



ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

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

Electrochemical impedance analysis with transmission line model for accelerated carbon corrosion in polymer electrolyte membrane fuel cells

Jeawoo Jung ^{a,b}, Young-Hoon Chung ^a, Hee-Young Park ^a, Jonghee Han ^{a,b},
 Hyung-Juhn Kim ^{a,c}, Dirk Henkensmeier ^{a,c}, Sung Jong Yoo ^{a,c},
 Jin Young Kim ^{a,b,c}, So Young Lee ^a, Kwang Ho Song ^{b,d,***},
 Hyun S. Park ^{a,**}, Jong Hyun Jang ^{a,b,c,*}

^a Fuel Cell Research Center, Korea Institute of Science and Technology (KIST), Seoul 02792, Republic of Korea

^b Graduate School of Energy and Environment, Green School, Korea University, Seoul 02841, Republic of Korea

^c Division of Energy & Environment Technology, KIST School, University of Science and Technology (UST), Seoul 02792, Republic of Korea

^d Department of Chemical and Biological Engineering, Korea University, Seoul 02841, Republic of Korea

ARTICLE INFO

Article history:

Received 30 November 2017

Received in revised form

23 April 2018

Accepted 14 June 2018

Available online xxx

Keywords:

Polymer electrolyte membrane fuel cell

Electrochemical impedance spectroscopy

Transmission line model

Cathode degradation

Ionic resistance

ABSTRACT

The effects of varying the applied voltage and relative humidity of feed gases in degradation tests of polymer electrolyte membrane fuel cells (PEMFCs) were analyzed using electrochemical impedance spectroscopy (EIS). A transmission line model that considers the proton-transport resistance in the cathode catalyst layer was used to analyze impedance spectra obtained from degraded PEMFCs. As the applied cell voltage was increased from 1.3 to 1.5 V to induce accelerated degradation, the cell performance decayed significantly due to increased charge- and proton-transfer resistance. The PEMFC degradation was more pronounced at higher relative humidity (RH), i.e. 100% RH, as compared with that observed under 50% RH. Furthermore, changes in the charge transfer resistance of the electrode accompanied changes in the ionic conductivity in the PEMFC catalyst layer. Although the initial ionic and charge-transfer resistances in the catalyst layer were lower under higher RH conditions, the impedance results indicated that the performance degradation was more significant at higher water contents in the electrode due to the consequential carbon corrosion, especially when higher voltages, i.e. 1.5 V, were applied to the PEMFC single cell.

© 2018 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

* Corresponding author. Fuel Cell Research Center, Korea Institute of Science and Technology (KIST), Seoul 02792, Republic of Korea.

** Corresponding author.

*** Corresponding author.

E-mail addresses: khsong@korea.ac.kr (K.H. Song), hspark@kist.re.kr (H.S. Park), jhjang@kist.re.kr (J.H. Jang).

<https://doi.org/10.1016/j.ijhydene.2018.06.093>

0360-3199/© 2018 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have been intensively researched and developed as environmentally friendly and highly efficient power sources for automobile and stationary applications [1]. As a result, several companies are introducing fuel cell electric vehicles and other mobile and stationary applications into the market. However, more reliable and economical systems are still required, and further development of PEMFCs is necessary to achieve durability (5000 h) and low cost (\$40/kW) for the wide deployment of fuel-cell technologies [2,3]. Accelerated degradation tests (ADTs) are frequently utilized to shorten the time required for durability evaluation, especially for PEMFC components [4–8]. For example, Mukundan et al. utilized open-circuit voltage (OCV) operation to evaluate the electrolyte membrane stability, combined with high-performance liquid chromatography (HPLC) analysis of released fluorine [6]; Macauley et al. repeatedly applied 0.6 V (3 s) and 0.95 V (3 s) potentials in a square wave form to compare the electrochemical durability of Pt and PtCo electrocatalysts [7].

In order to elucidate the degradation mechanisms of fuel cells, compositional and microstructural changes are commonly investigated using various techniques such as scanning electron microscopy [9,10], transmission electron microscopy [10–13], X-ray photoelectron spectroscopy [12], X-ray diffractometry [13], atomic force microscopy [14], and Fourier transform infrared spectroscopy [14]. However, these post-mortem analyses require interruption of long-term operation and disassembly of PEMFCs. In contrast, electrochemical techniques can be performed without cell destruction, and therefore, can be utilized as *in situ* techniques for analyzing degradation mechanisms. For example, cyclic voltammetry (CV) was used to measure the electrochemical surface area (ECSA) of Pt [15]. The ECSA loss was utilized to quantitatively analyze the degradation of fuel cells resulted from carbon support corrosion, ionomer/catalyst interface loss, dissolution or detachment, and particle growth [16]. The effects of ionic conductivity and gas-phase mass transport on PEMFCs have also been analyzed using rigorous physical models to fit polarization curves [17,18]. Lalit et al. reported that the primary mechanism of degradation can be identified using the shape of polarization-change curve (ΔV curve) which had a unique shape depending on the contribution of differed overpotentials (kinetics, ohmic, and transport) in different oxygen concentrations [19]. In addition, electrochemical impedance spectroscopy (EIS), in which alternating current (AC) or voltage signals are applied to electrochemical devices, has been used for *in situ* analysis of metal dissolution [20,21], carbon corrosion [20,22–25], hydration or flooding mechanisms [15,26–37], and catalyst-layer characteristics [38–45]. Erik et al. reported a localized EIS measurement to identify sectional membrane hydration level in a fuel cell [37]. Because only a small perturbation of the voltage or current is applied to the fuel cells during steady-state operation, the influence of EIS analysis on an operating electrochemical system is insignificant, thus making EIS suitable for *in situ* analysis.

EIS data, which include AC impedances at various frequencies, are generally plotted as Nyquist plots ($Z_{im}(f)$ vs. $Z_{re}(f)$) as well as various types of Bode plots ($Z_{im}(f)$ vs. f). These plots allow graphical analysis of the EIS data and provide information on ohmic resistance and charge-transfer resistance. Overlapped semicircles are typically observed in Nyquist plots, and the x-axis intercepts at higher and lower frequencies can be interpreted as the apparent ohmic resistance and total resistance, respectively. In addition, the difference between high- and low-frequency intercepts corresponds to the polarization resistance, which is related to the electrode processes that include charge-transfer and mass transport steps. This graphical analysis can be efficiently utilized for evaluating the effects of operating parameters and components on PEMFCs, as reported for inlet gas humidity [21] and hierarchical nanostructured carbons [23].

Furthermore, based on equivalent circuits, non-linear fitting analysis can be performed to determine resistance and capacitance values for each process. For PEMFC single cells, a resistance and parallel combination of a charge-transfer resistance and a double-layer capacitance (or a constant phase element) are utilized to represent the electrochemical characteristics of ohmic components, including polymer-electrolyte membranes [41], and cathodes, respectively [26–30]. For example, Silva and Rouboa reported that prolonged activation increased capacitance values while decreasing polarization resistance, which was correlated with the expansion of the triple-phase boundary [28]. It should also be noted that the hydrogen oxidation reaction at a PEMFC anode is much faster than the oxygen reduction reaction at the cathode; therefore, the anodic impedance terms can be neglected [46–48], with the exception of some special scenarios such as H_2 depletion [49].

More complicated equivalent circuits including the transmission line model (TLM) have also been successfully utilized for analyzing PEMFC single cells. The TLM was first introduced by R. de Levie to analyze the electrochemical characteristics of porous electrodes, such as Pt brush and Ag powder [42]. In a typical PEMFC, the cathode is composed of a carbon-supported Pt catalyst (Pt/C), Nafion ionomers, and pores, which are used as conduction pathways for electrons, protons, and gases, respectively. To describe the transport phenomenon, especially proton conduction through ionomer networks, TLM circuits with ionic resistance in the catalyst layer and reaction impedance of the oxygen reduction reaction have been utilized in several studies concerning PEMFC fabrication conditions [31–33,38,44], operation conditions [35,36], and catalyst-layer degradation, including carbon-support corrosion [1,25,38]. In addition, the reliability of the TLM model applied to gas diffusion electrodes was confirmed by comparison to the impedance spectra measured at a disk electrode in an aqueous solution [34]. When EIS data for cathodes are collected under a nitrogen atmosphere [25,31–34,38,44], instead of air [1,25,35,44], the interfacial-reaction impedance at the Pt and ionomer boundaries is represented by a simple capacitor. At high cathode potentials, the carbon support in the cathode layers is electrochemically oxidized, by combining with water molecules, to produce CO_2 and protons. This process is one of the major degradation

Download English Version:

<https://daneshyari.com/en/article/7705355>

Download Persian Version:

<https://daneshyari.com/article/7705355>

[Daneshyari.com](https://daneshyari.com)