage is lower than 0.1 in the anode catalyst layer (CL).

1. Introduction

Even though proton exchange membrane fuel cell (PEMFC) has been recognized as a leading candidate for a zero or low emission power source for transportation and backup power applications, there are still several hurdles to PEMFC commercialization, with one hurdle being carbon monoxide (*CO*) poisoning. Due to the use of platinum catalysts, the hydrogen electro-oxidation reaction occurring within conventional PEMFC (operating at lower than 100 °C) can be severely inhibited by the presence of more than 2 ppm of *CO* (by volume) in supplied hydrogen [1]. *CO* poisoning can be prevented if pure hydrogen is utilized as the fuel. However, a lack of hydrogen refueling infrastructure and on-board hydrogen storage problems result in pure hydrogen fuel being unattractive in the near term for practical applications. On-board reformation of a liquid hydrocarbon fuel, such as methanol, solves the infrastructure and on-board hydrogen storage problems of pure hydrogen fuel, but introduces *CO* contamination. The reformation of methanol results in about 1–2% of *CO* (by volume) in supplied fuel, and the *CO* volume fraction can be reduced to about 2–100 ppm by using a selective oxidation process [1,2].

Increasing the operating temperature is one of the most effective ways to enhance the *CO* tolerance of PEMFC [1], and this has become an important reason that high temperature PEMFC (HT-PEMFC) with operating temperatures higher than 100 °C has attracted growing interests in the past decade. By comparing with conventional PEMFCs operating at around 80 °C, HT-PEMFCs with elevated operating temperatures features not only higher *CO* tolerance (e.g. >1% *CO* at 150 °C [3]), but also faster electrochemical kinetics, simpler water management (presence of liquid water can be neglected), and easier cell cooling and waste heat recovery. Although HT-PEMFCs have many attractive features, technical challenges still remain and are mostly related to the proton exchange membrane (PEM). Perfluorosulfonic acid (PFSA) polymer membranes (e.g. Nation membranes) widely used in conventional PEMFCs suffer significant decrement in mechanical strength at the high operating temperature of HT-PEMFCs, and the much lower relative humidity (RH) in HT-PEMFCs than in conventional PEMFCs due to the significantly increased vapour saturation pressure with temperature also results in severe reduction of proton conductivity of the PFSA polymer membranes. Therefore, developing PEMs with high mechanical strength at the temperatures higher than 100 °C

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* Corresponding author. Tel.: +1 519 888 4567x36843; fax: +1 519 885 5862.
E-mail addresses: kjiao@uwaterloo.ca (K. Jiao), ialaefou@uwaterloo.ca (I.E. Alaefour), x6li@uwaterloo.ca (X. Li).

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Nomenclature

a, b	pre-exponential factors to calculate membrane proton conductivity
A	cell geometric area (m^2)
b_i	reaction rate constant of species i ($kmol\ m^{-3}$)
c	molar concentration ($kmol\ m^{-3}$)
CO	carbon monoxide
C_p	specific heat capacity ($J\ kg^{-1}\ K^{-1}$)
D	mass diffusivity ($m^2\ s^{-1}$)
DL	phosphoric acid doping level for PBI membrane
E_a	activation energy ($J\ kmol^{-1}$)
E_i^k	activation energy of species i($J\ kmol^{-1}$)
E_i^b	activation energy of species i($J\ kmol^{-1}$)
F	Faraday's constant ($9.6487 \times 10^7\ C\ kmol^{-1}$)
H	hydrogen atom
H_2	hydrogen
I	current density ($A\ cm^{-2}$)
j	volumetric current density ($A\ m^{-3}$)
j_0	volumetric exchange current density ($A\ m^{-3}$)
k	thermal conductivity ($W\ m^{-1}\ K^{-1}$)
K	permeability (m^2)
k_i	reaction rate constant of species i (s^{-1} or $kmol\ m^{-3}\ s^{-1}$)
$\dot{m}$	mass flow rate ($kg\ s^{-1}$)
M	molecular weight ($kg\ kmol^{-1}$); platinum catalyst reaction site
O	oxygen molecule
O_2	oxygen
p	pressure (Pa)
q_i	reaction rate ($kmol\ m^{-3}\ s^{-1}$)
R	universal gas constant ($8314\ J\ kmol^{-1}\ K^{-1}$)
RH	relative humidity
S	source terms, entropy ($J\ kmol^{-1}\ K^{-1}$)
t	time (s)
T	temperature (K)
T_{opt}	cell operating temperature (K)
$\vec{u}$	velocity ($m\ s^{-1}$)
V	electrical potential (V)
X	mole fraction
Y	mass fraction

Greek letters

α	transfer coefficient
γ_i	under relaxation factor for species i
ε	porosity
η	overpotential (V)
θ	coverage fraction
κ	electrical conductivity ($S\ m^{-1}$)
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
ads	adsorption/desorption
BP	bipolar plate
c	cathode
CO	carbon monoxide
$cell$	cell characteristic
CL	catalyst layer
eff	effective
ele	electronic
eox	electro-oxidation
g,s	gas and solid phases
GDL	gas diffusion layer
H	hydrogen atom
H_2	hydrogen
H_2O	vapour
i, j	the ith and jth species
in	inlet
m	mass (for source term)
mem	membrane
O	oxygen molecule
O_2	oxygen
ox	oxidation
opt	operating condition
out	outlet
p	previous iteration
pro	protonic
ref	reference state
rev	reversible
sat	saturation
sld	solid phase excluding the membrane electrolyte
T	energy (for source term)
u	momentum (for source term)

and with high proton conductivity in anhydrous environments becomes the major challenge, and most of the previous HT-PEMFC related researches focused on this important issue [4]. Polybenzimidazole (PBI) membranes first proposed by Aharoni et al. [5] have been investigated in the previous studies and recognized as a promising PEM when doped with a strong oxo-acid (e.g. phosphoric acid or sulfuric acid) for HT-PEMFCs [6–8]. Moreover, phosphoric acid doped PBI membrane first suggested for fuel cell applications by Wainright et al. [9] has attracted most of the attentions due to its relatively higher proton conductivity and mechanical strength by comparing with the other types of acid doped PBI membranes.

Experimental studies on HT-PEMFCs with phosphoric acid doped PBI membranes were mainly focused on the property characterizations of cell components [3,9–14] and in situ cell performance, durability and *CO* poisoning tests [11,15–18]. It was found that temperature, phosphoric acid doping level and surrounding RH all have significant effects on the proton conductivity of PBI membranes [3,9–12]. The thermal stability of a PBI membrane with a doping level of 4.8 (4.8 phosphoric acid molecules per PBI repeat unit) was confirmed to be more than enough for use as a PEM in HT-PEMFCs [13]. The electro-osmotic drag (EOD) effect was also found to be negligible in PBI membranes [14]. Good cell performances were obtained without any humidification from different in situ tests [11,15–18]. In situ tests involving both the continuous operation and shutdown-restart cycles demonstrated promising cell durability [15,16]. It was also confirmed that the *CO* tolerance of HT-PEMFC is much higher than conventional PEMFC [15,17].

Numerical models for HT-PEMFCs with phosphoric acid doped PBI membranes were also developed in the previous studies [18–24]. Cheddie and Munroe developed a one-dimensional model [19] and then further extended their model to three-dimensional [20]. A three-dimensional model similar to [20] was introduced in [18] as well. Both the steady and unsteady three-dimensional models were presented by Peng et al. [21,22]. A two-dimensional