Applied Energy 212 (2018) 1321–1332

Contents lists available at ScienceDirect

Applied Energy

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

Comprehensive analysis of galvanostatic charge method for fuel cell degradation diagnosis

Zunyan Hu[a,b,*], Liangfei Xu[a,b], Yiyuan Huang[c], Jianqiu Li[a,b,*], Minggao Ouyang[a,*], Xiaoli Du[c], Hongliang Jiang[a,b]

[a] *State Key Lab of Automotive Safety and Energy, Tsinghua University, Beijing 100084, PR China*
[b] *Collaborative Innovation Center of Electric Vehicles in Beijing, PR China*
[c] *Shanghai Shen-li High Tech Co., Ltd, Yuandong Rd., Industry Comprehensive Development Zone, Shanghai, PR China*

HIGHLIGHTS

- A correction algorithm has been proposed to improve the accuracy of GSC.
- The accuracy of GSC has been validated under different test conditions.
- Some useful rules have been concluded for the real application of GSC.
- GSC is applied to analyze the degradation reasons of a four-cell stack.

ARTICLE INFO

Keywords:
PEM fuel cell
Galvanostatic charge method
Cyclic voltammetry
Diagnosis
Degradation analysis

ABSTRACT

Cyclic voltammetry and linear sweep voltammetry are the most commonly used diagnosis methods to estimate the internal statement of fuel cell stack. However, both methods can only be applied in a single fuel cell. There is a lack of suitable in situ diagnosis methods for a multi-burl fuel cell stack. The galvanostatic charge method (GSC) is a very convenient in situ diagnosis method, which can be applied to a multi-burl fuel cell stack to calculate the electrochemical active surface area (ECSA), double-layer capacitance, and hydrogen crossover current. However, there are not enough experiments to analyze the adaption of GSC or apply this method to analyze fuel cell degradation process. In this study, we conducted experiments to validate the accuracy of GSC under different test conditions, and proposed a new correction algorithm to improve the accuracy. Next, this method was applied to analyze the performance degradation process of a four-cell stack. The experimental results showed that the estimated GSC parameters exactly coincide with the standard values. Additionally, for the degradation analysis of a four-cell stack, the GSC results showed that the ECSA reduction of cell four is the direct reason for performance degradation. Moreover, the assumptions of ECSA reduction and carbon corrosion were validated by material experiments. About 5° decrease in the contact angle of the gas diffusion layer (GDL) in the cathode catalyst was observed in the worst cell.

1. Introduction

Owing to their high efficiency and low environment impact [1], fuel cell vehicles have been recognized by several governments and research institutions as a potential solution. Nowadays, the performance of a fuel cell stack has met the commercial demand, and its service life is the major bottleneck [2]. The explanation of the degradation mechanism and prolonging of service life of the fuel cell stack are currently the hottest research topics. Especially for a high-power fuel cell stack, the degradation mechanism of the nafion membrane, catalyst, or carbon support [3] is more complex than that of a laboratory single fuel cell [4]. Additionally, the diagnosis methods of these parameters form the basis of durability research. In general, diagnosis methods can be separated into two categories: performance evaluation, which only considers voltage, and internal statement analysis.

The performance evaluation method is very convenient and does not require specific equipment. In general, a performance degradation of 10% under the reference current is the maximum allowable lifetime for a fuel cell system (FCS) in automotive applications [5]. This method is the most used approach for evaluating service life. However, a

* Corresponding authors at: State Key Lab of Automotive Safety and Energy, Tsinghua University, Beijing 100084, PR China.
E-mail addresses: huzy14@mails.tsinghua.edu.cn, hzy6608128@163.com (Z. Hu), xuliangfei@tsinghua.edu.cn (L. Xu), huangyy@sl-power.com (Y. Huang), lijianqiu@tsinghua.edu.cn (J. Li), ouymg@tsinghua.edu.cn (M. Ouyang), duxl@sl-power.com (X. Du), jhl15@mails.tsinghua.edu.cn (H. Jiang).

https://doi.org/10.1016/j.apenergy.2018.01.005
Received 17 October 2017; Received in revised form 30 December 2017; Accepted 2 January 2018

consistent opinion cannot be reached on the selection of reference current and end-up percentage. Furthermore, the voltage drop cannot offer a comprehensive explanation regarding which component is broken.

To get more information about the degradation reasons, a polarization curve test is applied in most situations [6]. In this way, performance degradation can be divided into three parts [7]: activation polarization, ohmic polarization, and concentration polarization. Using this method, we can know what happens in this fuel cell stack; however, what causes these phenomena is still unknown because the degradation of different components can lead to similar degradation phenomena.

For a fuel cell degradation process, resistance, crossover current, ECSA, and hydrophilicity are core indexes for health evaluation. To obtain this information, certain test technologies are required [8]. However, the ex situ analysis method is unsuitable for a high-power fuel cell stack, and certain in situ test technologies can only be applied to a single fuel cell stack.

Cyclic voltammetry (CV) [9–11] is the most common method for estimating ECSA. ECSA reduction is an important factor for fuel cell stack service life and a more active site can accelerate the reaction rate. However, this method can only be used in a single fuel cell stack [12]. Hu et al. [13] used a model-based method to estimate ECSA reduction; however, the accuracy of this method is still doubtful. Besides, some ex situ methods, such as scanning electron microscopy and transmission electron microscopy, can also be used for ECSA estimation. However, they are harmful for the fuel cell stack.

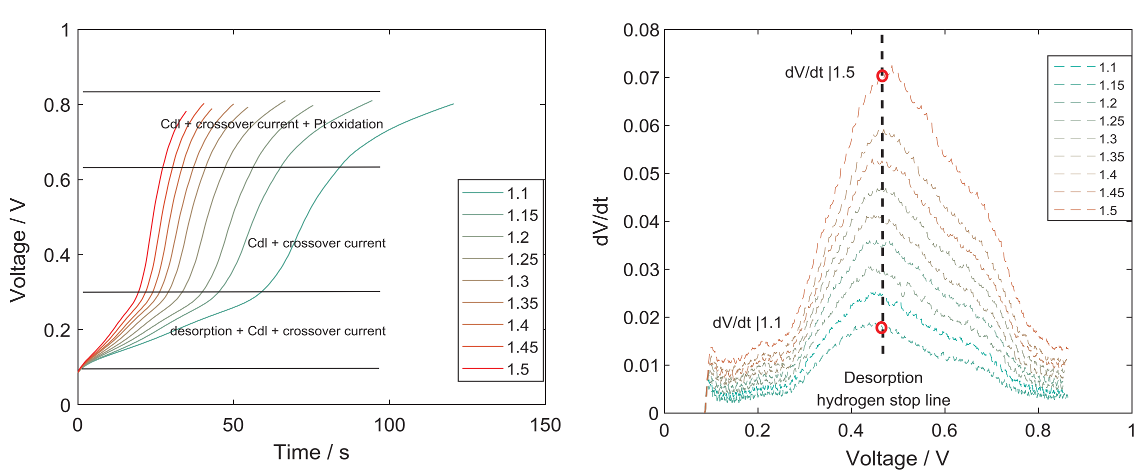
Linear sweep voltammetry (LSV) [14,15] is an effective in situ method for hydrogen crossover current estimation. The hydrogen crossover current is a membrane health indicator, and increasing the crossover current can result in fuel cell failure. However, even this method can only be used for a single fuel cell stack. Kundu et al. [16] suggested that increasing the hydrogen crossover current can lead to an open-circuit voltage (OCV) drop. Francia et al. [17] used a voltage model to estimate the value of the crossover current. However, experiments have shown that although OCV is an effective index for qualitative analysis, it is not effective for quantitative analysis. Moreover, using a drainage method to collect leaked gas is another useful method. However, it is difficult to identify the leakage rate of every cell of a high-power fuel cell stack.

Double-layer capacitance is related to the dynamic performance of a fuel cell [18], and can be measured by EIS [19] and CV [20]. However, CV cannot be applied to a high-power fuel cell stack. In contrast, EIS is feasible, but high accuracy equipment for EIS is very expensive.

EIS is a very important diagnosis method for multi-burl fuel cell stack performance analysis. And some internal state of heat and mass transfer process can be obtained by the mechanism EIS model [21–23]. Depernet et al. [24] applied EIS on a fuel cell system for embedded diagnosis or control improvement. Martin et al. [25] analyzed the degradation process of proton exchange membrane fuel cell without external humidification by EIS. And Wang et al. [26] used EIS to optimize the equivalence ratios control of a flame fuel cell unit. However, EIS is hard to provide some important parameters directly, like ECSA and crossover current. And the accuracy of internal state from EIS is dependent on the accuracy of mechanism model, which is very complex.

In conclusion, it is very difficult to monitor the health statement of a high-power fuel cell stack, and an effective in situ test method for a high-power fuel cell stack is still lacking. Thus, developing an in situ test method is important for the application of a high-power fuel cell stack. Stevens et al. [27] proposed a galvanostatic method for analyzing the electrochemical characterization of the active surface in carbon-supported platinum electrocatalysts. This method only needs a galvanostatic source for collecting voltage data. Since the current control and voltage collection are simpler, a galvanostatic method is more convenient than a CV method. Lee et al. [28] developed a new galvanostatic analysis technique to estimate ECSA, crossover current, and double-layer capacitance, and applied it to a single fuel cell stack and a five-cell PEMFC stack. Furthermore, Pei et al. [29] validated this method under different test conditions. Although these results showed reasonable trends, they were not were not comparable to the results of CV and LSV. Based on this method, Brightman et al. [30] evaluated the performance of an 18-cell PEMFC stack and Torija et al. [31] analyzed the basic characteristics of a six-cell PEMFC stack. However, all these experiments were conducted for one time. They didn't apply this method on a long period experiments to analyze the degradation process of fuel cell stack. Thus, there is not enough research to validate that this method can be used in a durability test to identify the degradation reasons.

This paper presents a comprehensive analysis of a galvanostatic charge method for fuel cell diagnosis. It validates the accuracy of GSC under different test conditions, and applies it to analyze the reasons for the performance degradation of a four-cell stack. Section 2 presents the mechanism model of the galvanostatic charge method and a correction algorithm for error elimination. Section 3 describes the experiments carried out in this study. Section 4 presents the analysis of the experimental data for a single fuel cell and a four-cell PEMFC stack. Section 5 presents the material experimental results to validate the degradation assumption. Section 6 presents the conclusion.



(a) Voltage curve during charging process

(b) dV/dt curve during charging process

Fig. 1. Mechanism of galvanostatic charge method.