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Degradation pattern prediction of a polymer electrolyte membrane fuel cell stack with series reliability structure via durability data of single cells

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HIGHLIGHTS

- Propose an accelerated degradation testing (ADT) procedure for a PEMFC stack with a series reliability structure.
- Estimate the lifetime of PEMFC stack using theory of the smallest order statistics.
- Propose a three-parameter Weibull distribution to fit the failure data of cells.
- Model the degradation paths of PEMFC stack based on ADT data of a single cell.

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ABSTRACT

The insufficient long-term durability of polymer electrolyte membrane fuel cell (PEMFC) stacks has been blocking commercialization of PEMFC technologies. An accelerated degradation test (ADT) is needed to facilitate the PEMFC development process by reducing the testing time. We propose an ADT procedure for a PEMFC stack with the concept of series reliability structure under startup–shutdown cycling testing conditions. The acceleration factor is estimated to fit the degradation paths of individual cells consisting of the PEMFC stack under normal use conditions via the accelerated degradation data of a single cell. We employ a nonparametric regression method to smooth the degradation curves observed from accelerated operating conditions. We illustrate the methodology for estimating the lifetime of the PEMFC stack using the theory of the smallest-order statistics. We propose a three-parameter Weibull distribution in fuel cell technology to fit the failure data of cells in a PEMFC stack.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have attracted broad attention as one of the most promising clean energy sources for stationary and large vessel applications due to their high power density, fast startup, and low pollutant emission at the point of use [1–5]. However, the insufficient long-term durability of PEMFC systems hinders the PEMFC technologies from penetrating commercial markets. Over the last decade, continuous effort has gone into extending PEFMC durability by improving membranes, anodic/cathode catalysts, and bipolar plate materials [6–9]. Most of all, to enable long-term durability for successful commercialization of PEMFCs, a fundamental understanding of the various degradation mechanisms that eventually lead to failure is required. To date, extensive research has sought to unveil the underlying degradation mechanisms of PEMFC by focusing mainly on mathematical modeling and experimental verification through electrochemical/physicochemical analysis [10–14].

In practice, studies on PEMFC durability have been based largely on the results of tests executed under the real operational mode of PEMFC-imbedded systems. However, observing failures under the real operation mode is time-consuming, because the degradation

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process is slow. To hasten the degradation mechanisms within a relatively short time, an accelerated degradation testing (ADT) has been employed to direct methanol fuel cells (DMFCs) [15,16]. Analogous to the accelerated life test (ALT), the purpose of the ADT is to expedite the degradation process by loading a higher level of stress than normal to extrapolate degradation rate at normal stress level, then to predict lifetime distribution or reliability at normal operating conditions more quickly, based on the extrapolated degradation rate. Because the ADT drastically reduces testing time, and the following post-mortem analysis can reveal critical causes of product degradation, the need for ADT has continuously increased in the area of fuel cells.

Recently, Bae et al. [17] proposed a straightforward ADT procedure for PEMFCs for easy and quick implementation of the procedure. However, existing ADT methods have mostly been performed for individual membrane electrode assemblies (MEAs) in the fuel cell engineering field [15–17]. In particular, long-term tests of stacks are vital for demonstrating the feasibility and durability of PEMFCs to enter the energy market, because the stack is composed of a large number of cells to meet the requirement of practical applications in vehicles and residential power generators. Therefore, the lifetime–stress relationship of the stack needs to be investigated with comparison of the result from the ADT for single cells.

The stack must undergo an emergency shutdown due to the risk of MEA damage if any cell's voltage in the stack falls below a critical safety level. Therefore, the stack lifetime is determined by the cell with the smallest lifetime in a PEMFC stack. The lifetime is defined as the time when the performance (e.g., power, voltage) falls below a critical threshold level. Suppose that a system consists of components, $X_1, X_2, \ldots, X_n$. In a series reliability structure, the reliability $R_s(t)$ of the system at time t is defined as $R_s(t) = R_{X_1}(t) \times R_{X_2}(t) \times \cdots \times R_{X_n}t)$. From this point of view, the stack has a series structure in terms of reliability, where the system lifetime is determined by the component with the minimum lifetime, and the system works if and only if all of its components work [18].

For the acceleration conditions of the PEMFC, a number of researchers reported that PEMFC performance is seriously deteriorated under continual startup–shutdown cycles, and that decay mechanisms in such conditions are closely related to local hydrogen starvation of the MEA in the PEMFC during startup–shutdown procedures [17,19–22]. In reality, for commercial use, a PEMFC system is subjected to repeated startup–shutdown cycles by the system's users. In this work, the startup–shutdown cycling frequency is chosen as an acceleration variable for the degradation of the PEMFC stack in the ADT by taking various experimental results and the real use environment into account. In addition, in order to realize cost savings in a PEMFC system, the stack was tested under dry air conditions through the removal of external gas humidification parts on the cathode side [23,24].

The research presented in this paper proposes an ADT procedure for a series-connected PEMFC stack under startup–shutdown cycling testing conditions. The degradation patterns and lifetime of the PEMFC stack operated under normal use conditions is estimated based on the accelerated degradation data of a single cell, using the statistical theory of the smallest order in a series reliability structure. This work is more challenging, because the degradation model of cells of the PEMFC stack is not known *a priori*, and the degradation paths show complicated nonlinear patterns. Furthermore, it is very meaningful in that the single cell ADT drastically reduces testing time and cost. In order to disclose the degradation mechanism of single cells and a PEMFC stack in different operating conditions, post-mortem analysis is limited in this research due to the limited experimental time available and scope.

2. Theoretical background

2.1. Nonparametric degradation model

It has been reported that the inherent degradation of MEA capacity approximately follows first-order kinetics [25]:

$$\eta(t) = \eta(0)e^{-\kappa t}, \quad t \geqslant 0 \tag{1}$$

where $\eta(t)$ is the capacity level at time t, $\eta(0)$ is the initial capacity, and $\kappa(>0)$ is the rate of degradation. The exponential decay model (1) can be linearized by log-transformation of the response. However, the exponential decay model hardly captures the degradation paths of individual cells, which present a steady decay in performance at the initial stage and progressive decay at a later stage. Instead of physics-based parametric models that require strict assumptions about the fitted model, we employ a nonparametric model to fit the complex degradation patterns of individual cells in the PEMFC stack without any model assumption. From accelerated degradation data, an acceleration factor is estimated under a scale-acceleration assumption. The scale-acceleration assumption means that the failure-times at an accelerated stress level can be obtained by simply multiplying a time-scale factor to the failure-times at a normal stress level. In the present work, this time-scale factor is estimated by smoothing the degradation curves observed from accelerated operating conditions, following the approach of Bae et al. [17].

Under the scale-acceleration assumption, the amount of degradation $\eta_0(t)$ at time t under normal operating conditions can be expressed by:

$$\eta_0(t) = \eta_i(t/\varsigma) \tag{2}$$

where $\eta_i(t)$ is the amount of degradation at time t under an accelerated operating condition i, $i = 1, 2, \ldots, I$, and $\varsigma(>1)$ is the time-scale factor, which is often called an acceleration factor in the sense that time moves more quickly in accelerated conditions than in normal operating conditions [26]. The first step in estimating the time-scale factor is to recover the underlying continuous curves from observed degradation data using smoothing techniques that capture the intrinsic nonlinearity in the data without reference to a parametric model. We employ locally weighted least squares with a kernel smoother. Specifically, the estimate of the degradation curve at time t is given by:

$$\hat{\eta}_i(t) = \frac{1}{m_i}\sum_{j=1}^{m_i} \frac{\{h_{2,i}(t;w) - h_{1,i}(t;w)(t_{ij} - t)\}\rho(t_{ij} - t;w)\eta_{ij}}{h_{2,i}(t;w)h_{0,i}(t;w) - h_{1,i}(t;w)^2} \tag{3}$$

where $h_{q,i}(t;w) = \left\{\sum_{j=1}^{m_i}(t_{ij} - t)^q \rho(t_{ij} - t;w)\right\}/m_i, \quad q = 0,1,2,$ η_{ij} is the observed degradation at measurement time $t_{ij}(j = 1, 2, \cdots, m_i)$ under test condition $i(i = 0, 1, \ldots, I)$, and $\rho(u;w)$ is the kernel smoother with bandwidth parameter w. As one of the most popular kernels in nonparametric regression, the Epanechnikov kernel smoother with second order is [27]:

$$\rho(u;w) = \begin{cases} (3/4\sqrt{5}) \cdot \left[1 - (u/w)^{2/5}\right] & \text{if } (u/w)^2 < 5 \\ 0 & \text{otherwise.} \end{cases} \tag{4}$$

Then, the time-scale factor is estimated using the algorithm suggested by Shiau and Lin [28]. See Bae et al. [25] for a detailed procedure to estimate the time-scale factor from accelerated degradation data.

2.2. Lifetime estimation of a PEMFC stack

The lifetime from the degradation data is defined as the time when the actual degradation path $\eta(t)$ reaches the pre-specified