INSIGHT

"ImplementatioN in real SOFC Systems of monItoring and diaGnostic tools using signal analysis to increase tHeir lifeTime"

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Document Abstract

The document provides a literature review on approaches to the SOFC degradation modelling and lifetime prediction. A survey of the modelling efforts is supported by the self-contained summary of dominating degradation mechanisms both at the cell level and the stack level as well as the chemistry/physics behind. The state of the art methods and algorithms employed for assessing the state of health are reviewed. This task provides the background for the SOFC lifetime modelling to be carried out in WP5.

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Abbreviations

1. Introduction

The most significant barriers to broader commercialization and market deployment of solid oxide fuel cells (SOFCs) are yet insufficient durability, reliability and cost. Reliability and durability, in particular, are significantly impacted by the degradation phenomena that emerge during the SOFC operation. Namely, the operation under high temperatures poses a number of challenges, cf. [1]:

1. Scaling up the cells to larger stacks generally decreases the reliability of the real system performance. Mechanical issues seem to be prevailing and the root causes are different. For example, chemical reactions across the cell generate large thermal gradients that implicate stress in materials. Similar implications may occur due to thermal cycling during operation as well as due to fabrication errors.
2. Within the porous electrode as well as cell components many concurrent physical processes occur in parallel. They pose difficulties in SOFC modelling because the governing equations that describe the involved variables form a system of coupled, nonlinear differential and algebraic equations with many parameters not independently measurable.
3. Elevated temperatures contribute to the growth of oxide layers between the interconnect plate and the electrodes, especially the cathode. A consequence of this phenomenon is also an increase in the cell's internal resistance, due to the increased Ohmic resistance along the conductive path. Another case is chromium oxide growth on the surface of the interconnect plate.

Understanding the mechanisms that bring to the deterioration is of paramount importance for the design, operation and management of the SOFC systems. Most of the work so far has focused on detailed modelling of the multiphysics processes in each point of the structure with the aim to understand the conditions that implicate the onset and rate of degradation as well as the relationship with the reliability and life span of the SOFC. There is also a rapidly growing interest in the methods for the online state of health assessment based on available operational data. Valuable information can be extracted by additionally perturbing the SOFC system. From the obtained responses the characteristic features that can be correlated with particular degradation modes are evaluated. Thanks to the versatile characterisation techniques there is a rich body of experimental runs supported by *post mortem* analyses, which sometimes provide unambiguous information on the nature of the degradation processes that were present during the experiments.

However, identification of the degradation mechanisms is an *inverse problem*, which is known to be difficult. A range of questions are encountered in practice:

- can the degradation phenomena be clearly related to a visible and unambiguous fingerprint in terms of features?
- how to associate changes in metrics with evolving degradation processes?
- how to cope with multiple degradation mechanisms evolving at the same time. Often the onset of one degradation mode implicates the emergence of other degradation modes.

The aim of this report is to deliver a summary of the state of the art in modelling the SOFC degradation and lifetime prediction. A self-contained description of the dominating degradation mechanisms both at the cell level and the stack level and the chemistry/physics behind them is provided. Given the fact that a lot of good and relevant results have been published in the domain of PEM fuel cells and batteries, some of them will be mentioned as well.

The organisation of the document is as follows. In Section 2 some basic notions and nomenclature are outlined. In Section 3 the diversity of SOFC modelling methods (related to durability and reliability) in the context of the PHM (see section 2) functionality is outlined. Hence modelling done in various contexts with different purpose in mind is put in a common framework. Section 4 provides a comprehensive review of the most important degradation mechanisms and the most notable related modelling results. Section 5 reviews results in SOFC state of health assessment and end of life prognosis. These topics have been receiving growing attention in the recent years in many disciplines (e.g. batteries and PEM fuel cells). The report ends up with some concluding remarks.

2. Basic notions

In this section, we will first review the main terminology and notions used in the diagnostic framework. Most of the terminology is suggested by the Technical Committee T.C.6.4 Fault Detection, Supervision and Safety of Technical Processes, a branch of the *International Federation of Automatic Control*.

States and signals

Fault: An unpermitted deviation of at least one characteristic property or parameter of the system from the acceptable/usual/standard condition.

Failure: A permanent interruption of a system's ability to perform a required function under specified operating conditions.

Malfunction: An intermittent irregularity in the fulfilment of a system's desired function

Error: A deviation between a measured or computed value (of an output variable) and the true, specified or theoretically correct value.

Disturbance: An uncontrolled (usually not known or directly measurable) unknown (and) input acting on a system.

Degradation: An instance of disturbance, which eventually causes the damaging implications for the system.

Perturbation: An input acting on a system, which results in a temporary departure from the current state.

Feature/Metric[1]*:* A fault indicator, generally obtained by some transformation of available sensed process variables. In the context of analytical model-based fault detection and isolation, a feature usually represents a deviation between measurements and model-equation based computations referred to as residual.

Symptom: A change of an observable quantity from normal behaviour.

Prognostics. An algorithm that tracks and predicts the growth of a fault mode with time. Prognostic algorithms may be data-driven, model-based or a hybrid.

Remaining Useful Life (RUL): the amount of time left for which a system under consideration is usable before some corrective action is required. It can be specified in relative or absolute time units, e.g., load cycles, flight hours, minutes, etc.

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[1] Both terms are used later on in the document, yet with the same meaning.

Run-to-Failure refers to a scenario where a system has been allowed to fail and corresponding observation data are collected for later analysis.

Failure Threshold: A limit on damage level beyond which a system is not usable. Failure threshold does not necessarily indicate a complete failure of the system but a conservative estimate beyond which risk of complete failure exceeds tolerance limits.

Functions

Fault detection: Determination of the faults present in a system and the time of detection.

Fault isolation: Determination of the kind, location and time of detection of a fault. Follows fault detection.

Fault identification: Determination of the size and time-variant behaviour of a fault. Follows fault isolation.

Fault diagnosis: Determination of the kind, size, location and time of detection of a fault. Follows fault detection. Includes fault isolation and identification.

Monitoring: A continuous real-time task of determining the conditions of a physical system, by recording information, recognising and indicating anomalies in the behaviour.

Supervision: Monitoring a physical system and taking appropriate actions to maintain the operation in the case of faults.

Prognostics and health management (PHM): The process of monitoring the health of a system and predicting its remaining useful life by assessing the extent of deviation or degradation from its expected state of health in its expected usage conditions.

Models

Diagnostic model: A set of static or dynamic relations which link specific input variables - the symptoms - to specific output variables - the faults.

Analytic redundancy: Use of two or more (but not necessarily identical) ways to determine a variable, where one way uses a mathematical process model in analytic form.

System properties

Reliability: Ability of a system to perform a required function under stated conditions, within a given scope, during a given period of time.

Safety: Ability of a system not to cause danger to persons or equipment or the environment.

Durability: Ability to resist permanent change in performance over time, i.e. degradation or irreversible degradation. This phenomenon is related to ageing.

Availability: Probability that a system or equipment will operate satisfactorily and effectively at any point in time.

<u>*A note on mathematical models*</u>

A mathematical model is an abstraction of reality designed for a particular purpose. A model is boldly conditioned by its *intended application*. In the process of building the resulting model $\mathcal{M}$ depends on [2]:

- the purpose of the model $\mathcal{P}$,
- the true physical system $\mathcal{S}$ and
- the set of experiments $\mathcal{E}$ performed on the system $\mathcal{S}$.

Achieving the purpose is a key objective in model building. The quality of a model is judged by the following attributes [3]:

Purposiveness: tells whether a model satisfies its purpose;

Falseness: a model is said to be falsified if it is contradicted by data;

Plausibility: a plausible model conforms to a priori knowledge about the process;

Precision: the level of resolution of the model output at which a model is reproducible and determined with many digits;

Accuracy: accurate model results in the close reproduction of the physical quantities.

3. A context view on the modelling approaches

The main factor that affects the model selection related to the SOFC degradation and lifetime is its *intended purpose*. With respect to the purpose in a particular phase of the SOFC system life cycle, two classes of modelling approaches can be distinguished.

In the *design phase* of the system, the main aim of the mathematical models is to describe the physical processes in a way that assure high precision, plausibility and accuracy with respect to the experimental evidence. Such models can help raise understanding of the internal mechanisms in the cell, help improve the design geometry and evaluate the influence of the operating parameters on durability, reliability and optimal operation. From the experiments performed in the design phase, the important knowledge required for online health assessment is acquired.

Knowledge and models obtained in the design phase are conveyed in various implicit and explicit forms to the *operational phase*. They will be reviewed from the perspective of their purposiveness in the context of PHM functionality. The main reason to emphasize PHM is due to the fact that online health monitoring will be mandatory for maximizing operational availability and safety and hence the overall economy of the operation and maintenance. At the time being, the PHM of SOFC systems needs to undergo a substantial progress in the near future. However, a good reference can be obtained from the advances in the related areas, like PEM fuel cells and batteries research.

In Figure 1 an integrated PHM architecture (see [4] for the most general cases) is presented and supportive data sources are indicated. The system design part requires substantial off-line experimental data and models built thereupon. These models are normally very detailed, of high resolution, based on first principles. They are aimed to analyse important issues related to the conditions leading to degradation, the evolution of degradation and impact on reliability. The same data sets and models are important in devising the models for support in online processing. The main steps of PHM system are briefly reviewed in the sequel.

Data Acquisition. Collects data from available sensors on the SOFC system and other instruments. Here are also included data like EIS and THD.

Data Processing. It performs feature extraction. This procedure may require a model or algorithm, which, generally speaking, maps the records into a vector of features $\boldsymbol{\theta}$.

Detection. Basically, it performs analysis in the feature space by comparing the actual feature patterns with reference ones. Reference patterns can be structured in terms of models or be available in the data format.

Diagnosis. The onset, type and origin of fault/degradation is assessed. A model that relates degradation mechanisms and the features play a crucial role.

Prognosis. The anticipated evolution of the system condition is evaluated and the remaining useful life is estimated. Information from reliability models or other priors on hidden degradation processes can be used.

Decision Support. Accommodation actions are plotted and advice on the maintenance steps to be taken.

4. Degradation mechanisms in SOFCs and related models

The objective of this section is to provide an overview of

- the most fundamental degradation mechanisms, which have the greatest impact on the deterioration of the cell/stack performance;
- chemical and physical processes responsible for the degradation mechanisms;
- metrics that have been suggested in the literature to detect and distinguish (isolate) the evolving degradation mechanism in online operation and
- models aimed to describe the evolution of degradation mechanisms over time.

Detailed understanding of the degradation mechanisms in most of the cases represents the main purpose of the modelling reported below. Some of the models were used to refine the design, for example, geometrical parameters, validate the selection of materials and verify reliability by estimating the life span.

Thermomechanical stress

Mechanism

The high temperatures – an SOFC is subjected to – cause a challenge for the technology and the used materials. Especially, at start-up and shut-down, thermal transients may arise in the stack and endanger the structural integrity of cell components and sealing material. The occurring thermal stresses can induce cracks in the cell, the sealing and the interfaces. From this further problems are evolving and can lead to additional failure modes (see following sections). Hence, in order to warrant safe operation, numerous studies focus on the thermomechanical response of materials. Simulations are used to determine thermomechanical critical locations in the stack configuration.

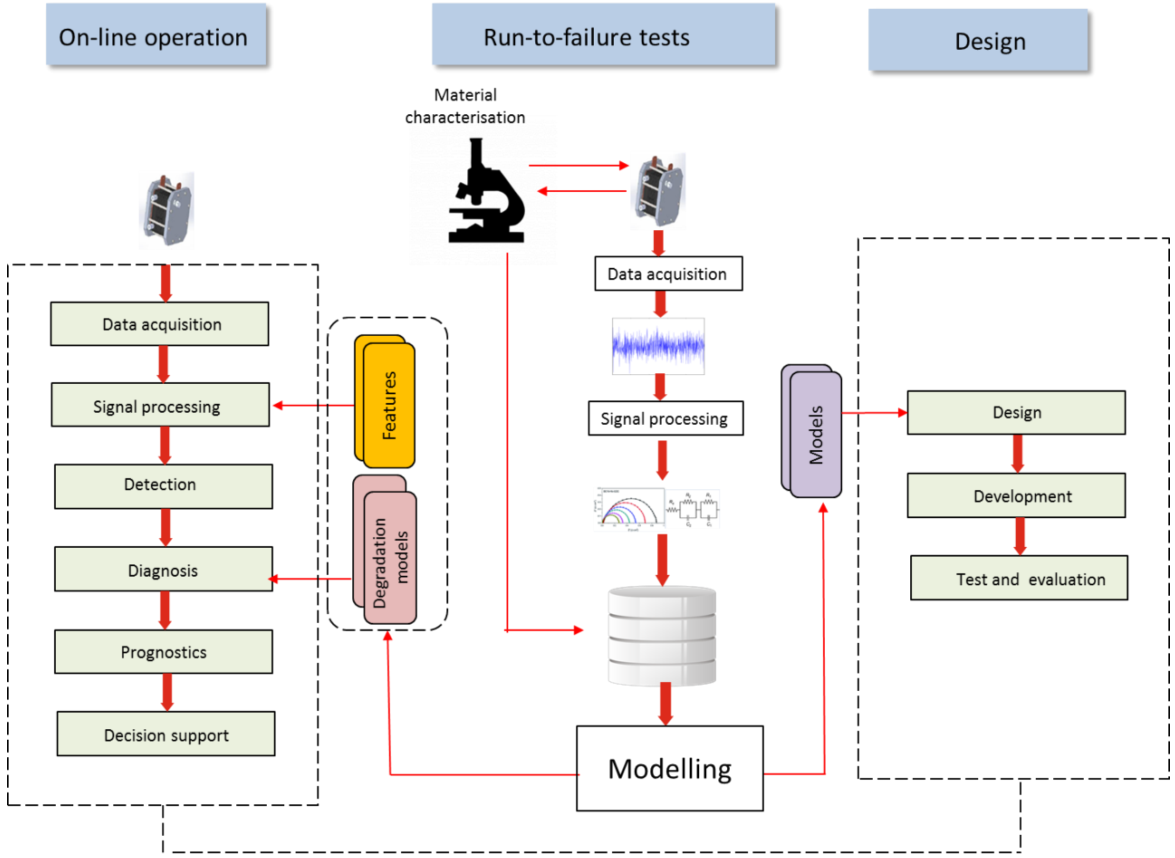

Figure 1: The PHM framework indicating that models of different purpose are needed depending on the support required in a particular PHM stage.

Causes

In practice, an SOFC-system may be frequently started and stopped when no power output is needed, so the system is subjected to temperature cycles. Rapid temperature changes introduce thermal shocks between surfaces and even in the bulk material and thus thermal expansion coefficient (TEC) mismatches between ceramic (cell, seal) and metallic material cause mechanical failure. In literature, one experimental study by Hanasaki et al. [5] is systematically investigating start-up and shut-down modes and proposes procedures to avoid rapid performance degradation of the stack by thermal cycling. But the majority of studies theoretically investigate thermal gradient distribution by means of computable fluid dynamics (CFD) and finite element method/analysis (FEM/FEA).

Modeling/metrics

The numerous thermomechanical CFD and FEM studies simulate thermal stresses either of single cells [6, 7] or of different stack configurations [8, 9, 10, 11, 12, 13, 14, 15, 16]. Advanced multi-physics models combine fluid dynamics and structural dynamic analysis to investigate the stress behaviour of cell and stack [17, 18]. Furthermore, an analytical model based on the classical beam bending theory has been published [19]. A detail literature overview of available thermomechanical models can be found in Ref. [9]

Detection

Some of the listed modelling methods additionally provide a probability of failure analysis [20, 21, 19]. In terms of detection, these analysis methods are useful to evaluate specific system configuration and their reliability. Thus, simulations allow the detection of weak points and prevention of failure modes before they occur, due to a proper cell design.
Other approaches towards failure detection make use of acoustic emission tools [22, 23]. It is a widely used non-destructive testing method for fracture analysis. In Ref [22] the damage progress was visualized via an adapted self-visualization map and furthermore, via a co-occurring cluster mining method, different damage patterns were separated.

4.2. Nickel oxidation

Description/Mechanism

Among major degradation phenomena of Ni-YSZ electrodes, the so-called redox-instability is the focus of many research efforts [24, 25, 26, 27, 28, 29, 30, 26, 31]. As it can lead to severe malfunctioning of a stack due to (i) fast electrochemical performance degradation, (ii) stress development and consequently (iii) mechanical failure, its occurrence is highly undesirable.

The underlying redox-processes cause an expansion of the cermet's microstructure and depending on the severity of the processes/cycle can either lead to small ionic network damages, cracks in the electrolyte or momentarily improved Ni/YSZ morphology followed by fast degradation [25]. In any case, re-oxidation is initiated by an overall or local increase of oxygen partial pressure. The thermodynamic limit is controlled by temperature and specific oxygen partial pressure. At high temperature and low partial pressures, O_2 gas diffusion is seen as the limiting factor while at low temperatures and high partial pressures, solid-state diffusion dominates the oxidation process. For a detailed mechanical overview, the reader may be referred to Ref. [24].

Causes

The oxidation process is heavily affected by cell geometry i.e. electrolyte supported cell (ESC) or anode supported cell (ASC), the cells' microstructure and composition, testing duration and testing conditions. Different faults may induce re-oxidation: (i) air leaks due to sealant failure or (ii) excessive fuel utilization conditions, causing high pH_2O/pH_2 partial pressures at the fuel electrode outlet (iii) emergency power shutdowns with insufficient fuel/inert gas supply or (iv) periodic air treatment of the fuel electrode as mitigation strategies for carbon deposition.

Modelling/Metrics

Besides fuel interruption, gradients in temperature and fuel composition can locally cause strong fuel depletion. Therefore CFD models evaluating temperature and fuel distributions shall be seen as preliminary modelling approaches to detect re-oxidation.

Modelling approaches specifically targeting the re-oxidation risk and the degree of oxidation of Ni/YSZ anodes [32, 33] are based on the thermodynamic equilibrium for Ni/NiO transition. In Ref. [32] the re-oxidation risk indicator is given by:

$$\mathrm{risk_{redox}} = \mathrm{p_{O2}^{eq}} - \mathrm{p_{O2}^{anode}} \tag{1}$$

The development of temperature and fuel gradients is sensitive towards fuel flow rate and flow geometry (i.e. cross-, counter, co-flow). This kind of sensitivity analysis for flow rate and two geometries were performed in [32]. Furthermore, Neidhardt [33] simulated the degree of Ni-Oxidation (DOO) in case of air-leakage and its dependency on spatial voltage and pH_2/pH_2O partial pressure distribution for the planar case. The resulting stress state in a stack after fault occurrence was moreover investigated by Laurencin et al [34]. The limiting strain for different cell geometries (ASC, ESC and ISC) was modelled by Sarantaridis et al. [35]

Detection

Primarily, electrochemical impedance measurements (EIS) are used as an in-situ tool for re-oxidation detection. As outlined in the former section, the severe re-oxidation process involves volume changes and so breaking the porous brittle ceramic cermet structure. In EIS this degradation process can be detected as a simultaneous increase of serial and polarization resistance with no corresponding change in peak frequency [36]. Similar EIS responses, however, are obtained if a delamination process occurs, as reported by Gazzarri et al [37]. Furthermore, a recent EIS study by Diethelm et al. [38] on redox-cycled cells showed similar fuel electrode responses, yet nearly no change in serial resistance [38]. In any case, such characteristic change gives a reason for a counteracting method.

In the work by Mosbæk [39], an advanced EIS setup was developed which allowed measuring EIS of each cell separately. Using this methodology allows monitoring gas distribution changes of the stack by analyzing gas conversion changes of each cell individually. Hence, this method allows to early detect possible fuel shortage, even in a stack to prevent re-oxidation. Additionally, the implementation of a total harmonic distortion tool was tested to detect fuel starvation.

4.3. Anode/Cathode delamination

Description/Mechanism

Degradation in SOFCs can occur due to detachment of the individual layers. Delamination is a phenomenon which is happening directly at the electrode-electrolyte interface and has a detrimental impact on mechanical strength and performance of SOFCs. De facto, when this failure mode occurs, the perpendicular directed open-gap between the layers blocks the charge conductive pathway and annihilates electrochemical reaction sides above and below the delamination points. Generally, this failure-mode is more pronounced at the oxygen-electrode-electrolyte interface. As Ni-YSZ anode and YSZ-electrolyte are customarily co-fired before applying the cathode material (to avoid chemical reactions), better bonding between the anode-electrolyte interfaces can be achieved.

Causes

Since SOFCs have to operate at elevated temperatures, the main cause for delamination can be ascribed to the differences in TECs of the adjacent layers. Repeated thermal cycling from room to operation temperature [5], the build-up of thermal stresses during manufacturing of the materials [40] and/or second phase formation during operation [41] can result in eventual detachment. Additionally, like investigated in Ref. [42] delamination can also be observed in SOFCs under local imbalanced operating conditions. Locally, the abnormally high pressure of O_2 can lead to detachment of the oxygen electrode and electrolyte. However, this mechanism is much more likely to arise in solid oxide electrolysers cells [43].

Detection

As outlined in section 4.3. on re-oxidation detection, a distinctive change in EIS allows identifying an occurring delamination process. In the work of Gazzari et al [37] an EIS of a delaminated SOFC and an intact cell are simulated and compared. By modelling delamination via an array of elements with the dielectric properties of air, they could identify diverse degradation mechanisms in a non-destructive way. In Ref. Gazzari and Kesler [44] extended the model.

4.4. Nickel coarsening

Description/Mechanism

The sintering process in the most commonly used fuel-electrode, namely Ni-YSZ is a well-known and highly studied degradation phenomenon [45, 46, 47, 48, 49, 50, 51]. The degradation phenomena associated with the microstructural changes of the electrodes during operation include Ni coarsening [52, 53, 54, 55, 56], Ni-Ni connectivity loss [57] as well as morphology changes [58].

Coarsening can be attributed to (i) solid diffusion processes and/or (ii) Ni surface and vapour transport. Mechanisms are well summarized in Refs. [59, 60].

Causes

The mobility of Ni-atoms can be influenced by operating parameters, i.e. mainly temperature [61, 62, 63], humidity of the fuel gas [64, 65, 66] and reduction and process parameters, thereby changing the initial microstructure [67, 29, 68, 57]. These effects result in lowering of the overall electrode performance by active surface area changes. Similarly, these effects were also reported for Ni-based catalysts by Sehested et al. [69]

Modelling/Metrics

The degradation of Ni-YSZ electrodes due to coarsening were modelled with different approaches, among them are simplified Oswald-ripening [55], the 'two-particle model' [70, 71, 72], the 'charge-capacitor model' [53, 54], a cellular automaton approach [73] and phase-field models [74, 75, 76, 77].

The two-particle model was firstly introduced by Vassen et al. [70] and then adapted in a modified way by Nakajo et al. [71] While for higher water contents the model seems to sufficiently simulate the sintering process, this seems to be not the case for Ni-YSZ exposed to lower pH_2O/pH_2 values [72].

Work by Tanasini et al [54] and Faes et al. [53] used the so-called semi-empirical charge capacitor model to connect microstructural morphology changes with cell degradation over time.

In contrast to the above-mentioned models, phase field models do not rely on empirical fitting parameters to simulate structural changes over time. Still, 3D Ni-YSZ images are used as starting point for the simulation. These structural evolution models generally assume YSZ to be immobile or to show very limited mobility. Recent work by Kennouche [78] suggests the need to modify this, in order to get more realistic structural evolution models.

Detection

To the best of our knowledge, no in-situ detection tool specifically concerning Ni-coarsening has been reported. Only EIS measurement and analysis of the Ni-charge transfer reaction resistance may be used. [64]

4.5. Interconnect oxidation

Description/Mechanism

In planar SOFC stacks, cheaper ferrite stainless steel interconnects are commonly used. This type of steel typically has a chromium content of 20-30 wt.% [79]. During SOFC operation, a chromium oxide scale forms on the steel, degrading the electrical conductivity of the interconnect-electrode interface. For practical applications, protective coatings are required especially for the oxygen side, to enhance the oxidation resistance and the electrical conductivity of the formed oxide scale and to reduce the chromium evaporation rate. It is important to ensure that the conductivity loss due to the oxide scale growth will remain within acceptable limits over the expected lifetime of an SOFC.

Causes

Recent progress on alloy and coating development for ferritic stainless steel interconnects has been reviewed by Shaigan et al. [80]. Extensive research work on the oxide scale growth has focused on the oxidation kinetics and on the ohmic resistance increase over time. Palcut et al. [79] investigated long-term oxidation behaviour of eight ferritic steels (uncoated) with 20-29 wt.% chromium at 850 ^{o}C in flowing, wet hydrogen, air and pure oxygen. The oxidation rate was found to increase with increasing oxygen partial pressure and decreasing chromium concentration. Crofer 22 APU and Crofer 22 H were reported to exhibit the lowest oxidation kinetics. Later Molin et al. from the same group conducted oxidation tests on uncoated and coated Crofer 22 APU in dry oxygen at three temperatures (800, 850, and 900 ^{o}C). By applying a dual layer coating, the oxidation rate constant at 850 ^{o}C was reduced by more than one order of magnitude. Park and Natesan [81] studied the oxidation kinetics of Cr at different temperatures and in different atmospheres. According to their data, a 20 μm thick layer of chromium oxide is expected to grow after 40,000 h at 850 ^{o}C in cathode-like atmospheres. Chen et al. [82] studied the effectiveness of Mn–Co–O spinel protective coating on 430SS. An area specific resistance (ASR) increase of approximately 0.5 Ω cm^2 was predicted after 50,000 h oxidation at 850 °C in air.

Modelling/Metrics

Due to its complex nature, previous efforts on quantitative modelling of the oxidation process were scarce and were limited to model alloy system. Hallstrom et al. [83] used the CALPHAD method and the DICTRA software to model chromium growth on pure Cr and compared with thermobalance results and TEM experiments at 625 and 700 °C in O_2. The modelling results were able to reproduce the experimental oxide thickness with good accuracy, allowing for an extension to multicomponent systems. Auinger et al. [84] investigated oxidation of two industrial steels with different chromium content (9 and 12 wt.%) oxidized for up to 120 h at 750 ^{o}C in the air by both experiments and numerical modelling. Here they have used a so-called “Applied Simulations of Thermodynamic Reactions and Interphase Diffusion - ASTRID” approach, which links the thermodynamic library

ChemAPP (GTT-Technologies, Germany) to the numerical program COMSOL (COMSOL Inc., USA). Satisfying agreements with experimental findings for the total oxidation depth and local oxide composition have been obtained. This model, however, cannot be applied to simulate the growth of an outer scale during oxidation which is common for SOFC interconnects. Gazzarri and Kesler [85] reported a two-dimensional impedance model of a working SOFC to study the effect of various degradation phenomena on the impedance spectrum for the purpose of non-invasive diagnosis. Interconnect oxidation was one of the degradation modes included. In their model, a 20 µm thick Cr_2O_3 layer was inserted between the interconnect and the cathode to simulate these phenomena. This thickness corresponds to the extrapolation of the oxidation kinetics data presented in [81] to 40,000 h, as the target lifetime of a stationary SOFC. The growth of the 20 µm thick Cr_2O_3 layer results in an increase of 0.4 Ω cm^2 in series resistance. The modelled IS also showed a slight increase in polarization resistance. They concluded that interconnect oxidation affects SOFC performance mainly by increasing the series resistance.

Detection

EIS and ASR measurements can be used to monitor the resistance increase due to IC oxidation.

4.6. Carbon deposition

Description/Mechanism

The flexibility of SOFCs to operate on different fossil fuels is a major advantage. However, the direct use of hydrocarbon fuels leads to additional degradation of the cells. For Ni-based fuel electrodes, a phenomenon known as coking can occur. This effect is also well-known from studies on metal-based catalysts, inevitable causing their deactivation [86, 87].

The principal reactions leading to the coking effect are as follows:

$$2\ \mathrm{CO}\ (\mathrm{g}) \rightarrow \mathrm{C(s)} + \mathrm{CO_2}\ (\mathrm{g}) \qquad (2)$$
$$\mathrm{C_nH_m} \rightarrow \mathrm{n\ C\ (s)} + \mathrm{m/2\ H_2} \qquad (3)$$
$$\mathrm{CO\ (g)} + \mathrm{H_2} \rightarrow \mathrm{C\ (s)} + \mathrm{H_2O\ (g)} \qquad (4)$$

The equilibrium of each reaction (2-4) depends on temperature and entropy. While Boudouard reaction (2) and reverse syngas formation (4) are favoured at a lower temperature, hydrocarbon cracking (3) seems to be the favoured reaction above 700^{o}C [88].

Furthermore, the type of formed carbon may change with temperature: while alpha-C forms at a temperature of 200-500^{o}C degrees, a polymeric form beta-C can be observed at 250-500^{o}C. The growth of whiskers and graphitic carbon takes place at for SOFC more relevant temperatures, at 300-1000^{o}C and 500-550^{o}C, respectively [89].

Depending on the reaction pathways and the form of deposited carbon, different deactivation scenarios may occur: (i) strong chemisorption of carbon as monolayer (ii) complete encapsulation of metal particles (iii) blockage of macro- and micro-gas diffusion channels (iv) growth of C-whiskers and (v) dissolution of the carbon into the metal, inducing volume expansion.

Causes

Several experimental studies in simulated synthesis gas [90, 91, 92, 93, 94] or methane [95, 96, 97, 98, 99, 100, 101, 102, 103, 104] performed thermodynamic analysis in order to identify the regions where carbon formation is favourable. However, as it was shown by Sasaki et al. [105] solid carbon can be formed even in the region where it was not predicted by equilibrium calculations.

A recent study by Kuhn and Kessler [106, 107] investigated thresholds for different operating parameters i.e. FU, S/C ratio, current density and temperature. Their thermodynamic threshold calculations were based on the assumption that carbon is deposited as solid graphite. They concluded that above 700°C thermodynamic data can be used to predict thresholds, while thresholds below 600°C strongly disagree. Similarly, He et al. [99] and Lee et al. [108] came to the conclusion that thermodynamic, physical and kinetic properties of graphite cannot solely explain the details for anode degradation. Different forms of deposited carbon are reported ranging from nanotubes and fibres to dissolved carbon [99] and furthermore whisker-type structures [104]. Yet, the major aspects determining coking are certainly (i) temperature [93] and (ii) polarization [109, 110, 111]. A recent literature overview can be found under [59].

Modelling/Metrics

In order to simulate carbon deposition, different computational studies were performed. Yurkiv et. al [112] presented an elementary kinetic model – combining (electro-)chemical, kinetic and degradation processes – in order to describe carbon deposition.
A detailed numerical study of thermodynamic equilibria for different carbon formation pathways was carried out by Schluckner [113]. Additionally, heterogeneous reaction kinetics were used to simulate elementary carbon adsorption. It was shown that carbon formation was most likely due to pure methane while CO-containing fuels seem to lead to the least carbon formation.

Moreover, a computational analysis on the effect of operating parameters i.e. H_2 molar ratio, temperature, pressure and operation voltage was performed by Ma et al [114]. The calculations revealed that low operating voltage can be helpful to inhibit carbon formation.

Detection

In-situ methods for carbon-detection are restricted. However, recently, a methodology based on an EIS method was proposed by Subotic et al. [115] to detect coking at a sufficiently early stage. The method would allow counteracting before the problem occurs.

Other in-situ detection strategies are combining EIS and additional detection techniques such as a novel microbalance sensor [97] or evolving gas analysis (EGA) sensor [116]. Although these studies allow in-situ detection, they can only detect deposition after it occurred.

4.7. Anode poisoning

Description/Mechanism

As commercially available hydrocarbon-based fuels incorporate additives and impurities, this leads to an additional degradation phenomenon of Ni-YSZ electrode due to poisoning effects.

Important constituents of natural (fossil and biogas) fuels are sulphur-containing species and are therefore of major concern. Sulphur has a detrimental effect on a metal catalyst, in particular, Ni because it strongly chemisorbs on the surface and thus hinders the catalytic activity. The adsorption causes altering of the surface energy of the metal-adsorbate system and reaction pathways of reactants to each other. The different mechanisms have been recently summarized in the literature [86, 59].

Causes

Available experimental studies mainly focus on H_2/H_2O based systems containing H_2S [117, 118, 119, 120, 121], however, newer studies are dedicated to investigating the effect in more admissible hydrocarbon-containing fuel mixtures [122, 123, 124, 125, 126, 127, 128, 129]. In any of the investigated cases, a fast performance decay can be observed, which in some cases is followed by an additional long-term degradation process [120, 121, 130].

The initial voltage drop is associated with the blockage of TPBs by adsorbed sulphur. A general agreement regarding the severity of the performance loss with respect to temperature [118, 120, 130] and concentration of sulphur species [117, 118, 119, 120, 121] exists. Lowering temperature and increasing sulphur concentration tend to enhance the phenomena as a result of higher sulphur coverage. Yet, the effect of current density is still controversial [120, 131, 130, 132, 133, 134, 135].

In hydrocarbon-based fuels the poisoning effect of sulphur is generally larger. Already at OCV conditions, an effect of sulphur can be observed [123, 122, 136, 137, 138, 139]. H_2S tends to severely alter the kinetics of the water-gas shift reaction. This impact seems to be even stronger than the impact on the electrochemical oxidation of hydrogen.

Long-term poisoning effects are less studied. Proposed explanations include (i) the formation of NiS_3 at high H_2S concentration [140], (ii) enhancement of Ni agglomeration due to dissolving sulphur in the Ni bulk structure [130, 134] (iii) fastening of Ni-diffusion away from the anode/electrolyte interface and so causing loss of percolation [132].

Modelling/Metrics

Articles for modelling sulphur-poisoning to predict the effect are quite limited. The few studies available make use of semi-empirical models [141], continuum damage modelling [142] and elementary kinetic models [143, 144, 145, 146].

Cayan et al. present a 1D model to predict degradation rates due to the adsorption of different impurities including H_2S. Diffusion and adsorption processes are considered while (electro-) chemical reactions rely on experimentally obtained parameters.

The degradation model presented by Ryan at al. [142] introduces a damaging factor to predict effects for various degradation phenomena. The factor used for sulphur poisoning is obtained by fitting experimental data from Ref. [130].

The 1D-elementary kinetic models presented by Riegraf et al. and Janandhardan et al. are based on different approaches to capture fundamental physical and (electro-)chemical processes in the composite electrode problem. The geometrical structure of a button cell is considered in both cases. A multistep reaction mechanism for sulphur formation and coverage [147] is used to simulate the poisoning effect. The models seem to be able to explain the apparently contradicting experimental trends regarding current density. Additionally, the models seem to clarify the experimental differences between two common anode structures i.e. Ni/CGO and Ni/YSZ. The lower degree of poisoning of Ni/CGO might be an effect of lower anode polarization resistance.

Furthermore, Papurello et al. [129] introduced a simple model to predict time-to-coverage depending on the sulphur concentration in anode gas feed.

Detection

Similar to degradation caused by Ni coarsening, no specific detection tool for sulphur poisoning or other impurities has been reported.

4.8. Fuel starvation

The fuel starvation condition may cause local oxidant environment (i.e. very low concentrations of H_2 and CO), leading to the oxidation of Ni metal to NiO. The Ni oxidation (i.e. reoxidation cycles) causes irreversible mechanical degradation of the electrolyte and electrode interface by the dimensional expansion of the anode support [148]. Larrain et al. [149] and Van Herle et al. [150] investigated the risk of cell reoxidation due to fuel starvation by introducing degradation submodels into a repeat-element model. In [151] Gaynor et al. conducted a numerical investigation on the prevention of the fuel starvation occurrence. It was demonstrated that the fuel starvation can occur with rapid load increase. At this aim, the authors developed and compared different methods to prevent fuel depletion within the fuel cell. Laurencin et al. [152] investigated the effects of anode re-oxidation in an SOFC caused by a direct oxidation in air (i.e., fuel shutdown) and an ionic current (i.e., fuel starvation), throughout a damage model. In [153] Angeloni et al. developed an SOFC model based on partial differential equations. The authors simulated the evolution of the most important physical variables leading to local gas starvation at both high fuel and oxidant utilization. Moreover, they affirmed that a reduction of local gas starvation could be achieved by increasing electrode porosity. In [154] Brus et al. analysed the effect of the reoxidation cycle on anode microstructure caused by fuel starvation. The microstructure changes were quantified throughout a 3D reconstruction of electrochemical, ion beam and scanning electron microscopy measurements for parameters such as the tortuosity factor, triple phase boundary density, volume fraction, connectivity and average grain size. The authors concluded that the fuel starvation might cause significant changes in microstructure morphology. In [155] da Silva and Heck demonstrated that under fuel starvation conditions nickel sulphide activity is greatly increased, indicating a strong interaction between Ni and sulphur, which can lead to severe deactivation of Ni. Esposito et al. [156] applied the Continuous Wavelet Transform (CWT) methodology to the SOFC voltage signal to detect the presence of anode re-oxidation caused by high fuel utilization (i.e. local fuel starvation).

4.9. Chromium poisoning

Description/Mechanism

One of the major degradation mechanisms in SOFCs is poisoning of the cathode by chromium species when chromium-containing alloys are used as the interconnect material [157]. At SOFC operating conditions, volatile Cr-containing species, such as CrO_3 and $CrO_2(OH)_2$, are generated over the chromia scale on the interconnect surface [158]. These gas species are transported via the gas phase or via surface diffusion to the active cathode layer, causing rapid performance deterioration in SOFCs due to the poisoning of cathodes towards the oxygen reduction reaction [159], [160], [161], [162], [163], [164].

Causes

Extensive efforts have been devoted to investigating chromium poisoning of SOFC cathodes and the mechanisms behind them. A detailed literature review on this topic was made by Jiang and Chen [165]. Representative reactions to the evaporation of Cr to form gaseous species can be formulated as follows:

Cr_2O_3 (s) + $1.5O_2$ (g) $\rightarrow$ $2CrO_3$ (g)
Cr_2O_3 (s) + $1.5O_2$ (g) + $2H_2O$ (g) $\rightarrow$ $2CrO_2(OH)_2$ (g)

The partial pressure of Cr-containing gas species depends strongly on temperature, $P(O_2)$, $P(H_2O)$, and composition of oxide scale. In general, the vaporization of Cr species in the SOFC anode environment could be neglected [158]. The Cr vaporization from Cr_2O_3 has been experimentally investigated by a number of groups and a set of Gibbs energy functions have been provided which can be used to predict the vapour pressure of Cr-containing gas species at any given condition [[166], [167], [168], [169]].

In the literature different mechanisms have been proposed on chromium poisoning of SOFC cathodes. From a thermodynamic stability point of view, Yokokawa et al. [[170]] proposed that for LSM, Cr_2O_3 deposition or formation of $CrMn_2O_4$ at the TPB is the direct cause of chromium poisoning. Badwal et al. [160] and Taniguchi et al. [[171]] proposed an electrochemical reduction mechanism, where they suggested that the deposition of Cr is mainly due to the electrochemical reduction of Cr-containing gaseous species and it is in competition with the ORR. A correlation between the polarization losses and the increase and accumulation of chromium at the LSM/YSZ interface was clearly shown In Taniguchi et al.'s studies. Konysheva et al. [159] however suggested that chromium poisoning could have two causes: 1) deposition of chromium oxide blocking oxygen diffusion and transportation to active TPBs, and 2) reaction of Cr-containing gaseous species with cathode materials forming poorly conductive phases, such as $SrCrO_4$. Jiang et al. [[163], [162]] conducted a series of studies on chromium poisoning and proposed that the deposition of Cr is a non-electrochemical process and is kinetically limited by nucleation reactions between Cr-containing gaseous species and the nucleation agents. The reactions can be written as follows [[165]]:

CrO_3 (g) + N (s) $\rightarrow$ $Cr\text{-}N\text{-}O_{(nuclei)}$ (s) + O_2 (g)
$Cr\text{-}N\text{-}O_{(nuclei)}$ (s) + CrO_3 (g) $\rightarrow$ Cr_2O_3 (s)
$Cr\text{-}N\text{-}O_{(nuclei)}$ (s) + N + CrO_3 (g) $\rightarrow$ $N\text{-}Cr\text{-}O_x$ (s)

where N represents the nucleation agent and is identified to be Mn^{2+} and SrO for the LSM and LSCF cathodes, respectively. According to the mechanism proposed by Jiang et al. [[165]], cathodes which are free of such nucleation agents would be more tolerant towards Cr deposition.

Modeling/Metrics

Cr poisoning is influenced by a number of factors including the cathode material and its composition, temperature and $P(O_2)$, cathode polarization, Cr source etc. Kulikovsky [2011Kul] developed a model for Cr poisoning of mixed conducting SOFC cathodes in a planar SOFC. The model includes an ionic current conservation equation, Ohm's law, and a rate equation for the concentration of deposited Cr_2O_3.

Detection

Cr poisoning can be easily detected in situ via EIS measurements (indicated by polarization resistance increase) or ex-situ via post-test characterization of SOFC cathodes.

5. Modelling for on-line condition assessment

Models required for condition assessment are largely available in the form of qualitative rules based on metrics derived from experimental evidence. Metrics are extracted from polarisation curves, EIS curves, THD characteristics, by parameter estimation of the stack model. All these metrics are strictly linked to the operational functioning points of the system and can be considered as lumped parameters representative of the SoH. It is worth remarking that characteristic quantities are fundamental to evaluate the state of the degradation processes causing loss of cell performances.

5.1. Evaluation of the polarisation curve

The durability of SOFCs is significantly affected by several degradation mechanisms, which reduce cell performance during the time and can lead to failures in the stack. Methods to directly observe degradation phenomena and measure their behaviour over time are difficult to implement. Usually, indirect SoH indicators, related to the decay of the voltage over time and coupled with temperature and current density are adopted [172]. Indeed the effect of operating parameters, such as temperature, voltage and current density has been studied in the literature.

In [173] Offer and Brandon studied the effect of experimental temperature and current density upon carbon deposition degradation mechanism, showing that, under not extreme current density values, carbon deposition doesn't affect seriously the electrochemical performances of the anode. In [174] Nakajo et al. investigated the distribution and the evolution of the degradation under practical operating conditions by means of VI characterisations performed at fixed operating times, underlining that these underestimate the severity of the degradation due to temperature effects. In [175] de Haart et al. studied the degradation behaviour over 3000 h functioning of several stacks operated at different current densities and the effect of chromium poisoning. In particular, they affirmed that degradation evolution is highly affected by the fuel utilization. In [176] Zaccaria et al. developed a simplified real-time model of degradation relating the voltage degradation rate per 1000 h of operation to current density, fuel utilization and temperature, by means of the increment in the ohmic resistance. In [177] Yan et al. investigated the degradation of the SOFC for more than 750 h under a fixed current density in order to evaluate the behaviour of the cells and detrimental mechanisms of sealing, contact resistance and oxidation of metal interconnect which might lead the cell to performance losses. Post-test examination ascribed 1/3 of degradation to the *ASR* increasing of the LCN ($LaCo_{0.6}Ni_{0.4}O_{3-\delta}$) contact material, 1/3 to the stainless steel interconnect oxidation and 1/3 to the leakage of the stack.

5.2. EIS modelling

Electrochemical Impedance Spectroscopy (EIS) is a useful technique for the analysis of fuel cells, which provides a wealth of information about the system analysed. It is a non-destructive tool extremely useful to give an insight of the SoH of the cell and to evaluate how a degradation process could affect the overall performance losses [178]. Thus, it is fundamental to link degradation processes to the EIS spectra, in order to individuate the SoH metrics for diagnostic tools. An overview can be found in [179], where Huang et al. investigated over 150 journal papers with respect to AC impedance modelling in SOFC aiming at SOFC diagnosis. Correlated to the EIS is the modelling approach of the Equivalent Circuit Model (ECM), in order to interpret the data for the characterization of the system. These models are based on experimental data to estimate the parameters that describe adequately, according to a non-linear fitting, the behaviour of the system, in order to test it in different conditions and under degradation mechanisms. Elements used for the impedance modelling are clearly described in [180], where Khan and Rizvi proposed ECMs for different kinds of SOFC cathode materials. In [181] Hofmann and Panopoulos developed a mathematical model for planar SOFC to simulate steady-state performance characteristics and in particular to simulate EIS spectrum. The model was applied in a detailed parametric analysis of the losses in order to deconvolute the impedance spectrum, by relating each main transport process to an impedance arc. Parametric analysis of EIS by varying characteristic parameters such as porosity and tortuosity (strictly correlated to some degradation mechanisms) were performed. Similarly, in [182], Zhu et al. developed a modelling study aiming at explaining the influences of detailed surface chemistry within SOFC composite anode structures on EIS. By exploiting a 6-elements ECM based on a physical model, they proposed qualitative trends of frequency shifts measured on the complex impedance of SOFCs operating on hydrogen, carbon monoxide and syngas mixtures. In [183] Fadaei and Mohammadi performed a parametric study on the effects of overvoltage, inlet fuel concentration, temperature, anode thickness, inflow velocity and porosity on the impedance spectrum using physical models. Similarly, in [184] Lang et al. investigated on the electrochemical testing of the SOFC short stacks with sintered anode-supported cells and identified the nature of losses by fitting the impedance spectra to an equivalent circuit based on 5 elements, and testing the impedance spectra at different operating gases and current densities. Finally, in [185] Montinaro et al. tested an SOFC with LSCF cathode at different operating conditions (e.g. gas partial pressure, H_2S poisoning, temperature) through EIS, in order to identify the main mechanisms contributing to the polarization resistance, especially at the anode side. In particular, they presented the evolution of VI curves and Nyquist plots under different conditions of S/C ratio, H_2S poisoning, voltage and raw materials.

EIS technique is a key tool to monitor the behaviour of the polarization losses during the time, in order to try to individuate the causes of degradation happening in the system. For this purpose, Comminges et al. in [186] monitored the impedance spectra of 5-cell SOFC stack in order to analyse the evolution of ohmic and polarisation resistances during 10000 h. In Figure 2 the evolution of the Nyquist plots of two cells in time is reported. They found that stack degradation was mainly attributed to the increased ohmic resistance by means of possible interconnect corrosion, reduced effective contact areas between cells and interconnects and partial re-oxidation of the anode.

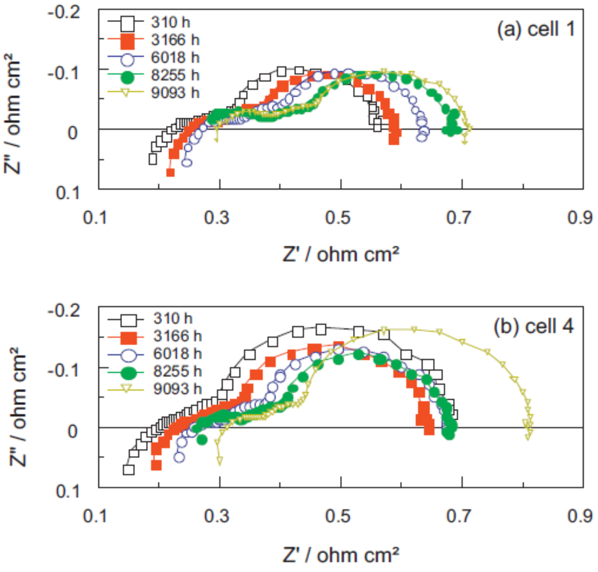

Figure 2: Selected EIS spectra of two cells recorded at 0.5 A cm−2 at 750 ◦C under simulated reformate gas after 310, 3166, 6018, 8255 and 9093 h of operation [186].

In [187] Shy et al. investigated how flow distributors could improve significantly the degree of flow uniformity of a planar SOFC and then its performances by reducing ohmic and polarization resistances. Electrochemical impedance measurements through a 5-elements equivalent circuit model were used to describe the evolution of ohmic and polarization resistances both in a cell with guide vanes and in a classic one. In this latter case, an anode-reoxidation phenomenon was detected. In [188] a finite element model was applied by Gazzari and Kesler to investigate the degradation mechanisms of an SOFC, in particular, the electrode delamination, which causes significant changes in the impedance spectrum. In this study, an impedance model was developed to simulate degradation mechanisms of anode and cathode delamination, sulphur poisoning, chromium deposition and their effects on the spectra in terms of arcs dimensions and peak frequencies. In [189] Papurello et al. investigated the performance of anode-supported SOFCs under different trace compounds. In particular, they deconvoluted the impedance spectra of the SOFC through EIS in order to identify the main losses under H_2S, HCl and other compounds poisoning. They found that H_2S poisoning minimally affects the ohmic contribution, while the polarization losses increase due to the TPB decrease. Similarly, in [190] Papurello et al. showed how H_2S poisoning doesn't affect the ohmic resistance, but it leads to an increase of the high-frequency arc of the EIS spectra due to a deactivation of Ni by the sulphur. The low-frequency arc is also affected, due to a slower gas conversion phenomenon, as shown in Figure 3.

In [191] Tanasini et al. studied the effect of particle coarsening in SOFC electrodes. In particular, they performed EIS at fixed operation times for 4 identical cell tests. In this way, they found that "the activation period" of nickel coarsening led to a reduction of the low-frequency arc, while ohmic resistance remained constant. At the same time, the high frequencies intercept shifted towards smaller values and the polarization resistance increased even if water saturation could have falsified the analysis. In [192] Kubota et al. investigated the effects of redox treatments on performances of Ni-based anode SOFC due to varying temperatures. They found that the changes in anode microstructure led to an increase of polarization resistance due to TPB length reduction, in particular, the ohmic resistance increased slightly together with cycles with an increase of the high-frequency impedance arc, as shown in Figure 4.

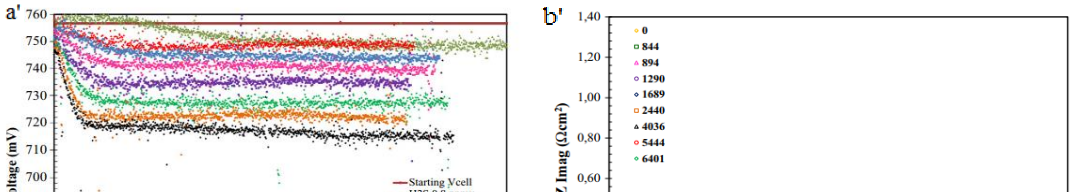

Figure 3: (a' and a'') SOLIDpower cell increasing and decreasing H_2S concentration impact on cell performance and (b' and b'') the corresponding EIS diagrams [190]

Due to the high complexity of the systems, the individual impedance-related processes cannot be easily separated by the semi-empirical equivalent circuit models evaluated by the Complex Non-Linear Least Squares (CNLS) Algorithm, due to overlapping, and because different arrangements of the circuit elements can yield the same impedance curves [193]. For these reasons, the Distribution of Relaxation Time approach has proved to be a complementary tool to identify and target the processes with the highest polarization losses in order to improve cell performance. In this approach, the system is modelled through a quasi-infinite series of resistive-capacitive elements without specific consideration about the occurring phenomena, thus eliminating the need for an a priori circuit model choice [194]. Individual processes are separated by means of their typical time constants and allow separating different polarization losses in order to develop a physical model for the ECM analysis. In [195] Kromp showed that unlike the imaginary part of the complex impedance curve, where the individual polarization processes overlap, four peaks can be distinguished clearly in the DRT, otherwise unrecognizable (see Figure 5).

Furthermore, by exploiting this approach it is possible to identify the characteristic frequencies of the individual polarization processes and a qualitative information about their contribution to the overall polarization resistance. In [196] Leonide et al. analysed anode-supported SOFC experimental data through a DRT approach. This latter allows identifying five different processes contributing to the total polarization loss that an EIS might not do. By means of a CNLS fitting, an equivalent circuit model was developed, by modelling all polarization loss processes identified. By doing so, the diffusivity of oxygen in the bulk, gas-phase diffusion in the cathode, gas diffusion in the anode substrate, charge transfer reaction and ionic transport at the anode side were identified and modelled. In [197] Weiβ et al. studied the application of the Distribution of Relaxation Times approach in the analysis of the impedance spectra of high-temperature fuel cells, in order to separate polarization losses by means of their typical time constants without any a priori knowledge about the physics of the system. This methodology, coupled with the EIS allows individuating the most appropriate ECM describing the real system. More detailed information about the DRT method can be found in [198], [199], [200].

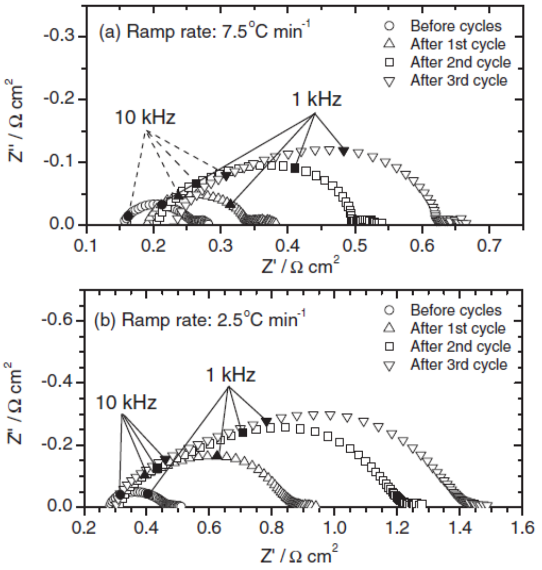

Figure 4: Impedance spectra of Ni-YSZ anode under the open circuit condition before and after thermal-redox cycles. Ramp rate of heat-treatment: a) 7.5°C min^{-1}; b) 2.5°C min^{-1}; Temperature 1000°C; Anode gas: 20% H_2O - 80% H_2; Cathode gas 100% O_2 [192]

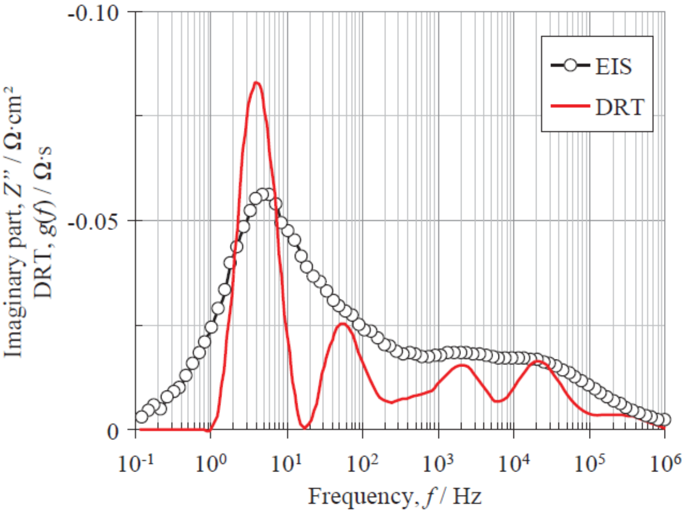

Figure 5: Imaginary part of the impedance spectrum along with the corresponding Distribution of Relaxation Times (in red) [195]

A rather comprehensive overview of the EIS based features tailored for the SOFC diagnosis is given in [201]. The authors indicate the qualitative changes occurring in the parameters of the EIS curve in a similar way as in the papers above. In spite of a wide range of documented cases, to the best of the author's knowledge, no paper addresses the SOFC monitoring based on *in situ* reasoning applied to the calculated EIS and DRT features.

5.3. Metrics based on analytical models and model-free approaches

Using analytical models in fault detection has been around for several decades and a solid body of theory has been developed and applied in many diverse applications. A good overview can be found in [202]. The most common approaches to features (metrics) extraction [203] build on (i) parameter estimation, (ii) parity relations and (iii) observers. The idea of the first group of approaches is to build a physical model of the system and associate faults with one or more parameters of the model. Hence model parameters serve as metrics. Parity relations are consistency relationships among the available process variables and are used to build metrics referred to as *residuals*. If the system is in the nominal condition. i.e. without fault, the parity relations return values near zero. A fault in the component causes certain parity relations to become different from zero. A fault is detected when at least one residual exceeds a given threshold. Fault isolation can be performed from the set of non-zero residuals. In the ideal case, each fault is associated with a specific combination of zero and non-zero residuals. In the third case, the process model is in the form of the state space model while a fault is modelled as an unknown input and/or parameter in the state model. Depending on the issues addressed there are different ways how to generate residuals [203].

The number of feature extraction approaches for SOFCS, based on the mathematical models is rather limited. One of the few contributions to the residual based diagnosis is available in [204]. The residuals are calculated by means of a lumped model of the stack and BoP components. Evaluation of the residuals is based on a fault-symptom matrix FSM presented in [205]. The approach builds on the physical model of the SOFC system. FSM was first developed by using fault-trees analysis and then improved via faults simulation. It should be stressed that a key issue in model-based diagnosis is diagnostic resolution i.e. the ability to distinguish unambiguously among different faults. This property significantly depends on selection and placements of the sensors. A profound study on optimal selection of sensors in SOFC in order to achieve the best resolution is performed in [206].

The use of a first principles model to generate residuals is described in [207]. The model is validated both in steady state as well as dynamic states. It is used to simulate faults and generate residuals and hence provide training examples for a fault classification algorithm.

A completely black-box approach based on a neural network model of the nominal SOFC behaviour has been demonstrated in [208], [209]. The authors also suggest a selection procedure for the determination of the most descriptive variables in the model [204].

Shortcomings of the analytical model-based approaches

Obtaining accurate analytical models of SOFCs behaviour from standard instrumentation is laborious and takes good quality data for validation. By relying only on the operational data, without additionally targeted system excitation, condition assessment can be complicated if only model-based. The main problem is that without excitation in the high-frequency part of the spectrum it is not possible to get good information on electrochemical processes. Models obtained from the operational records are able to describe only dominant dynamics related to the temperature and flow processes.

Model-free approaches

Few attempts to apply signal processing to analyse frequency content of the voltage have been reported. In [210] the wavelet transform (WT) is used to decompose the SOFCs voltage signals and to find out the effective feature variables that are discriminative for distinguishing the normal and abnormal operating conditions of the system. Another approach to the problem is in [172]. The authors propose a regression model to describe the three components of the long-term degradation process in a SOFC stack, i.e. smooth voltage decay over time on each cell, variability of voltage decay across the cells and random fluctuations due to noise. Both approaches are applicable provided stationary operational conditions apply.

A glimpse into the PEM domain

Unlike SOFCs, substantially more work in model-based features extraction has been performed on PEM fuel cells. Experience obtained from there can be valuable in SOFC research. For example, some of the methods like [211], [212], [213] have used parity relations. Use of other approaches like neural networks, fuzzy models and support vector machines have been reported in the literature. A comprehensive review of almost 50 papers on analytical feature extraction models in PEM can be found in [214]. A review of non-model based techniques like signal processing, statistical and AI methods is available in [215].

6. Diagnostics

The theory of fault detection and diagnosis is very well developed and a range of tools have already been used in many fields of applications [203]. Fault diagnosis is preceded by detection. In the detection step, one has to reveal eventual departure of the current system condition from the nominal condition. Change can be assessed by using statistical decision making, see [216] for an excellent overview. An application of the statistical evaluation of residuals in the area of SOFCs is demonstrated in [204].

The first step after detection is *isolation* where one has to localize the origin of the fault. If possible, this is followed by *fault identification*, which is understood as an estimation of the size of fault. To isolate the fault or degradation mechanism some sort of discrimination in the feature space is required. There is a rich arsenal of tools for fault isolation widely used in other communities. One can refer to [203] for a comprehensive overview.

There are two major classes of approaches to fault isolation. One is based on *inference methods* and the other on *classification methods*.

Classification methods come into play when a sufficient number of experimental case studies is available. There is a range of algorithms at disposal which aims to discriminate between clusters of points in the feature space that belong to the same degradation mechanism. Again, very little has been done in the SOFC domain. An approach employing support vector machine has been proposed in the context of SOFCs in [217]. Experiments show that incipient faults can be distinguished quite reliably. More specifically, the minimum size of the fault corresponds to a 5% deviation of the associated variable from its nominal value.
A classification approach to SOFC diagnosis based on fuzzy clustering is proposed in [218].

The main drawback of the classification approach is that their successful operation requires a considerable set of case examples. Also, the experiments must contain examples from all the degradation modes of interest, which takes a substantial experimental effort and cost. It seems there are more papers reporting the successful application of classification approaches in the domain of PEMFCs, see [219], [220], [221] and [222] for a nice overview.

Inference methods incorporate prior or heuristic knowledge about the features and faults. This relationship can be expressed in terms of Boolean IF-THEN-ELSE rules or their fuzzy version. In the SOFC context, there are only very few works addressing isolation. This can be done by using Boolean reasoning [204]. The fault-symptom matrix corresponds to a set of logical rules, where it is usually assumed that only one fault is acting in the system at the time. In case FSM is fully isolated also multiple faults can be unambiguously revealed.

However, knowing the root cause of the malfunction is a valuable information, yet insufficient for managing maintenance. What is important to know is that even if diagnosis helps identifying failure causes, it can only be performed after the fault occurs. Consequently, the diagnosis does not offer the possibility to anticipate when the system will break down, and hence the end of the operation, occur. In the PHM concept, this task is assigned to prognostics.

7. Prognostics

Prognostics predicts the future health evolution and estimates the remaining useful life of the system. Hence it can improve system reliability while reducing maintenance costs and downtimes. This has been a topic of interest over different disciplines, from mechanical systems [223] to electrochemical ones [222].

The prognostics take two phases: a learning phase and the prediction phase. During the learning phase, the prognostic model is learned from the system behaviour up to time t_p (see Figure 6). During the prediction phase, the prognostics gives RUL predictions of the system and determines when the critical threshold is reached. The time length between the predicted time of failure (we define it as $t_{failure}$) and the starting point of prognostics t_p is the RUL.

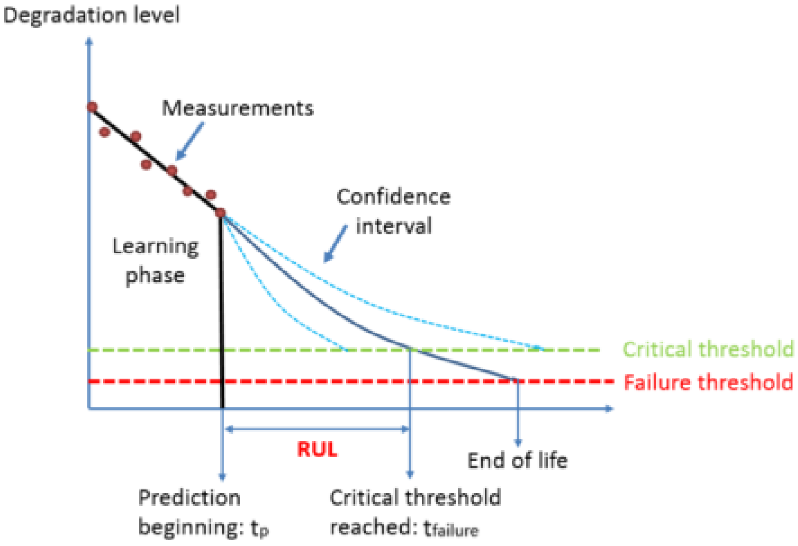

Figure 6: The prognostics process

So far, almost no attention has been devoted to the development of algorithms for on-line prediction of RUL in SOFC systems. There are only 4 papers that address the topic.

In [208] the authors adopt a neural network model in which time is used as an explicit independent variable, hence allowing to describe the decay of voltage as a function of time and operational parameters. To train the model, the data from run-to-failure tests are required. The approach is shown to predict the evolution of the stack voltage decay under implicit assumption that the degradation mechanisms present during the validation phase are similar to those in the learning stage.

The authors in [224] study the RUL prediction under two degradation mode types i.e. anode poisoning, and cathode humidification. They apply a qualitative model for the state of health and probabilistic transition between the discrete instances of the state of health. The whole study is performed in the simulation environment. From a series of simulated life-long tests they learn the parameters of the transition model by the data-driven method (Least Squares – Support Vector Machine). In the validation stage, the model shows rather a high prediction accuracy with ~20% absolute error. In this work cell voltage is utilised as the state of health indicator. Again stationary operating conditions are assumed. ~~Similar approach can be found in~~

Unfortunately, the output voltage is directly affected by operating conditions imposed on the system. Therefore, it is difficult to distinguish whether the voltage drop is caused by degradation of the fuel cells, a change in load condition, or if it is a response of the system due to the controller. The recent paper [225] seems to be the first attempt to RUL prediction of SOFC stacks that allows for rather general non-stationary operating conditions, thus rendering the need for constant operation unnecessary. The idea is to estimate the parameter ASR online, by employing a nonlinear lumped process model. The temporal evolution of the ASR is then described by another model whose parameters are identified on-line based on past records. Hereupon the RUL predictions are evaluated by means of Monte Carlo simulation. An excerpt of the algorithm performance is shown in Fig. 7.

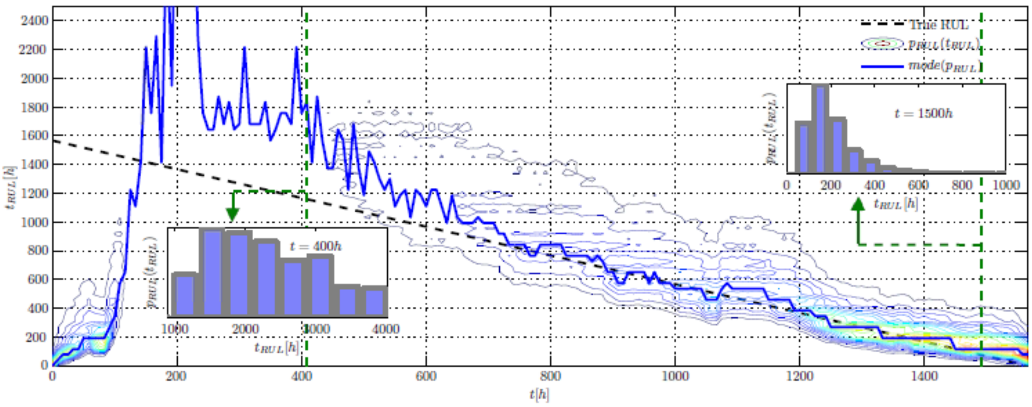

Figure 7: The evolution of RUL prediction during operation of an SOFC stack. The dashed line is true RUL. The graph indicates that e.g. at the time instance t=400 the prediction is highly uncertain since the spread of the anticipated end of life is in the interval 1000-4000h. At t=1500h the spread narrows to ~ [0-500] with most expected RUL~150h, which fits the true time remained till the end.

A glimpse on the PEM domain

However, more work has been done in the area of PEM fuel cells. For example, in [226], the review summarizes the challenges related to the PEM fuel cell prognostics and RUL predictions. They identify the importance of suitable health indicators for RUL prediction and address the definition of the end-of-life point of the cells. Works related to RUL prognosis in a PEM are aimed at modelling the temporal evolution of stack voltage, a voltage related power output, or efficiency loss due to degradation. The most common approach is to consider voltage as state of health (SoH) indicator and perform RUL upon evident drift in stack/cell voltage. Such a characterization of SoH is often justified because the voltage is directly associated with power output, and hence the efficiency of power conversion. On the other hand, the authors of [227] employ electro-chemical surface area as an indicator for SoH.

For describing the temporal evolution in SoH, the authors usually employ various empirical models to predict voltage drop in the future and to estimate RUL. The employed models range from simple ones with linear, polynomial, and exponential structures [228], to complex structures common in machine learning society [229], [230], [231], [232].

An approach that exploits the equivalent circuit model parameters of the fuel cell prognostics is given [233]. An idea using simple linear, or polynomial, models describing impedance, is presented in [234] and then the identified models are utilized to evaluate SoH and RUL prediction [235].

A more thorough review of the EIS based techniques for diagnostics and prognostics of PEM is available in [236] and [237] where over 100 papers addressing the topic are listed.

8. Conclusions

The literature review addresses modelling of the degradation mechanisms and models aimed to support the state of health monitoring in solid oxide fuel cells. A comprehensive description of main degradation phenomena, their root-causes and related models is provided, which is valuable for further monitoring design.

The main findings and achievements can be summarised as follows:

a. The modelling approaches related to the degradation phenomena are diversified with respect to the purpose assigned in the PHM context. PHM is suggested as a common framework for treating the system design (off-line part) and on-line operation (on-line part). The design part includes knowledge acquired through the experiments and on the laboratory systems and the related modelling. Those models are mainly purposed for the simulation of the degradation processes, evaluation of the reliability, optimisation of the operational parameters and optimisation of the system parameters.
b. The majority of the models dedicated to the degradation are usually high-resolution first principles models that help gain a better understanding of the underlying phenomena and hence directly contribute to the improved design of the fuel cell.
c. Relatively little is done in modelling for the context of *in situ* PHM. Although a lot of work has been conducted to gain an understanding of the correlation between failure mechanisms and features *ex situ*, there is still practically no algorithm reported, which solves the diagnostic problem *in situ*.
d. Very little work has been done in the area of diagnostics and prognostics of SOFCs, in particular.

9. Bibliography

[1] J. Irvine and P. Connor, Solid Oxide Fuell Cells: Facts and Figures: Past, Present and Future Perspectives for SOFC Technologies, Springer, 2013.

[2] K. Hangos and I. Cameron, Process Modelling and Model Analysis, 2001.

[3] T. Bohlin, Interactive system identification: prospects and pitfalls, Springer, 1991.

[4] H. M. Elattar, K. H. Elminir and A. M. Riad, "Prognostics: a literature review," *Complex & Intelligent Systems,* vol. 2, no. 2, p. 125–154, 2016.

[5] M. Hanasaki, C. Uryu, T. Daio, T. Kawabata, Y. Tachikawa, S. M. Lyth, Y. Shiratori, S. Taniguchi and K. Sasaki, "SOFC durability against standby and shutdown cycling," *J. Electrochem. Soc.,* vol. 161, no. 9, pp. F850-F860, 2014.

[6] P. Fan, G. Li, Y. Zeng and X. Zhang, "Numerical study on thermal stresses of a planar solid oxide fuel cell," *International Journal of Thermal Sciences,* vol. 77, pp. 1-10, 2014.

[7] B. Sun, R. A. Rudkin and A. Atkinson, "Effect of thermal cycling on residual stress and curvature of anode-supported SOFCs," *Fuel Cells,* vol. 9, no. 6, pp. 805-813, 2009.

[8] J. Kuebler, U. F. Vogt, D. Haberstock, J. Sfeir, A. Mai, T. Hocker, M. Roos and U. Harnisch, "Simulation and validation of thermo-mechanical stresses in planar SOFCs," *Fuel Cells,* vol. 10, no. 6, pp. 1066-1073, 2010.

[9] M. Peksen, "Numerical thermomechanical modelling of solid oxide fuel cells," *Progress in Energy and Combustion Science,* vol. 48, pp. 1-20, 2015.

[10] K. Weil and B. Koeppel, "Thermal stress analysis of the planar SOFC bonded compliant seal design," *International Journal of Hydrogen Energy,* vol. 33, no. 14, pp. 3976-3990, 2008.

[11] T. L. Jiang and M.-H. Chen, "Thermal-stress analyses of an operating planar solid oxide fuel cell with the bonded compliant seal design," *International Journal of Hydrogen Energy,* vol. 34, no. 19, pp. 8223-8234, 2009.

[12] A. Nakajo, F. Mueller, J. Brouwer, J. Van herle and D. Favrat, "Mechanical reliability and durability of SOFC stacks. Part II: Modelling of mechanical failures during ageing and cycling," *International Journal of Hydrogen Energy,* vol. 37, no. 11, pp. 9269-9286, 2012.

[13] C.-K. Lin, T.-T. Chen, Y.-P. Chyou and L.-K. Chiang, "Thermal stress analysis of a planar SOFC stack," *Journal of Power Sources,* vol. 164, no. 1, pp. 238-251, 2007.

[14] A. Selimovic, M. Kemm, T. Torisson and M. Assadi, "Steady state and transient thermal stress analysis in planar solid oxide fuel cells," *J. Power Sources,* vol. 145, no. 2, pp. 463-469, 2005.

[15] Z. Qu, P. Aravind, S. Boksteen, N. Dekker, A. Janssen, N. Woudstra and A. Verkooijen, "Three-dimensional computational fluid dynamics modeling of anode-supported planar SOFC," *International Journal of Hydrogen Energy,* vol. 36, no. 16, pp. 10209-10220, 2011.

[16] K. Recknagle, R. Williford, L. Chick, D. Rector and M. Khaleel, "Three-dimensional thermo-fluid electrochemical modeling of planar SOFC stacks," *Journal of Power Sources,* vol. 113, no. 1, pp. 109-114, 2003.

[17] P. Pianko-Oprych, T. Zinko and Z. Jaworski, "A numerical investigation of the thermal stresses of a planar solid oxide fuel cell," *Materials,* vol. 9, no. 10, 2016.

[18] M. Peksen, A. Al-Masri, L. Blum and D. Stolten, "3D transient thermomechanical behaviour of a full scale SOFC short stack," *International Journal of Hydrogen Energy,* vol. 38, no. 10, pp. 4099-4107, 2013.

[19] T. Zhang, Q. Zhu, W. L. Huang, Z. Xie and X. Xin, "Stress field and failure probability analysis for the single cell of planar solid oxide fuel cells," *J. Power Sources,* vol. 182, no. 2, pp. 540-545, 2008.

[20] L. Liu, G.-Y. Kim and A. Chandra, "Modeling of thermal stresses and lifetime prediction of planar solid oxide fuel cell under thermal cycling conditions," *Journal of Power Sources,* vol. 195, no. 8, pp. 2310-2318, 2010.

[21] A. Nakajo, Z. Wuillemin, J. Van herle and D. Favrat, "Simulation of thermal stresses in anode-supported solid oxide fuel cell stacks. Part I: Probability of failure of the cells," *Journal of Power Sources,* vol. 193, no. 1, pp. 203-215, 2009.

[22] K.-i. Fukui, K. Sato, T. Hashida, J. Mizusaki and M. Numao, "Intelligent analysis for evaluating physical degradation using acoustic emission," *ECS Transactions,* vol. 57, no. 1, pp. 571-580, 2013.

[23] W. Kong, J. Li, S. Liu and Z. Lin, "The influence of interconnect ribs on the performance of planar solid oxide fuel cell and formulae for optimal rib sizes," *Journal of Power Sources,* vol. 204, pp. 106-115, 2012.

[24] A. Faes, A. Hessler-Wyser, A. Zryd and J. Van herle, "A review of redox cycling of solid oxide fuel cells anode," *Membranes,* vol. 2, no. 3, pp. 584-664, 2012.

[25] T. T. Klemensø, C. Chung, P. H. Larsen and M. Mogensen, "The mechanism behind redox instability of anodes in high-temperature SOFCs," *J. Electrochem. Soc.,* vol. 152, no. 11, pp. A2186-A2192, 2005.

[26] M. Pihlatie, A. Kaiser and M. Mogensen, "Redox stability of SOFC: Thermal analysis of Ni-YSZ composites," *Solid State Ionics,* vol. 180, no. 17-19, pp. 1100-1112, 2009.

[27] B. Iwanschitz, J. Sfeir, A. Mai and M. Schütze, "Degradation of SOFC anodes upon redox cycling: a comparison between Ni/YSZ and Ni/CGO," *J. Electrochem. Soc.,* vol. 157, no. 2, pp. B269-B278, 2010.

[28] J. Brabandt, Q. Fang, D. Schimanke, M. Heinrich, B. E. Mai and C. Wunderlich, "System relevant redox cycling in SOFC stacks," *ECS Trans.,* vol. 35, no. 1, pp. 243-249, 2011.

[29] K. V. Manukyan, A. G. Avetisyan, C. E. Shuck, H. A. Chatilyan, S. Rouvimov, S. L. Kharatyan and A. S. Mukasyan, "Nickel oxide reduction by hydrogen: kinetics and structural transformations," *J. Phys. Chem. C,* vol. 119, no. 28, pp. 16131-16138, 2015.

[30] M. Pihlatie, "Stability of Ni-YSZ composites for solid oxide fuel cells during reduction and re-oxidation," 2010.

[31] M. Pihlatie, A. Kaiser, P. H. Larsen and M. Mogensen, "Dimensional behavior of Ni/YSZ composites during redox cycling," *J. Electrochem. Soc.,* vol. 156, no. 3, pp. B322-B329, 2009.

[32] D. Larrain, J. Van herle and D. Favrat, "Simulation of SOFC stack and repeat elements including interconnect degradation and anode reoxidation risk," *Journal of Power Sources,* vol. 161, no. 1, pp. 392-403, 2006.

[33] J. Neidhardt, "Nickel Oxidation on Solid Oxide Fuel Cells: Modeling and Simulation of Multi-Phase Electrochemistry and Multi-Scale Transport," 2013.

[34] J. Laurencin, G. Delette, F. Lefebvre-Joud and M. Dupeux, "A numerical tool to estimate SOFC mechanical degradation: Case of the planar cell configuration," *Journal of the European Ceramic Society,* vol. 28, no. 9, pp. 1857-1869, 2008.

[35] D. Sarantaridis and A. Atkinson, "Mechanical modelling of redox cycling damage in solid oxide fuel cells," *Proceedings of 7th European Fuel Cell Forum,* 2006.

[36] J. Laurencin, G. Delette, B. Morel, F. Lefebvre-Joud and M. Dupeux, "Solid oxide fuel cells damage mechanisms due to Ni-YSZ re-oxidation: case of the anode supported cell," *Journal of Power Sources,* vol. 192, no. 2, pp. 344-352, 2009.

[37] J. Gazzarri and O. Kesler, "Non-destructive delamination detection in solid oxide fuel cells," *Journal of Power Sources,* vol. 167, no. 2, pp. 430-441, 2007.

[38] S. Diethelm, V. Singh and J. Van herle, "Investigation of 2R-cell degradation under thermal cycling and redox cycling conditions by electrochemical impedance spectroscopy," *ECS Trans.,* vol. 68, no. 1, pp. 2285-2293, 2015.

[39] R. R. Mosbæk, J. Hjelm, P. V. Hendriksen and R. G. Barfod, "Solid Oxide Fuel Cell Stack Diagnostics," 2014.

[40] B. Charlas, H. L. Frandsen, K. Brodersen, P. V. Henriksen and M. Chen, "Residual stresses and strength of multilayer tape cast solid oxide fuel and electrolysis half-cells," *J. Power Sources,* vol. 288, pp. 243-252, 2015.

[41] M. J. Heneka and E. Ivers-Tiffée, "Influence of high current cycling on the performance of SOFC single cells," *J. Fuel Cell Sci. Technol.,* vol. 9, no. 1, pp. 11001-11001, 2011.

[42] K. Park, S. Yu, J. Bae, H. Kim and Y. Ko, "Fast performance degradation of SOFC caused by cathode delamination in long-term testing," *Int. J. Hydrogen Energy,* vol. 35, no. 16, pp. 8670-8677, 2010.

[43] A. V. Virkar, "Mechanism of oxygen electrode delamination in solid oxide electrolyzer cells," *Int. J. Hydrogen Energy,* vol. 35, no. 18, pp. 9527-9543, 2010.

[44] J. Gazzarri and O. Kesler, "Electrochemical AC impedance model of a solid oxide fuel cell and its application to diagnosis of multiple degradation modes," *Journal of Power Sources,* vol. 167, no. 1, pp. 100-110, 2007.

[45] Z. Fang, B. Patterson and M. Turner, "Influence of particle size distribution on coarsening," *Acta Metallurgica et Materialia,* vol. 40, no. 4, pp. 713-722, 1992.

[46] J. S. Cronin, J. R. Wilson and S. A. Barnett, "Impact of pore microstructure evolution on polarization resistance of Ni-Yttria-stabilized zirconia fuel cell anodes," *Journal of Power Sources,* vol. 196, no. 5, pp. 2640-2643, 2011.

[47] D. Kennouche, Y.-c. K. Chen-Wiegart, K. J. Yakal-Kremski, J. Wang, J. W. Gibbs, P. W. Voorhees and S. A. Barnett, "Observing the microstructural evolution of Ni-Yttria-stabilized zirconia solid oxide fuel cell anodes," *Acta Mater.,* vol. 103, pp. 204-210, 2016.

[48] M. O. Pecho, A. Mai, B. Münch, T. Hocker, J. R. Flatt and L. Holzer, "3D microstructure effects in Ni-YSZ anodes: influence of TPB lengths on the electrochemical performance," *Materials,* vol. 8, no. 10, pp. 7129-7144, 2015.

[49] Y.-H. Lee, H. Muroyama, T. Matsui and K. Eguchi, "Degradation of nickel-yttria-stabilized zirconia anode in solid oxide fuel cells under changing temperature and humidity conditions," *Journal of Power Sources,* vol. 262, pp. 451-456, 2014.

[50] G. J. Nelson, K. N. Grew, J. R. Izzo Jr., J. J. Lombardo, W. M. Harris, A. Faes, A. Hessler-Wyser, J. Van herle, S. Wang, Y. S. Chu, A. V. Virkar and W. K. Chiu, "Three-dimensional microstructural changes in the Ni-YSZ solid oxide fuel cell anode during operation," *Acta Mater.,* vol. 60, no. 8, pp. 3491-3500, 2012.

[51] S. P. Jiang, "Sintering behavior of Ni/Y2O3-ZrO2 cermet electrodes of solid oxide fuel cells," *J. Mater. Sci.,* vol. 38, p. 3775 – 3782, 2003.

[52] M. Pihlatie, A. Kaiser, M. Mogensen and M. Chen, "Electrical conductivity of Ni-YSZ composites: Degradation due to Ni particle growth," *Solid State Ionics,* vol. 189, no. 1, pp. 82-90, 2011.

[53] A. Faes, A. Hessler-Wyser, D. Presvytes, C. G. Vayenas and J. Van herle, "Nickel-zirconia anode degradation and triple phase boundary quantification from microstructural analysis," *Fuel Cells,* vol. 9, no. 6, pp. 841-851, 2009.

[54] P. Tanasini, M. Cannarozzo, P. Costamagna, A. Faes, J. Van Herle, A. Hessler-Wyser and C. Comninellis, "Experimental and theoretical investigation of degradation mechanisms by particle coarsening in SOFC electrodes," *Fuel Cells,* vol. 9, no. 5, pp. 740-752, 2009.

[55] D. Simwonis, F. Tietz and D. Stoever, "Nickel coarsening in annealed Ni/8YSZ anode substrates for solid oxide fuel cells," *Solid State Ionics,* vol. 132, no. 3-4, pp. 241-251, 2000.

[56] T. Iwata, "Characterization of Ni-YSZ Anode degradation for substrate-type solid oxide fuel cells," *J. Electrochem. Soc.,* vol. 143, no. 5, pp. 1521-1525, 1996.

[57] A. Hauch, P. S. Jørgensen, K. Brodersen and M. Mogensen, "Ni/YSZ anode - Effect of pre-treatments on cell degradation and microstructures," *J. Power Sources,* vol. 196, no. 21, pp. 8931-8941, 2011.

[58] Y. Liu and C. Jiao, "Microstructure degradation of an anode/electrolyte interface in SOFC studied by transmission electron microscopy," *Solid State Ionics,* vol. 176, no. 5-6, pp. 435-442, 2005.

[59] M. S. Khan, S.-B. Lee, R.-H. Song, J.-W. Lee, T.-H. Lim and S.-J. Park, "Fundamental mechanisms involved in the degradation of nickel-yttria stabilized zirconia (Ni-YSZ) anode during solid oxide fuel cells operation: A review," *Ceram. Int.,* vol. 42, no. 1, Part A, pp. 35-48, 2016.

[60] H. Yokokawa, H. Tu, B. Iwanschitz and A. Mai, "Fundamental mechanisms limiting solid oxide fuel cell durability," *J. Power Sources,* vol. 182, no. 2, pp. 400-412, 2008.

[61] A. Hagen, R. Barfod, P. V. Hendriksen, Y.-L. Liu and S. Ramousse, "Degradation of anode supported SOFCs as a function of temperature and current load," *Journal of The Electrochemical Society,* vol. 153, no. 6, pp. A1165-A1171, 2006.

[62] K. Thydén, "Microstructural degradation of Ni-YSZ anodes for solid oxide fuel cells," Risø-PhD-32 2008.

[63] M. Ananyev, D. Bronin, D. Osinkin, V. Eremin, R. Steinberger-Wilckens, L. de Haart and J. Mertens, "Characterization of Ni-cermet degradation phenomena I. Long term resistivity monitoring, image processing and X-ray fluorescence analysis," *J. Power Sources,* vol. 286, pp. 414-426, 2015.

[64] A. Hauch, M. Mogensen and A. Hagen, "Ni/YSZ electrode degradation studied by impedance spectroscopy - Effect of p(H2O)," *Solid State Ionics,* vol. 192, no. 1, pp. 547-551, 2011.

[65] L. Holzer, B. Iwanschitz, T. Hocker, B. Münch, M. Prestat, D. Wiedenmann, U. Vogt, P. Holtappels, J. Sfeir, A. Mai and T. Graule, "Microstructure degradation of cermet anodes for solid oxide fuel cells: Quantification of nickel grain growth in dry and in humid atmospheres," *Journal of Power Sources,* vol. 196, no. 3, pp. 1279-1294, 2011.

[66] A. Ploner, A. Hagen and A. Hauch, "Study of operating parameters for accelerated anode degradation in SOFCs," *Fuel Cells,* In Press.

[67] P. Jørgensen, S. Ebbehøj and A. Hauch, "Triple phase boundary specific pathway analysis for quantitative characterization of solid oxide cell electrode microstructure," *J. Power Sources,* vol. 279, pp. 686-693, 2015.

[68] Z. Jiao and N. Shikazono, "Quantitative study on the correlation between solid oxide fuel cell Ni-YSZ composite anode performance and reduction temperature based on three-dimensional reconstruction," *J. Electrochem. Soc.,* vol. 162, no. 6, pp. F571-F578, 2015.

[69] J. Sehested, J. A. Gelten and S. Helveg, "Sintering of nickel catalysts: Effects of time, atmosphere, temperature, nickel-carrier interactions, and dopants," *Applied Catalysis A: General,* vol. 309, no. 2, pp. 237-246, 2006.

[70] R. Vassen, D. Simwonis and D. Stöver, "Modelling of the agglomeration of Ni-particles in anodes of solid oxide fuel cells," *Journal of Materials Science,* vol. 36, no. 1, pp. 147-151, 2001.

[71] A. Nakajo, P. Tanasini, S. Diethelm, J. Van herle and D. Favrat, "Electrochemical model of solid oxide fuel cell for simulation at the stack scale II: Implementation of degradation processes," *J. Electrochem. Soc.,* vol. 158, no. 9, pp. B1102-B1118, 2011.

[72] J. G. Maillard and R. Steinberger-Wilckens, "Development of modelling and testing for analysis of degradation in solid oxide fuel cells," *ECS Transactions,* vol. 68, no. 1, pp. 1879-1887, 2015.

[73] X. Wang and A. Atkinson, "Modeling microstructure evolution of Ni cermet using a cellular automaton approach," *J. Electrochem. Soc.,* vol. 161, no. 5, pp. F605--F614, 2014.

[74] Z. Jiao and N. Shikazono, "Simulation of solid oxide fuel cell anode microstructure evolution using phase field method," *Journal of The Electrochemical Society,* vol. 160, no. 6, pp. F709-F715, 2013.

[75] H.-Y. Chen, H.-C. Yu, J. Scott Cronin, J. R. Wilson, S. A. Barnett and K. Thornton, "Simulation of coarsening in three-phase solid oxide fuel cell anodes," *J. Power Sources,* vol. 196, no. 3, pp. 1333-1337, 2011.

[76] Q. Li, L. Liang, K. Gerdes and L.-Q. Chen, "Phase-field modeling of three-phase electrode microstructures in solid oxide fuel cells," *Appl. Phys. Lett.,* vol. 101, no. 3, pp. 033909--, 2012.

[77] F. Abdeljawad, B. Völker, R. Davis, R. M. McMeeking and M. Haataja, "Connecting microstructural coarsening processes to electrochemical performance in solid oxide fuel cells: An integrated modeling approach," *Journal of Power Sources,* vol. 250, pp. 319-331, 2014.

[78] D. Kennouche, Y.-c. K. Chen-Wiegart, C. Riscoe, J. Wang and S. A. Barnett, "Combined electrochemical and X-ray tomography study of the high temperature evolution of Nickel â€“ Yttria Stabilized Zirconia solid oxide fuel cell anodes," *Journal of Power Sources,* vol. 307, pp. 604-612, 2016.

[79] M. Palcut, L. Mikkelsen, K. Neufeld, M. Chen, R. Knibbe and P. V. Hendriksen, "Corrosion stability of ferritic stainless steels for solid oxide electrolyser cell interconnects," *Corros. Sci.,* vol. 52, pp. 3309-3320 , 2010.

[80] N. Shaigan, W. W. Qu, D. G. Ivey and W. Chen, "A review of recent progress in coatings, surface modifications and alloy developments for solid oxide fuel cell ferritic stainless steel interconnects," *J. Power Scources,* vol. 195, pp. 1529-1542, 2010.

[81] J.-H. Park and K. Natesan, "Electronic transport in thermally grown Cr2O3," *Oxidation of Metals,* vol. 33.1, pp. 31-54, 1990.

[82] X. Chen and soauthors, "Protective coating on stainless steel interconnect for SOFCs: oxidation kinetics and electrical properties," *Solid State Ionics,* vol. 176.5, pp. 425-433, 2005.

[83] S. Hallstrom, M. Halvarsson, L. Hoglund, T. R. Jonsson and J. Agren, "High temperature oxidation of chromium: Kinetic modeling and microstructural investigation," *Solid State Ionics,* vol. 240, pp. 41-50, 2013.

[84] M. Auinger, R. Naraparaju, H.-J. Christ and M. Rohwerder, "Modelling high temperature oxidation in ironâ€“chromium systems: combined kinetic and thermodynamic calculation of the long-term behaviour and experimental verification," *Oxidation of Metals,* vol. 76, p. 247, 2011.

[85] J. I. Gazzarri and O. Kesler, "Short stack modeling of degradation in solid oxide fuel cells - Part II. Sensitivity and interaction analysis," *Journal of Power Sources,* vol. 176, pp. 155-166, 2008.

[86] P. Boldrin, E. Ruiz-Trejo, J. Mermelstein, J. M. Bermédez Menúndez, T. Ramárez Reina and N. P. Brandon, "Strategies for carbon and sulfur tolerant solid oxide fuel cell materials, incorporating lessons from heterogeneous catalysis," *Chem. Rev.,* vol. 116, no. 22, pp. 13633-13684, 2016.

[87] C. H. Bartholomew, "Mechanisms of catalyst deactivation," *Applied Catalysis A: General,* vol. 212, no. 1-2, pp. 17-60, 2001.

[88] K. Hou and R. Hughes, "The kinetics of methane steam reforming over a Ni(alpha)-Al2O catalyst," *Chemical Engineering Journal,* vol. 82, no. 1-3, pp. 311-328, 2001.

[89] C. Bartholomew, P. Agrawal and J. Katzer, "Sulfur poisoning of metals," *Advances in Catalysis,* vol. 31, pp. 135-242, 1982.

[90] M. Drewery, E. Kennedy, F. Alenazey, B. Dlugogorski and M. Stockenhuber, "The effect of synthesis gas composition on the performance of Ni-based solid oxide fuel cells," *Chem. Eng. Res. Des.,* vol. 101, pp. 22-26, 2015.

[91] H. Miao, G. Liu, T. Chen, C. He, J. Peng, S. Ye and W. G. Wang, "Behavior of anode-supported SOFCs under simulated syngases," *J. Solid State Electrochem.,* vol. 19, no. 3, pp. 639-646, 2015.

[92] Y. Zhang, Z. Yang and M. Wang, "Understanding on the carbon deposition on the Nickel/Yttrium-Stabilized Zirconia anode caused by the CO containing fuels," *Journal of Power Sources,* vol. 279, pp. 759-765, 2015.

[93] T. Chen, W. G. Wang, H. Miao, T. Li and C. Xu, "Evaluation of carbon deposition behavior on the nickel/yttrium-stabilized zirconia anode-supported fuel cell fueled with simulated syngas," *J. Power Sources,* vol. 196, no. 5, pp. 2461-2468, 2011.

[94] V. Alzate-Restrepo and J. M. Hill, "Carbon deposition on Ni/YSZ anodes exposed to CO/H2 feeds," *Journal of Power Sources,* vol. 195, no. 5, pp. 1344-1351, 2010.

[95] P. Fan, X. Zhang, D. Hua and G. Li, "Experimental study of the carbon deposition from CH4 onto the Ni/YSZ anode of SOFCs," *Fuel Cells,* vol. 16, no. 2, pp. 235-243, 2016.

[96] Y. Jiao, L. Zhang, W. An, W. Zhou, Y. Sha, Z. Shao, J. Bai and S.-D. Li, "Controlled deposition and utilization of carbon on Ni-YSZ anodes of SOFCs operating on dry methane," *Energy,* vol. 113, pp. 432-443, 2016.

[97] J. Millichamp, T. J. Mason, N. P. Brandon, R. J. Brown, R. C. Maher, G. Manos, T. P. Neville and D. J. Brett, "A study of carbon deposition on solid oxide fuel cell anodes using electrochemical impedance spectroscopy in combination with a high temperature crystal microbalance," *Journal of Power Sources,* vol. 235, pp. 14-19, 2013.

[98] J. Macek, B. Novosel and M. Marincek, "Ni-YSZ SOFC anodes: Minimization of carbon deposition," *J. Eur. Ceram. Soc.,* vol. 27, no. 2-3, pp. 487-491, 2007.

[99] H. He and J. M. Hill, "Carbon deposition on Ni/YSZ composites exposed to humidified methane," *Applied Catalysis A: General,* vol. 317, no. 2, pp. 284-292, 2007.

[100] N. C. Triantafyllopoulos and S. G. Neophytides, "The nature and binding strength of carbon adspecies formed during the equilibrium dissociative adsorption of CH4 on Ni-YSZ cermet catalysts," *J. Catal.,* vol. 217, no. 2, pp. 324-333, 2003.

[101] J.-H. Koh, Y.-S. Yoo, J.-W. Park and H. C. Lim, "Carbon deposition and cell performance of Ni-YSZ anode support SOFC with methane fuel," *Solid State Ionics,* vol. 149, no. 3-4, pp. 157-166, 2002.

[102] T. Takeguchi, Y. Kani, T. Yano, R. Kikuchi, K. Eguchi, K. Tsujimoto, Y. Uchida, A. Ueno, K. Omoshiki and M. Aizawa, "Study on steam reforming of CH4 and C2 hydrocarbons and carbon deposition on Ni-YSZ cermets," *J. Power Sources,* vol. 112, no. 2, pp. 588-595, 2002.

[103] A. Lanzini, C. Guerra, P. Leone, M. Santarelli, F. Smeacetto, S. Fiorilli, A. Gondolini, E. Mercadelli, A. Sanson and N. Brandon, "Influence of the microstructure on the catalytic properties of SOFC anodes under dry reforming of methane," *Materials Letters,* vol. 164, pp. 312-315, 2016.

[104] A. Lanzini, P. Leone, C. Guerra, F. Smeacetto, N. Brandon and M. Santarelli, "Durability of anode supported Solid Oxides Fuel Cells (SOFC) under direct dry-reforming of methane," *Chemical Engineering Journal,* vol. 220, pp. 254-263, 2013.

[105] K. Sasaki and Y. Teraoka, "Equilibria in Fuel Cell Gases: II. The C-H-O Ternary Diagrams," *Journal of The Electrochemical Society,* vol. 150, no. 7, pp. A885--A888, 2003.

[106] J. Kuhn and O. Kesler, "Carbon deposition thresholds on nickel-based solid oxide fuel cell anodes I. Fuel utilization," *Journal of Power Sources,* vol. 277, pp. 443-454, 2015.

[107] J. Kuhn and O. Kesler, "Carbon deposition thresholds on nickel-based solid oxide fuel cell anodes II. Steam:carbon ratio and current density," *Journal of Power Sources,* vol. 277, pp. 455-463, 2015.

[108] W. Y. Lee, J. Hanna and A. F. Ghoniem, "On the predictions of carbon deposition on the nickel anode of a SOFC and its impact on open-circuit conditions," *Journal of The Electrochemical Society,* vol. 160, no. 2, pp. F94--F105, 2013.

[109] Y. Lin, Z. Zhan, J. Liu and S. A. Barnett, "Direct operation of solid oxide fuel cells with methane fuel," *Solid State Ionics,* vol. 176, no. 23-24, pp. 1827-1835, 2005.

[110] Y. Lin, Z. Zhan and S. A. Barnett, "Improving the stability of direct-methane solid oxide fuel cells using anode barrier layers," *Journal of Power Sources,* vol. 158, no. 2, pp. 1313-1316, 2006.

[111] J. Liu and S. A. Barnett, "Operation of anode-supported solid oxide fuel cells on methane and natural gas," *Solid State Ionics,* vol. 158, no. 1-2, pp. 11-16, 2003.

[112] V. Yurkiv, "Reformate-operated SOFC anode performance and degradation considering solid carbon formation: A modeling and simulation study," *Electrochimica Acta,* vol. 143, pp. 114-128, 2014.

[113] C. Schluckner, V. Subotic, V. Lawlor and C. Hochenauer, "Carbon deposition simulation in porous SOFC anodes: A detailed numerical analysis of major carbon precursors," *Journal of Fuel Cell Science and Technology,* vol. 12, no. 5, pp. 051007--051007-12, 2015.

[114] T. Ma, M. Yan, M. Zeng, J.-l. Yuan, Q.-y. Chen, B. Sunden and Q. Wang, "Parameter study of transient carbon deposition effect on the performance of a planar solid oxide fuel cell," *Applied Energy,* vol. 152, pp. 217-228, 2015.

[115] V. Subotic, C. Schluckner, J. Strasser, V. Lawlor, J. Mathe, J. Rechberger, H. Schroettner and C. Hochenauer, "In-situ electrochemical characterization methods for industrial-sized planar solid oxide fuel cells Part I: Methodology, qualification and detection of carbon deposition," *Electrochim. Acta,* vol. 207, pp. 224-236, 2016.

[116] J. Kuhn and O. Kesler, "Method for in situ carbon deposition measurement for solid oxide fuel cells," *J. Power Sources,* vol. 246, pp. 430-437, 2014.

[117] J. F. Rasmussen and A. Hagen, "The effect of H2S on the performance of Ni-YSZ anodes in solid oxide fuel cells," *Journal of Power Sources,* vol. 191, no. 2, pp. 534-541, 2009.

[118] Y. Matsuzaki and I. Yasuda, "The poisoning effect of sulfur-containing impurity gas on a SOFC anode: Part I. Dependence on temperature, time, and impurity concentration," *Solid State Ionics,* vol. 132, no. 3-4, pp. 261-269, 2000.

[119] Z. Cheng and M. Liu, "Characterization of sulfur poisoning of Ni-YSZ anodes for solid oxide fuel cells using in situ Raman microspectroscopy," *Solid State Ionics,* vol. 178, no. 13-14, pp. 925-935, 2007.

[120] K. Sasaki, K. Susuki, A. Iyoshi, M. Uchimura, N. Imamura, H. Kusaba, Y. Teraoka, H. Fuchino, K. Tsujimoto, Y. Uchida and N. Jingo, "H_2S poisoning of solid oxide fuel cells," *Journal of the Electrochemical Society,* vol. 153, no. 11, pp. A2023-A2029, 2006.

[121] L. Yang, Z. Cheng, M. Liu and L. Wilson, "New insights into sulfur poisoning behavior of Ni-YSZ anode from long-term operation of anode-Supported SOFCs," *Energy & Environmental Science,* vol. 3, pp. 1804-1809, 2010.

[122] J. F. B. Rasmussen and A. Hagen, "The Effect of H_2S on the performance of SOFCs using methane containing fuel," *Fuel Cells,* vol. 10, no. 6, pp. 1135-1142, 2010.

[123] T. R. Smith, A. Wood and V. I. Birss, "Effect of hydrogen sulfide on the direct internal reforming of methane in solid oxide fuel cells," *Applied Catalysis A: General,* vol. 354, no. 1-2, pp. 1-7, 2009.

[124] T. Yoshizumi, S. Taniguchi, Y. Shiratori and K. Sasaki, "Sulfur poisoning of SOFCs: Voltage oscillation and Ni oxidation," *Journal of the Electrochemical Society,* vol. 159, no. 11, pp. F693-F701, 2012.

[125] A. Weber, S. Dierickx, A. Kromp and E. Ivers-Tiffee, "Sulfur poisoning of anode-supported SOFCs under reformate operation," *Fuel Cells,* vol. 13, no. 4, pp. 487-493, 2013.

[126] T. S. Li, M. Xu, C. Gao, B. Wang, X. Liu, B. Li and W. G. Wang, "Investigation into the effects of sulfur on syngas reforming inside a solid oxide fuel cell," *J. Power Sources,* vol. 258, pp. 1-4, 2014.

[127] A. Hagen, "Sulfur poisoning of the water gas shift reaction on anode supported solid oxide fuel cells," *Journal of the Electrochemical Society,* vol. 160, no. 2, pp. F111-F118, 2013.

[128] Y. Shiratori, T. Ijichi, T. Oshima and K. Sasaki, "Internal reforming SOFC running on biogas," *International Journal of Hydrogen Energy,* vol. 35, no. 15, pp. 7905-7912, 2010.

[129] D. Papurello, A. Lanzini, S. Fiorilli, F. Smeacetto, R. Singh and M. Santarelli, "Sulfur poisoning in Ni-anode solid oxide fuel cells (SOFCs): Deactivation in single cells and a stack," *Chemical Engineering Journal,* vol. 283, pp. 1224-1233, 2016.

[130] S. Zha, Z. Cheng and M. Liu, "Sulfur Poisoning and regeneration of Ni-based anodes in solid oxide fuel cells," *Journal of the Electrochemical Society,* vol. 154, no. 2, pp. B201--B206, 2007.

[131] P. Lohsoontorn, D. Brett and N. Brandon, "The effect of fuel composition and temperature on the interaction of H2S with nickel-ceria anodes for solid oxide fuel cells," *Journal of Power Sources,* vol. 183, no. 1, pp. 232-239, 2008.

[132] A. Hauch, A. Hagen, J. Hjelm and T. Ramos, "Sulfur poisoning of SOFC anodes: effect of overpotential on long-term degradation," *J. Electrochem. Soc.,* vol. 161, no. 6, pp. F734-F743, 2014.

[133] D. G. Ivey, E. Brightman and N. Brandon, "Structural modifications to nickel cermet anodes in fuel cell environments," *Journal of Power Sources,* vol. 195, no. 19, pp. 6301-6311, 2010.

[134] H. Kishimoto, T. Horita, K. Yamaji, M. E. Brito, Y.-P. Xiong and H. Yokokawa, "Sulfur poisoning on SOFC Ni anodes: Thermodynamic analyses within local equilibrium anode reaction model," *Journal of the Electrochemical Society,* vol. 157, no. 6, pp. B802-B813, 2010.

[135] E. Brightman, D. Ivey, D. Brett and N. Brandon, "The effect of current density on H2S-poisoning of nickel-based solid oxide fuel cell anodes," *Journal of Power Sources,* vol. 196, no. 17, pp. 7182-7187, 2011.

[136] A. Hagen, G. B. Johnson and P. Hjalmarsson, "Electrochemical evaluation of sulfur poisoning in a methane-fuelled solid oxide fuel cell: Effect of current density and sulfur concentration," *Journal of Power Sources,* vol. 272, pp. 776-785, 2014.

[137] A. Hagen, J. F. Rasmussen and K. Thydén, "Durability of solid oxide fuel cells using sulfur containing fuels," *Journal of Power Sources,* vol. 196, no. 17, pp. 7271-7276, 2011.

[138] M. Noponen, M. Halinen, J. Kiviaho and J. Saarinen, "Feasibility of autothermally reformed natural gas on anode supported solid oxide fuel cells," *Journal of Fuel Cell Science and Technology,* vol. 3, no. 4, pp. 438-444, 2006.

[139] J. Rostrup-Nielsen, J. Hansen, S. Helveg, N. Christiansen and A.-K. Jannasch, "Sites for catalysis and electrochemistry in solid oxide fuel cell (SOFC) anode," *Applied Physics A,* vol. 85, no. 4, pp. 427-430, 2006.

[140] J. Dong, Z. Cheng, S. Zha and M. Liu, "Identification of nickel sulfides on Ni-YSZ cermet exposed to H2 fuel containing H2S using Raman spectroscopy," *J. Power Sources,* vol. 156, no. 2, pp. 461-465, 2006.

[141] F. N. Cayan, S. R. Pakalapati, I. Celik, C. Xu and J. Zondlo, "A degradation model for solid oxide fuel cell anodes due to impurities in coal syngas: Part I Theory and validation," *Fuel Cells,* vol. 12, no. 3, pp. 464-473, 2012.

[142] E. Ryan, W. Xu, X. Sun and M. Khaleel, "A damage model for degradation in the electrodes of solid oxide fuel cells: Modeling the effects of sulfur and antimony in the anode," *Journal of Power Sources,* vol. 210, pp. 233-242, 2012.

[143] M. Riegraf, G. Schiller, R. Costa, K. A. Friedrich, A. Latz and V. Yurkiv, "Elementary kinetic numerical simulation of Ni/YSZ SOFC anode performance considering sulfur poisoning," *Journal of the Electrochemical Society,* vol. 162, no. 1, pp. F65-F75, 2015.

[144] M. Riegraf, V. Yurkiv, G. Schiller, R. Costa, A. Latz and K. A. Friedrich, "The influence of sulfur formation on performance and reforming chemistry of SOFC anodes operating on methane containing fuel," *Journal of the Electrochemical Society,* vol. 162, no. 12, pp. F1324-F1332, 2015.

[145] V. M. Janardhanan and D. S. Monder, "Sulfur poisoning of SOFCs: A model based explanation of polarization dependent extent of poisoning," *Journal of the Electrochemical Society,* vol. 161, no. 14, pp. F1427-F1436, 2014.

[146] B. V. R. S. N. Prasad and V. M. Janardhanan, "Modeling sulfur poisoning of Ni-based anodes in solid oxide fuel cells," *Journal of the Electrochemical Society,* vol. 161, no. 3, pp. F208--F213, 2014.

[147] S. Appari, V. M. Janardhanan, R. Bauri, S. Jayanti and O. Deutschmann, "A detailed kinetic model for biogas steam reforming on Ni and catalyst deactivation due to sulfur poisoning," *Applied Catalysis A: General,* vol. 471, pp. 118-125, 2014.

[148] T. H. Lee, K. Y. Park, J.T. Kim, Y. Seo, K.B. Kim, S. J. Song, B. Park, J.Y. Park, "Degradation analysis of anode-supported intermediate temperature-solid oxide fuel cells under various failure modes," *Journal of Power Sources,* vol. 276, pp. 120-132, 2015.

[149] D. Larrain, "Solid Oxide Fuel Cell Stack simulation and optimization, including experimental validation and transient behaviour," PhD thesis, Ecole Polytechnique Fédérale deLausanne (EPFL), Lausanne, CH, 2005.

[150] J. Van herle, D. Larrain, N. Autissier, Z. Wuillemin, M. Molinelli and D. Favrat, "Modeling and experimental validation of solid oxide fuel cell materials and stacks," *Journal of the European Ceramic Society,* vol. 25, p. 2627–2632.

[151] R. Gaynor, Mueller, F, F. Jabbari and J. Brouwer, "On control concepts to prevent fuel starvation in solid oxide fuel cells," *Journal of Power Sources,* vol. 180, pp. 330-342, 2008.

[152] J. Laurencin, G. Delette, B. Morel, F. Lefebvre-Joud and M. Dupeux, "Solid oxide fuel cells damage mechanisms due to Ni-YSZ re-oxidation: Case of the anode supported cell," *Journal of Power Sources,* vol. 192, pp. 344-352, 2009.

[153] M. Angeloni, P. Lisbona and R. Bove, "A PDE model for microscopic simulation of solid oxide fuel cells," *Journal of Power Sources,* vol. 201, pp. 184-195, 2012.

[154] G. Brus, K. Miyoshi, H. Iwai, M. Saito and H. Yoshida, "Change of an anode's microstructure morphology during the fuel starvation of an anode-supported solid oxide fuel cell," *International Journal of Hydrogen Energy,* vol. 40, pp. 6927-6934, 2015.

[155] A. L. da Silva and N. C. and Heck, "Thermodynamics of sulfur poisoning in solid oxide fuel cells revisited: The effect of H 2 S concentration, temperature, current density and fuel utilization," *Journal of Power Sources,* vol. 296, pp. 92-101, 2015.

[156] A. Esposito, L. Russo, C. Kändler, C. Pianese, B. Ludwig and N. Y. Steiner, "High fuel utilization in solid oxide fuel cells: Experimental characterization and data analysis with continuous wavelet transform," *Journal of Power Sources,* vol. 317, pp. 159-168, 2016.

[157] C. Sun, R. Hui and J. Roller, "Cathode materials for solid oxide fuel cells: a review," *Journal of Solid State Electrochemistry,* vol. 14, pp. 1125-1144, 2010.

[158] K. Hilpert, D. Das, M. Miller, D. H. Peck and R. Weiß, "Chromium vapor species over solid oxide fuel cell interconnect materials and their potential for degradation processes," *Journal of the Electrochemical Society,* vol. 143.11, pp. 3642-3647, 1996.

[159] E. Konysheva, H. Penkalla, E. Wessel, J. Mertens, U. Seeling, L. Singheiser and K. Hilpert, "Chromium poisoning of perovskite cathodes by the ODS alloy Cr5Fe1Y2O3 and the high chromium ferritic steel Crofer22APU," *Journal of the Electrochemical Society,* vol. 153.4, pp. A765-A773, 2006.

[160] S. P. S. Badwal, R. Deller, K. Foger, Y. Ramprakash and J. P. Zhang, "Interaction between chromia forming alloy interconnects and air electrode of solid oxide fuel cells," *Solid State Ionics,* Vols. 99.3-4, pp. 297-310, 1997.

[161] S. C. Paulson and V. I. Birss, "Chromium poisoning of LSM-YSZ SOFC cathodes I. Detailed study of the distribution of chromium species at a porous, single-phase cathode," *Journal of The Electrochemical Society ,* vol. 151.11, pp. A1961-A1968., 2004.

[162] S. P. Jiang, S. Zhang and Y. D. Zhen, "Deposition of Cr species at (La, Sr)(Co, Fe) O3 cathodes of solid oxide fuel cells," *Journal of The Electrochemical Society,* vol. 153.1, pp. A127-A134., 2006.

[163] S. P. Jiang, J. P. Zhang and K. Foger, "Deposition of chromium species at Sr-doped LaMnO3 electrodes in solid oxide fuel cells II. Effect on O2 reduction reaction," *Journal of the Electrochemical Society,* vol. 147, pp. 3195-3205, 2000.

[164] J. W. Fergus, "Effect of cathode and electrolyte transport properties on chromium poisoning in solid oxide fuel cells.," *International Journal of Hydrogen Energy ,* vol. 32.16, pp. 3664-3671, 2007.

[165] S. P. Jiang and X. Chen, "Chromium deposition and poisoning of cathodes of solid oxide fuel cells - a review," *International Journal of Hydrogen Energy,* vol. 39, pp. 505-531, 2014.

[166] B. B. Ebbinghaus, "Thermodynamics of gas phase chromium species: the chromium oxides, the chromium oxyhydroxides, and volatility calculations in waste incineration processes," *Combust Flame,* vol. 93, p. 119–137, 1993.

[167] E. J. Opila, N. S. Jacobson, D. L. Myers and E. H. Copland, "Predicting oxide stability in high-temperature water vapor," *JOM,* vol. 58, p. 22–28, 2006.

[168] C. Gindorf, L. Singheiser and K. Hilpert, "Vaporisation of chromia in humid air," *J Phys Chem Solids,* vol. 66, p. 384–387, 2005.

[169] C. Gindorf, L. Singheiser and K. Hilpert, "Chromium vaporisation from Fe, Cr base alloys used as interconnect in fuel cells," *Steel Res,* vol. 72, p. 528–533, 2001.

[170] H. Yokokawa, T. Horita, N. Sakai, K. Yamaji, M. E. Brito, Y. P. Xiong and H. Kishimoto, "Thermodynamic considerations on Cr poisoning in SOFC cathodes," *Solid State Ionics,* vol. 177.35, pp. 3193-3198, 2006.

[171] S. Taniguchi, M. Kadowaki, H. Kawamura, T. Yasuo, Y. M. Y. Akiyama and T. Saitoh, "Degradation phenomena in the cathode of a solid oxide fuel cell with an alloy separator," *Journal of power sources,* vol. 55.1, pp. 73-79, 1995.

[172] M. Guida, F. Postiglione and G. Pulcini, "A random-effects model for long-term degradation analysis of solid oxide fuel cells," *Reliability Engineering & System Safety,* vol. 140, pp. 88-98, 2015.

[173] G. J. Offer and N. P. Brandon, "The effect of current density and temperature on the degradation of nickel cermet electrodes by carbon monoxide in solid oxide fuel cells," *Chemical Engineering Science,* vol. 64(10), pp. 2291-2300, 2009.

[174] A. Nakajo, F. Mueller, J. Brouwer and D. Favrat, "Progressive activation of degradation processes in solid oxide fuel cells stacks: Part I: Lifetime extension by optimisation of the operating conditions," *Journal of Power Sources,* vol. 216, pp. 449-463, 2012.

[175] L. G. J. De Haart, J. Mougin, O. Posdziech, J. Kiviaho and N. H. Menzler, "Stack degradation in dependence of operation parameters; the real-SOFC sensitivity analysis," *Fuel Cells,* vol. 9, pp. 794-804, 2009.

[176] V. Zaccaria, D. Tucker and A. Traverso, "A distributed real-time model of degradation in a solid oxide fuel cell, part I: Model characterization," *Journal of Power Sources,* vol. 311, pp. 175-81, 2016.

[177] D. Yan, L. Liang, J. Yang, T. Zhang, J. Pu, B. Chi and J. Li, "Performance degradation and analysis of 10-cell anode-supported SOFC stack with external manifold structure," *Energy,* vol. 125, pp. 663-670, 2017.

[178] X. Z. R. Yuan, C. Song, H. Wang and J. Zhang, Electrochemical impedance spectroscopy in PEM fuel cells: fundamentals and applications., Springer Science & Business Media, 2009.

[179] Q. A. Huang, R. Hui, B. Wang and J. Zhang, "A review of AC impedance modeling and validation in SOFC diagnosis," *Electrochimica Acta,* vol. 52(28), pp. 8144-8164, 2007.

[180] S. Khan, S. A. Rizvi and S. Urooj, "Equivalent circuit modelling using electrochemical impedance spectroscopy for different materials of SOFC," in *Computing for Sustainable Global Development (INDIACom), 2016 3rd International Conference on*, 2016, March.

[181] P. Hofmann and K. D. Panopoulos, "Detailed dynamic solid oxide fuel cell modeling for electrochemical impedance spectra simulation.," *Journal of Power Sources,* vol. 195(16), pp. 5320-5339, 2010.

[182] H. Zhu, A. Kromp, A. Leonide, E. Ivers-Tiffée, O. Deutschmann and R. J. Kee, "A model-based interpretation of the influence of anode surface chemistry on solid oxide fuel cell electrochemical impedance spectra," *Journal of The Electrochemical Society,* vol. 159(7), pp. 255-266, 2012.

[183] M. Fadaei and R. Mohammadi, "A comprehensive simulation of gas concentration impedance for solid oxide fuel cell anodes.," *Energy Conversion and Management,* vol. 106, pp. 93-100, 2015.

[184] M. Lang, C. Auer, A. Eismann, P. Szabo and N. Wagner, "Investigation of solid oxide fuel cell short stacks for mobile applications by electrochemical impedance spectroscopy," *Electrochimica Acta,* vol. 53(25), pp. 7509-7513, 2008.

[185] D. Montinaro, A. R. Contino, A. Dellai and M. Rolland, "Determination of the impedance contributions in anode supported solid oxide fuel cells with (La,Sr)(Co,Fe)O3−δ cathode," *International Journal of Hydrogen Energy,* vol. 39(36), pp. 21638-21646, 2014.

[186] C. Comminges, F. Q. X. M. Zahid, N. Y. Steiner and O. Bucheli, "Monitoring the degradation of a solid oxide fuel cell stack during 10,000 h via electrochemical impedance spectroscopy," *Electrochimica Acta,* vol. 59, pp. 367-375, 2012.

[187] S. S. Shy, C. M. Huang, H. H. Li and C. H. Lee, "The impact of flow distributors on the performance of solid oxide fuel cell—Part II: Electrochemical impedance measurements," *Journal of Power Sources,* vol. 196(18), pp. 7555-7563, 2011.

[188] J. I. Gazzarri and O. and Kesler, "Electrochemical AC impedance model of a solid oxide fuel cell and its application to diagnosis of multiple degradation modes," *Journal of power Sources,* vol. 167(1), pp. 100-110, 2007.

[189] D. Papurello, A. Lanzini, D. Drago, P. Leone and M. Santarelli, "Limiting factors for planar solid oxide fuel cells under different trace compound concentrations," *Energy,* vol. 95, pp. 67-78, 2016.

[190] D. Papurello, A. Lanzini, S. Fiorilli, F. Smeacetto, R. Singh and M. Santarelli, "Sulfur poisoning in Ni-anode solid oxide fuel cells (SOFCs): Deactivation in single cells and a stack," *Chemical Engineering Journal,* vol. 283, pp. 1224-1233, 2016.

[191] P. Tanasini, M. Cannarozzo, P. Costamagna, A. Faes, J. Van Herle, A. Hessler-Wyser and C. Comninellis, "Experimental and theoretical investigation of degradation mechanisms by particle coarsening in SOFC electrodes," *Fuel Cells,* vol. 9(5), pp. 740-752, 2009.

[192] M. Kubota, T. Okanishi, H. Muroyama, T. Matsui and K. Eguchi, "Microstructural evolution of Ni–YSZ cermet anode under thermal cycles with redox treatments," *Journal of the Electrochemical Society,* vol. 162(4), pp. 380-386, 2015.

[193] H. Schichlein, A. C. Müller, M. Voigts, A. Krügel and E. Ivers-Tiffée, "Deconvolution of electrochemical impedance spectra for the identification of electrode reaction mechanisms in solid oxide fuel cells," *Journal of Applied Electrochemistry,* vol. 32(8), pp. 875-882, 2002.

[194] A. Hauch and M. B. Mogensen, "Testing of electrodes, cells, and short stacks," in *Advances in Medium and High Temperature Solid Oxide Fuel Cell Technology*, Springer International Publishing, 2017, pp. 31-76.

[195] A. Kromp, "Model-Based Interpretation of the Performance and Degradation of Reformate Fueled Solid Oxide Fuel Cells", KIT Scientific Publishing, 2013.

[196] A. Leonide, V. Sonn, A. Weber and E. vers-Tiffée, "Evaluation and modeling of the cell resistance in anode-supported solid oxide fuel cells," *Journal of The Electrochemical Society,* vol. 155(1), pp. 36-41, 2008.

[197] A. Weiß, S. Schindler, S. Galbiati, M. A. Danzer and R. Zeis, "Distribution of relaxation times analysis of high-temperature PEM fuel cell impedance spectra," *Electrochimica Acta,* vol. 230, pp. 391-398, 2017.

[198] A. Leonide, Y. Apel and E. Ivers-Tiffee, "SOFC modeling and parameter identification by means of impedance spectroscopy," *ECS Transactions,* vol. 19(20), pp. 81-109, 2009.

[199] E. Barsoukov and J. Macdonald, "Impedance Spectroscopy: Theory, Experiment and Applications," John Wiley & Sons, 2005.

[200] Y. Zhang, Y. Chen, M. Yan and F. Chen, "Reconstruction of relaxation time distribution from linear electrochemical impedance spectroscopy.," *Journal of Power Sources,* vol. 283, pp. 464-477, 2015.

[201] L. Barelli, L. Barluzzi and G. Bidini, "Diagnosis methodology and technique for solid oxide fuel cells: A review," *J. Hydrogen Energy,* pp. 5060-5074, 2013.

[202] V. Venkatasubramanian, R. Rengaswamy, Y. Kewen and S. N. Kavuri, "A review of process fault detection and diagnosis Part I: Quantitative model-based methods," *Computers and Chemical Engineering,* vol. 27, pp. 293- 311, 2003.

[203] R. Isermann, "Model-based fault-detection and diagnosis—Status and applications," *Annu. Rev. Control,* vol. 29, no. 1, p. 71–85, 2005.

[204] D. Marra, C. Pianese, P. Polverino and M. Sorrentino, "Models for Solid Oxide Fuel Cell Systems - Exploitation of Models Hierarchy for Industrial Design of Control and Diagnosis Strategies," Springer, 2016.

[205] P. Polverino, C. Pianese, M. Sorrentino and D. Marra, "Model-based development of a fault signature matrix to improve solid oxide fuel cell systems on-site diagnosis," *J. Power Sources,* vol. 280, p. 320–338, 2015.

[206] P. Polverino, M. Sorrentino and C. Pianese, "A model-based diagnostic technique to enhance faults isolability in solid oxide fuel cell systems," *Applied Energy,* vol. 204, pp. 1198-1214, 2017.

[207] A. Sorce, A. Greco, L. Magistri and P. Costamagna, "FDI oriented modeling of an experimental SOFC system, model validation and simulation of faulty states," *Applied Energy,* vol. 136, p. 894–908, 2014.

[208] D. Marra, M. Sorrentino, C. Pianese and B. Iwanschitz, "A neural network estimator of solid oxide fuel cell performance for on-field diagnostics and prognostics applications," *J Power Sources ,* vol. 241, p. 320–9, 2013.

[209] M. Sorrentino, D. Marra, C. Pianese, M. Guida, F. Postiglione, K. Wang and A. Pohjoranta, "On the use of neural networks and statistical tools for nonlinear modeling and on-field diagnosis of solid oxide fuel cell stacks," *Energy Procedia,* vol. 45, pp. 298-307, 2014.

[210] E. Pahon, N. Yousfi Steiner, S. Jemei, D. Hissel, M. Péra, W. K. and P. Mocoteguy, "Solid oxide fuel cell fault diagnosis and ageing estimation based on wavelet transform approach," *International Journal of Hydrogen Energy,* vol. 41, pp. 13678-13687, 2016.

[211] A. Niroumand, W. Merida and M. Saif, "PEM fuel cell low flow FDI," *J. Process. Control,* vol. 21, p. 602–612, 2011.

[212] L. Pellaco, P. Costamagna, A. De Giorgi, A. Greco, L. Magistri, G. Moser and A. Trucco, "Fault diagnosis in fuel cell systems using quantitative models and support vector machines," *Electron. Letters,* vol. 50, p. 824– 826, 2014.

[213] T. Escobet, D. Feroldi, S. De Lira, V. Puig, J. Quevedo, J. Riera and M. Serra, "Model-based fault diagnosis in PEM fuel cell systems," *J. Power Sources,* vol. 192, p. 216–223, 2009.

[214] R. Petrone, Zheng, D. Hissel, M. Péra, C. Pianese, M. Sorrentino, M. Becherif and N. Yousfi-Steiner, "A review on model-based diagnosis methodologies for PEMFCs," *International Journal of Hydrogen Energy,* vol. 38, no. 17, pp. 7077-7091, 2013.

[215] Z. Zheng, R. Petrone, M. Péra, D. Hissel, V. Becherif, C. Pianese, N. Yousfi Steiner and M. Sorrentino, "A review on non-model based diagnosis methodologies for PEM fuel cell stacks and systems," *International Journal of Hydrogen Energy,* vol. 38, no. 21, pp. 8914-8926, 2013,.

[216] M. Basseville and I. Nikiforov, "Detection of Abrupt Changes: Theory and Application," Prentice Hall, 1993.

[217] P. Costamagna, A. De Giorgi, L. Magistri, G. Moser, L. Pellaco and A. Trucco, "A classification approach for model-based fault," *IEEE Transactions on Energy Conversion,* pp. 676-678, 2016.

[218] K. Wang, "Ex-situ and in-situ Diagnostic Algorithms and Methods for Solid Oxide Fuel Cell System," Ph.D. Dissertation, L'Université de Franche-Comté; Besançon, France, 2012.

[219] L. A. M. Riascos, M. G. Simoes and P. E. Miyagi, "A Bayesian network fault diagnostic system for proton exchange membrane fuel cells," *J. Power Sources,* vol. 165, p. 267–278, 2007.

[220] J. Cho and B. Zhou, "Diagnosis of PEM fuel cell stack dynamic behaviors," *J. Power Sources,* vol. 177, p. 83–95, 2008.

[221] J. Kim, I. Lee, Y. Tak and B. H. Cho, "State-of-health diagnosis based on hamming neural network using output voltage pattern recognition for a PEM fuel cell," *Int. J. Hydrogen Energy,* vol. 37, p. 4280–4289, 2012.

[222] D. Hissel and M. C. Pera, "Diagnostic & health management of fuel cell systems: Issues and solutions," *Annual Reviews in Control,* vol. 42, pp. 201-211, 2016.

[223] M. Gašperin, Đ. Juričić, P. Boškoski and J. Vižintin, "Model-based prog- nostics of gear health using stochastic dynamical models," *Mechanical Systems and Signal Processing,,* vol. 25, no. 2, p. 537–548, 2011.

[224] X. Wu and Q. Ye, "Fault diagnosis and prognostic of solid oxide fuel cells," *J Power Sources,* vol. 321, p. 47–56, 2016.

[225] B. Dolenc, P. Boškoski, M. Stepančič, A. Pohjoranta and Đ. Juričić, "State of health estimation and remaining useful life prediction of solid oxide fuel cell stack," *Energy Conversion and Management,* vol. 148, p. 993–1002, 2017.

[226] M. Jouin, M. Bressel, S. Morando, R. Gouriveau, D. Hissel, M. Péra and e. al., "Estimating the end-of-life of PEM fuel cells: guidelines and metrics," *Appl Energy ,* vol. 177, p. 87–97, 2016.

[227] X. Zhang and P. Pisu, "An unscented Kalman filter based approach for the health monitoring and prognostics of a polymer electrolyte membrane fuel cell," in *Annual Conference of Prognostics and Health Management Society*, 2012.

[228] J. Kimotho, T. Meyer and W. Sextro, "PEM fuel cell prognostics using particle filter with model parameter adaptation," in *IEEE Conference on Prognostics and Health Management*, 2014.

[229] R. Silva, R. Gouriveau, S. Jemei, D. Hissel, L. Boulon, K. Agbossou and N.Y. Steiner, "Proton exchange membrane fuel cell degradation prediction based on adaptive neuro-fuzzy inference systems," *Int J Hydrogen Energy,* vol. 39, p. 11128–44, 2014.

[230] S. Morando, S. Jemei, R. Gouriveau, N. Zerhouni and D. Hissel, "Fuel cells remaining useful lifetime forecasting using echo state network," in *IEEE Vehicle Power and Propulsion Conference*, p. 1–6.

[231] K. Javed, R. Gouriveau and N. Zerhouni, "Data-driven prognostics of proton exchange membrane fuel cell stack with constraint based summation-wavelet extreme learning machine," in *6th International Conference on Fundamentals and Development of Fuel Cells*, p. 1-8, 2015.

[232] A. Hochstein, H. Ahn, Y. Leung and M. Denesuk, "Switching vector autoregressive models with higher-order regime dynamics," in *IEEE Conference on Prognostics and Health Management (PHM)*, p. 1–10, 2014.

[233] E. Lechartier, E. Laffly, M. Péra, R. Gouriveau and D. H. Zerhouni, "Proton exchange membrane fuel cell behavioral model suitable for prognostics," *Int. J. Hydrogen Energy,* vol. 40, p. 8384–97, 2015.

[234] W. Vianna, I. de Medeiros, B. Aflalo, L. Rodrigues and J. Malere, "Proton exchange membrane fuel cells (PEMFC) impedance estimation using regression analysis," in *IEEE Conference on Prognostics and Health Management (PHM)*, p. 1–8., 2014.

[235] T. Kim, H. Kim, J. Ha, K. Kim, J. Youn and J. Jung, "A degenerated equivalent circuit model and hybrid prediction for state-of-health (SOH) of PEM fuel cell," in *IEEE Conference on Prognostics and Health Management*, p. 1–7, 2014.

[236] M. Jouin, M. Bressel, S. Morando, R. Gouriveau, D. Hissel and M. Péra, "Estimating the end-of-life of PEM fuel cells: guidelines and metrics," *Appl. Energy,* vol. 177, p. 87–97, 2016.

[237] T. Sutharssan, D. Montalvao, Y. K. Chen, W.-C. Wang, C. Pisac and H. Elemara, "A review on prognostics and health monitoring of proton exchange membrane fuel cell," *Renew. Sustain. Energy Rev.,* vol. 75, pp. 440-50, 2017.