



Study of Operating Parameters for Accelerated Anode Degradation in SOFCs

Ploner, Alexandra; Hagen, Anke; Hauch, Anne

Published in:
Fuel Cells

Link to article, DOI:
[10.1002/fuce.201600193](https://doi.org/10.1002/fuce.201600193)

Publication date:
2017

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):

Ploner, A., Hagen, A., & Hauch, A. (2017). Study of Operating Parameters for Accelerated Anode Degradation in SOFCs. *Fuel Cells*, 17(4), 498-507. DOI: 10.1002/fuce.201600193

DTU Library

Technical Information Center of Denmark

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Study of operating parameters for accelerated anode degradation in

SOFCs

Alexandra Ploner^{1*}, Anke Hagen¹, Anne Hauch¹

Technical University of Denmark, Department of Energy Conversion and Storage, 4000 Roskilde,

Denmark

[]Corresponding author: aplo@dtu.dk*

Abstract

Solid oxide fuel cell (SOFC) applications require lifetimes of several years on the system level. A big challenge is to demonstrate such exceptionally long lifetimes in ongoing R&D projects. Accelerated or compressed testing are alternative methods to obtain this. Activities in this area have been carried out without arriving at a generally accepted methodology. This is mainly due to the complexity of degradation mechanisms on the single SOFC components as function of operating parameters. In this study, we present a detailed analysis of approx. 180 durability tests regarding degradation of single SOFC components as function of operating conditions. Electrochemical impedance data were collected on the fresh and long-term tested SOFCs and used to de-convolute the individual losses of [single](#) SOFC cell components – electrolyte, cathode and anode. The main findings include a time-dependent effect on degradation rates and domination of anode degradation for the evaluated cell types and operating conditions. Specifically, the steam content as determined by fuel inlet composition, current density and fuel utilization was identified as major parameter, more important than for example operating temperature. The obtained knowledge is adopted to identify optimal operation profiles in order to acquire accelerated testing for lifetime investigation of SOFCs.

Key words: accelerated testing, solid oxide fuel cell, impedance spectroscopy, degradation, durability

1 Introduction

Life time evaluation for Solid Oxide Fuel Cells (SOFCs) is a time-consuming and expensive task. Generally, fuel cells are tested under galvanostatic conditions and in most cases, the degradation rate of SOFCs is quoted as average or linearized decay of cell voltage or increase of cell resistance over time [1]. Low degradation rates of only a few mV per 1000 h, which are achieved for state-of-the-art cells [2] demand testing over several thousand hours to overcome the experimental error and to identify the major degradation mechanisms.

Among recent attempts to develop lifetime prediction models of SOFC was the European project ‘[EU SOFC-LIFE](#)’. The aim of the project was to understand degradation by systematically testing single elements and interfaces of the interconnect-electrode-electrolyte-assembly, separately. The project revealed that the dominant contribution affecting degradation of single repeating units (SRU) is due to an increased contact resistance of the cathode/interconnect interface. Unfortunately, the project could not succeed in relating degradation phenomena of isolated elements to the total SOFC or SRU unit [3].

It is therefore highly desirable to develop a testing strategy to predict the durability of the complete SOFCs in a fast and still appropriate manner. Accelerated lifetime testing (ALT), as a possible method, is conducted by provoking degradation under heavy-duty operating conditions ideally without causing any new failure processes [4]. However, it is challenging to choose relevant aggravated operating conditions for SOFCs, as degradation mechanisms of SOFC components (i.e. cathode, anode and electrolyte) show different dependencies on parameters such as temperature, current load or fuel composition. For example, decreasing the operating temperature caused an increase of cathode degradation while anode degradation decreased or remained constant for a certain SOFC generation

[5]. Even though major failure mechanisms are known, no general agreement has been reached regarding which degradation phenomena dominates the overall cell degradation and even less how it can be accelerated in appropriate way by different testing conditions.

Despite these known challenges, attempts for accelerated testing were carried out in a pragmatic approach under non-steady operation conditions (current cycling, temperature cycling) [6]. Following the concept of acceleration, the aim was to increase degradation rates by cycling conditions and relate these to steady state operation. However, when applying fast current load cycling on stack level, no acceleration of the degradation was observed [7]. Furthermore, tests done at different current load cycling profiles revealed a strong deviation between predicted and measured lifetime [8].

These considerations motivated a detailed analysis of durability tests using results of electrochemical impedance spectroscopy (EIS). This approach was used in previous studies [9,10] mostly during operation. While valuable results are obtained for time constants of different degradation mechanisms, it is difficult to compare test series, where more than one or two parameters or materials are changed. A robust approach that allows comparison of degradation between tests of different cell generations, setups and operating parameters is to compare the area specific resistance (ASR) of the fresh and degraded cell obtained under standardized conditions for all cells.

The total ASR of the cells obtained before and after the test at open circuit voltage (OCV) was split up into contributions from anode, cathode and electrolyte. In this study, data were selected from about 180 long-term tests of anode supported cells.

The analysis of the EIS included the break-down of losses employing distribution of relaxation times (DRT) and analysis of difference of impedance spectra (ADIS) for qualitative assessment, followed by quantitative analysis via fitting of the experimental IS to an equivalent circuit model applying complex-

non-linear-least-square (CNLS) method. In that way it was possible to determine the degradation rate for each cell component separately as a function of operating conditions.

The aim was to identify parameters which accelerate the degradation of the cell component with the lowest electrochemical performance, i.e., that dominates the ASR of the full cell to design a reliable ALT sequence for SOFCs.

2 Experimental

2.1. Cell specifications

All tested cells were anode supported SOFCs, consisting of a Ni-3YSZ anode support, a Ni-8YSZ anode and an 8YSZ electrolyte. The cells had an active electrode area of 4 cm x 4 cm. Cells with different kinds of cathodes were studied: a mixed ionic and electronic conducting (MIEC) electrode (LSCF-CGO, LSC-CGO), together with a CGO barrier layer or a composite LSM-YSZ electrode. The main cell components, as well as the parameters for selected durability tests are summarized in Table 1.

2.2. Testing procedure

The testing procedure started by sealing the setup and reducing the NiO in the anode and the support layer in a 9:91 H₂:N₂ mixture after heating the cell to either 850°C (procedure I) or 1000°C (procedure II). Details for the two different start-up and reducing procedures can be found elsewhere [11, 12].

Before and after durability testing under constant current load each cell was electrochemically characterized by EIS and current-voltage curves at a set of different standardized temperatures and gas compositions. This information was used to identify the individual responses of each cell component and to allow the quantitative break-down of losses by CLNS fitting. Figure 1 shows an illustration of

the performed testing sequence. Herein ‘fingerprint’ (FP) refers to the initial and final electrochemical characterization.

2.3. Degradation rate and impedance analysis

EIS recorded at OCV before and after performing durability testing was used to determine degradation rates of single cell components. If not stated otherwise, the ASR values for each cell component were determined from EIS, measured either at 700°C or 750°C and a 20/80 H₂O/H₂ fuel mixture and air to the cathode. [The impedance spectra for determining the initial ASR was measured between 1h-96 h before the durability test started.](#)

The degradation rate r_i related to 1000 h was calculated according to

$$r_i / \% \text{ kh}^{-1} = (\text{ASR}_{i,\text{final}} - \text{ASR}_{i,\text{start}}) / \text{ASR}_{i,\text{start}} \cdot 1000 / t_{\text{aging}} \cdot 100 \quad (1)$$

where ASR_i the initial or final ASR value for the component i (i.e. anode, cathode, electrolyte) and t_{aging} the time for durability testing excluding the time of the conducted fingerprint.

The deconvolution of the obtained EIS was carried out with an equivalent circuit model based on the work by Barfod et al. [14] for the anode response and full cells with LSM-YSZ cathodes. The response of the MIEC electrode was approximated by a Gerischer-type response as outlined in the work by Hjelm et al. [15]. For the ASR value of the anode, the resistance contributions assigned to electrochemical process (arc at ~ 0.5-10 kHz) at the Ni /YSZ interface [14,16] and contributions due to the ionic transport in the YSZ matrix (arc at ~ 11-40 kHz) were considered [16]. For cells with LSM/YSZ electrodes, the HF frequency arc consists of contributions from both anode and cathode (ionic transport [in YSZ matrix](#)) and hence was split up equally among the two electrodes for estimation of individual ASR values. The approach for EIS analysis is shown for a selected cell in Figure 2 and Figure 3.

The accuracy of the impedance fit was checked by

$$\text{relative residuals} / \% = (Z(\omega_i)^{\text{fit}} - Z(\omega_i)^{\text{exp}}) / Z(\omega_i)^{\text{exp}} \cdot 100 \quad (2)$$

as function of Z' and Z'' . While the residual calculation for freshly prepared cells showed consistently good fitting results (1 % down to 100 Hz, below 5 % in the whole frequency range), the impedance fit for degraded cells show about 2 % higher fitting errors but still allowed an estimation of changes of the ASR value for the component.

The ASR contribution of the [gas conversion](#) arc was used as indication that no change of the cell's active area had occurred during durability testing.

3 Results and Discussions

Typically, SOFC degradation rates are related to the operating conditions (e.g. current density, steam content, testing time, fuel utilisation etc.). The current study followed this approach. However, instead of a total cell degradation the ASR degradation rates for single SOFC components are related to the operation parameter.

3.1. Selection of data

For the evaluation a data base of approx. 180 long-term (>500 h) single cell tests was available. A preselection was performed based on the total polarization resistance (R_p) of the cells at the initial characterization. Exceptionally well or poor performing cells were excluded from the further durability analysis. [The data set data was selected based on:](#)

$$R_p = R_{p,\text{med}} \pm \text{IQR} \quad (3)$$

[where \$R_{p,\text{med}}\$ corresponds to the median and IQR to the interquartile range of each data set.](#) Figure 4 depicts how the selection was conducted. For single cells with LSM-YSZ electrode R_p values between

0.33-0.52 Ωcm^2 at 750°C were included. R_p data for cells with a MIEC electrode were allowed to vary from 0.21-0.44 Ωcm^2 at 700°C and 0.16-0.28 Ωcm^2 at 750°C, respectively. The purpose for this preselection was to ensure a fair comparison of the different cells and to exclude potential outliers. As the degradation rate is normalized to the initial ASR value, exceptionally high starting values would lead to, in some respect misleading smaller r and vice versa [17]. [After exclusion of these outliers about 135 cells were further analyzed.](#)

3.2. Cell component

Understanding degradation phenomena of Ni/YSZ electrodes has been subject of many recent studies [9, 18-20]. In the investigated anode supported cells, with MIEC electrodes, about 50 % of the total initial cell resistance at 750°C can be assigned to the anode (and approx. 35 % in anode supported cells with LSM/YSZ). From impedance analysis (see Figure 2), it became furthermore evident that a change of cell resistance occurred in a frequency range (\sim 0.5-10 kHz) which can be assigned to the anode triple phase boundary (TPB) charge transfer reaction [21].

[Figure 5 depicts the ASR development of the single resistance contribution of an example cell \(No. 52\) over time.](#) Obviously, the anode resistance contribution is the electrochemically performance limiting component of the cell. Degradation rates up to 100 % of its initial value in the first 1000 h (see following sections) was found and subsequently it is essential to pinpoint its critical operation conditions to design meaningful operating conditions for ALT.

Hence, this study is focused on identifying operating parameters which might lead to accelerated aging of the Ni/YSZ cermet electrodes to enable further and faster degradation studies of this electrode.

3.3. Operating time effect

One major observation from the large number of available tests carried out under different conditions and with different types of cathodes was a strong operating time dependency effect on the degradation rates. Likewise, analysis with focus on the anode degradation led to the same conclusion. Figure 6 shows the analysis results for single cell tests in the range between 596 h to 4813 h of durability testing (time at constant conditions). The calculated r was considerably larger for tests shorter than 1000 h and leveled off to a similar degradation rate for tests longer than ca. 2500 h of testing. Thus, the duration of the durability test seemingly has a larger or at least a similar effect on degradation as the operating conditions. To some extent a change in anode degradation rate is expectable because the driving force for some single degradation phenomena e.g. particle growth might be high in the initial period of testing and reach stagnation at longer operating times [22].

This result also highlights the ineffectiveness of estimating degradation for commercially relevant time scales (40.000 h-80.000 h) by degradation tests shorter than ca. 2500 h. [A fast loss of performance in the initial period will shift linearized degradation rates related to the initial performance to higher values and ergo extrapolation of these rates will predict poorer long-term performances.](#)

Subsequently, to exclude an operating time effect on the degradation analysis, tests with durations between 1000-2500 h were evaluated.

3.4. Fuel considerations

As outlined before, the degradation analysis focussed on the cells with MIEC cathodes where the anode resistance is dominating the overall SOFC resistance, i.e. the anode is considered the weakest point. [In order to relate anode degradation to various operating conditions, tests which were operated either with methane or large amounts of CO in the inlet fuel are excluded from the further discussion. 30 tests were considered to fulfil all requirements for a direct comparison \(see table 1\).](#)

3.5. Degradation as function of initial anode resistance

To develop a model for accelerated lifetime prediction puts naturally special emphasis on the absolute initial anode resistance in the SOFC and how it affects the degradation. Figure 7 shows the degradation rate of the anode vs. the initial anode resistance. There seems to be a weak trend. Apparently, a low anode ASR starting value results in faster degradation, i.e. more active anodes are prone to faster degradation. However, conclusions must be made with care as the tests comprise different cell generations, along with the fact that durability testing was performed at different operating conditions. Notwithstanding these shortcomings, the results indicate that the anode reaches a final, rather stable state independently from the initial structure.

It is known that a low anode ASR value can be correlated to a high TPB density and this can be related to the existence of finely distributed Ni particles [22, 23]. The driving force for one of the major degradation phenomena in anodes, namely nickel particle growth, is therefore more pronounced the smaller the initial particles are [24] and would explain the trend in Figure 7. Consequently, it can be of relevance to study anode structures with an initial coarser Ni/YSZ microstructure when considering long-term degradation. This would allow setting the particle growth as degradation aside and permit investigating of other failure mechanism occurring at long exposure times (>2500 h).

3.6. Establishing of a single parameter that determines anode degradation

It is clearly the ultimate aim to explain the degradation – here of the anode – as function of a universal set of parameters that combines all important operating conditions. In order to establish such a set of parameter, the anode degradation was analysed as function of the operating parameters i.e. temperature, current density, steam content in the hydrogen fuel and fuel utilization. Figure 8 shows the results. For the same reasons mentioned in the former section, the comparability is complicated by the multitude of

varied parameters. Despite this complexity, neither, the operating temperature from 600°C to 950°C nor the current density in the range between 0 Acm⁻² and 1.93 Acm⁻² resulted in trends of the anode degradation. Moreover, even fuel utilization values up to 80% do not seem to amplify the degradation of Ni/YSZ. Only an increase of steam content in the initial hydrogen fuel seems to lead to an increase of anode degradation rate [20], though the trend is rather weak with large scatter of the results (Figure 8b)

The initial steam content thus seems to be a relevant parameter for the anode degradation but including more parameters seems necessary to achieve a more straightforward correlation.

One could, for example, consider using the *initial anode ASR value at testing conditions* (in contrast to the ASR at standard conditions used in the previous analysis Figure 8). The ASR value of the Ni/YSZ electrode is then a function of all operating parameters (i.e. temperature, current density and steam content) and decreases with increased temperature, current load and steam content [21,25]. This value would merge all testing conditions to one single value.

Figure 9 displays the degradation rate of the anode as a function of its starting value at testing conditions. Lower starting values result in a higher degradation rate. This observation would indicate that increasing any of the mentioned parameters leads to higher anode degradation.

That, of course, does not give an idea which one on of them is dominating but it highlights the interplay of all operating parameters and points out the necessity to find proper parameter combinations to compare degradation for different testing conditions.

Returning to the observed weak trend of steam content on the anode degradation, it was attempted to establish a more appropriate determination of the steam content in the cell depending on the operating conditions. In addition to the steam in the initial fuel feed, steam is formed depending on the current density and also related to the fuel utilisation and as ‘side product’ when carbon containing fuel is used.

A descriptive way taking into account the actually relevant steam content might be the steam flow rate of the outlet fuel in mol h⁻¹.

The theoretical outlet steam flow for H₂/H₂O fuel mixtures can be calculated according to:

$$\text{H}_2\text{O}_{\text{out}} / \text{mol h}^{-1} = v(\text{H}_2\text{O})_{\text{produced}} + v(\text{H}_2\text{O})_{\text{in}} = I / 2F \cdot 3600 \text{ s h}^{-1} + v(\text{H}_2\text{O})_{\text{in}} \quad (4)$$

For H₂/CO₂/CO gas mixtures as fuel, the reverse gas shift reaction needs to be considered, namely



In this study the calculation of the outlet steam flow rate for H₂/CO₂ was performed based on an algorithm of the free available software RFCcontrol [26]. It includes the relevant parameters at different temperatures and by dividing the cell into multiple segments the water equilibrium is iteratively derived for each segment based on the previous one and finally the outlet segment.

In Figure 10 the anode degradation rate vs. the overall outlet steam flow are shown. Only cells which were operated at 700°C or 750°C are included to eliminate significant temperature influences.

A rather clear trend of increase of the anode degradation with increasing steam flow is obtained. The scatter of degradation rate is most likely a result of comparable but not identical anode structures.

However, the trend is much clearer compared to r_{anode} as a function of inlet steam (see Figure 8b)

Despite this scatter an overall trend that the overall steam seems to enhance degradation can be seen from Figure 10. On the other hand the results for the different applied current densities in the range from 0.25 to 1.19 Acm⁻² nicely follow the overall trend. Obviously the (potential) effect of current density on anode degradation was circumvented by integrating it into the steam flow, indicating the current density affects anode degradation indirectly by regulating the steam and not by overpotential related effects at these operating conditions. That is in line with studies on the effect of current density on anode degradation reported previously. Hagen et al.[5], for example, investigated the effect of

current load on anode-supported cells. It was concluded that high current loads primarily lead to higher degradation of the LSM/YSZ cathode at 750 °C while anode degradation seemed to be less severe. Further, Hauch et al. [9] studied the effect of different current densities on the stability of Ni/YSZ electrodes. Increasing the current density from 0.75 Acm⁻² to 1 Acm⁻² did not lead to higher anode degradation. Thus, it is conceivable that this range is not severe enough to initiate any accelerated degradation.

The effect of the steam outlet flow rate on the degradation rate of R_s can be seen from Figure 11. Comparing r_{R_s} for cells with MIEC and LSM/YSZ cathodes, an increase of r_{R_s} can be noticed for both cell types. The magnitude for cells with LSM/YSZ (Figure 11a) is roughly is about twice as high compared to cells with MIEC electrodes (Figure 11b). Based on previous durability studies on cells with LSM/YSZ cathodes, a part of the R_s increase can be related to the cathode degradation [27]. The degradation processes in LSM/YSZ electrodes seem to influence the losses of R_s to a high extent, so that no clear trend is detectable due to different steam contents on the anode side.

Due to the smaller contribution of MIEC R_p to the total ASR of this SOFC generation and also a negligible degradation of these cathodes, r_{R_s} seems to be closely correlated to a degradation process in Ni/YSZ electrodes. Higher steam content seems to amplify r_{R_s} . Consequently, changes in the anode microstructure might affect the R_s degradation to a higher extent than intrinsic degradation process of 8YSZ electrolytes (ionic conductivity loss). It makes it worthwhile to consider either migrating Ni particles away from the Ni-YSZ/YSZ interface or loss of Ni-Ni connectivity as degradation phenomena [23].

Conductivity studies by Philatie et. al. suggest [28] that electronic conductivity of Ni-YSZ anodes appears to decay faster in presence of higher steam content. This correlates well with the observation made in this work. Note that R_s of cell No.10 does not follow the overall trend in Figure 11b. This cell

was operated with water on both electrodes and therefore a part of the R_s degradation can have origin at the cathode. Furthermore, SEM analysis available for this cell indicates an additional degradation process of YSZ evolving from the cathode side.

4 Conclusion

An analysis of impedance data for 180 single cell durability tests has been conducted with the aim to identify accelerating parameters for compressed testing. The degradation behavior has been determined for each cell component individually and correlated with different operating parameters. In order to enable comparison of tests ranging over different temperatures, current densities, cell types etc., the individual resistances measured under standard conditions before and after the durability tests were used. The Ni/YSZ electrode for anode-supported cells with the state-of-the-art MIEC electrodes contribute the most to the overall ASR change in the degraded cells and therefore it is worthwhile to focus on its limitation when designing accelerated testing methods.

For calculating an appropriate degradation rate the duration of the long-term test plays a significant role. There is a trend towards smaller degradation rates with longer durations of the tests. It is therefore critical to compare degradation rates of cells which have been operated under <1000 h and > 2500 h. The degradation rate tends to level off at much smaller values after 2500 h, so it is doubtful to predict cell durability for commercial applications on tests conducted less than ca. 3 months. The effect of duration of testing on the anode degradation even seems to overshadow any effects of operating conditions such as temperature, current density or fuel utilization or specific cell generation.

Evaluating these operating parameters, no clear trend of the anode degradation was found. However, it was possible to relate an increase of the anode degradation to the increase the overall steam content. The analysis in this work showed that it is not sufficient to consider the steam content at the fuel inlet

but also the steam that is generated through application of current density and through the adjustment of the fuel utilization have to be included leading to a clear trend. The increase of the anode resistance could be coupled to an increase of the serial resistance, probably due to loss of Ni or loss of Ni percolation at the anode/electrolyte interface. A combination of all parameters that determine the steam content was thus the key to explain anode degradation over a large range of operating conditions and specific cell compositions, providing a basis for a potential controlled acceleration of anode degradation.

Acknowledgement

The authors thank colleagues at the DTU Energy department for providing the data used for the analysis, especially Dr. Christopher R. Graves, Dr. Per Hjalmarsson and Dr. Johan Hjelm. Furthermore, the authors thank Henrik Henriksen for valuable technical assistance. Funding by Energinet.dk (project 2014-1-12231 ForskEL ‘SOFC4RET’) is gratefully acknowledged.

List of Symbols

ASR	area specific resistance / Ωcm^{-2}
FU	fuel utilization
I	current / A
j	current density / Acm^{-2}
OU	oxygen utilization
r_i	degradation rate of component i / $\% \text{kh}^{-1}$
R_p	polarization resistance / Ωcm^{-2}
R_s	serial resistance / Ωcm^{-2}

t	time / h
T	temperature / °C
U	voltage / V

References

- [1] R. S. Gemmen, M. C. Williams, K. Gerdes, *J. Power Sources* **2008**, *184*, 251.
- [2] S. C. Singhal in *Solid Oxide Fuel Cells: Facts and Figures*, (Eds. J. T. S. Irvine, P. Conner), Springer, London, **2013**.
- [3] *Solid Oxide Fuel Cells - Integrating Degradation Effects into Lifetime Predictions Models*, can be found under http://cordis.europa.eu/rcn/97947_en.html, **2016**.
- [4] W. Nelson in *Accelerated Life Testing: Statistical Models, Test Plans and Data Analysis*, John Wiley & Sons, New York, **2004**.
- [5] A. Hagen, R. Barfod, P. V. Hendriksen, Y.-L. Liu, S. Ramousse, *J. Electrochem. Soc.* **2006**, *153*, A1165.
- [6] M. J. Heneka, E. Ivers-Tiffée, *J. Fuel Cell Sci. Tech.* **2011**, *9*, 11001.
- [7] A. Hagen, J. V. T. Høgh, R. Barfod, *J. Power Sources* **2015**, *300*, 223.
- [8] M. J. Heneka, E. Ivers-Tiffée, *ECS Trans.* **2006**, *1*, 377.
- [9] A. Hauch, M. Mogensen, *Solid State Ionics* **2010**, *181*, 745.
- [10] C. Endler-Schuck, A. Leonide, A. Weber, S. Uhlenbruck, F. Tietz, E. Ivers-Tiffée, *J. Power Sources* **2011**, *196*, 7257.
- [11] A. Hauch, S. H. Jensen, S. Ramousse, M. Mogensen, *J. Electrochem. Soc.* **2006**, *153*, A1741.
- [12] P. Hjalmarrsson, X. Sun, Y.-L. Liu, M. Chen, *J. Power Sources* **2014**, *262*, 316.
- [13] P. H. Larsen, K. Brodersen, *US Patent, US 2008124602-A1*, **2008**.
- [14] R. Barfod, M. Mogensen, T. Klemensø, A. Hagen, Y.-L. Liu, P. Vang Hendriksen, *J. Electrochem. Soc.* **2007**, *154*, B371.
- [15] J. Hjelm, M. Søgaaard, R. Knibbe, A. Hagen, M. Mogensen, *ECS Trans.* **2008**, *13*, 285.
- [16] T. Ramos, M. Søgaaard, M. B. Mogensen, *J. Electrochem. Soc.* **2014**, *161*, F434.
- [17] T. L. Skafte, J. Hjelm, P. Blennow, C. Graves, *Proc. 12th European SOFC & SOE Forum* **2016**, *8*.

- [18] M. V. Ananyev, D. I. Bronin, D. A. Osinkin, V. A. Eremin, R. Steinberger-Wilckens, L. G. J. de Haart, J. Mertens, *J. of Power Sources* **2015**, 286, 414.
- [19] D. Kennouche, Y.-c. K. Chen-Wiegart, K. J. Yakal-Kremiski, J. Wang, J. W. Gibbs, P. W. Voorhees, S. A. Barnett, *Acta Mater.* **2016**, 103, 204.
- [20] A. Hauch, M. Mogensen, A. Hagen, *Solid State Ionics* **2011**, 192, 547.
- [21] J.-C. Njodzefon, *Ph.D. Thesis*, Technical University of Denmark, Roskilde - Denmark, **2015**.
- [22] L. Holzer, B. Iwanschitz, T. Hocker, B. Münch, M. Prestat, D. Wiedenmann, U. Vogt, P. Holtappels, J. Sfeir, A. Mai, T. Graule, *J. Power Sources* **2011**, 196, 1279.
- [23] M. S. Khan, S.-B. Lee, R.-H. Song, J.-W. Lee, T.-H. Lim, S.-J. Park, *Ceram. Int.* **2016**, 42, 35.
- [24] C. Herring, *J. Appl. Phys.* **1950**, 21, 301.
- [25] A. Leonide, V. Sonn, A. Weber, E. Ivers-Tiffèe, *J. Electrochem. Soc.* **2008**, 155, B36.
- [26] S. Koch, *OCV_corr, RFCcontrol Version 5.5.1*, **2016**, Software Control System for electrochemical devices.
- [27] A. Hagen, Y. L. Liu, R. Barfod, P. V. Hendriksen, *J. Electrochem. Soc.* **2008**, 155, B1047.
- [28] M. H. Pihlatie, A. Kaiser, M. Mogensen, M. Chen, *Solid State Ionics* **2011**, 189, 82.
- [29] A. Müller, *Ph.D. Thesis*, Universität Fridericiana Karlsruhe, Karlsruhe - Germany, **2004**.
- [30] A. Faes, A. Hessler-Wyser, D. Presvytes, C. G. Vayenas, J. Van herle, *Fuel Cells* **2009**, 9, 841.
- [31] H. Yokokawa, H. Tu, B. Iwanschitz, A. Mai, *J. Power Sources* **2008**, 182, 400.
- [32] A. Weber, J. Szász, S. Dierickx, C. Endler-Schuck, E. Ivers-Tiffée, *ECS Trans.* **2015**, 68, 1953.
- [33] N. M. Sammes, Z. Cai, *Solid State Ionics* **1997**, 100, 39.

Figure Captions

Figure 1 The testing procedure was initiated with a detailed characterization, followed by galvanostatic durability testing and ended with a final characterization.

Figure 2 Nyquist plot of EIS of a selected cell (No. 39) at FP (top). DRT plot illustrating the cell's impedance responses at different frequencies (bottom). The fuel electrode response is indicated by red dashed lines.

Figure 3 EIS fit of cell from test No.39. The contributions used for estimating the ASR value of Ni/YSZ cermet electrodes are simulated.

Figure 4 R_p values from the initial FP for all the tested cells are plotted vs. the years when the durability testing was conducted (a). Pre-selection of data by comparison of polarization resistance values for single cells with LSM-YSZ electrodes (b) and MIEC electrodes (c). The borders for the excluded data are represented by dashed lines. Cells marked with (*) were made via a different (half cell) manufacturing route.

Figure 5 Time dependency of different ASR-contributions to the overall resistance overtime (cell No. 52)

Figure 6 Degradation rates of the polarization resistance (r_{Rp}) as function of test duration. Cells have different cathodes and were operated at a large number of different operating conditions (i.e. $T = 600-950^\circ\text{C}$, $j = 0-1.93 \text{ Acm}^{-2}$ and for details see Table 1).

Figure 7 Relation between anode degradation and initial anode ASR value (obtained at $T=750^\circ\text{C}$, 20/80 $\text{H}_2\text{O}/\text{H}_2$ fuel, air to the cathode and OCV)

Figure 8 Influence of current load (a), steam content in the inlet fuel (b), temperature (c) and fuel utilization (d) on anode degradation (for testing conditions see Table 1).

Figure 9 Relation between anode degradation and initial ASR value (obtained at testing conditions see Table 1, **only cells are included where an initial impedance measurement at long-term testing conditions was available**)

Figure 10 Anode degradation as function of the steam outlet flow rate. Cells marked with (*) were made via a different half cell manufacturing route.

Figure 11 Serial resistance R_s degradation rate vs. steam outlet flow rate in the anode compartment.

Table Captions

Table 1 Cell specifications and durability testing parameters (**not shown are tests <1000 h or >2500 h, and tests operated with CH₄ or CO in the inlet fuel**)

test	start-up	anode	cathode	barrier	T/°C	t/h	j / Acm ⁻²	fuel	H ₂ O in / %	FU / %	oxidant	OU / %
4	II	Ni/YSZ ⁵	LSCF/CGO ¹	CGO ¹	700	2302	0.25	H _{2,dry}	0	45	air	21
10	II	Ni/YSZ ⁵	LSC ¹	CGO ¹	700	2026	0.50	H ₂ :H ₂ O	4	58	air _{humidified}	20
12	I	Ni/YSZ ⁵	LSC/CGO ¹	CGO ²	750	1514	0.75	H ₂ :CO ₂ (4:1)	16	79	air	9
17*	I	Ni/YSZ ⁶	LSC/CGO ¹	CGO ³	700	1512	0.75	H ₂ :H ₂ O	5	61	air	9
18	I	Ni/YSZ ⁵	LSC/CGO ¹	CGO ²	600	1004	0.4	H ₂ :H ₂ O	4	16	air	16
37	II	Ni/YSZ ⁵	LSC/CGO ¹	CGO ³	650	1817	0.75	H ₂ :CO ₂ (4:1)	15	20	air	18
39*	II	Ni/YSZ ⁶	LSCF/CGO ¹	CGO ¹	750	1013	0.75	H ₂ :H ₂ O	39	28	O ₂	5
49	I	Ni/YSZ ⁵	LSCF/CGO ¹	CGO ¹	800	1220	0	H ₂ :H ₂ O	80	0	O ₂	0
50	II	Ni/YSZ ⁵	LSCF/CGO ¹	CGO ¹	700	1321	0.5	H ₂ :H ₂ O	40	20	air	20
51	II	Ni/YSZ ⁵	LSCF/CGO ¹	CGO ¹	700	1508	0.5	H ₂ :H ₂ O	4	62	air	20
52	II	Ni/YSZ ⁵	LSCF/CGO ¹	CGO ¹	700	1500	0.5	H ₂ :H ₂ O	39	19	air	20
53	II	Ni/YSZ ⁵	LSCF/CGO ¹	CGO ¹	800	1632	0.5	H ₂ :H ₂ O	4	63	air	20
63	I	Ni/YSZ ⁵	LSCF/CGO ¹	CGO ¹	800	1214	0	H ₂ :H ₂ O: CO ₂ (4:1)	50	0	O ₂	0
81	II	Ni/YSZ ⁴	LSM/YSZ ⁴	non	850	1585	1.76	H ₂ :CO ₂ (4:1)	16	75	air	20
83	II	Ni/YSZ ⁵	LSM/YSZ ⁴	non	750	1508	0.25	H ₂ :CO ₂ (4:1)	17	43	air _{humidified}	9
85	II	Ni/YSZ ⁴	LSM/YSZ ⁴	non	750	1575	0.25	H ₂ :CO ₂ (4:1)	16	83	air	9
86	II	Ni/YSZ ⁴	LSM/YSZ ⁴	non	850	1524	1.0	H ₂ :CO ₂ (4:1)	17	77	air	11
87	II	Ni/YSZ ⁴	LSM/YSZ ⁴	non	850	1699	0.25	H ₂ :CO ₂ (4:1)	16	73	air	4
92a	II	Ni/YSZ ⁵	LSM/YSZ ⁴	non	750	1506	0.75	H ₂ :CO ₂ (4:1)	17	86	air	9
94	II	Ni/YSZ ⁴	LSM/YSZ ⁴	non	750	1513	0.75	H ₂ :CO ₂ (4:1)	15	77	air	9
95	II	Ni/YSZ ⁴	LSM/YSZ ⁴	non	750	1502	0.75	H ₂ :H ₂ O: CO ₂ (4:1)	26	71	O ₂	3
97	II	Ni/YSZ ⁴	LSM/YSZ ⁴	non	950	1515	1.66	H ₂ :CO ₂ (4:1)	17	63	air	20

98	II	Ni/YSZ ⁴	LSM/YSZ ⁴	non	750	1503	1.19	H ₂ :H ₂ O: CO ₂ (4:1)	23	76	O ₂	4
111	II	Ni/YSZ ⁴	LSM/YSZ ⁴	non	850	1991	1.93	H ₂ :CO ₂ (4:1)	16	79	air	22
139	II	Ni/YSZ ⁵	LSM/YSZ ⁴	non	850	1500	0.25	H ₂ :CO ₂ (4:1)	17	48	air _{,humidified}	9
143	II	Ni/YSZ ⁵	LSM/YSZ ⁴	non	750	1243	0.75	H ₂ :CO ₂ (4:1)	15	79	air _{,humidified}	9
144	II	Ni/YSZ ⁴	LSM/YSZ ⁴	non	750	1565	0.75	H ₂ :CO ₂ (4:1)	16	76	air	9
150	II	Ni/YSZ ⁵	LSM/YSZ ⁴	non	800	2001	0.5	H ₂ :CO ₂ (4:1)	16	80	air _{,humidified}	6
185	I	Ni/YSZ ⁵	LSM/YSZ ¹	non	750	1000	0.5	H ₂ :H ₂ O	25	37	O ₂	9

¹screen printed ²spin-coated ³physical-vapor deposition ⁴sprayed ⁵tape-casted ⁶multi-layer tape casting

process [13]