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# Advancements regarding in-operando diagnosis techniques for Solid Oxide Cells NiYSZ cermets

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**Abstract.** Solid Oxide Cell (SOC) is a promising technology, featuring versatile applications from combined heat and power generation to power-to-gas storage. Whilst their commercial readiness is poor, their advantages in terms of efficiency and environmental sustainability are undeniable. However, lifetime is an overriding concern. In the normal practice, in-operando experimental investigation of degradation is performed through volt-amperometric measurements and electrochemical impedance spectroscopy. Despite their implementation simplicity, it is hard to correlate the measurements output with the corresponding chemical/physical change at the microscopic scale. Ex-situ analysis on exhausted materials partially answers this question. Conversely, in-situ and in-operando material analysis provides insight on processes occurring during operating cycles (i.e. temperature range 650-900°C, pressure at least atmospheric, electrodes exposure to flammable gases, electric current flow across the membrane-electrodes assembly). Many techniques are available to this matter, yet their implementation usually results challenging. This review aims at presenting the advantages of in-situ and in-operando diagnosis techniques for the detection of specific degradation mechanisms affecting SOC cermets.

## INTRODUCTION

Solid Oxide Cells (SOCs) are advanced electrochemical energy conversion devices suitable for both power generation and power-to-gas storage. Beside their commercial maturity is still yet to come, their advantages in terms of efficiency and environmental sustainability in many applications are undeniable<sup>1-3</sup>. Nonetheless, to achieve commercial roll-out, SOC's lifetime is an overriding concern. Performance decay over the time of operation may be amplified by both unfavorable combination of operating conditions and wrong management procedures. Under controlled operation, SOC's have demonstrated good performances when used as fuel cells, reaching more than 40000 hours of operation in stationary systems, and more than 5000 hours in mobile devices<sup>4</sup>. Real operation of SOC's implies cyclic temperature variation (following the need to shut the SOC down periodically)<sup>5</sup>, as well as exposure to fuel gases containing impurities<sup>6</sup>. These extrinsic factors are responsible for undesired side reactions involving the SOC materials, ending in a loss of performances<sup>7</sup>. To investigate the main issues attempting the long lifetime of SOC materials, diagnosis techniques to observe specific degradation mechanisms are necessary. Research on the field is focused on methodologies and techniques to understand the causes of material degradation, looking at: i) developing technical solutions at system level to reduce performance decay<sup>8</sup>, ii) designing advanced materials<sup>9</sup>.

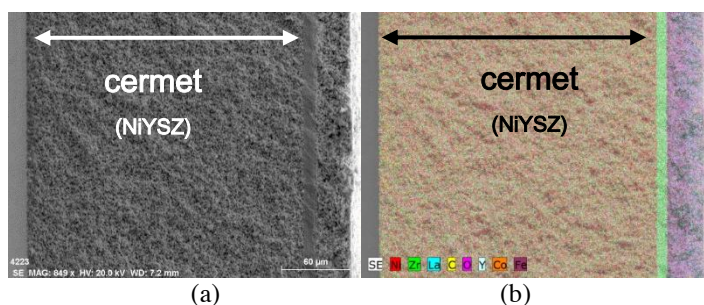
In the normal practice, in-operando experimental investigation of degradation is performed through volt-amperometric measurements (i-V), electrochemical impedance spectroscopy (EIS), gas-chromatographic analysis (GC) of outlet gases<sup>10</sup>. While these techniques are easy to be implemented, it is rather hard to correlate the measurements output with the corresponding chemical/physical transformation at the microscopic scale. This question is partially answered by ex-situ analysis on exhausted SOC materials<sup>11</sup>. However, all of them depict the status of the materials after a series of modifications occurred during operation, including the final cooling down to ambient temperature after the SOC shut down. Thus, they do not allow understanding the cause of ongoing

degradation and to correlate it to conventional electrochemical characterization (i-V, EIS) and online gas analysis (GC). Moreover, SOC materials are particularly challenging, since the real operation requires high temperature, while, as cited above, a complete cooling down has to be performed under a reducing atmosphere to prepare the material for the ex-situ characterization. This is expected to introduce additional causes of modification, concealing the effects produced by the operating conditions. To produce advancements and increase knowledge on SOC degradation, in-operando material analysis is the key-point. At best of its potentiality, this means investigating the physical and chemical status of a complete SOC during a normal operating cycle – in other word, when SOC materials are operated under the following conditions: temperatures in the range of 650-900°C, pressure at least atmospheric, exposure to flammable gases, electric current flow across the membrane-electrodes assembly (MEA). Several techniques are available to this matter, yet their implementation usually results challenging for the severe operating conditions of SOCs.

This review aims at discussing the predominant degradation mechanisms leading to SOC performance decay and classifying the most promising techniques that can be used for their detection. Therefore, the advantages of in-situ and in-operando diagnosis techniques are clearly highlighted.

## SOC Cermets

Referring to the operation as a fuel cell, the SOC anode is the electrode where the fuel oxidation takes place (also defined as the fuel electrode). It is made of two interconnected solid phases: a porous ceramic material and a metallic catalyst – what is called a “*cermet*”. The first realizes the cell structural support, hosts the catalyst particles and allows a proper gas distribution. The second promotes chemical and electrochemical reactions, as well as provides electric conductivity. Looking at commercial products, the most common catalyst is Nickel (Ni), while the supporting layer consists of Zirconia, doped with Yttrium Oxide (YSZ) to improve the cell ionic conductivity and to keep the Zirconia lattice stable against thermal transitions. Beside other materials specifically developed to make SOC lifetime longer<sup>9</sup>, Nickel Gadolinia-Doped Ceria (NiGDC)<sup>12</sup> and Nickel Scandia-Stabilized Zirconia (NiScSZ)<sup>13</sup> have similar properties to NiYSZ. Yet, among the Nickel-based cermets, NiYSZ is preferred, for it is rather inexpensive and has very good electro-catalytic activity for the hydrogen conversion at high temperature<sup>14</sup>. Figure 1 shows the cross-sectional image of a commercial MEA where the cermet is the thicker layer (anode-supported SOC, NiYSZ/8YSZ/LSCF).



**FIGURE 1.** SOC cross-section: SEM image (a), EDX mapping (b).

For the good operation of the fuel cell, the catalyst particles are finely and homogeneously distributed in the YSZ<sup>15</sup>. Moreover, the latter has to preserve a crystallographic structure that minimize the electric resistance (i.e. cubic/tetragonal lattice instead of monoclinic)<sup>11</sup>. Moreover, the spatial distribution of the two solid phases determines also the porosity, which is an essential feature concurring to the electrochemical performance of the material. Beside the homogeneous elemental distribution highlighted in Fig. 1b, from the SEM characterization a marked change in porosity is clear comparing the anode to the electrolyte (dense layer, at the anode right). SOC materials have to be stable up to high temperature typical of their operation (650-900°C), and to show a thermal expansion behavior matching the other components of the cell (sealants, interconnects).

## CERMETS DEGRADATION MECHANISMS

Commercial SOCs have shown excellent long-term stability over thousand hours of operation as fuel cells under controlled operating conditions. Yet, performance degradation over long time is something physiologic for a

material exposed to high temperature and electrochemical processes. It might be accelerated by the unfavorable combination of certain operating conditions, that is to say mainly temperature distribution and feeding gas chemical composition (temperature higher than 700°C is the main driver pushing the kinetics of any process to happen more quickly<sup>16</sup>).

Generally, degradation is defined by a loss in performance due to a single component or to the interaction of different components. At a macroscopic level, this is observable in the form of voltage loss or, in the most severe cases, material cracks and delamination. To be rigorous, concerning SOC electrodes components, degradation mechanisms are classified according to 3 main categories: i) deactivation and passivation, ii) material transport (intrinsic solid particles/impurities from the feeding gases), iii) thermomechanical mechanisms<sup>17</sup>.

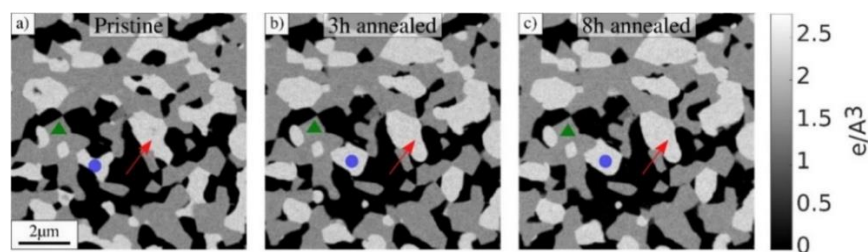
However, talking of the NiYSZ electrode (the anode, when the SOC is used as fuel cell), it is useful to correlate the degradation phenomena to the cermet phase affected. In other words, this brief overview classifies degradation mechanisms as it follows: Nickel Coarsening, Nickel poisoning, Carbon-induced degradation, Red-ox instability, (Nickel oxidation and Zirconia relaxation). Table 1 shows a synoptic classification of most studied mechanisms. Whilst each mechanism brings to peculiar changes at microscopic level, at macroscopic scale the resulting evidence is an increase in the polarization losses. Each mechanism is further commented in this section.

**TABLE 1.** Main degradation mechanisms for SOC cermets. Legend: MT: Material Transport, TMS: Thermomechanical Stress, D&P: Deactivation and Passivation.

Phase	Degradation mechanisms	Type	Microscopic change	Effect on performances
Metal Catalyst <i>Nickel</i>	Coarsening	MT	Migration and agglomeration Ni particles (sintering)	Reduction of catalytic surface Reduction of electric connectivity
	Metal dusting corrosion	MT D&P	Loss of catalyst	→ Increase in charge transfer resistance
	Carbon deposition	D&P	Coverage of catalyst surface	Reduction of catalytic surface Gas distribution losses
		MT	Pores occlusions	→ Increase in charge transfer and gas distribution resistance
Ceramic Support <i>Ytria stabilized Zirconia</i>	Poisoning	D&P	Adsorption and reaction with Nickel particles, catalysis inhibition	Reduction of catalytic surface → Increase in charge transfer and gas distribution resistance
	Nickel oxidation	TMS	Oxidation of Ni to NiO Loss of active catalyst	Reduction of catalytic surface Reduction of electric connectivity → Increase in electric resistance
				Volume increase (metal phase) → Mechanical stress, cracks Porosity decrease → Increase in gas diffusion resistance
	Red-ox cycles	TMS	Transition of tetragonal/cubic Zirconia to Monoclinic	Volume increase → Mechanical stress, cracks Decrease of conductivity

### Coarsening

Coarsening is a general term used to describe the degradation in the distribution and granulometry of the catalyst. In the “healthy” anode, Nickel particles are finely and homogeneously distributed. However, high temperature favors Nickel particles diffusion in the Zirconia lattice and their agglomeration in bigger grains. Therefore the catalyst distribution becomes “coarse”<sup>15</sup> (Fig. 2).



**FIGURE 2.** NiYSZ electrodes: progressive Nickel coarsening<sup>18</sup>

This process is called sintering and it is one of the most prominent problem leading performance decay. Because of the agglomeration of Nickel grains, the active area available for the electrochemical reactions at the triple phase boundaries (TPBs) decreases - TPBs are the spot where the electrochemical reaction occurs, thanks to the simultaneous presence of three items: the catalyst, the anode fuel gas (diffused through the pores) and oxygen anions. Due to the same reason, less Nickel particles are connected to create a path for the charge transfer, resulting in a decrease of the cell conductivity. Moreover, a change in the catalyst particle size and distribution has also a repercussion on the electrode porosity<sup>18</sup>. The process described accompanies physiological ageing of the electrode, yet it might be accelerated by certain operating conditions. For instance, non-uniform temperature distribution on the anode surface as the effect of local chemical reactions may cause hot spots that speed sintering up.

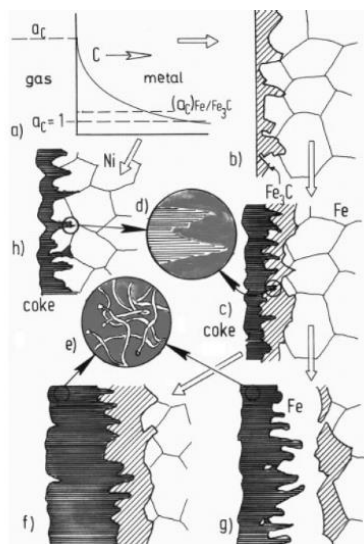
### Carbon-Induced Degradation

Carbon deposition (also referred to as coking) is one of the main dangers arising when fuels containing carbon monoxide and/or hydrocarbons (i.e. methane, light tars) are used. The chemistry of this phenomenon is complex, but it could be simplified considering the following reactions<sup>19</sup>: i) Boudouard  $2\text{CO} \rightarrow \text{C} + \text{CO}_2$ , ii) Hydrocarbon cracking  $\text{C}_n\text{H}_m \rightarrow n\text{C} + m/2\text{H}_2$  and iii) Heterogeneous water gas shift  $\text{CO} + \text{H}_2 \rightarrow \text{C} + \text{H}_2\text{O}$ .

Those reactions occur in the gas phase and lead to the formation of solid carbon, either amorphous (graphite) or in the form of nanotubes/whiskers<sup>20</sup>. Moreover, the kinetic of coking reactions is favored by the presence of the Nickel catalyst. The deposition of solid carbon particles produces several effects. First of all, for the interaction with the Nickel catalyst, solid carbon is responsible for the reduction of the catalytic activity (Nickel surface coverage). Second, the formation of bulk carbon deposit may occlude the material pores, counteracting gas diffusion through the electrode.

Both effects reduce the number of TPBs and they are measured as an increase in the electrochemical impedance at a higher level. In addition to that, pores occlusion may interfere with gas distribution, producing locally higher oxygen partial pressure. As it is further explained, this even causes re-oxidation phenomena.

Besides the inhibition of the catalytic activity, solid carbon may also nucleate inside the catalyst grain causing the so-called *metal dusting corrosion*<sup>21,22</sup>. The reaction mechanism leading to metal dusting corrosion on metal alloys (iron based), as well as on Nickel is represented in the scheme at Fig. 3. According to the notation reported in the figure, the metal dusting mechanism follows this path: a) carbon is transferred from the gas phase to the metal phase, until the metal phase is oversaturated with carbon, b) on the surface of the metal phase, carbon-metal compounds nucleate and grow, c) graphite nucleates and grows into the carbon-metal compounds, h) inward growth of the carbon-metal layer and outward disintegration under coke formation (temperature less than 600°C) / formation of a metal layer in between the carbon-metal and the graphite ones and further diffusion of carbon (temperature higher than 700°C). At steady state, the metal dusting corrosion leads to a loss of the metal catalyst.



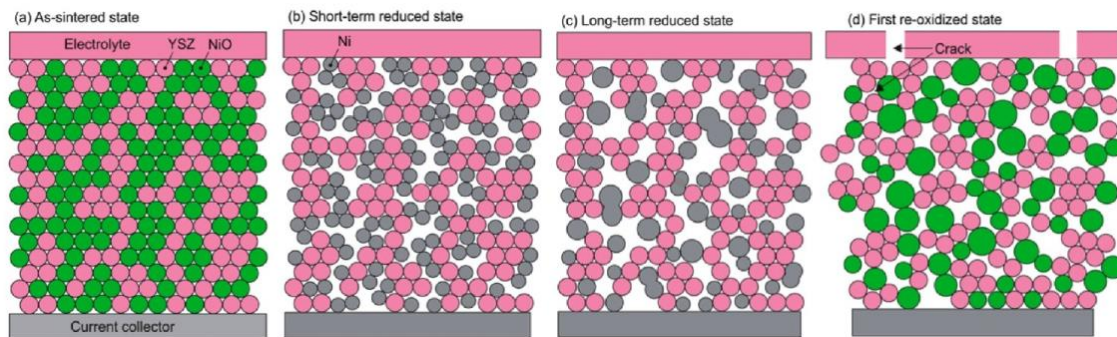
**FIGURE 3.** Metal dusting corrosion on metal alloys – schematic drawing<sup>22</sup>.

### Poisoning

Similarly to coking, other chemical species may favor passivation mechanisms. This is a well-known problem when it is up to Sulphur compounds, as Hydrogen Sulphide ( $H_2S$ ), which are abundant in many fuel gases suitable for SOCs (grid natural gas, biogas, landfill gas...). For instance,  $H_2S$  is likely to react with oxygen in the anode chamber, delivering water and realizing Sulphur. This settles onto the catalyst particle, creating bonds (permanent) so as to deactivate the catalytic activity<sup>23,24</sup>. This phenomenon is defined poisoning and it is claimed reversible to a very low extent. Otherwise, the reaction between the catalyst and Sulphur produces volatile compounds that are flushed away by the gas flow and result in a loss of catalytic mass.

### Re-Oxidation Instability

Red-oxidation is one of the main limitations of Nickel cermet electrodes. This mechanism refers to chemo-mechanical variations which may occur at the electrode at high temperature (typically for SOC in the range 650–900°C) and high oxygen partial pressure. A schematic of the cermet Re-oxidation cycle is reported in Fig. 4, based on Cassidy's and following works<sup>25</sup>. First, the cermet reduction (from NiO in Fig. 4a to Ni in Fig. 4b and 4c) increases the electrode porosity because of the associated volume change (roughly -40%vol). During re-oxidation, Nickel expands up to +66%vol. As a consequence of the volume increase, the mechanical stability of both the electrolyte and the NiYSZ electrode itself is jeopardized. The operating conditions producing higher oxygen partial pressure, enhancing this phenomenon are: high load/high fuel utilization (excess of oxidative ions flux), air leakage through seals, accidental fuel supply interruption, shut-down and start-up performed without protective gas. Re-oxidation may occur locally, creating stress gradients in the electrode. This is a precursor for severe mechanical cracks and delamination, leading to the cell irreversible failure<sup>26</sup>.



**FIGURE 4.** Schematic of reoxidation of SOC cermet electrode<sup>25</sup>

In addition to the catalyst degradation, severe thermal and oxidative conditions are dangerous also for the ceramic bone (YSZ). In state-of-the-art cermets, stabilization through Yttria doping enhance the ionic conductivity. Zirconia phase is fully stabilized in the tetragonal phase ( $t\text{-ZrO}_2$ ), which normally does not exist at temperatures lower than  $1000^\circ\text{C}$ , where the monoclinic form ( $m\text{-ZrO}_2$ ) is the most stable polymorph.  $t\text{-ZrO}_2$  has a more compact structure and, for this reason, the distance between two reticular sites is shorter if compared to  $m\text{-ZrO}_2$ <sup>27</sup>. Thereby, the energy required to displace oxygen anions is lower, enhancing the ionic conductivity. YSZ is subject to ageing, which appear as a loss of ionic conductivity during operation at high temperature. Usually, ionic conductivity worsens as the lattice structure faces relaxation. Either thermal or mechanical stresses cause the martensitic transition from tetragonal to monoclinic Zirconia, which is accompanied by a significant increase in volume<sup>11</sup>.

## DEGRADATION DETECTION: STATE OF THE ART

As Table 1 summarizes, notwithstanding different causes and effects at microscopic level, usually all of the degradation mechanisms are detected and related to polarization losses and cell impedance increase. This can be observed with in-operando measurement techniques. Then, common practice also implements ex-situ material analysis. Table 2 reports most common MEA characterization techniques, summarizing the main limitations.

**TABLE 2.** State-of-the-art experimental methods to characterize Solid Oxide Cells.

Technique	Type	Measurements	Drawbacks
Electrochemical voltammetry	In operando	Current, Voltage, Power density	Ultimate performance metric, but often chemically ambiguous
Electrochemical Impedance Spectroscopy	In operando	Electrolyte resistance, activation barriers, gas diffusion and charge transfer resistance	Chemically ambiguous and Model specific
GC	In operando	Off-gases composition	Results affected by calibration standards, equilibria completion out of the MEA
MS /GC/ TPO/TPR	Ex-situ	Adsorbates composition	Thermal alteration of adsorbates
SEM	Ex-situ	Surfaces morphology	SOC cools alter morphology, Vacuum
EDX	Ex-situ	Material elemental composition	Qualitative distribution of elements
TEM	Ex-situ	Structural defects, impurities, inner structure and stress state	Difficult sample preparation, susceptible to artefacts introduction
XRD/XAS	Ex-situ	Crystallographic and local structure, Electronic structure	Optimization of sample thickness and absorption

## Electrochemical In-operando

Then, common in-operando analytical techniques are electrochemical voltammetry (i-V curve) and electrochemical impedance spectroscopy (EIS). The first describes the sum of polarization losses as a function of current, with no highlights on specific phenomena causing performance losses. A basic interpretation of i-V curves

is based on the slope method, so that activation, ohmic and concentration losses can be quantified. The second is based on the electrical measurements on the MEA, after it is excited with a sinusoidal wave at variable frequency. High frequencies (>100 kHz) identify the pure resistance, while low frequencies detect the other contribution to the cell impedance. In particular, charge transfer resistance at the electrode-electrolyte interfaces are highlighted, as well as low dynamic processes like gas distribution (< 1-10 Hz)<sup>28</sup>. Moreover, the elaboration of EIS measurement through Relaxation Times analysis (DRT) allows a better identification of losses<sup>29</sup>, trying to find a correlation between cell impedance components and degradation causes. However, since the mathematical elaboration of experimental data is based on hypothesis concerning the SOC equivalent electric circuit, results are strongly model specific<sup>30,31</sup>.

Finally, concerning the chemical processes occurring at the cermet active site, an additional real-time information is provided by the on-line gas chromatographic (GC) analysis of off-gases. Their composition is determined by the extent of electrochemical processes, as well as by simultaneous chemical equilibrium. Therefore, a continuous sampling of off-gases is a good indicator about the actual catalyst activity. Yet, GC analysis has two limitations: first, some equilibria are completed out of the MEA (before the sampled gas enters the separation columns) and second, on-line fast gas chromatography output suffers from typical pre-calibration issues.

These kinds of characterization are widespread for a matter of simplicity regarding both the technique itself (sensors, data sampling, data analysis) and the realization of a proper experimental setup. Nonetheless, they do not allow isolating the single phenomena derating NiYSZ features over the time of operation.

## Ex-Situ

A strategy to deduce the chemistry of reactions occurring in the SOC is represented by extensive ex-situ analyses. This kind of characterization is also called “*post mortem*”, since it depicts the status of the materials at the end of its useful life –once the MEA has been cooled down to room temperature and disassembled from the test apparatus. For this purpose, multiple analytical techniques have been used. Typical ex-situ methods include:

- analysis of chemicals released by the specimen, often performed heating the sample under a controlled atmosphere (Mass spectrometry MS, GC, Temperature Programmed Oxidation or Reduction TPO/TPR)<sup>32</sup>.
- characterization of the morphology of surfaces (Scanning Electron Microscopy - SEM) and inner structure (Transmission Electron Microscopy - TEM)<sup>33</sup>. Both offer high spatial resolution and high magnifications (up to 1000 kX), but require a vacuum chamber. Moreover, the sample preparation may introduce artefacts.
- characterization of element distribution on the material, carried out by electron spectroscopy (EDX). This technique is easy to be implemented, yet it does not investigate how the elements are bonded and what is the crystal structure. Elemental mapping obtained features high surface coverage, yet results have to be assumed from a qualitative point of view rather than quantitative<sup>34</sup>.
- characterization of chemical compounds and lattice structure, by means of X-ray diffraction (XRD) and X-ray adsorption spectroscopy (XAS).

## Limitations of Current Diagnosis Techniques

Current diagnosis techniques have many limitations for the complete investigation of degradation and its causes. First, traditional electrochemical methods (i-V and EIS) report on macroscopic electrochemical behavior, but cannot identify specific reaction pathways, resulting ambiguous with regard to degradation mechanisms exposed in Table 1.

Secondly, regarding ex-situ measurements, although findings from these methods might be informative on the chemical composition (intrinsic and adsorbates), distribution and material surface/inner morphology, the conclusions drawn must acknowledge that results can be affected by chemistry occurring as the SOC cools down. This is the first cause of error and it is impossible to be overcome when ex-situ methods are implemented. Moreover, the specimens have to be transferred from the testing apparatus to the analysis chamber and this practice can introduce additional artefacts that modify the status of the material. For instance, the improper transfer may produce cracks or release the components that have been adsorbed onto the specimen. Also, some ex-situ techniques require a pre-treatment for the specimen (like metal deposition, grinding, exfoliation in thinner layer).

## DEGRADATION DETECTION: ADVANCEMENTS

### In-Situ

In order to overcome the main issues of ex-situ analysis, degradation observation and measurement have to be performed with advanced in-situ techniques. For the in-situ characterization, the sample is placed in an analysis chamber where both temperature and atmosphere are controlled. These chambers are accessible to probing signal and response detector, so that it is possible to collect measurements in real time, keeping the SOC specimen in the desired conditions, reproducing real operation. This allows investigating directly the interaction with the fuel gas and the SOC. Therefore, problems related to the specimen transfer and preparation are completely avoided. Further, measurements performed on real time on the materials can be correlated to macroscopic electrochemical measurements, enabling the correlation between the material change and the overall loss of performance.

From the literature survey, it emerges that some well-known analytical techniques can be implemented also for the in-situ characterization – as XRD and XAS. Moreover, Raman vibrational spectroscopy is very promising, since it gives real-time information on molecular composition, kinetic aspects. Both X-rays and Raman, however, investigate limited areas of the sample. In order to have a broader spatial coverage and sufficient resolution, thermal imaging is preferable. It can identify spatial variations related to thermal processes occurring on the SOC electrodes, therefore are suitable to observe temperature changes due to carbon deposition (i.e. graphite formation), current flow, material phase changes, or the buildup of intermediates occurring during feeding gases components oxidation/reduction. Nonetheless, their main drawback is related to the lack of molecular specificity. Table 3 summarizes the main points emerged from the survey. For that, spectroscopic methods are far more promising. Among them, vibrational spectroscopy - as Infra-Red and Raman - well allows performing unambiguous in-situ and real time characterization. Moreover, these techniques have the great advantage of being non-invasive for the specimen. The main pitfall of Infra-red for the in-situ and in-operando characterization of SOC is ascribed to the materials available to build detectors. Normally, infra-red detectors are not enough sensitive in the visible wavelengths range and, since the very high operating temperature makes the specimen optically behave like a black-body, infra-red detectors may easily get saturated from radiations emitted by such signal sources. Also, there are a few materials able to transmit infra-red wavelength signals<sup>35</sup>. Conversely, Raman uses conventional optics and detectors matched to ultraviolet, visible, and near-infrared wavelengths, so that Raman is suitable to identify heterogeneous samples with high resolution (this is relevant because it gives information about the electro-catalytic activity of the material). In addition, this can be integrated into microscopes. Many works reporting SOC materials diagnosis by Raman spectroscopy were published, but most of them investigated either half cells or SOC materials pellets/powders. Recently, this techniques was demonstrated to be valid on real NiYSZ cells under operation, measuring the formation of graphite and validating i-V and EIS measurement thereby<sup>36</sup>. Similarly, this techniques is suitable to investigate Sulphur-driven degradation<sup>37</sup>.

Comparing Table 3 with previous Table 2, it appears that mostly used SEM and EDX are absent, for they fail to this purpose. In fact, although they offer the highest spatial resolution and sensitivity to identify structure, morphology and composition of materials, they require a high degree of vacuum, which is in strong contrast with the expected operating conditions of SOC materials.

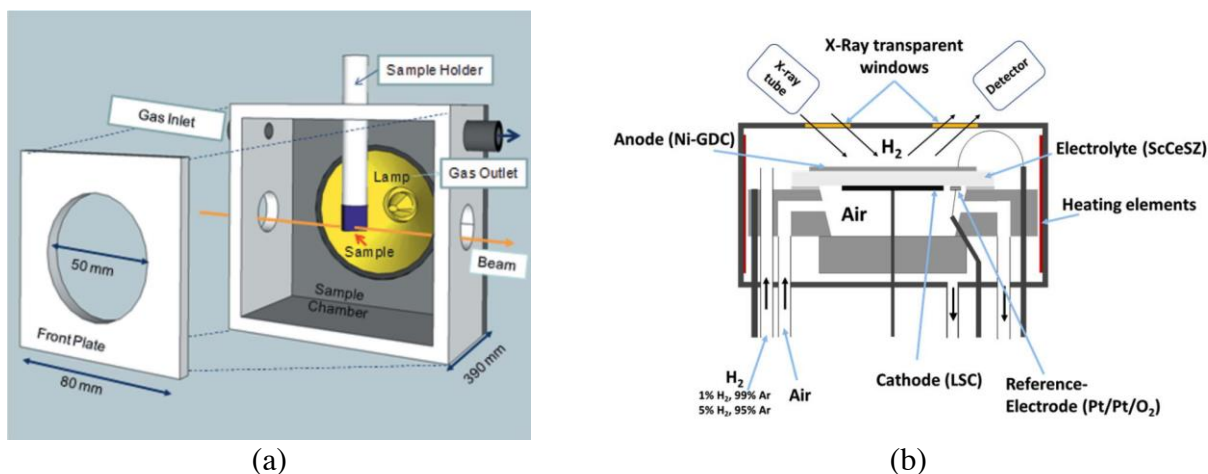
**TABLE 3.** Advanced experimental methods to characterize SOC materials<sup>38,39</sup>

Technique	Type	Measurements	Drawbacks
XPS	In-situ Ex-situ	Material composition and electronic structure	Difficult in situ, only elemental analysis, surface sensitivity
XRD	In situ	Crystallographic and local structure, Electronic structure	Experimentally challenging, needs brilliant and tunable sources, used for a single position at time
XAS	In situ	Atomic and electronic structure	Used for a single position at time
Raman spectroscopy	In situ	Material composition and adsorbates	Experimentally challenging
Infra-red	In situ	Surfaces species, adsorbates	
Thermal Imaging	In situ	Thermal emissions (Temperature mapping)	No molecular specificity

### In-Operando

To the end of in-operando SOC material analysis, XRD and XAS are very promising tools to monitor the occurrence of different phases, their structure, as well as redox processes even when amorphous or nano-crystalline components are formed. Although these techniques are largely employed when it comes to low temperature electrochemical devices, for the operation features of SOC, it is very challenging to build a suitable test housing compatible with the XAS and XRD set-ups. A few apparatuses have been realized pointing at this target and the techniques have been mainly applied only for the characterization of half-cells operating according to simplified conditions. To the best of the authors' knowledge, at present only two works present real advancements in this field, yet the results obtained are still far from a complete in-operando SOC material characterization.

Lund et al.<sup>40</sup> used a spectro-electrochemical cell to provide simultaneous EIS and XANES under relevant conditions for the SOC cermet. A schematic of the measurement chamber is reported in Fig. 5a: the SOC material sample is placed onto a holder in front of a Kapton frame, which is resistant to typical high temperature of SOC operation and suitable for the transmission of X-rays. Nonetheless, the experiments are carried in pseudo in-operando conditions (i.e. high temperature, yet electrodes expose to an oxygen-helium gas atmosphere).



**FIGURE 5.** Schematic drawings of analysis chamber for in-situ/pseudo operando SOC characterization through synchrotron based X-ray techniques: (a) spectro-electrochemical cell for XANES measurements<sup>40</sup> and (b) high temperature cell for simultaneous characterization of crystallographic and electrochemical properties<sup>41</sup>

Finally, Korjus et al.<sup>41</sup> implemented a dual chamber Anton Paar HTK 1200N to perform simultaneous electrochemical and synchrotron-based x-ray characterizations on a SOC specimen. Fig. 5b depicts a scheme of the test apparatus, showing electrodes probes, specimen holder and X-rays frames. Again, notwithstanding this research recently reported very interesting findings, the SOC material is operated in “mild” conditions, very far from the ones occurring in a typical application (i.e. only 5% hydrogen is supplied, argon balanced). Both experiences report results collected on tiny-area specimen: this does not highlight degradation phenomena that are driven by a spatial distribution of temperature, current, mechanical stresses and gas flow (local reactants starvation).

## CONCLUSIONS

NiYSZ is the most common cermet used to manufacture SOC electrodes. Since SOC durability is an overriding technological problem, the investigation of degradation mechanisms to prevent the early SOC failure is of great interest. While electrochemical techniques (i-V and EIS) are state-of-the-art practice, they do not allow understanding the specific cause of performance decay without ambiguities. In fact, most of degradation mechanisms are interconnected. This means the occurrence of an unfavorable condition may trigger a series of several mechanisms leading quickly to the cell failure. Material characterization provides information on the chemical and morphological structure of the SOC cermet. Yet, ex-situ analysis conceals the correlation with the operating condition which is responsible for degradation mechanisms to be initiated. To this matter, in-operando material characterization appears as the only answer to gain insight on specific degradation mechanisms. Although advanced diagnostic techniques (such as synchrotron-based X-rays and optical spectroscopy as Raman) show high potentialities, their implementation is not trivial since a testing apparatus accessible to probes and detectors needs to

be built. This has to comply with the normal operation of the SOC material, encountering several challenges (pressure, high temperature, gas flow, flammable gas fraction).

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