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Towards a practical tool for online monitoring of solid oxide fuel cell operation: An experimental study and application of advanced data analysis approaches

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HIGHLIGHTS

- Detailed electrochemical investigation of industrial-sized planar SOFCs.
- Determination of frequency responses for online-monitoring tools.
- Insight into processes and mechanisms in SOFCs.
- Identification of carbon deposition by means of DRT.
- Identification of carbon removal by means of DRT.

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ABSTRACT

Reliability and durability are key criteria for solid oxide fuel cell (SOFC) systems in order to gain a market acceptance and establish a positive reputation. To ensure SOFCs reach their reliability and durability targets, feedback regarding the stack degradation sources is required in order to balance the system operation for acceptable power supply; while maintaining longevity. Indeed, a compromise on one or both accounts may be required for many systems that will enter the field for the first time, since there are so many unknowns for the SOFC technologies. Systems including SOFC stacks are being designed and tested for small stationary power generators and large-scale plants, as well as for automotive auxiliary power and range extension systems. This ensures that appropriate contermeasures can be taken, thereby considerably extending lifetime of SOFC systems.

An advanced approach, the distribution of relaxation time analysis of electrochemical impedance spectra is used to identify excitation frequencies altered by SOFC regulation or degradation effects. The technique used and results contained in this paper provide key information, which can be used in the development of a low cost and practical online monitoring hardware tailored specifically for SOFCs. The impacts of diverse operating parameters on an industrial sized SOFC cell performance are identified. Moreover, specific time constants for a practically relevant example stack degradation mode (carbon deposition) are determined. In a further step, the key frequencies for carbon deposition may be monitored online using the tool. A key finding of this work is that the processes can be successfully isolated via EIS excitation without using a reference electrode. This is of great importance for using the methods developed to isolate the key feedback frequencies in a practical experimental setup. Furthermore, this paper demonstrates why avoiding, and if necessary, the removal of carbon deposits, on the SOFC anode, are essential to understand and enact for reliable and durable SOFCs systems to break into and hold a market position.

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1. Introduction

Solid oxide fuel cells (SOFCs) are an economically and environmentally attractive technology that generate electrical power. They directly convert chemical energy stored in fuel to electrical energy with up to 60% efficiency. Furthremore, the high-quality heat by-product of SOFCs can be used as heat source for domestic or industrial purposes, thus even further increasing their overall efficiency. [1,2] SOFCs are also seen as a promising technology for combined heat and power generation in wastewater treatment plants. They are extremely attractive for practical applications since they tolerate a wide range of readily available fuels. Studies have already shown that utilizing biogas [3], urea [4], diesel, kerosene [5], bioethanol [6] and even coal gas [7] as a fuel is possible. When using urea, AdBlue could be considered as an interesting alternative SOFC fuel, which is available, safe and low cost product, as shown in [4].

The ability to monitor online and quickly identify operating conditions, and the onset of stack degradation, is currently not available as complementary and practical tool for SOFC systems. As part of an SOFC system, this feature would provide a feedback for timely counteraction implementation and preserve the reliability and durability of the SOFC stack. Such counteractions could include alterations to the system operation, indicate a future maintenance is required or even trigger a safe state, where data can be analyzed and control algorithms can be updated. The durability of stationary SOFC systems is particularly demanding since 40–80 k hours of operation will be expected. Demonstrating that these SOFC systems are reliable and durable to the degree of established technologies will be extremely expensive and, in any case, not achievable without extensive field testing. Systems entering the field will benefit from a method of monitoring and providing feedback to the manufactures. Such a tool and feedback will help manufacturers learn rapidly about their systems in various conditions and applications, and support simultaneously preserving the products reliability, durability, and critically reputation. Thus, future generations of these systems will benefit greatly from the lessons learned with upgraded hardware and optimized control algorithms.

Determining which degradation processes are occurring at early stages requires in-depth knowledge of individual mechanisms and the selection of appropriate methods for their identification. Since the process of carbon deposition on the porous SOFC anode is very complex, and includes a wide variety of mechanisms, gaining a full understanding of the basic processes that occur within the cell constitutes a first step to ensure complete understanding of this degradation mechanism. The phenomenon of carbon deposition and its effect on the performance of planar SOFCs have been extensively investigated in literature, see Refs. [8–15]. Carbon formation on the surface of the catalyst, or elsewhere on and in the anode and fuel channels, can block the active catalyst sites and gas pores, thus significantly diminishing cell performance, [16]. Carbon deposits can also induce the delamination of the anode-electrolyte boundary layer, catalyst-dusting or even Ni-reoxidation, see Refs. [17,11,12,18]. With high operating temperatures of between 600 °C and 1000 °C and porous anodes with Ni-catalysts support, SOFCs allow direct internal fuel reforming of hydrocarbons [19,20], which results in a high fuel flexibility. Although the commonly used Ni-based anodes have good catalytic performance, they demonstrate a propensity for carbon depositions to form on the anode when they are operated with carbon-containing fuels. In order to avoid carbon deposition, alternative materials can be used, such as e.g. Ir/CGO or other gadolinium- or samarium-stabilized ceria-based materials or conducting ceramic materials that however result in significant decreased electrochemical performance, [6,21–23].

This paper focuses on carbon deposition on the anode. However, the technique applied may also be used for determining the onset and evolution of other degradation mechanisms, such as Ni-agglomeration, nickel oxidation, anode poisoning, chrome deposition on the cathode, humidity degrading the cathode, sintering of the cathode contact materials, etc., all of which can decrease the lifetime of the practical SOFC power generation devices, [24]. This paper also provides experimental examples and comparisons for why cells must be tested on industrial sized samples to provide relevant data for monitoring cells in industrial applications with EIS based tools.

1.1. Research aims of this study

Hydrocarbon fuels contain many components and impurities, diverse interactions and processes occur simultaneously each during the gas processing stages in an SOFC system. The fuel undergoes these processes during evaporation, pre-reforming and mixing stages. After the gas processing a fuel composition then enters the SOFC anode and further processes occur. To identify of all individual processes possible in the SOFC anode, a basic examination and isolation of single processes is necessary. The technique for performing this and isolating carbon deposition is thus the primary goal of this study. Three steps were followed with an additional 4th step to investigate carbon removal, should it occur in an industrial system and the potential for the eventual SOFC stack recovery.

In the *first step* volume fractions of hydrogen, nitrogen, and water vapor were varied and the effects on the frequency response were analyzed. In the *second step*, the fuel and air volume flow rates were varied, which represents the effects of fuel and air starvation, and the frequency responses were analyzed. The results obtained from this analysis are subsequently used as a basis for *step three*; the identification of the carbon deposition process, and finally in the *fourth step* for the removal of carbon deposits investigation.

Industrial-scale planar SOFC cells were used in this study, which are of great importance to SOFC research since they are suitable for the eventual commercial use of SOFC technology. To date, detailed investigation of a variety of chemical and electrochemical processes and degradation mechanisms have primarily been performed on SOFC cells with a small active area. This typically does not exceed 16 cm^2, and they are even often button-shaped, which limits the assessment of the results for industrially relevant sized SOFCs. In comparison to these small area cells, the studies on large-area, planar, single SOFCs, have demonstrated that it is more difficult to attain optimal operating conditions or to achieve excellent cell performance resulting from a number of factors, including cell sealing, contacting, etc., [25–28,]. The test rig used in this study has proven to be extremely effective and sufficient for the types of experimentation required on industrial relevant SOFC cells, [29,30]. Moreover, it is well known that operating conditions strongly affect the electrochemical performance of large planar cells. For smaller cells, it can be seen that many operating parameters, such as the fuel utilization, current density, potential and temperature can easily be regulated and handles on the smaller cells with limited scope for comparison with larger industrially relevant cells. In our previous studies, we have performed extensive analyses of industrial-sized SOFCs, on the following topics: the distribution of gas phase species and molar species fractions considering different reaction mechanisms, carbon formation activity and surface coverage along the cell, as well as temperature, current density, and potential distribution as functions of the cell length (see [27,31,32]). To understand the operation and examine failure modes on SOFC cells, larger cells must be used since that larger dimensions cause physical and thermodynamic gradients that cannot be replicated on the small cells. Generating these gradients like in an industrial application is essential for developing an algorithm for online monitoring of SOFC stack. It is hypothesized that low cost single cell testing provides a first insight into the application on development for such online monitoring tools prior to investigations on more expensive SOFC stacks, which will be investigated in the future by the group.