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A model-based approach for current voltage analyses to quantify degradation and fuel distribution in solid oxide fuel cell stacks

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HIGHLIGHTS

- Identification of fuel leakages and fuel distribution in SOFC stacks.
- Determination of internal resistances from (V,I)-data by eliminating fuel effects.
- Real-time, model-based identification of malfunctioning of SOFC stacks.
- Time dependent evolution of degradation phenomena from (V,I)-data.
- Simulated local species concentrations and current densities along fuel channels.

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ABSTRACT

Reliable quantification and thorough interpretation of the degradation of solid oxide fuel cell (SOFC) stacks under real conditions is critical for the improvement of its long-term stability. The degradation behavior is often analyzed based on the evolution of current–voltage (V,I) curves. However, these overall resistances often contain unavoidable fluctuations in the fuel gas amount and composition and hence are difficult to interpret. Studying the evolution of internal repeat unit (RU) resistances is a more appropriate measure to assess stack degradation. RU-resistances follow from EIS-data through subtraction of the gas concentration impedance from the overall steady-state resistance. In this work a model-based approach where a local equilibrium model is used for spatial discretization of a SOFC stack RU running on hydrocarbon mixtures such as natural gas. Since under stack operation, fuel leakages, uneven fuel distribution and varying natural gas composition can influence the performance, they are taken into account by the model. The model extracts the time-dependent internal resistance from (V,I)-data and local species concentration without any fitting parameters. RU resistances can be compared with the sum of the resistances of different components that allows one to make links between laboratory degradation experiments and the behavior of SOFC stacks during operation.

1. Introduction

For commercially available stationary solid oxide fuel cell (SOFC) applications a lifetime of at least 40,000 h with a power degradation lower than 1% per 1000 h are required [1–5]. To meet these goals the performance of SOFC stacks needs to be monitored during operation and the obtained results need to be properly interpreted [6].

Stack performance data can be used to identify operation errors and irregularities such as changes in the fuel supply. Performance data are often extrapolated over time to make predictions regarding the stack life-time. However, to get the maximum benefit from stack performance data combined experimental and theoretical methods have to be applied.

Performance losses are generally characterized by monitoring an operation parameter such as current, voltage or power or by current–voltage (V,I) data analysis at different time steps [7–12].

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The main parameters extracted from (V,I)-curves are open circuit voltages (OCV) and overall area specific resistances (ASR_{tot}) of a individual or all repeat unit(s) (RU) [8,13]. Ideally the ASR_{tot} obtained from (V,I)-data of the stack can be correlated with partial resistances of local degradation phenomena, that are most suitably studied in button cell or other laboratory experiments. However, the ASR_{tot} is affected by fuel gas effects which make comparisons with partial resistances difficult. In addition, these fuel gas effects show fluctuations resulting from fuel leakages, unequal fuel distribution between the different repeat units within the stack and unavoidable variations in the fuel composition provided by the natural gas from the local grid. As a result, experimental (V,I)-data from SOFC stacks operated e. g. with natural gas from the local grid often shows significant scatter. Variations in the observed degradation data can happen from one stack to another and within a single stack from one RU to another [13,14]. Deviations between the measured and theoretical OCVs can be caused, for example, by unusual fuel reformer operation or fuel leakages that affect the anode and/or cathode gas composition by direct oxidation of a certain amount of fuel and air upstream to the RU, respectively [13,15,16]. In addition, deviations in the (V,I)-characteristic can be related to the overall amount of fuel available [13]. This can be affected by unequal fuel distribution between the different repeat units of a single stack e. g. by manufacturing and assembling tolerances. It can also be caused by fuel leakages [17,18] (e. g. by cracks and sealing points) and by sensor malfunctions such as drifts in the output of upstream located thermal mass flow controllers [19]. Furthermore, the overall temperature level and the temperature distribution over the stack both can vary and therefore cause additional scatter in observed stack performances. This is because temperature influences the cell potential, but also ohmic and polarization losses [20,21]. Note however that recent advances in the thermal management of SOFC stacks led to well controllable and rather homogeneous stack temperatures [16,22]. Fuel gas effects are often the main cause for deviations from normal stack behavior for the Hexis SOFC stack. The separation of fuel gas effects from the “true”, internal resistance of a stack repeat unit ($ASR_{RU} \neq ASR_{tot}$) can be accomplished by electrochemical impedance spectroscopy (EIS) shown in section 2 [13,23,24]. However, EIS measurements are generally not available for SOFC stacks running in the field. There is hence a need for extracting internal stack repeat unit resistances from commonly available, time-dependent (V,I)-data, to accurately predict and interpret the performance of SOFC stacks under real conditions (using e. g. natural gas as fuel).

A method for extracting ASR_{RU} from (V,I)-data has already been published earlier by the authors [11]. There a 0D thermodynamic equilibrium model assuming a uniform distribution of fuel and air over the entire RU to calculate ASR_{gas} for hydrocarbon-containing fuels is used [25]. If this 0D-approach is applied to fuel cells with an active cell area of several square centimeters, e. g. 100 cm^2, the calculated gas concentration resistance ASR_{gas} is significantly overestimated. Such a deviation is obvious, since the fuel composition and oxygen partial pressure variations along the gas channels between corresponding inlet and outlet is not considered in a 0D-approach.

In this work we propose a model-based approach to extract repeat unit resistances ASR_{RU} from experimental (V,I)-data without using any fitting parameters. The model separates internal ohmic and polarization losses from fuel gas concentration effects and takes into account different types of fuel leakages and possible fluctuations in the fuel gas composition from the grid. The comparison of time dependent ASR_{RU} evolution during stack operation with averaged ASR trends obtained from single experiments under laboratory conditions has a number of applications. It allows one to verify if the degradation phenomena observed in single experiments under laboratory conditions can explain the degradation behavior within stacks using the same components. The model enables furthermore to extract local species concentration in the flow channels as well as local current densities and potentials for a given fuel utilization (FU).

2. Conceptual approach

Depending on the cell and stack design, ASR_{RU} includes the contributions of the different RU layers and their mutual interfaces. For Hexis stacks based on electrolyte-supported cells (ESCs) including metallic interconnects (MICs), the main contributions comprise ohmic losses (ASR_{ohm}) from the electrolyte (ASR_{el}), contact resistances (ASR_{con}) and oxide layers formed on metallic interconnect as well as ohmic and polarization losses from the electrodes (ASR_{an}, ASR_{ca}).

Electrochemical impedance spectroscopy (EIS) enables to separate internal repeat unit resistances ASR_{RU} from gas concentration losses (ASR_{gas}) since the overall resistance is defined as follow:

$$ASR_{tot} = ASR_{RU} + ASR_{gas}. \tag{1}$$

Fig. 1 shows impedance data for one repeat unit in a 5-cell Hexis stack operated at 900 °C with catalytic partial oxidized (CPOx) reformed natural gas. The mass flux of natural gas was varied between 0.02 $g\,h^{-1}\,cm^{-2}$ and 0.06 $g\,h^{-1}\,cm^{-2}$. Fig. 1a presents the EIS-data in a Nyquist plot whereas each spectrum was measured at about 50% FU. Variations of the fuel amount basically affects the gas concentration arc in the low frequency region (<0.5 Hz) on the right whereby this arc is scaled-down with increasing fuel amount. For a large surplus of fuel, typically delivered in button cell experiments, the gas concentration arc disappears since gas concentration losses are inverse proportional to the fuel feed [25–27]. Furthermore fuel variations have a negligible impact on the electrode resistances ASR_{an} and ASR_{ca} compared to the overall resistance ASR_{tot}. This behavior is also representative for other stacks with different cell types at OCV [21,28,29].

The internal resistance ASR_{RU} extracted from EIS-data consist of the ohmic resistances ASR_{ohm}, at the high frequency intercept in the Nyquist plot (Fig. 1a), and the electrode losses ASR_{an} and ASR_{ca} represented by the two smaller not fully formed arcs in the frequency range >0.5 Hz. Effects of the fuel amount variations are also shown in Fig. 1b whereby Im(Z)-part is plotted against the frequency. Variations related to electrodes processes are identifiable in the frequency range >0.5 Hz.

Reliable separation and quantification of fuel gas concentration effects from internal resistances (ASR_{RU}) based on experimental (V,I)-data are the main purposes of this work. Since the further discussion is about fuel leakages and uneven fuel distributions over the stack it is important to define the term “nominal fuel supply” as the ideal case. The nominal fuel supply corresponds to the preset amount of fuel entering each RU. However, in reality a specific RU will most probably be fed with an amount of fuel that differs somewhat from the nominal one. In any case, the nominal fuel implies the absence of the following unwanted effects:

i) leakages effecting the upstream fuel composition by a partially direct oxidation of fuel caused by air leaking from the air to the fuel supply denoted by fm
ii) fuel oversupply caused by uneven fuel distribution within the stack or/and by positive deviations in the overall fuel caused by malfunctions of the flow controllers denoted by fo