Solid State Ionics xxx (2013) xxx–xxx

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

One-dimensional modeling and analysis for performance degradation of high temperature proton exchange membrane fuel cell using PA doped PBI membrane

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ARTICLE INFO

Article history:
Received 15 May 2013
Received in revised form 27 August 2013
Accepted 29 August 2013
Available online xxxx

Keywords:
One-dimensional model
Degradation modeling
Lifetime prediction
PA-doped PBI
High-temperature PEMFC

ABSTRACT

The cell degradation in high-temperature proton exchange membrane fuel cells (HT-PEMFCs) using phosphoric acid (PA)-doped polybenzimidazole (PBI) membranes is one of the most important challenges to be improved for its early commercialization since the reported lifetime of the HT-PEM is too deficient to meet the commercially required target. The aim of this paper is to numerically investigate the effects of operating conditions on the performance degradation of HT-PEMFC. In order to resolve this problem, a one-dimensional model for the HT-PEM with PA-doped PBI membrane has been developed based on the hybrid modeling method and the model validated with HT-PEMFC polarization curves obtained by ourselves. Using the developed model, activation and ohmic overpotentials at each layer could be analyzed through membrane electrode assembly (MEA). The simulation results demonstrate that the durability of HT-PEMFC is changeable with respect to current density and PA doping level. In addition, the lifetimes have been predicted according to different operating conditions and thus we found whether any conditions are helpful to improve lifetime of HT-PEM or not.

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1. Introduction

Traditional PEM fuel cells using persulfonated polytetrafluoroethylene (PTFE) as the proton conductor face several obstacles such as easy contamination of Pt catalyst, water management problem, system's complexity, and relatively lower temperature of recovered hot water. In order to improve these problems, it has been developing HT-PEMFC which is based on polybenzimidazole (PBI) operating from 393.15 K to 473.15 K. HT-PEMFC system component is simple and easy because of a high tolerance to CO and sulfur as well as a no humidification [1]. However, HT-PEM that has lower performance and lifetime compared to conventional PEMFC has relatively few experimental data for initial performance and durability due to short research period and it has also few modeling study works until now.

As experimental studies, Andreasen et al. [2] presented the performance change in HT-PEM according to current, temperature and components of anodic gas. Hu et al. [3] and Modestov et al. [4] found degradation reason using the cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), but they did not mention the effect of temperature on the durability. Oono et al. [5,6] experimented on leakage of PA in membrane, platinum (Pt) agglomeration in catalyst layer and lifetime according to temperature. Li et al. [7] presented and analyzed experimental data that start-up/shut-down, relative humidity (RH), sulfur dioxide (SO_2) affect the cell performance and durability. From these research works, it is noted that change of operating condition affect initial performance and lifetime.

As modeling studies, Cheddie et al. [8–10] experimentally compared Nafion with PBI membrane and developed one phase and two phase numerical model to predict the cell performance but not durability. Olapade et al. [11] developed one-dimension isothermal model to estimate the effects of pressure, RH, temperature, gas diffusion layer and micro porous layer on the cell performance. Scott et al. [12,13] developed one dimension model to simulate effect of catalyst loading and Pt/C ratio on the cell performance. These studies were mainly focused on the initial performance and reason of degradation according to various operating conditions in fuel cells. However they did not estimate degradation rate and predict their lifetime according to various operating conditions. Liu et al. [14], Sousa et al. [15], Hu et al. [3] partly built the degradation model that deal with durability data for a relatively short time.

In this paper, one-dimensional degradation model for HT-PEMFC with PA-doped PBI membranes has been developed and the model showed the activation and ohmic overpotentials at each layer of electro-catalyst and membrane inside MEA. As a result of the simulation with the developed degradation model, the degradation phenomenon and its lifetime of HT-PEMFCs could be predicted under different operating conditions.

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http://dx.doi.org/10.1016/j.ssi.2013.08.036

Nomenclature

A	pre-exponential coefficient for PA doping level
a	activity
B	pre-exponential coefficient for humidity
b	activation energy of membrane, J
c	molar fraction
DL	doping level
E	electrical potential, V
E_c	activation energy for catalyst, J mol^{-1}
F	Faraday's constant, C mol^{-1}
H	enthalpy, J mol^{-1}
j	current density, A m^{-2}
k_m	proton conductivity, S m^{-1}
n	number of transfer electrons
p	pressure, Pa
R	universal gas constant, J mol^{-1} K^{-1}
RH	effective relative humidity
S	entropy, J mol^{-1} K^{-1}
T	temperature, K
t	time, h

Greek letters

α	transfer coefficient
Δ	difference
δ	thickness, m
ξ	coefficient of pressure and molar fraction
η	overpotential, V

Superscripts and subscripts

0	exchange
act	activation
m	membrane
ohm	ohmic
ref	standard, reference conditions
r	reversible

2. Model development

2.1. Model description and assumptions

We have been developed one dimensional and isothermal HT-PEM single cell model using gPROMS ModelBuilder (PSE Ltd). The effects of the following components are reflected in the model; membrane, catalyst layers, gas diffusion layers, bipolar plates and current collector but not gas channels. The following assumptions are adopted in the developed model.

- Single phase flow
- Ideal gas mixture
- Ignore contact resistance between components
- Isotropic macro-homogeneous porous media
- Negligible activation and concentration over-potential at anode side

2.2. Governing equations

The most of governing equations used in the developed model are referred to [8]. The other references [9–11,15,17] also give a good guideline. Continuity equation of the fluid flow is used because consumption or generation of materials does not occur in gas diffusion area. In order to apply to transfer of multicomponent gas in porous media, Stefan–Maxwell equation is used. Momentum equation in this porous media is dominated by Darcy's equation and mixture viscosity is calculated by the averaged mass value. Decomposition and combination of protons and electrons at catalyst layer are fulfilled, and thus charge conservation equation is considered for the rate of charge transfer between the solid and electrolyte phases. Electrochemical reaction occurs due to transfer of charge and therefore ohmic or joule heat and heat of reaction are spontaneously generated. The energy equation accounts for generation, convection and conduction of heat. Source terms are also considered by the rate of reaction in the catalyst layer. The overall cell voltage (E_{cell}) in the cell is given by the following equation

$$E_{cell} = E_r - \eta_{act} - \eta_{ohm} \tag{1}$$

where E_r is reversible potential including effect of gas concentration using Nernst equation according to data of thermodynamics, η_{act} is activation overpotential by Butler–Volmer equation, and η_{ohm} is ohmic overpotential by Ohm's law. Experiments for PA-doped PBI-based HT-PEMFC were performed to estimate the parameters in the model explained above. In the experiments, the single cell uses a commercial MEA, Celtec P 1100 provided from BASF, with an active cell area of 45 cm^2.

2.3. Constitutive relations

The hybrid model combining fundamental and empirical models are developed to predict the rate of degradation for the HT-PEMFC with respect to operating conditions. The empirical equations are derived based on the experimental data reported by Oono et al. [5]. Oono et al. performed long-term durability tests with the PA-doped PBI-based HT-PEMFC at 0.2 A cm^{-2} and 150, 170, and 190 °C and then analyzed the cause of the PEMFC degradation in the overpotential levels.

2.3.1. Electrochemical kinetics

The Butler–Volmer equation was used to calculate activation overpotential and is given by

$$j_r = j_{ref}\xi\left(\exp\left(\frac{a_{Rd}F\eta_{act}}{RT}\right) - \exp\left(\frac{a_{ox}F\eta_{act}}{RT}\right)\right) \tag{2}$$

$$j_{ref} = j_{ref0}exp\left(-\frac{E_c}{R}\left(\frac{1}{T} - \frac{1}{T^{ref}}\right)\right) \tag{3}$$

where j_r is reaction exchange current density, j_{ref} is reference exchange current density, η_{act} is activation overpotential at cathode side, α_{Rd} is reduction charge transfer coefficient at cathode side, α_{Ox} is oxidation charge transfer coefficient at cathode side, j_{ref0} is reference exchange current density parameter, E_c is activation energy for catalyst, and ξ is coefficient about pressure and molar fraction.

Oono et al. reported that activation overpotential of HT-PEM during long term continuing operation has been mostly increased due to agglomeration of Pt, and reduction of an active surface area. Thus we defined that the reference exchange current density parameter is the function of time and operating temperature. The following empirical equation based on exponential and polynomial expression finally leads the activation overpotential in the HT-PEM cell.

$$j_{ref0} = \left(a * e^{b*T}\right) * t + (c * T + d) \tag{4}$$

where T is operating temperature, t is time, a, b, c and d are coefficients of j_{ref0}. A least square errors technique was used to decide the proper values of the coefficients.

Please cite this article as: M. Kim, et al., Solid State Ionics (2013), http://dx.doi.org/10.1016/j.ssi.2013.08.036

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