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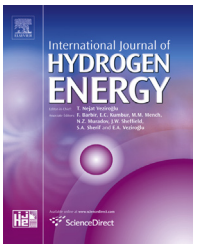

Numerical modeling of the degradation rate for membrane electrode assemblies in high temperature proton exchange membrane fuel cells and analyzing operational effects of the degradation

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ABSTRACT

The numerical model of the degradation rate in high temperature proton exchange membrane fuel cells (HT-PEMFC) using phosphoric acid (PA) doped polybenzimidazole (PBI) membranes is developed and expressed as a semi-empirical relationship. The model accounts for the degradation factors in terms of activation, ohmic, and concentration over-potentials and the subsequent degradation rate for high temperature membrane electrode assemblies (MEAs). Furthermore, the model considers the operating temperature effects on the degradation rate, because the degradation rate is highly dependent on the operating temperature. The developed model is validated with HT-PEMFC polarization curves obtained by ourselves and with degradation data after long-term operations reported in the literature. The agreement between the model predictions and the experimental data is good. The model is used to investigate the effects of operating temperature, PA doping level, and inlet gas pressure on the HT-PEMFC initial performance and its degradation rate. The analysis suggests that the predicted lifetime and average performance for high temperature MEAs exhibit a trade-off by changing the operating temperature. In particular, the performance of an HT-PEMFC operated at higher temperature shows a slight degradation at first but a fast degradation rate later. The degradation at higher temperature is mainly caused by activation over-potential.

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Introduction

Fuel cells have taken center stage as more eco-friendly and substantial energy technology than conventional fossil energy sources. Fuel cells are widely used in stationary, portable and transportation applications due to high energy conversion efficiency and excellent load conformability. Proton exchange membrane fuel cells (PEMFC) mostly use perfluorosulfonic acid (PFSA) polymers in the membrane. This system has high conductivity, chemical stability, mechanical strength and potentially long term durability [1], but it has material problems such as poisoning of carbon monoxide (CO) and difficult water and heat management [2]. To solve these problems, a high temperature PEMFC (HT-PEMFC) based on polybenzimidazole (PBI), which is operated from 393.15 K to 473.15 K, has been developed. The HT-PEMFC system is relatively simple because of a high tolerance to CO and sulfur as well as no humidification [3]. However, the HT-PEM has a lower performance and shorter lifetime compared to conventional low temperature PEMFC and has relatively little experimental data for its initial performance and durability due to short study periods compared to low temperature PEMFC. Modeling studies with for an HT-PEM are nearly nonexistent until now.

S. J. Andreasen et al. [4] presented a study of the performance change according to current, temperature and components of the anodic gas. J. Hu et al. [5] and A. D. Modestov et al. [6] determined the degradation cause using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), but they did not mention the effect of temperature on the durability. Y. Oono et al. [7,8] experimented on the spilling of phosphoric acid in the membrane, platinum (Pt) agglomeration in the catalyst layer and the lifetime according to temperature. Q. Li et al. [1] experimented and analyzed how the start-up/shutdown, relative humidity (RH), and sulfur dioxide (SO_2) affected the performance and durability. Many researchers found that the operating conditions affect the initial performance and lifetime. The cell temperature was found to have the most important effect on the initial performance and durability. However, it is difficult to experimentally determine the lifetime of HT-PEMFC at various conditions, because experiments for measuring lifetimes are time and money consuming processes. Therefore, modeling studies are used to solve this experimental problem. D. Cheddie and N. Munroe [9,10,11] experimentally compared Nafion and PBI membranes, developed a one phase and two phase numerical model, and predicted its performance. P. O. Olapade et al. [12] developed a one-dimensional isothermal model and presented the impact on performance with regard to change of pressure, RH, temperature, gas diffusion layer and microporous layer. K. Scott et al. [13,14] developed one-dimensional to simulate the effects of catalyst loading and Pt/C ratio and verified the model accuracy by comparison with experimental data. These studies were focused on the change in the initial performance and investigated the cause of degradation according to the operating conditions of the fuel cells. A. R. Korsgaard et al. [15] presented a simple performance model including the effects of temperature, reactant stoichiometry, RH and over-potential at the cathode side, but they did not predict lifetime based on these operating conditions. D. Liu and S. Case [16], T. Sousa et al. [17], and J. Hu et al. [5] proposed experiments and modeling that deal with relatively short lifetimes for performance and durability, but they did not mention the cause of degradation and the operating conditions did not vary. The previous studies only include the effect of activation over-potential in short lifetimes [5,6,7,8,18].

In this paper, the development of a degradation model including the effect of over-potentials is used to predict the long term lifetime with regard to various operating conditions, because the operating conditions significantly affect the lifetime of HT-PEM, which has been partially investigated through previous experiments. Thus, we develop a semi-empirical model that includes the effects of over-potentials to predict the lifetime of HT-PEM, for which it is hard to design an analysis of the degradation at various operating conditions, and to determine the initial performance and degradation rate using the developed model at various operating conditions.

Experimental description

The aim of this work is to develop a degradation model for predicting the lifetime of HT-PEMFC. Because determining the durability performance data of HT-PEM require long-term experiments and a change of over-potentials, we utilized experimental data from Y. Oono et al. [7], T. J. Schmidt et al. and J. Baurmeister [18] to ensure reliability of the model. Also, we directly experimented on the initial performance of HT-PEM using a Celtec-P1100 membrane electrode assembly (MEA) from BASF Company Ltd. in the Germany to increase the accuracy in predicting performance of model. The size of the active area of the used MEA was 23.92 cm^2. An MEA using a phosphoric acid (PA) doped PBI membrane and a gas diffusion electrode (GDE) made of carbon fiber are used. The bipolar plate (BP) is made of carbon. The geometric structure of the BP consists of a parallel serpentine of three channels, with a lib of 1 mm width and depth, a land of 1 mm width and a channel of 280 mm length. We used hard type gaskets made of thermal resistant polymer to maintain a constant clamping thickness and used insulation gaskets. To prevent leakage and decrease contact resistance between the BP and end plate (EP), we used graphite sheets.

Fig. 1 shows the schematic diagram of the test station for our experiment. The cell is located in a furnace. The temperature of inside of the furnace was controlled by a PID controller from the outside. The cell temperature is measured at the center point of the EP as the representative value of cell temperature, because the size of cell was so small and the temperature gradient not large. We assumed that the cell temperature was equal to the temperature of the EP. The reactants were supplied in a pre-heated and non-humidified condition at both the anode and the cathode. We made progress with the experiment at room temperature. The range of measured temperatures in experiment was from 423.15 K to 443.15 K. We used air at the cathode side and hydrogen and mixed gas (H_2 80%, CO_2 18%, CO 0.5%, CH_4 1.5%), imitating reformed gas, at the anode side. Before the main test, a PBI

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