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Classical statistical methodology for accelerated testing of Solid Oxide Fuel Cells

Alexandra Ploner*, Anke Hagen, Anne Hauch

Technical University of Denmark, Department of Energy Conversion and Storage, Frederiksbergvej 399, 4000 Roskilde, Denmark

HIGHLIGHTS

- Semi-empirical degradation prediction model for Solid Oxide Fuel Cells.
- Parameterization of degradation on an extensive quantity of experimental data.
- Temperature and steam dependency for accelerated aging of Solid Oxide Fuel Cells.

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ABSTRACT

Solid Oxide Fuel Cell (SOFC) lifetime prognosis is a substantial challenge for market introduction. This paper illustrates an accelerated testing approach based on an extensive quantity of experimental degradation data and suggests derivable degradation quantities for SOFC with focus on a large number of tests. The semi-empirical degradation models are based on the underlying physical degradation phenomena in the cell and are used for projection of temperature and steam impact on SOFC aging. Degradation tests performed at seven different temperatures and four different p(H_2O) in the fuel gas are used for evaluation. The key contribution of this study is parameterization of the aging model by experimental data while physical simulations in literature usually lack such robust empirical foundation.

1. Introduction

Solid Oxide Fuel Cells (SOFCs) are a promising technology for stationary and mobile power applications. Research activities over the last decades were dedicated to improve the performance and durability of the individual cell and stack components to reach commercial viability targets. For stationary applications (e.g. domestic combined heat and power generators) a lifetime of 40,000–80,000 h is expected to be competitive with current generalized generation or diesel generator technologies [1]. However, the estimation of lifetime and reliability of cells and stacks is a remaining critical issue for commercialisation. Long-term tests from 1 kh up to 70 kh are reported [2]. Yet, with enhancing durability of the SOFC technology, longer lifetime tests will be needed to identify failures and quantify long-term degradation rates. Logically, these tests are costly and often impractical. Hence, it will be desirable to determine SOFC lifetime by other means and in shorter times.

Accelerated testing is a widely used approach in reliability engineering [3]. Within the reliability discipline, accelerated tests (ATs) are divided into two complementary but important approaches to derive reliability and lifetime information. For *qualitative ATs* (‘torture testing’) devices are subjected to a harsher-than-usual combination of operating parameters. This methodology is already implemented in SOFC long-term durability tests for example by performing redox-cycle tests and deliberate poisoning tests [4,5]. In general, this detrimental failure should be avoided under actual use. However, the experiments are necessary to assess and to contribute to improving e.g. electrode structure, composition or the stack design.

On the other hand, the *quantitative AT* approach attempts to obtain degradation-time distribution at a specific level of operating conditions and utilizes models to justify extrapolation to the nominal level. In many cases, the relationship between an accelerating variable (stressor) and the actual degradation mechanism based on physical/chemical theory can be extremely complex. Efforts within the physical/chemical interpretation approach are frequently based on a small number of experiments [6,7] and lack the measurement around the mean life. Thus, an empirically derived model building on statistical data may be an attractive alternative. This approach is routinely used in batteries [8,9] and microelectronics [10], but not yet in the field of SOFC/SOEC.

In analogy to lifetime tests of rechargeable batteries, SOFC lifetime

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* Corresponding author.
E-mail address: apl@dtu.dk (A. Ploner).

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tests can be separated into '*cycle life*' and '*calendar life*' tests. Aging of SOFCs leads to resistance changes due to e.g. mechanical and electrochemical aging processes. Mechanical failures occur for example due to mismatches of the temperature expansion coefficients of the different materials which the SOFC is composed of. Therefore, this failure is mainly introduced at start-up and shut-down procedures and dynamic operation of SOFC stacks and can be evaluated by simulating e.g. temperature cycles ('*cycling life*').

On the other hand, under constant operating conditions ('*calendar life*') primarily electrochemical aging takes place. It includes chemical and structural processes that all lead to an increase of the area specific resistance (ASR) over time, such as degradation of the fuel electrode (e.g. Ni-coarsening, Ni-Ni percolation loss, carbon and sulfur poisoning [11]), the oxygen electrode (e.g. Cr-poisoning [12], second phase formation [13]) and electrolyte (e.g. conductivity loss [13]). Aging phenomena for instance poisoning effects or secondary phase formation can be avoided to a certain extent via adjustments of fuel composition, choice of oxygen electrode or choice of operating conditions. On the other hand, microstructural degradation of the Ni-YSZ electrode and Cr-poisoning are critical processes, which are hardly preventable in state-of-the-art technology and therefore targeted aging phenomena.

This study focusses on classical accelerated '*calendar life*' testing methods for SOFCs by semi-empirical ATs. The results are analyzed with a reliability methodology and experimentally derivable degradation quantifications for ATs are proposed in the field of SOFC.

2. SOFC degradation analysis

Degradation is fundamental to all devices. As the cell degrades, a decrease of performance follows. The progress of the performance degradation depends on time and stressor, i.e. one or more operating parameters. In Fig. 1a a common SOFC voltage degradation [14] curve of a degradation test under constant operating conditions is shown, i.e. a so-called '*calendar life*' test.

Obviously, an initial degradation trend (wear-in) is followed by a relatively linear intrinsic degradation rate (IDR) and finally if the test is operated long enough a progressive degradation rate (= wear-out) region might occur [14,16]. The degradation pattern over time follows therefore typically a bathtub-shaped curve for device degradation [15]. Particularly, the wear-in (= initial degradation) causes challenges for lifetime prediction and complicates reporting of degradation rates for SOFC tests, because a simple extrapolation is not possible for short testing times. In fact, different lifetime limits are obtained whether or not a wear-in period is considered (see Fig. 1a). By extrapolation of the IDR, the corresponding end-of-life equals to approx. 23,300 h vs. 87,900 h and demonstrates the impact of the wear-in region on lifetime prediction. In the field of reliability engineering such an effect is not unfamiliar and can be encountered if large differences of degradation rates of two different degradation populations exist for one device. Each population is a sum of various degradation phenomena. If the two degradation modes are clearly separated in time, it is possible to discriminate between the two processes. For SOFC lifetime it is crucial to eliminate the wear-in region, so that the end-of-life target of e.g. 10% voltage loss for SOFC as proposed by the U.S. Department of Energy [17] becomes a feasible objective. In SOFCs, this could be achieved by designing an adequate accelerated *conditioning* treatment which removes the initial degradation, i.e. the wear-in period.

As seen in previous work [18,19] the degradation in the wear-in region is dominated by degradation processes due to the fuel electrode in state-of-the-art cells. Therefore, particularly stressors affecting fuel electrode degradation can be considered relevant to design an accelerated *conditioning* process. According to many experimental studies high steam/hydrogen ratio [20,21] in the fuel or high temperature [22,23] can be possible degradation 'controllers', as they tend to accelerate microstructural changes of the fuel electrode and thereby yielding faster performance stabilization. Furthermore, as SOFCs are mostly operated in galvano- or potentiostatic mode – current density or overpotential can be considered as additional stressors. However, so far current density/overpotential seem to have no effect on the microstructural degradation of the Ni-YSZ electrode [24] or only show a subordinate impact by regulation of the steam content in the fuel during operation of a SOFC [18]. In the following sections, the semi-empirical accelerating approach is outlined with focus on temperature and steam partial pressure.

2.1. Models for evaluation of degradation

Different semi-empirical fitting models may be used for quantitative ATs. Most common are scale-acceleration models. These models presume that degradation D at a particular stressor level s is scaled by an accelerating factor AF

$$D(s) = D(s_o)\cdot AF(s) \tag{1}$$

Here $AF(s)$ is a positive function of s, fulfilling $AF(s_0) = 1$. Furthermore, as D will be represented as distribution of degradation data rather than a discrete value at a specific stressor level s an appropriate distribution function (e.g. exponential, log-normal, Weibull) needs to be identified to describe D with the mean value μ and the spread σ of the distribution. This distribution is naturally caused by arbitrary random effects (e.g. different operators, differences in microstructure etc.)

With the focus on accelerating fuel electrode degradation, the major stressors temperature and steam content in the fuel are considered for determining the *AF*. First, the empirically derived Arrhenius type lifetime equation is used to take the accelerating impact of temperature into account [25]:

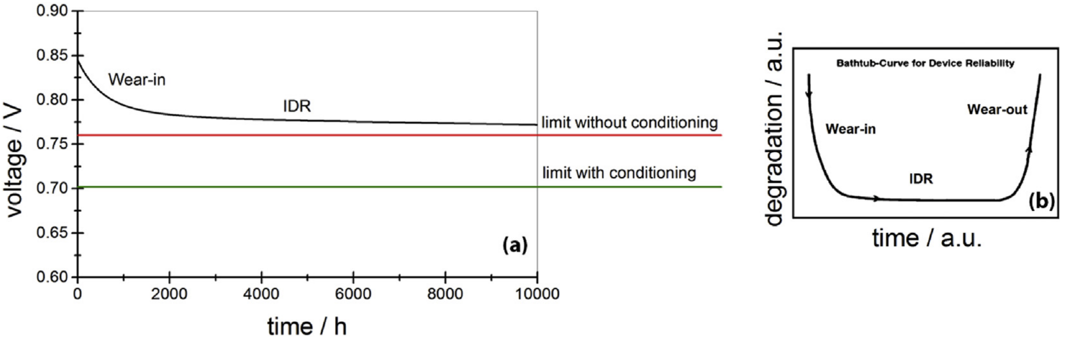

Fig. 1. Voltage degradation curve for a long-term SOFC single cell test. End-of-life limits were calculated using a 10% voltages loss ($\Delta V/V_o$) based on the initial voltage with a wear-in period V_0 (0 h) = 0.84 V, red line and without a wear-in period V_0 (2000 h) = 0.78 V, green line (a). The bathtube curve is a modified illustration taken from Ref. [15], showing degradation over time (b). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)