



In-situ electrochemical characterization methods for industrial-sized planar solid oxide fuel cells Part I: Methodology, qualification and detection of carbon deposition



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ABSTRACT

Failure modes such as carbon deposition must be avoided or controlled in order to ensure the safe operation of auxiliary power units running on diesel reformat or other carbon-containing fuels. Electrochemical impedance spectroscopy (EIS) technology and methodology combined with the distribution of relaxation times (DRT) method could be promising technique to investigate the critical operating conditions or play a role in an online monitoring techniques such as total harmonic distortion analysis (THDA) or fast EIS thus allowing counteractions, for example changing of the operating conditions or cell-protecting regeneration. The sample anode-supported solid oxide fuel cells for industrial application are analyzed and characterized with the aim of isolating anode processes and enabling fast detection of carbon depositions. Different process mechanisms are successfully separated using this methodology and without a reference electrode, which is of great importance for the practical usage. This study represents a first step in a broader study which will investigate more into carbon depositions and also other ways of deposition and poisoning of the anode and the cathode.

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1. Introduction

Solid oxide fuel cells represent a very promising technology which is gaining increased interest because of its numerous advantages. The ability for direct conversion of chemical energy from gaseous fuel and an oxidant gas into electricity make SOFCs one of the most efficient of all energy conversion units. High operating temperatures between 600 °C and 1000 °C enable the usage of affordable non-precious catalysts such as nickel and ensure significant fuel flexibility, high-quality waste heat and high power-density, [1,2]. Furthermore, high operating temperatures and the very good catalytic performances of Ni enable internal reforming of hydrocarbons.

Different in-situ and ex-situ techniques are applied as a means of characterizing the performance of fuel cells. The measurement of the polarization curve, as the most ubiquitous electrochemical method, is used for the quantitative evaluation of the cell

performance. The dependence of voltage and current as well as available power density under the prevalent operating conditions are shown by this means. This method only quantifies the cell's electrochemical performance, which may also be used to monitor its degradation over time. In order to give more detailed information about the involved loss mechanisms such as ohmic, activation or concentration losses and to attempt an explanation of why the cell performs the way it does, electrochemical impedance spectroscopy is applied [1]. Electrochemical impedance spectroscopy is a very important tool and a sophisticated technique for the online examination of cells and also for an evaluation of experimental results. Its usefulness lies in the ability to distinguish between the electrical and electrochemical properties of fuel cells under investigation and to provide feedback regarding real-time processes such as cell performance changes. These can be, for example, cell degradation through carbon formation on the anode side, nickel oxidation or cathode degradation. Electrochemical impedance spectroscopy is a non-intrusive in-situ method, which is often used in laboratories, where tests are performed under a range of conditions, including accelerated stress test operation. The fundamental advantage of the EIS-method is its ability to

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characterize the cell behavior and to enable differentiation of the impact made by specific operating conditions. In order to correctly interpret the fuel cell behavior based on the EIS-measurements, appropriate equivalent circuit (EC) has to be chosen. Numerous studies have addressed the absolutely central importance of applying electrochemical impedance measurements to the field of fuel cells characterization technique, see Refs [3–14].

The measured electrochemical impedance spectra show many overlapped processes and furthermore how the alternation of the parameters on one electrode impacts the electrochemistry of the second electrode. Differentiating between air and the fuel electrode is a challenging and non-trivial approach, if the measurements are performed for industrially-sized SOFCs without reference electrode. Altogether, a detailed electrochemical analysis of the cell behavior and sample early identification of adverse changes of the cell performance caused by wide variety of degradation mechanisms is missing in the literature and is essential for the further investigation of solid oxide fuel cells. In our study we perform an entire electrochemical analysis of SOFCs relevant for the industrial usage that are examined under various operating conditions. In the first part of this paper different parameters such as gas composition, humidity content or load were varied in order to identify the specific cell behavior and to create a base model which will be used in a second part for detailed investigation of several degradation mechanisms and identification of critical operating conditions. The temperature dependency of all the processes involved is examined. The importance of the load during the impedance measurements, which simultaneously impacts the operating environment, needs to be mentioned and it is analyzed in detail. Moreover, different equivalent-circuits were analyzed and compared with each other. Polarization curves were calculated based on the fit plots and subsequently verified by measured U/i characteristic curves thus evaluating single electric circuit elements and specifying the size of single loss mechanisms. An easy and fast identification of carbon deposition is also represented in this first part. The focus is to investigate the impact of SOFC operation with simulated reformed diesel as expected for an auxiliary power unit (APU) application, see Ref. [15]. The feeding with carbon-containing gas mixtures can lead to carbon formation on the cell anode. Carbon deposition in SOFCs must be avoided during operation, because it accelerates the cell and stack degradation due to pore blocking, fuel starvation, anode electrochemical reoxidation, and the nickel dusting. The mentioned degradation processes change the cell and stack electrochemical activity and performance. SOFCs operated with carbon-building fuels have already been investigated in the literature, see Refs. [16–21]. Further possibility for distinguishing between the anode and cathode processes is distribution of relaxation times analysis (DRT), which is briefly described and shown in the first part of this study. The DRT method was applied in order to separate out the processes that occurred and to make a basis for the further investigation. The real part of the measured impedance data was used to calculate the DRT-function using the software package FTIKREG [22]. Distribution of relaxation times analysis is already shown in the literature, but for SOFCs with small chemical active area ($\leq 16 \text{ cm}^2$). Sonn et al. [23] used the DRT to separate polarization processes with different time constants. The DRT-analysis performed in their study shows 4 processes represented with 4 characteristic frequencies, which characterize gas diffusion in both the flow channels and the contact mesh and also charge transfer reaction and ionic transport in the YSZ matrix. Fang et al. [24] and Leonide et al. [25] differentiated three processes for the cells operated under hydrogen. In these studies, the processes between 1 Hz and 10 Hz were temperature independent, while the process between 10 Hz and 300 Hz and also between 200 Hz and 10 kHz indicated strong temperature dependency. Kromp et al. [26] distinguished five different processes in their study. The identified

high-frequency processes were referred to both anode and cathode reactions. The anode processes included gas diffusion, charge transfer reaction and ionic transport within the anode functional layer. The high-frequency related process of the cathode side referred to the oxygen surface exchange kinetics of the LSCF cathode used and the diffusivity of oxygen ions within the LSCF bulk. At lower frequencies mass-transfer processes caused by gas diffusion in the pores of the Ni/YSZ-anode substrate could be recognized.

2. Experimental setup

2.1. Cell geometry

Anode-supported SOFC single cells are examined in this study. The Ni-YSZ anode substrate with an average thickness of $250 \mu\text{m}$ has an area of $10 \times 10 \text{ cm}^2$, on which a Ni/ZrO₂ anode functional layer with an approximate thickness of $10 \mu\text{m}$ is added. The YSZ-electrolyte layer has the same dimension as the anode and is fabricated with a thickness of approximately $10 \mu\text{m}$. The cathode functional layer consisting of lanthanum strontium cobalt ferrite (LSCF) is approximately $30 \mu\text{m}$ thick with a chemical active area of 81 cm^2 , whereby the around $5 \mu\text{m}$ thick CeO₂ barrier layer is added between the cathode and the electrolyte.

2.2. Experimental setup and testing procedure

The single cells were embedded in the ceramic cell housing appropriate for the testing of the cells with the dimension $10 \times 10 \text{ cm}^2$. The anode side was contacted with a Ni-mesh, while platinum was used to contact the cathode side. The anode was fed with several fuel combinations containing CO, CO₂, H₂, CH₄, H₂O and N₂, see Table 1. Gas mixtures **e** and **g** shown in this table correspond to the commercially used diesel reformat, with varying concentration of methane. The partial pressure of single gas components was varied and controlled by separate mass flow controllers. The temperature was varied in a range between 700°C and 800°C . The analysis of the gas mixture before and after the cell was performed using a gas analyzer, see Ref. [27]. For more detailed information about the experimental setup we refer the reader to Refs. [28–30]. At this point it must be mentioned that all the measurements for every single gas mixture noted in Table 1 were carried out at 700°C , 750°C and 800°C , but to keep track of the overview, they are not all shown in every figure.

Impedance measurements were performed using a Bio-Logic impedance analyzer with a $\pm 40\text{A}$ booster over the whole possible load range and in a frequency range from 10 kHz to 100 mHz, see Ref. [31]. This in-situ electrochemical method was used to investigate the impact of different parameters on the cell behavior, such as partial pressure of single gas components, flow rate or humidity on anode side on the cell performance. DC galvanostatic technique was applied and AC sinusoidal amplitude was superimposed for the purpose of the measurements under load. An AC current amplitude of 40 mA was chosen so as to ensure the linearity principle and cell potential as a function of AC current was measured.

Table 1
Volume fraction of single gas components.

Gas mixture	H ₂ vol%	CO vol%	CO ₂ vol%	CH ₄ vol%	H ₂ O vol%	N ₂ vol%
a	45	0	0	0	0	55
b	25	0	0	0	0	75
c	25	0	0	0	10	65
d	25	5	0	0	10	60
e	15.4	13.7	9.8	2.5	11	29.8
f	25	0	0	0	20	55
g	15.4	13.7	9.8	9.5	11	22.8

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