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Modeling of high temperature proton exchange membrane fuel cells with novel sulfonated polybenzimidazole membranes

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ABSTRACT

In this study, a three-dimensional, steady-state, non-isothermal numerical model of high temperature proton exchange membrane fuel cells (HT-PEMFCs) operating with novel sulfonated polybenzimidazole (SPBI) membranes is developed. The proton conductivity of the phosphoric acid doped SPBI membranes with different degrees of sulfonation is correlated based on experimental data. The predicted conductivity of SPBI membranes and cell performance agree reasonably with published experimental data. It is shown that a better cell performance is obtained for the SPBI membrane with a higher level of phosphoric acid doping. Higher operating temperature or pressure is also beneficial for the cell performance. Electrochemical reaction rates under the ribs of the bipolar plates are larger than the values under the flow channels, indicating the importance and dominance of the charge transport over the mass transport.

Introduction

Proton exchange membrane (PEM) fuel cells (PEMFCs) are promising green power sources for electronic products, backup power and transportation applications [1,2]. In recent decade, high temperature proton exchange membrane fuel cells (HT-PEMFCs) have received considerable attention due to their potential benefits and advantages, such as simple water management, high tolerance to CO poisoning (increasing CO tolerance with temperature [3]), fast reaction kinetics at elevated temperatures, less external humidification requirement and easy waste heat recovery.

Proton exchange membrane is a key component in HT-PEMFCs. Up to date, high temperature PEMs can be classified into four groups: (a) sulfonated aromatic hydrocarbon polymer membranes, (b) inorganic–organic composite membranes, (c) blend polymer membranes, and (d) acid–base polymer membranes [4]. Among them, the aromatic polybenzimidazole (PBI) membranes have attracted significant attention because of their outstanding thermal, chemical, oxidative and hydrolytic stabilities particularly at high

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Nomenclature

A_1	active surface area of the catalyst layer, cm^2
A_2	inlet area for anode and cathode, m^2
c	molar concentration, mol m^{-3}
C_p	specific heat capacity, J kg^{-1} K^{-1}
D	mass diffusivity, m^2 s^{-1}
F	Faraday's constant, 96,487 C mol^{-1}
I	current density, A cm^{-2}
j	electrochemical reaction rate, A cm^{-3}
j_0	volumetric exchange current density, A cm^{-3}
$\vec{J}$	diffusive mass flux vector
m	mass flow flux, kg s^{-1} m^{-2}
M	molecular weight, kg mol^{-1}
p	pressure, Pa
R	universal gas constant, 8.314 J mol^{-1} K^{-1}
S	source terms, entropy, J mol^{-1} K^{-1}
T	temperature, K
$\vec{u}$	superficial velocity, m s^{-1}
V	electric potential, V
$\vec{v}$	real velocity, m s^{-1}
x	mole fraction

Greek letters

α	transfer coefficient
ε	porosity
η	overpotential, V
κ	permeability, m^2
λ	thermal conductivity, W m^{-1} K^{-1}
σ	electrical conductivity, S m^{-1}
μ	dynamic viscosity, kg m^{-1} s^{-1}
ξ	stoichiometry ratio
ρ	density, kg m^{-3}
φ	electric and ionic potential, V
ω	volume fraction of electrolyte in catalyst layer
γ	mass fraction
$\vec{\tau}$	shear stress tensor

Superscripts

eff	effective value
in	inlet
ref	reference state

Subscripts

a	anode
act	activation
c	cathode
cell	fuel cell characteristic
ele	electronic
gas	gas phases
H_2	hydrogen
H_2O	water vapor
i, j	different species
m	mass (for source term)
mem	membrane
O_2	oxygen
op	operating conditions
pro	protonic
rev	reversible
sol	solid phases excluding the membrane
T	energy (for source term)

temperatures. However, PBI must be modified since it is not a proton-conductive material itself [5].

One of the modification methods is acid-doping [6,7]. Phosphoric acid doped PBI membranes show high proton conductivities under low relative humidity (RH) even in completely anhydrous state [8–11]. The proton conductivity is mainly determined by the phosphoric acid doping level, and the higher the doping level, the higher the proton conductivity. These doped PBI membranes exhibit excellent properties such as electro-osmotic drag number nearly approaching zero and high proton conductivity at high temperatures (120–200 °C) [12]. However, high doping level usually results in poor mechanical strength [13]. Another method for the application is to introduce sulfonic acid groups into PBI membranes forming ionic cross-linking between sulfonic acid groups and imidazole rings. The cross-linked sulfonated polybenzimidazole (SPBI) membranes have been reported to have excellent mechanical properties and better radical oxidative stability, which are beneficial for fuel cell lifetime [13,14]. However, the ionic cross-linking has a negative effect on the conductivity of these SPBI membranes since some of the sulfonic acid groups become neutralized by basic imidazole groups and hence no longer available for proton conduction [15]. Consequently, there is an urgent need to optimize the degree of ionic cross-linking and the levels of phosphoric acid doping for phosphoric acid doped SPBI membranes. Conventionally, such optimization is often accomplished through trial and error approach experimentally in the realism of material development.

On the other hand, numerical simulation has increasingly become an effective and useful tool in the development of fuel cells by considering in detail the effect of internal transports and electrochemical phenomena within fuel cells. HT-PEMFCs models which predict the cell performance under different design or operating conditions have been developed in previous studies [16–21]. Cheddie and Munroe [16,17] first proposed a model of HT-PEMFC, which was extended into two- and their three-dimensional isothermal models. The three-dimensional model predicted a greater ohmic loss, because of the presence of ribs, than the two-dimensional model [17]. Peng and Lee [18] developed a three-dimensional, non-isothermal model and pointed out that the current collector land area was important for fuel cell performance. However, this model did not consider the ohmic loss in bipolar plates (BPs), gas diffusion layers (GDLs) and catalyst layers (CLs). Peng et al. [19] also developed a transient three-dimensional, non-isothermal model which considered the electrochemical charge double-layer effect. A pseudo two-dimensional, steady-state and isothermal model was developed by Shamardina et al. [20] to account for the crossover of gases through the membrane. Jiao and Li [21] fully considered the effects of temperature, phosphoric acid doping level and surrounding RH on PBI membranes in the HT-PEMFC model. It is clear that most of the HT-PEMFC models available in