



ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

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

Catalyst layer doped with phosphotungstic acid for degradation mitigation in Polymer Electrolyte Membrane Fuel Cells

Guang-Ying Chen^a, Cheng Wang^{a,*}, Yi-Jie Lei^a, Jianbo Zhang^{b,**},
Zong-Qiang Mao^a, Jian-Wei Guo^a, Jian-Long Wang^a

^a Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084, China

^b State Key Laboratory of Automotive Safety and Energy, Tsinghua University, Beijing 100084, China

ARTICLE INFO

Article history:

Received 19 January 2016

Received in revised form

4 March 2016

Accepted 29 April 2016

Available online xxx

Keywords:

Proton exchange membrane fuel cell

Durability

Phosphotungstic acid

Accelerated stress test

Mitigation

ABSTRACT

The aim of this study was to enhance durability and performance of Polymer Electrolyte Membrane Fuel Cells (PEMFCs) for transportation application. A modified catalyst coated membrane (CCM) with phosphotungstic acid (PTA) in catalyst layer was fabricated using a heating ultrasonic-spray method, and durability study of both the modified CCM and traditional CCM was carried out according to the DOE CCM/stack durability protocol. During the accelerated stress test of CCM durability, cyclic voltammetry, polarization curves, linear sweep voltammetry and electrochemical impedance spectroscopy were employed for diagnosis of the CCM performances. The experimental results indicate that the power density of the modified CCM decreased only 14% while the traditional CCM decreased 33% after 100-h aging time, which confirms that addition of PTA in the catalyst layer of CCM is an effective way to improve the durability for CCM attributed to the enhancement of intermediates removal and the increasing of proton transfer channels by using the PTA excellent properties, both redox property and proton conductivity.

© 2016 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

PEMFCs are considered to be a promising energy conversion device for transportation and stationary applications due to their high efficiency, high energy density and zero or low pollution [1]. Durability, apart from performance and cost requirements is one of the significant barriers to PEMFC industrialization. In the past few years, numerous studies have shown that several factors including proton exchange membrane thinning, catalyst layer degradation and gas diffusion

layer degradation can affect the durability of a PEMFC. More and more experimental results have shown catalyst layer degradation in the component of CCM is one of the most critical factors for performance degradation in PEMFC [2]. The catalyst layer in CCM for current PEMFC is mainly composed of platinum based catalyst and Nafion ionomer used generally in the membrane. Without the Nafion ionomer addition, the majority of the platinum based catalyst sites are inactive [3]. It is known that the intermediates such as hydrogen peroxide, OH radicals produced during the fuel cell working process are potential species that damage perfluorosulfonic acid polymer

* Corresponding author. Tel./fax: +86 01062797595.

** Corresponding author. Tel./fax: +86 01062797595.

E-mail addresses: wangcheng@tsinghua.edu.cn (C. Wang), jbzhang@tsinghua.edu.cn (J. Zhang).

<http://dx.doi.org/10.1016/j.ijhydene.2016.04.222>

0360-3199/© 2016 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

in Nafion ionomer by attacking at the alpha hydrogen [4]. The dissolution and chemical degradation of Nafion ionomer in the catalyst layer might be more severe than that in the membrane because of it is located adjacent to the fuel cell reaction active sites. Xie et al. [5] revealed the degradation of the ionomer network in the catalyst layer after 500 h of operation under high humidity and constant current using cell impedance trends. Zhang et al. [6] detected the catalyst layer ionomer degradation after 300 h of fuel cell operation using XPS quantitative analysis. According to their report, the catalyst layer surface concentration of fluorine reduced from 50.1% to 38.9%, consistent with a decrease of CF_3 and CF_2 species and an increase in oxidized forms of carbon. Which undoubtedly was a proof for the Nafion ionomer change in catalyst layer. Therefore, increasing catalyst layer durability is becoming a major challenge and growing focus of research attention in PEMFC durability studies. Possible mitigation methods for degradation of Nafion ionomer in the catalyst layer include reducing peroxide from electrochemical reaction by using radical inhibitors or peroxide-decomposition catalysts deposited within catalyst layer to decrease the severity of radical attacks. Research results show that solid heteropoly acids have excellent redox property and proton conductivity, and the addition of heteropoly acid to Nafion membrane is a significant route to achieve the objective of improving durability attributed to the enhancement of intermediates removal and increase of proton transfer channels [7]. According to this principle of the degradation mitigation for Nafion membrane, we expect that adding heteropoly acid into the catalyst layer is also an effective way to improve the durability for CCM. Zhou et al. [8] developed a novel proton exchange membrane using phosphotungstic acid (PTA, $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$) as proton carrier and mesoporous silica as matrix (PTA-meso-silica). The study provided us the idea of using phosphotungstic acid as both proton carrier and peroxide-decomposition catalyst to improve the durability of PEMFC without apparent decrease in proton conductivity.

In this study, the PEMFC durability was investigated by impregnating phosphotungstic acid into catalyst layer in CCM (the modified CCM). The DOE PEMFC durability test protocol [2] was employed to evaluate the durability difference between the modified CCM and the traditional CCM (no phosphotungstic acid). During durability test of CCMs, cyclic voltammetry (CV), polarization curves (IV), linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) were adopted for performance status diagnosis of PEMFC.

Experimental

Preparation of CCM

The CCMs were fabricated using a heating ultrasonic-spray method, where the catalyst ink was sprayed directly onto the Nafion XL membrane (DuPont, USA) at a temperature of 100 °C. The catalyst ink was prepared by mixing Pt/C catalyst (Johnson Matthey, Pt 40 wt%), isopropanol, and a Nafion ionomer solution (DuPont, 5wt%), with or without 3wt% phosphotungstic acid (PTA, $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$, reagent grade obtained from Sigma Aldrich, FW2880.05) adding respectively.

The two categories of CCMs (traditional CCM and modified CCM) were prepared with the following membrane and electrode components given in Table 1.

Accelerated stress test

The prepared CCMs with active area of 25 cm² were sandwiched between two gas diffusion layers (SGL-25BC, Germany), then assembled into a single fuel cell using graphite bipolar plates with serpentine flow channels (Shanghai Hong Feng Industrial Company Limited), and the clamping force of the single cell was 5 N m by eight lubricated bolts. This single fuel cell was connected to the HS-150 Fuel Cell Test Equipment (Hephas Energy Co., Ltd). For the CCM accelerating degradation test, the fuel cell was evaluated at 80 °C with pure Air and H₂ (99.999%) being used as cathode and anode reactant respectively. The current density and gas flow rate were changed every 30 s, and a test cycle finished after 20 test points. The complete operational protocol is presented schematically in Table 2 and diagrams of the cycles for accelerated stress test are shown in Fig. 1.

Electrochemical characterization

At 0, 100, 200, and 300 h, the accelerating stress test was paused to conduct characterizations of CCM degradations, such as CV, IV, LSV and EIS. And the electrochemical performances were measured by an electrochemical workstation (ZAHNER IM6ex). During the CV and LSV measurements humidified hydrogen (300 mL/min, dew point: 68 °C) and N₂ (500 mL/min, dew point: 68 °C) were supplied to the anode and the cathode respectively. The scan range is 0.05–1.4 V for CV with scan rate of 20 mV/s, while the scan range is 0.05–0.6 V with 1 mV/s rate for LSV. The EIS was conducted at a constant current of 200 mA/cm² with an AC frequency range of 100 kHz–0.05 Hz and an amplitude of 5 mV.

Results and discussion

Overall performance degradation in accelerated stress test

Fig. 2 shows the overall performance change of the traditional and modified CCM during the aging time from 0 to 6000 min. From the top to the bottom the three parts of the figure exhibit the voltage behaviors of the two CCMs under different constant current operation of 0.02 A/cm², 0.1 A/cm² and 1.2 A/cm² respectively. It can be seen that the voltage distinction between the modified and traditional CCM became more and more obvious with the increase of current density. Furthermore, during the aging time from 0 to 6000 min, the performance of modified CCM was better than the traditional CCM under the constant current operation of 0.02 A/cm², 0.1 A/cm² and 1.2 A/cm², respectively. Even though the performance of the two CCM was almost the same under lower constant current operation of 0.02 A/cm² during the aging time from 0 to 1000 min. From the result, an obvious conclusion can be summarized that the modified CCM showed an enhanced performance and stability over the traditional one, especially at higher current density. And the reasons for the

Download English Version:

<https://daneshyari.com/en/article/5147889>

Download Persian Version:

<https://daneshyari.com/article/5147889>

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