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Online monitoring tools for SoH diagnostic and prognostic of remaining lifetime of reversible solid oxide cell (rSOC) systems

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Abstract

In order to ensure the continuous operation of (i) solid oxide fuel cells (SOFC) as the main parts of auxiliary power units (APUs) or stationary power generators, and (ii) solid oxide electrolysis cells (SOEC) as highly-efficient systems for advanced fuel generation, it is of crucial importance to be able to determine specific cell processes and to identify diverse potential degradation mechanisms at the earliest possible stage. This ensures the electrochemical processes within reversible solid oxide cell (rSOC) systems to be optimized with the aim to achieve the maximum overall efficiency for energy and fuel generation. Moreover, if degradation is identified at early stage, appropriate countermeasures can be taken, thereby considerably extending the lifetime of the rSOC system under operation.

In this study, industrial-scale rSOCs are analyzed by means of electrochemical impedance spectroscopy (EIS) as well as advanced electrochemical tools – (i) distribution of relaxation times (DRT) analysis, and (ii) total harmonic distortion (THD) analysis. The DRT approach is applied in order to isolate the processes involved in both operating modes and to deliver suggestions for the overall operation optimization. Eventually, a practical tool applicable for online-monitoring systems - total harmonic distortion analysis (THD) is applied to identify carbon deposition degradation mechanisms in a high temperature fuel cell system, which was induced by fueling SOFC with methane. This method enabled detection of specific frequencies for the failure mode mentioned, thus making a basis for fast development of cost-effective and practical online monitoring tool. This technique enables to in-operando control rSOC systems, to identify diverse degradation mechanisms at initial state and to prolong the lifetime of the technology used.

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Nomenclature

APU	Auxiliary Power Unit	SOC	Solid Oxide Cell
EIS	Electrochemical Impedance Spectroscopy	SOEC	Solid Oxide Electrolysis Cell
OCV	Open Circuit Voltage	SOFC	Solid Oxide Fuel Cell
SoH	State of the Health	THD	Total Harmonic Distortion Analysi

1. Introduction

High-temperature solid oxide cell (SOC) technology marks a significant step towards emission-free energy and fuel production, thus creating a global sustainable energy system. Auxiliary power units (APUs) or combined heat and power (CHP) systems with solid oxide fuel cells (SOFC) as the main component provide solution for highly efficient and low emission energy system of tomorrow. The great advantage of SOFCs is that they can be operated under a wide range of various fuels, such as hydrogen, diesel reformate, methane, ammonia, etc. Next, they are highly efficient when operating in both part- and full-load modes, due to direct conversion of chemical energy into electrical energy. Compared to low-temperature fuel cells, which require noble metals as catalysts and pure hydrogen as fuel, SOFCs have great fuel flexibility and use affordable metallic catalysts. Moreover, they are capable of operating in a reversible mode, as solid oxide electrolysis cells (SOEC), converting excess electrical energy into fuels, such as hydrogen, carbon monoxide, or even methane, with an overall efficiency significantly higher than in low-temperature electrolysers.

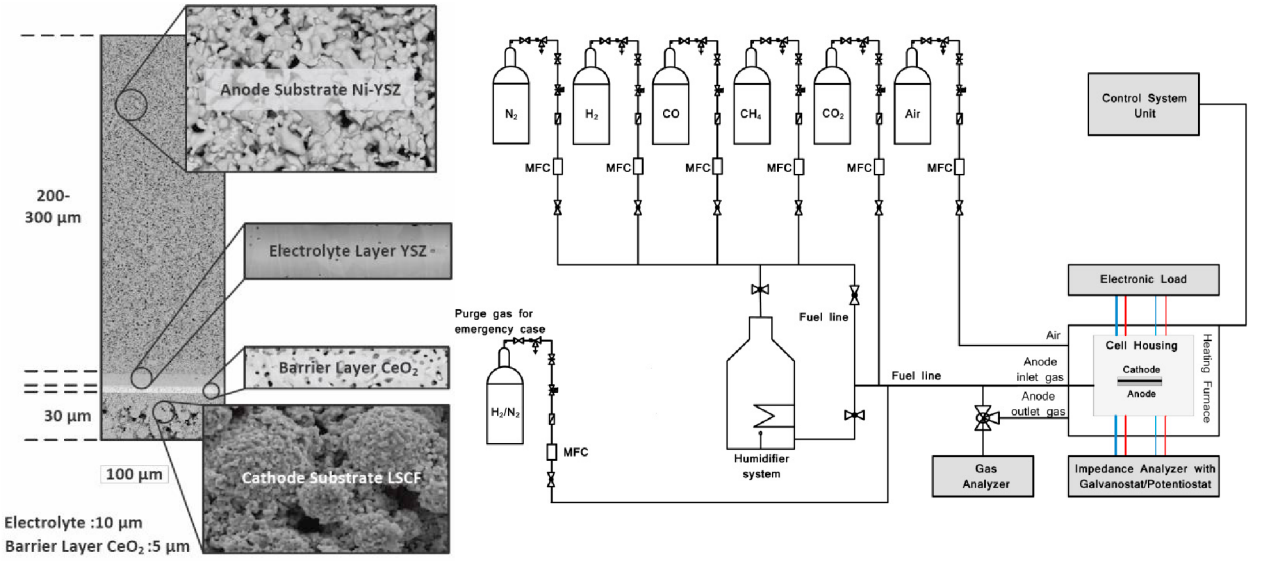
However, the high operating temperatures, great fuel flexibility and internal reforming can lead to various degradation mechanisms, as a result of which the cell's lifetime can be significantly shortened. For instance, feeding SOFC with carbon-containing fuels or operating SOEC in Co-electrolysis mode brings risk of carbon formation and its deposition on the porous Ni-based anode, [1-3]. Moreover, high operating temperature and gas supply starvation can accelerate other degradation phenomena and thus distinctly reduce the lifetime of the rSOC technology. The examination and accurate identification of mechanisms that occur when rSOCs are operated under conditions that can provoke specific degradation mechanisms are important topics for the continuing application of reversible SOC systems. 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 fuel electrode is very complex and includes a wide variety of mechanisms, and degradation is one of the main drawbacks in fuel cell development and operation, the impact of changes in the cell on its performance is of special interest. A full understanding of the basic processes that occur within an SOFC during feeding with different fuels can be found in our previous studies [1,4]. It represents a first step to ensure complete understanding of the reversible SOC operation as well as degradation mechanisms during the SOFC operation that will be explained within this study.

In order to prolong the lifetime of the future-oriented rSOC technology and to accelerate its commercialization, it is necessary: (1) to optimize operating conditions in order to increase the overall efficiency, and (2) to develop in-situ methods and tools that are able to identify individual degradation mechanisms at an early stage, predict future degradation trends, and provide accurate information about the remaining useful lifetime, which are two main topics of the present study.

2. Experimental setup

Commercial available solid oxide cells manufactured by CeramTec GmbH in an industrial size were employed as rSOC for the purpose of investigations of single processes within this study. Furthermore, in order to investigate carbon deposition phenomenon, SOFC cells manufactured at Forschungszentrum Jülich were used. The both cell types had the same anode, but different cathode. The cells' dimensions are also the same. The cell size (100 cm^2) is of great importance, since such large cells are candidates for the eventual commercial use of SOFC technology. The

average thickness of the cells used was 350-400 µm. The anode, fabricated as Ni-YSZ, was directly connected to the YSZ electrolyte. The cathode was LSCF; between the cathode and the YSZ electrolyte a CeO barrier layer was implemented in order to inhibit undesired chemical reactions. The cell microstructure can be seen in Fig. 1a. In order to ensure good electronic conductivity, the anode was contacted with Ni-meshes, while platinum was used as a current collector on the anode side. The tested single cells were embedded in a ceramic cell housing, which was positioned in a temperature-programmed furnace. The schematic overview of the test rig is presented in Fig. 2.



(a) Microstructure of the SOC cell employed [5] (b) Test rig [6]

Fig. 1: SOC and test rig used for the investigations performed within this study.

Different fuels were applied to characterize the cell performance. In the SOFC mode, the cells were supplied with dry and humidified hydrogen, in order to determine its performance under degradation-free conditions. To determine the SOC flexibility and to compare performance under both fuel cell and electrolysis mode, the gas mixture containing from 45 vol% H_2, 15 vol% H_2O and 40 vol% N_2 was supplied to the fuel electrode, while the air electrode was purged with air. Moreover, internal reforming of SOFC was analyzed by fueling it with methane. The methane was diluted in water vapor in order to decrease the probability for carbon to be formed. However, the S/C ratio was set to be 0.5, which exceeded the critical value, with the aim to accelerate the carbon deposition process and therefore the cell degradation. The gas mixtures used, thus volume percentage and volumetric flow of each gaseous component, were defined by means of separate mass flow controllers. The measurements were performed at the temperature of 800°C.

Advanced electrochemical investigations were performed by applying sophisticated in-situ electrochemical impedance spectroscopy technique, as well as distribution of relaxation times method and total harmonic distortion analysis. The EIS method was used to estimate overall losses that occur during the cell operation under varying operating conditions, while DRT enabled to determine which processes result in highest losses. Furthermore, the THD, which is estimated to have a great potential for application in practical online-monitoring tools was applied to identify specific frequencies of carbon deposition induced cell degradation. A fast determination of critical operating conditions was possible by occurring signal distortion at specific frequencies.

3. Results and discussion

Initially, electrochemical impedance spectroscopy based on a typical single sine excitation signal method was applied as an online-monitoring tool. This method was applied on the cells in a reversible mode, thus investigating the complex cell behavior both under fuel cell and electrolysis mode. The obtained spectra are visible in Fig. 2, for which the rSOC used was fed with a gas mixture of 45 vol% H_2 and 15 vol% H_2O in N_2. The impedance measurements were performed in a frequency range between 10 kHz and 100 mHz. The gas composition used is appropriate for both operating modes: SOFC, since hydrogen is available for electrochemical production of water, and SOEC, since water vapor is available, which can be dissociated into hydrogen and oxygen during electrochemical electrolysis. At OCV no electrochemical reactions occur, and only catalytic chemical processes are visible. When increasing the current and leading the cell into the fuel cell mode, the overall losses decrease; the enhanced electrochemical reactions decrease activation losses, hydrogen is being utilized and water vapor is generated. The higher current the lower the losses, as long as fuel and air supply are sufficient. In contrast to this, when operating the cell in electrolysis mode, the overall losses increase with the increasing current. The spectra observed in Fig. 2 show strong increase of impedance in the range of middle and low frequencies in SOEC mode, thus referring to the increasing losses and resistance of slow processes. In the SOFC mode, the impedance does not change such strongly with varying current. Thus conclusion can be made that operating parameters set are more appropriate for the SOFC mode, because amount of hydrogen fuel is sufficient, whereby amount of water vapor is not sufficient for the electrolysis mode. Such information obtained from EIS measurements are of crucial importance for further adjustment of operating conditions and optimization of the electrochemical processes that occur.

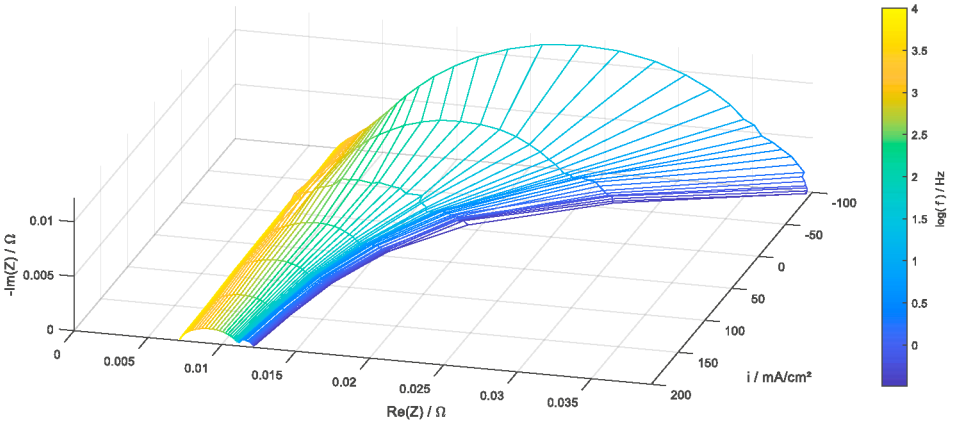


Fig. 2: Electrochemical impedance spectra obtained during reversible SOC operation under 45/15/40 $H_2/H_2O/N_2$.

The impedance data observed were used as a basis to obtain more precise information on specific frequencies using distribution of relaxation times analysis. The DRT analysis is used as complementary method to simplify the separation of kinetics, transport mechanisms, and to identify major loss sources in the system used. When comparing the DRT spectra observed in Fig. 3, it is obvious that independent on the operation mode, the fast processes do not change strongly. The slow processes observed at relaxation times between 10^{-3} and $5 \cdot 10^{-2}$ s are mainly influenced when varying between SOFC and SOEC mode. In the fuel cell mode such processes are not distinctly affected, since hydrogen fuel is available in a sufficient amount for electrochemical processes and no fuel starvation occurs. In the case when fuel utilization is too high and fuel starvation effect occurs, strong increase in low-frequency range is observable, but no significant changes in the range of medium frequencies could be observed, as shown in [7]. In the electrolysis mode the resistance (DRT) of medium-frequency processes significantly rise as amount of hydrogen produced increases and the amount of remaining water vapor available for further reactions decreases, respectively. Increasing H_2O/H_2 dilution in nitrogen, and thus inhibited gas diffusion and gas conversion on the fuel electrode led to significant increase of the medium-frequency arcs, as shown in study

in [8]. Therefore, such peak may be related to the water dissociation and refer to insufficient amount of water vapor in SOEC mode in the present study. Moreover, increasing current shift the peak to the right on the time axis, which means that the relaxation time increases and diffusion processes are influenced.

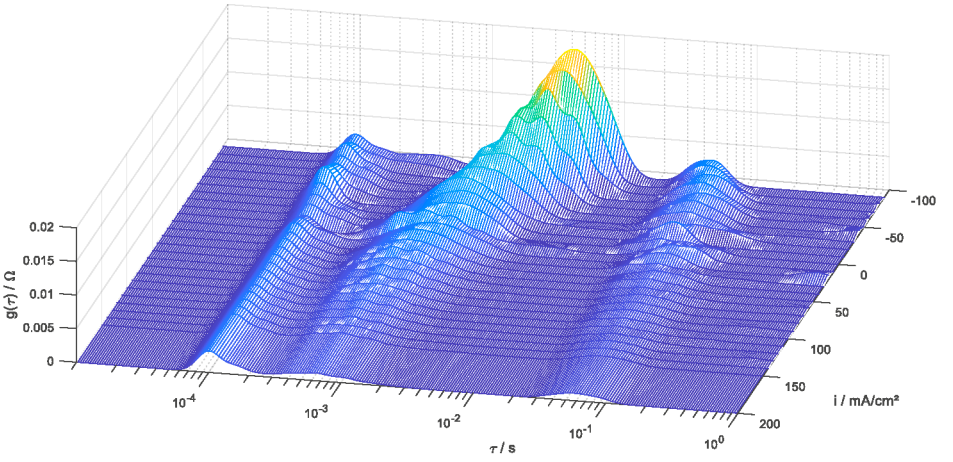
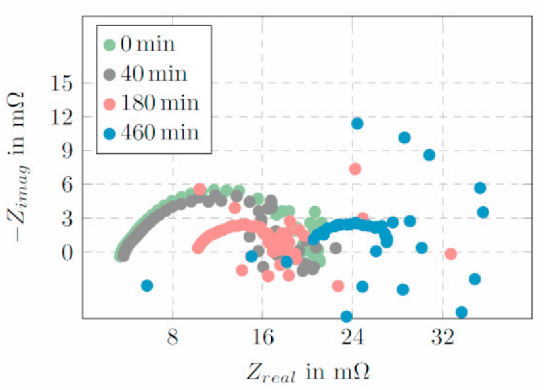
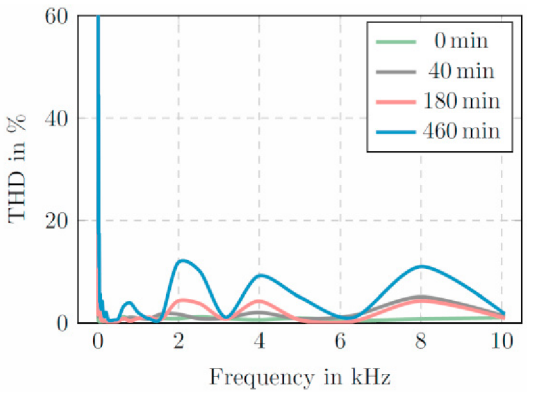


Fig. 3: DRT spectra obtained during reversible SOC operation under 45/15/40 $H_2/H_2O/N_2$.

Eventually, THD method was applied during SOFC operation under carbon-containing methane fuel. Electrochemical characterization measurements were performed every 20 minutes in order to continuously monitor performance variations. For that purpose, both EIS measurements (Fig. 4a) and THD measurements (Fig. 4b) were performed. In order to obtain accurate information when fueling SOFC with methane, frequency range had to be extended down to 50 mHz. EIS spectra represented in Fig. 4a show strong increase of the ohmic resistance as a function of time and increasing amount of carbon on the fuel anode. It is also visible that first measurements (0 min and 40 min) were very stable, while in the course of the experiment the measurements became very unstable. The stability of the initial state was also confirmed by THD measurements, e.g. green solid curve in Fig. 4b, for which THD was 0%. Further, it is obvious that during experiment, as amount of carbon formed increased and degradation was more pronounced, distortion of the measured signal increased (see y-axis), while the specific frequencies remained unchanged. Non-linear state could be identified only at frequencies 0.5 kHz, 2 kHz, 4 kHz and 8 kHz, as can be seen in Fig. 4b. The approximate signal distortion was observed to be between 10% and 20% for this degradation case.



(a) Electrochemical impedance spectra



(b) Total harmonic distortion spectra

Fig. 4: Electrochemical measurements performed during SOFC fueling with methane, S/C=0.5 at 800°C.

One EIS measurement cycle took approximately 15 minutes, while applying the THD method, which means performing the measurements only at the characteristic frequencies determined, can decrease the overall measurement time down to several seconds.

4. Conclusion

The present study reveals non-traditional methods for in-situ characterization of solid oxide cell systems, which can be seen as a significant step towards implementation of the techniques described into a practical and cost-effective online-monitoring devices. The application of the methods described enabled: (1) to determine the overall losses in both SOFC and SOEC mode and to seaparate them, (2) to make suggestions for performance optimization, and (3) to identify degradation at early stage in a time-efficiently manner. When using the THD method described, the overall measurement time can be reduced from 15-20 minutes down to several seconds. The online-monitoring tools employed within the present study can be applied for the same purpose not only for fuel and electrolysis systems, but also for a wide spectrum of electrochemical systems, power and fuel generation systems, to determine their performance, optimize the operation and increase the overall efficiency, as well as to extend the lifetime of the technology used.

Acknowledgements

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