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Degradation studies using machine learning on novel solid oxide cell database

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Abstract
With the current progress in solid oxide cell (SOC) technology towards commercial products, better durability is vital. Continuous advancements in technology and material discovery demand the understanding of underlying degradation mechanisms. It remains a challenge to experimentally assess the lifetime using conventional mapping by long-term testing.

In this work, a statistical approach based on machine learning was utilized for assessing the lifetime of SOCs. An in-house SOC dataset consisting of about 2135 tests under different test conditions over the past ca. 20 years with different cell materials was used as the basis for a novel database. Degradation parameters were defined using values obtained from impedance analysis at open-circuit voltage before (and after) durability testing and parameters recorded during the durability tests. To apply machine learning approaches, data visualization was first carried out, followed by correlation analysis between the different input parameters. Machine learning approaches such as single and multivariable linear regression were applied. Such a study on a diverse dataset would enable an inclusive lifetime prediction for wider datasets, independent of changes in testing environments as well as for various cell operation modes.

KEYWORDS
database, fuel cell, lifetime studies, machine learning, solid oxide cells

INTRODUCTION

Solid oxide cells (SOCs) are being employed in a wide range of applications such as power generation, Power-to-X, and so forth [1–6]. These large-scale applications require long operational lifetimes, in the range of several 10 000 h. Lab and pilot-scale tests in these time scales have been carried out in the past [7–9]. It is known that during such long-term tests several parameters influence the cell performance. These are both intrinsic characteristics of the cell - microstructure, materials, and so forth and external factors during operation - temperature, current density, reactant flows, cell voltage, and so forth. In addition, variations of the parameters can occur or test setups can vary (e.g., auxiliary components). Thus, to deduce conclusions on the long-term behavior of cells operated under similar conditions, expensive repetition and reproduction of experiments are crucial. Furthermore, with rapid technology advancements, a longer durability of cells and stacks is achieved and conclusions based on short-term testing prove to be insufficient [10]. A strategy to overcome the needed long testing time is accelerated stress testing. In order to perform these stress tests, a set of accelerating parameters and their influence on a suitable degradation
measure need to be identified. For SOCs, identification of such acceleration parameters has not been accomplished yet due to the complex interplay of the various operating parameters on the cell performance over time. This work aids to gain an understanding of this interplay using experimental results from a large pool of durability tests including a large variety of cell generations, operating conditions, and test setups. Machine learning (ML) approaches are used for the first time to visualize the test parameters and to evaluate their influence on cell degradation on such a large SOC dataset. In a previous work carried out by Ploner et al. [11], it was shown that in the fuel cell (FC) operation, a strong correlation between one single operation parameter and cell degradation could not be obtained with the selected dataset of durability tests, only weak correlations, which became stronger through the combination of several single operating parameters.

Definition of a suitable degradation measure and identification of corresponding operating parameters is vital. In literature [8,10,12], various definitions of degradation for FC operation have been stated, primarily based on current and voltage measurements over time or impedance spectroscopy measurements taken at different temperatures and with different gas compositions before and after durability testing.

In the past, research groups have reported the use of statistical approaches [13–15] to capture the performance of various electrochemical devices over time, but not for SOCs across different material compositions and test conditions. Such approaches have been limited for FCs including SOCs due to the limited availability of long-term test data. Simulation models for solid oxide FCs (SOFCs) have been developed and tested based on previously validated empirical correlations or a limited number of cells tested under certain conditions. In this way, such a model is valid only for a limited number of tests, that is, only for tests operated under those specific test conditions for the specific cell technology. New models have to be developed when changing the test conditions or the cell technology.

ML approaches have been used on large datasets in the field of electrochemistry, for example, in battery characterization [13]. It involves the following main steps: (i) creation of the database, (ii) data visualization, (iii) definition of the dataset (after filtering and target selection), (iv) identification of correlated and non-correlated input parameters, (v) ML model training (input and target parameters) and testing, and (vi) evaluation of the model fit. In this work, the authors aim to apply machine learning models on a novel dataset, which contains data from SOCs tested at the Technical University of Denmark (DTU) over different operating times, specific operating parameters, and cell compositions (see approach illustrated in Figure 1). Unlike simulations, such an approach relies on data to give information on the hidden patterns and information across the test sets. Deconvolution of valuable information based on cell degradation was carried out using a dataset that contains variations in both cell test conditions as well as operating modes, by utilizing ML routines for the first time on a diverse dataset in the field of SOC.

**EXPERIMENTAL SECTION**

**Database structure**

A unique database, which consists of 2135 SOC tests performed at the Department of Energy Conversion and Storage at DTU over a period of two decades, was created (tests were performed at Risø National Lab until 2019). The data was extracted for all tests from the existing data servers and implemented into data frames using Python Pandas open source library. The database consists of tests under different operation modes (FC, electrolysis [EC], and reversible operation) in either potentiostatic or galvanostatic, constant, or dynamic operation for planar cells with different materials and structural compositions with a large variety of operating parameters. Figure 2 illustrates the structure of this database.

The data servers provided numerous information for each test. Each test consists of time series data from the start of the test for different parameters such as temperatures recorded at several places (like cell inlet and outlet), gas compositions, cell voltages (across the cell and in-plane), current, pO2 measurements which is the oxygen partial pressure at the electrodes that is measured using an electrochemical sensor (It gives the potential measured between the gas at the electrode versus a reference electrode, which is air provided separately outside the FC), and so forth. These test parameters were logged using an automated data logging system at regular intervals (from 1 to 15 min). Furthermore, unique classifiers of the tests are included as attributes. Those contain additional information about the tests, such as details entered by the user at the start of the test (e.g., cell material, auxiliary components, etc.). In addition, initial resistance values from electrochemical impedance spectroscopy (EIS) and current-voltage (I-V), recorded at a set of standardized specific gas compositions and temperatures were also extracted. Tests were also classified according to the used fuel, constant or dynamic modes (for the current density or temperature, FC or EC mode), and so forth. These attributes help select the relevant tests for a specific degradation evaluation. Furthermore, each test typically includes a set of EIS and I-V
curves recorded throughout the cell operation as separate data frames.

It is noteworthy that the tests have been performed over the past several decades with different test interests (to evaluate the performance of cell generations, to identify the effect of operating conditions on degradation, etc.) and differing cell test setups like sealants, contact layers, flow configurations, and so forth. Thus, a direct comparison of the data is very complex and cannot be captured by simple analysis; here ML approaches could prove to be a unique tool. After the establishment of the database, data visualization and filtering were performed to select the relevant tests for the preliminary evaluation (for example durability tests in specific operating modes) and to eliminate erroneous measurements in test data (improper connections, broken sensors, etc.).
Data visualization and filtering

For the initial selection of tests, time-based filters were applied to extract FC durability tests, which is the focus of the present contribution, that is, to exclude short-term tests and durability tests in other modes.

Figure 3 illustrates the distribution of the duration of tests in the complete database of the 2135 SOC tests. The time filter was chosen to capture the degradation over a sufficiently long testing time. Typically, the degradation rate is larger in the initial operating period and decreases over time. In order to accommodate for this non-linear degradation behavior of the cells, the time filter to extract the durability tests was set to values longer than 300 h operating under load. Furthermore, tests with erroneous data (for example power or other technical failures) were filtered out. Finally, only tests in FC mode operated galvanostatically were selected for this work. These filters reduce the number of tests for the model from 2135 to 151. The conditions used to filter out the desired long-term FC tests carried out on ceramic cells (either anode or electrolyte supported cells) are summarized in Figure 4.

It is very crucial to visualize the dataset before a selection of ML models can be done, for example, to evaluate how the test results cover the input parameter space such as temperature, current density, and so forth. Ideally, the tests should have been carried out over a large range of these parameters. The different distributions of the input parameters indicate the variations within the data set and the appropriate transformations (such as normalization of the data points, mean values, etc.) that need to be applied in order to accommodate for this non-linear degradation behavior of the cells, the time filter to extract the durability tests was set to values longer than 300 h operating under load. Furthermore, tests with erroneous data (for example power or other technical failures) were filtered out. Finally, only tests in FC mode operated galvanostatically were selected for this work. These filters reduce the number of tests for the model from 2135 to 151. The conditions used to filter out the desired long-term FC tests carried out on ceramic cells (either anode or electrolyte supported cells) are summarized in Figure 4.

From a statistical point of view, in addition to the wide variation of the dataset (i.e., range of temperatures, current densities, etc.), a large number of data points is desirable at each test condition so that the outliers in the data, that may affect the models, can be identified easily - a requirement
that is not always fulfilled with the available tests of SOCs, where repetition of long-term tests at identical conditions are still rare. This is a general challenge of SOFC durability tests due to the costly tests and test items. In Figure 5d it can be seen that there are only carried out a few long-term FC tests at current densities above 1.0 A/cm², which can make the dataset biased if not treated properly. On the other hand, a fair number of tests have been carried out at temperatures of ca. 700, 750, and 850°C giving a better statistical basis for this range.

Box plots further help to identify the variance within a given dataset and thus obtain the outliers based on interquartile ranges. In the box plots for cell operating temperatures, shown in Figure 6, a further possible classification of subsets of the data is by using the compositions of the materials of the cathode (either Lanthanum Strontium Manganite/Yttria-stabilized Zirconia [LSM/YSZ] composite or Lanthanum Strontium Cobalt Ferrite/Gadolinium-doped Ceria [LSCF/CGO] composite). The height of the box indicates the range from the first to the third quartile of the selected input parameter (here, the temperature of durability test), and the median value is indicated by the horizontal line within the box. It is interesting to notice

the shift of the median value (orange line in the box in Figure 6) for the different subsets when looking at all tests (left) and then dividing them by cells with two different cathode materials in Figure 6. This shift indicates that cells
with LSM/YSZ based cathodes were typically operated at higher temperatures than cells with LSCF/CGO cathodes. This is a result of the more active mixed ionic electronic conducting LSCF containing cathodes, which were developed to decrease the operating temperature of SOFC. Such variation in the data would be hidden when considering an overall dataset with all the operated cells. Thus, it is important to see if such differences exist within the database that may affect the correlations with the degradation measures and potentially lead to wrong conclusions.

RESULTS AND DISCUSSION

Target parameter: Degradation measures

The next important step to analyze cell performance over time is the selection of a suitable target parameter, reflecting cell degradation. An illustration of a typical durability test is shown in Figure 7. The cells are characterized for electrochemical performance (I-V curves, EIS) at a set of standard conditions prior to the long-term testing, followed by the long-term operation, and a final characterization after completion of the durability test, as well.

In order to involve a large dataset with tests at constant or changing current load or operated under potentiostatic conditions, Ploner et al. [11] considered the change of the area-specific resistance (ASR) of the cell or a cell component, determined at standard conditions before (pre-test) and after (post-test, see Figure 7) executing the durability test as a valid degradation measure. With this approach, durability tests carried out under widely varying conditions can be evaluated and compared to each other. This also ensures that fluctuations within the test operation period do not affect the quality of the data for the statistical degradation models.

A more common target variable to quantify degradation is the decrease of the cell voltage under the durability operation (at galvanostatic conditions), more specifically the % degradation per 1000 h. This approach limits evaluation to tests operated at similar conditions and complicates it for example for tests at changing current load or excludes potentiostatic tests. The degradation value is also heavily dependent on the operating time in case of non-linear voltage decrease over time (as illustrated in Figure 7).

Degradation as a change of anode ASR at open-circuit voltage before and after durability test

Previous degradation analysis revealed that there is a weak correlation between the total steam content in the fuel gas and the anode degradation, expressed as anode ASR increase, where the resistance was determined at standard conditions before and after the durability test from deconvolution of the EIS spectra [11]. By using ASR values determined before and after the durability tests, various fluctuations that may induce noise in the data during operation or varying operating conditions under durability testing and non-linear behavior of the cell voltage degradation will be omitted to achieve a good quality degradation measure. Furthermore, when extracting the anode ASR, tests carried out with different cathode materials can be compared. For this chosen degradation measure, an FC test subset with a total of 19 tests was available in the previous study [8].

The same degradation measure and dataset were evaluated in the present work. To study the multi-collinearity that exists in the dataset, the different input parameters (test conditions) are plotted against each other. Linear correlations were examined between the input pairs. This would make it possible to identify those input parameters, which affect each other, and to isolate individual or sets of parameters, which affect degradation and could serve as potential accelerating parameters for durability testing. The correlations are shown in the form of a heat map in the correlation matrix in Figure 8. The diagonal elements in the heat map are indicated by a correlation of 1, as they are plotted against the same parameter. The areas above and below the diagonal are identical as the parameter combinations remain the same. In this figure, strong positive correlations appear in red, strong inverse correlations in blue, and weak/no correlations in white. The strongest correlations were observed between the current density and V_start (voltage at the start of the durability conditions, intense blue squares in Figure 8). This inverse correlation can be understood since the higher the current density, the lower the cell voltage in fuel cell operation. Another interesting observation is the cell resistance at the
The start of the cell testing at specified conditions (R_start) and the voltage measurement of the fuel inlet (pO2_in) (dark orange square in Figure 8). These values are seen to be correlated with each other in the present dataset, that is, the higher the pO2_in, the higher the R_start in the chosen dataset. However, one parameter is a test condition while the other is a cell property. The observed correlation might indicate that, incidentally, cells with a higher initial resistance also were operated with high pO2_in. This finding is thus a result of the limited amount of available data in the dataset. Another observation is a positive correlation of the duration of the test (load duration) and temperature in (orange square in Figure 8); these are two independent parameters, as well. These examples underline that all correlations have to be evaluated for true correlation between the parameters and those, which may have emerged incidentally or due to the limited number of data. The used format gives a unique opportunity, due to the condensed nature of the data presentation, to evaluate these correlations between the input parameters within a chosen dataset. Already from the first glance of revealing the many correlations, it is easy to understand why identification of one single accelerating parameter for SOFC degradation testing is a challenging undertaking.

The next step is to observe any correlations of the input parameters with the degradation measure. More specifically, the change of anode ASR was chosen and correlated with the input parameters. Figure 9 shows the results for the parameters current density and inlet steam fraction. The correlations were evaluated using Spearman’s correlation value, which shows the correlation strength ranged from −1 to +1 (from strongly inverse correlation to strong positive correlations). Linear correlations as shown in Figure 9 were obtained using simple linear regression. The change of anode ASR (i.e., anode degradation) is observed to have a positive correlation with both the current density as well as the molar fraction of steam at the fuel inlet. These results confirm that anode degradation increases with applied current density and increase of steam in the fuel.

Another important observation is with respect to the confidence intervals (shaded region) at each parameter value which is determined around the regression line using bootstrapping. The confidence intervals indicate the error in the predictions from the regression line, a narrow confidence interval throughout the parameter range would be ideal. Availability of more long-term tests could improve the confidence intervals. The found positive correlation has a correlation strength of 0.27 Spearman’s correlation coefficient for the current density (see Figure 9a), and 0.39 for the steam molar fraction at the inlet (see Figure 9b). These values must be >0.5 to be statistically significant and to allow for generalized conclusions, which will hold true irrespective of the selected dataset. While the obtained trends are in line with Ploner et al. [11], the statistical relevance needs to be improved. In order to further expand this approach to obtain statistically significant correlations and establish robust models across different cell types and operation conditions, a larger test set is needed.

A multi-variable linear regression was performed on the same data set with selected input parameters during the durability conditions to see if there is a linear correlation giving higher statistical significance (for example combination of steam at an inlet in the fuel, current density, fuel utilization, etc.). This regression evaluation did not result in a satisfactory coefficient of determination (R^2 score), which is a measure of accuracy in the target predictions. A solution to identify multi-variable correlations with statistical significance is the use of non-linear approaches and also to increase the number of test data in the dataset. This approach would potentially also help to reach statistically more significant results for a degradation target measure which is known to be dependent on the interplay of input parameters.

Degradation as a change of cell voltage overtime during durability test

The change of cell voltage versus time was selected as another degradation measure. With this approach, 151 long-term FC tests could be included from the database. Again, correlation plots were made to identify linear correlations between the input parameters as shown in Figure 10. It was observed that true correlations for example...
between initial cell voltage ($V_{\text{start}}$) and current density remain strong (blue squares, compare Figures 8 and 10). Other correlations changed by including more tests in the data set. For example, $pO_2_{\text{in}}$ and $R_{\text{start}}$, now show a very weak correlation (orange in Figure 8 vs. light orange in Figure 10). The same was observed for the independent input parameters load duration and temperature (white square in Figure 10). These observations indicate that larger data populations would eventually lead to reveal the true (physically meaningful) correlations and separate them from incidental correlations due to the limited range of operating parameters in a smaller dataset.

When evaluating the effect of input parameters on the degradation measure cell voltage decrease over time, correlations were found. For example, the cell voltage degradation decreased with the testing year (Figure 11a). Since there are a large number of tests operated under a wide range of operating parameters and material compositions over these years, the spread of degradation rate is wide (see data points in Figure 11a). It is difficult to explain why the year when the test was executed should affect the degradation rate. The observed decreasing trend is rather an indication of the technological and material advancements over the years, that is, more durable cell versions were tested in more recent years. Figure 11b shows the correlation between the target cell voltage degradation and the operating parameter steam molar fraction at the inlet. The cell voltage degradation increases with increasing inlet steam molar fraction. The same trends are thus observed for both degradation target parameters. The highest correlation significance is found to be around 0.25 for the steam molar fraction, which is still not statistically significant to make generalized conclusions, but the confidence intervals throughout the parameter space (shaded areas in Figure 11), indicate a $\pm0.05\%$/kh, which is in a satisfactory range. Similarly, in the case of the effect of current density, the cell voltage degradation increased with Spearman’s correlation significance of 0.27. The linear correlations show the same trends with the higher number of tests in Figure 11c as compared to fewer tests in Figure 9b. In other words, even though there was a larger data set for correlating the cell voltage degradation to operating parameters, the significance was lower than for the smaller dataset with the anode ASR degradation. This is clearly due to the nature of the degradation target. In contrast to the target increase of anode ASR, where only the anode degradation is considered, the target cell voltage degradation is certainly affected by both
FIGURE 11  Linear correlations for selected input parameters for SOFC durability tests >300 h under operation to the degradation measure cell voltage increase over time (A) versus operation year, (B) versus steam molar fraction at the inlet, and (C) versus current density.

CONCLUSIONS

A novel database was created with all SOC tests performed on planar cells at the Department of Energy Conversion and Storage at DTU over the past decades. These tests include a large variety of cell generations (materials and structures), test setups (sealings, contacting layers, etc.), and operating modes (short and long terms, FC and EC modes, constant and dynamic conditions, etc.). The database was created using existing data from test servers. It served as the fundament for applying machine learning routines for the very first time on revealing prevailing correlations between operating parameters and degradation in FC mode in order to get new insight in understanding degradation of SOC and in order to harvest more intensely the comprehensive existing data. The ultimate goal is a model for the prediction of the lifetime of the SOCs and the identification of parameters for accelerated degradation tests. The present work focused on tests in FC mode and with durations longer than 300 h under current in order to evaluate the effect of input parameters (operating conditions) on a target measure for degradation.

The authors have implemented data visualization and initial statistical models on input parameters and different target measures for degradation (anode resistance change and change of cell voltage over time). It was observed that a number of input parameters have an interplay between each other, for example, the current density and the initial voltage at the start of the durability conditions, which is an expected correlation. Further, some correlations between input parameters are only observed due to the limited population of the current datasets. This makes the isolation of the effects of a single parameter on the target variable (degradation measure) and the identification of a single accelerating parameter for SOFC degradation testing challenging. It was shown that by increasing the population of the data set, true correlations with a physical meaning remained strong, while those related to the limited data got weaker.

When evaluating how the input parameters affect the degradation target for a chosen subset, weak correlations were identified by correlating the degradation measures increase of anode resistance before and after durability testing and the increase of cell voltage over time during durability testing to the parameter current density and to the steam molar fraction at the inlet. In order to achieve high statistical significance and make generalized conclusions for durability, more test data and potentially more complex (non-linear) correlation models are required. In future studies, model creation and analysis will be extended to include more tests with different operating modes like EC and reversible FC/EC operation. Furthermore, time-dependent target variables are of interest in
order to be able to predict the lifetime of cells with the identified correlation of the input to cell degradation.

List of Acronyms

- FC: fuel cell
- EC: electrolysis
- ASR: area-specific resistance (Ω cm²)
- I-V curve: current-voltage curve
- EIS: electrochemical impedance spectra
- R_start: cell resistance before the start of durability testing at specified conditions (at 850°C with 80/20 composition and no-load) (Ω cm²)
- V_start: voltage at the start of the durability test (mV)

Abbreviations in Figure 2 Test

- Test Time: time since the start of test
- T_center: cell temperature at inlet
- T_corner: cell temperature at outlet
- Air: flow rate of air on the air electrode
- O₂ cathode: flow rate of pure oxygen on the air electrode
- H₂: flow rate of hydrogen on fuel electrode
- H₂O: flow rate of steam on fuel electrode
- O₂: flow rate of oxygen on fuel electrode (for producing steam by combustion)
- CO₂: flow rate of CO₂ on fuel electrode
- CH₄: flow rate of CH₄ on fuel electrode
- CO: flow rate of CO on fuel electrode
- pO₂_in: potential measured between the gas composition at fuel inlet versus air
- pO₂_out: potential measured between the gas composition at fuel outlet versus air
- Cell voltage: voltage measured across cell

Current density effective current density applied/extracted: Attributes

- Duration: total test duration since mounting
- CO₂ test (classifier): if it is a pure CO₂ test
- Cyclic test (classifier): if it is operated in cyclic mode
- FP Resistance values: resistance measured at fingerprint conditions
- EIS Tests (Pandas Dataframe)
- t_imp: time at the start of EIS measurement
- Rs: Ohmic resistance
- Rp: polarisation resistance
- T_imp: temperature at cell inlet at the start of EIS measurement
- Air_imp: air flow rate during EIS
- H₂_imp: H₂ flow rate during EIS
- O₂_imp: O₂ flow rate on fuel electrode during EIS
- O₂ cathode_imp: O₂ flow rate on air electrode during EIS
- Current_imp: current applied during EIS
- V_imp: voltage recorded at the start of the impedance test
- I-V curves: (Pandas Dataframe)
- t_iv: time at the start of I-V measurement
- ASR secant: ASR calculated from the slope of the I-V curve
- T_imp: average temperature at the start and stop of the I-V curve at the cell inlet.
- V_iv: voltage at open circuit conditions measured at start and end of I-V
- Air iv: air flow rate during I-V
- H₂ iv: H₂ flow rate during I-V
- O₂ iv: O₂ flow rates on fuel electrode during I-V
- O₂ cathode iv: O₂ flow rates on air electrode during I-V
- Fuel utilization: fuel utilization calculated based on the I-V curve

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES


