Applikationsbericht

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Single cell THD measurements

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. 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. 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.

Experimental Setup

Commercial available solid oxide cells manufactured in an industrial size were employed as rSOC for the purpose of investigations of single processes and carbon deposition phenomenon. The cell size (100 cm²) 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. 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. 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. 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.

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. 1a) and THD measurements (Fig. 1b) 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. 1a 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. 1b, 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
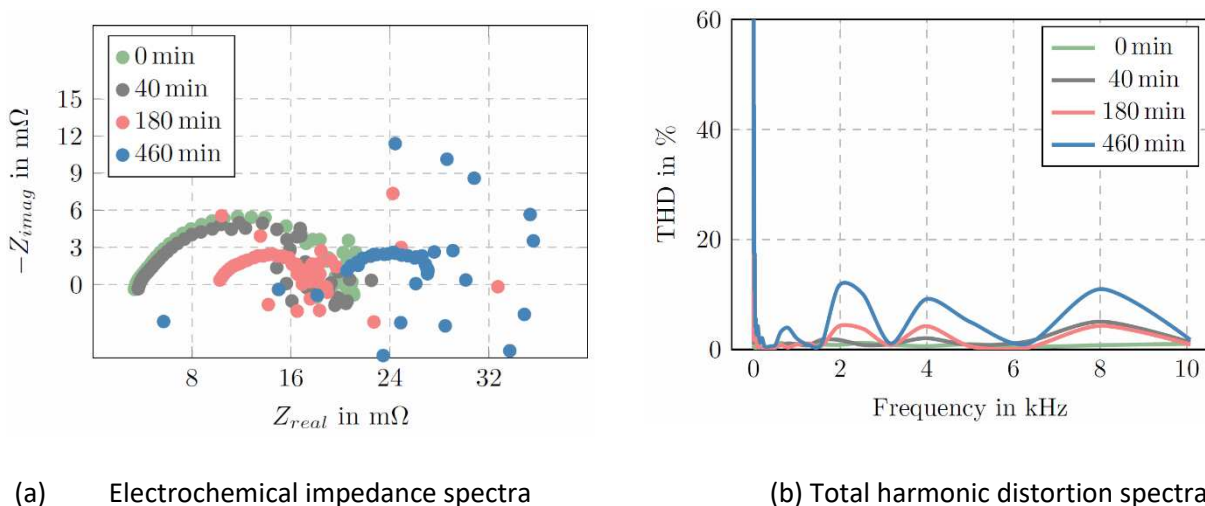
(a)   Electrochemical impedance spectra   (b) Total harmonic distortion spectra

Fig. 1: Electrochemical measurements performed during SOFC fueling with methane, S/C=0.5 at 800°C.

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. 1b. The approximate signal distortion was observed to be between 10% and 20% for this degradation case.

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.

Stack measurements

An AC characterization in terms of Electrochemical Impedance Measurements (EIS) was performed on a reversible solid oxide cell stack (rSOC). Measurements were carried out at OCV as well as during charging and discharging for both individual cells and the stack. For that purpose, the Reference 3000™- Potentiostat/Galvanostat was used in combination with the Reference 30K Booster, both from GAMRY. The 30K Booster adds an additional current range to the Reference 3000™, thus providing final output currents of +30A to -30A at voltages up to +20V. The Reference 3000™ is equipped with a Multi-channel Auxiliary Electrometer, which enables the independent acquisition of EIS from a total of eight cells in a multi-cell stack.

The modified EIS measurement mode, based on the common galvanostatic EIS, known as the Hybrid EIS, was used in order to inhibit high DC current and undesired errors. When using potentiostatic EIS, low impedances that are typical for SOCs, may lead to high DC currents if small fluctuations in the applied DC voltage occur. Moreover, using the galvanostatic EIS with a fixed AC current amplitude can result in high AC voltages, and artifacts at high frequencies and low impedances may arise. All this effects could bring the stack from the linear in the non-linear state. The applied hybrid EIS combines the advantages of both galvanostatic and potentiostatic mode, and ensures the safe operation during the IS measurements. The Hybrid technique uses galvanostatic cell control, as found in the galvanostatic mode, though the amplitude of the applied AC current is changed to obtain a nearly constant desired AC voltage response. By adjusting the AC current continuously ensures that the AC voltage is not extended beyond the linear, non-destructive range. Thus, destroying the cell is prevented and furthermore, it is much less sensitive to mutual induction artifacts. The AC voltage is not controlled exactly by the system, certainly it is satisfied with an AC voltage close to the desired value of the AC voltage. However, due to an accurately measured AC voltage used for the impedance calculation, this inaccuracy does not carry over into the measured impedance. Additionally, the AC current is also adjusted throughout the frequency range as the impedance of an SOC varies with the frequency, which optimizes the measured potential at every single frequency. The frequencies applied for the EIS ranged from 20 kHz to 20 mHz with 10 points per decade, while the desired AC voltage was set to 10mV.
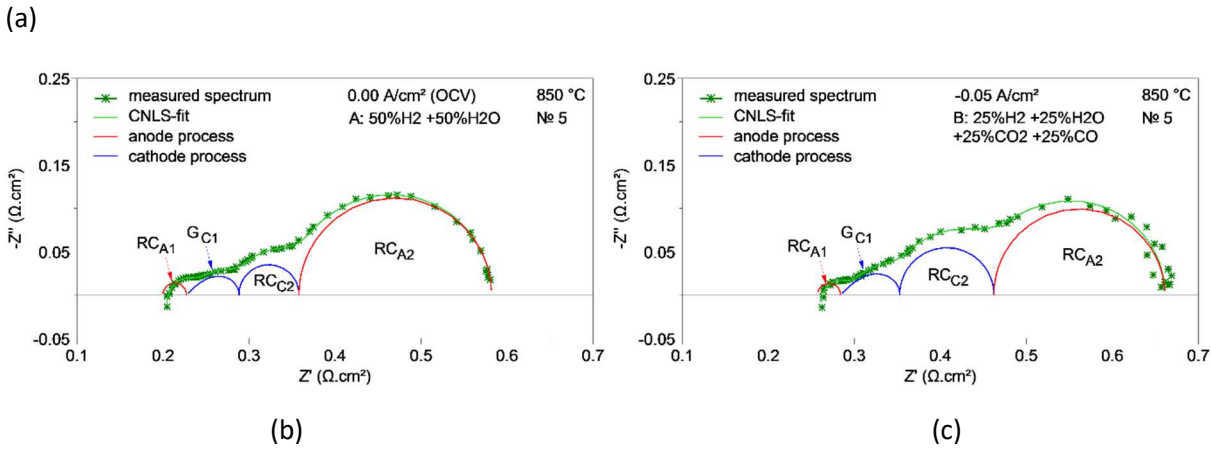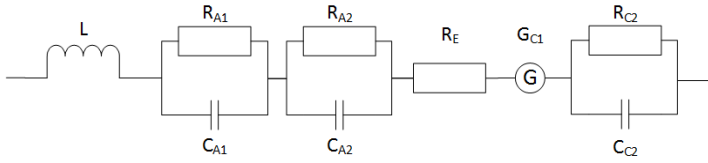
Figure 2: (a) Electrical equivalent circuit (EEC) model used for CNLS fit of impedance data. Superimposition of the CNLS-fit and the experimental data measured under (b) 50%H2+50%H2O, and (c) 25%H2+25%H2O+25%CO2+25%CO. [1]

The measured impedance data were fitted using the Simplex Method implemented in the *GAMRY Echem Analyst* Software, and all IS diagrams are obtained using the fit principle mentioned. Based on the fitted data, it is possible to analyze and determine the contribution of each process to the overall losses. The EEC used for fitting is given in Fig. 2a consisting of an inductance, three RC-equivalent circuits, a Gerischer Element, and a serial resistance. Fig.2b and Fig.2c show the superimposition of the experimental data and the numerical fits for H_2O- and co-electrolysis mode, respectively. Analyzing the IS, four semicircles can be identified.

Fig. 3 shows a comparison of the IS of the stack's individual cells, which were recorded at the same time as the impedance of the whole stack at 0.10A/cm² at 800 and 850°C. The cells chosen therein are representative of five repeating units in the stack: the two bottom cells (No1 and No2), a center cell (No5), and two top cells (No9 and No10). The decrease of Z' as the current density increases is ascribed to the smaller low frequency arc impedance at both temperatures. The impedance decreases as the current increases due to anodic polarization as well as the additional steam generated at the fuel electrode. (i) The noticeable decrease in the ASR values, from 800°C to 850°C, corresponds to an increase in the ionic conductivity of the electrolyte and the electrode functional layers. (ii) The middle frequency arc includes considerable contributions from the oxygen ion diffusion and charge transfer at the air electrode. From the spectra, it is possible to see that the air electrode-specific losses are reduced as the temperature increases, while the fuel electrode-specific losses remain almost unchanged. (iii) The almost unchanging low frequency arc capacitance mainly includes contributions from the gas conversion in the fuel electrode (concentration gradients connected with Nernst voltage distribution over the cell and gas diffusion in fuel electrode), and is more or less independent of both position and temperature.
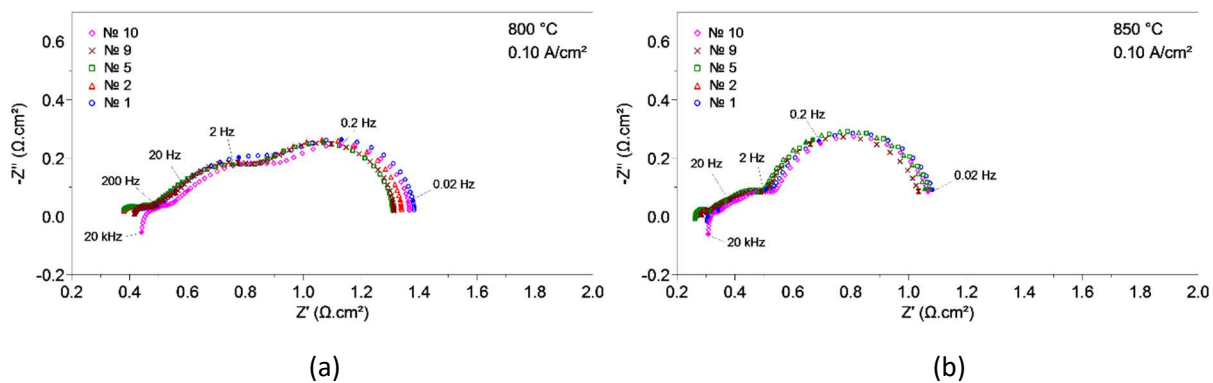
Figure 2: (a) Nyquist plots of the impedance spectra of five individual cells within the stack in fuel cell mode at (a) 800°C / 0.10A/cm², (c) 850°C / 0.10A/cm² in mixtures of 60% H2+40% N2. Total gas flow rate: 490l/h - Air flow rate: 1500l/h. [1]