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A review on solid oxide fuel cell durability: Latest progress, mechanisms, and study tools



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ABSTRACT

The commercial breakthrough of solid oxide fuel cells (SOFCs) is still hampered by degradation related issues. Most SOFCs that perform well do not possess good stability. To achieve a targeted degradation rate of 0.2%/1000 h important to a durable SOFC device, it is vital to identify the sources of degradation. So far, the longest stable performance was given by F1002-97, a short stack from Forschungszentrum Jülich GmbH, which reached 93,000 h of operation at 700 °C under 0.5 A cm⁻² constant current density with a degradation rate of 0.5%/1000 h. In this review, we discuss the most detrimental degradation mechanisms for the core components of the SOFC, mainly poisoning, microstructural deformations, and strains. Electrochemical, chemical, and structural characterization tools for quantifying degradation mechanisms are also presented. The following section addresses the most recent progress in SOFC durability and the associated methods for analyzing degradation. These techniques include different doping techniques (including Mo, Nb, Co, Ce, Ta, Sn, etc.), surface modifications (e.g.infiltration, exsolution techniques, protective coatings), and interface engineering. Finally, the factors that inhibit the enhancement of SOFC durability are briefly discussed, such as inadequate knowledge of the degradation process and limitations in the material choices.

1. Introduction

The limited fossil fuel resources and their destructive impacts on the environment and climate in particular call for developing alternative sustainable energy sources [1-3]. In this regard, fuel cells are a promising power supply technology with significant efficiency, fuel flexibility nature, combustion-free operation, and almost zero-emission [1,4,5]. Fuel cells are also key elements in a hydrogen-based energy system.

A fuel cell converts the chemical energy in a fuel, such as H_2 and hydrocarbons, directly into electricity. The operation is comparable to batteries, except that fuel cells have gaseous electrodes; they do not require recharging and run as long as both fuel and oxidant are supplied to the electrodes [6–8]. Moreover, their efficiency is not limited by the Carnot cycle as in heat engines [9,10]. Generally, fuel cells are categorized by their electrolyte characteristics into six main groups: alkaline (AFC), phosphoric acid (PAFC), polymer electrolyte membrane (PEM), direct methanol (DMFC), molten carbonate (MCFC), and solid oxide (SOFC).

Among the different fuel cells, the SOFC is one of the most efficient

technologies for power generation as it is flexible to fuel choice, noiseless, showing low CO_2 emissions, and has a potentially long lifetime of 40,000–80,000 h [8]. A SOFC typically employs yttrium-stabilized zirconia (YSZ) electrolyte. The cathode of the SOFC adsorbs oxygen molecules from the oxidant gas (air) and reduces them to negative oxygen ions. The chemical potential gradient passes these ions through the electrolyte to the anode fed by fuel. Then, the oxygen ions oxidize the diffused fuel catalytically leading to the generation of electrons. Finally, an external circuit transfers the released electrons to the cathode to complement the discharge process [11]. A schematic of a typical SOFC and its working principles is shown in Fig. 1.

The high working temperature of SOFC, necessary to reach an adequate ionic conductivity, provides excellent heat byproducts for combined cycle operations or co-generation of energy. Another merit is their solid-state electrolyte, which is manageable and does not cause corrosion to the cell or handling issues. Furthermore, SOFCs are cost-effective for mass production since they do not use expensive noble metals [7,8,13].

Considering SOFCs harsh operating conditions, such as high working temperatures, redox and thermal cycling, and poisonous atmosphere

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Abbreviations

Acronyms	s & Abbreviations Definition
SOFC	Solid oxide fuel cell
AFC	Alkaline fuel cell
PAFC	Phosphoric acid fuel cell
PEM	Polymer electrolyte membrane fuel cell
DMFC	Direct methanol fuel cell
MCFC	Molten carbonate fuel cell
YSZ	Yttrium-stabilized zirconia
0-SOFC	Oxide-ion solid oxide fuel cell
GDC	Gadolinia-doped ceria
LSGM	La _{0.8} Sr _{0.2} Ga _{0.8} Mg _{0.2} O _{3$-\delta$}
H-SOFC	Proton conducting solid oxide fuel cell
DCZI	$BaCe_{0.7}Zr_{0.1}Y_{0.2}U_{3-\delta}$
LOW	$La_{1-x}Sr_xWiiO_3$
LOUP	$La_{0.6}SI_{0.4}CO_{0.2}Fe_{0.8}O_3$
NDCaCO	NuBa _{1-x} Ga _x G0 ₂ O _{5+δ}
DIC	$Ba_2 I Cu_3 O_{6+\delta}$
DCFZ I DE7D	$Ba_x C 0_{0.4} Fe_{0.4} L I_{0.1} I_{0.1} U_{3-\delta}$
DNOE	$Dare_{0.8}ZII_{0.1}DI_{0.1}U_{3-\delta}$
PNOF	$Pr_2 NIO_{3.9+\delta} r_{0.1}$
PBCI	$PrBaCo_{2-x}Ta_xO_{5+\delta}$
SDC	Samarium-doped certa
SFIN	$Sr_2FeMOO_{6-\delta}$
LSCM	$La_{0.7}Sr_{0.3}Cr_{0.5}Will_{0.5}O_{3-\delta}$
CFUL	Ceramic Fuel Cells Limited
CHP	Combined Heats and Power
DOE	U.S. Department of Energy
ASK	Triale above boundary
	Cocondomy for Mass Spectrometry
	Secondary for mass spectrometry
UKK	Thermal expansion appficient
SSC	$Sm_{0.2}Sm_{2-\delta}$
55C ScS7	$(7rO_{1})_{1}$, $(Sc_{1}O_{2})_{2}$
OCV	Open circuit voltage
nnh	Darts per hillion
ppp	Parts per million
ss	Stainless Steel
ISCM	LasSraOra -Mna -Ora -
DTU	La(),7551(),2551(),51111(),503_8
	$= 50 \text{ mole} (200 \text{ mole} 7 \text{ mole} 7 \text{ mole} 8 \text$
CZD3 TEM	Transmission electron microscopy
ILIVI	Current voltage
I-V FIS	Electrochemical impedance spectroscopy
DC	Direct Current
	Alternating current
IN	
DRSCE	$La_2NIO_{4+\delta}$
I SCrN	$L_{2a} = Sr_{a} = Cr_{a} = Ni_{a} = O_{a}$
SECM	$La_{0.6510,2}C_{10.851110,15}C_{3}$
DNM	3121701.30a0.2000.506-8
YRD	Y-ray diffraction
HTYPD	High-temperature XBD
FTIR	Fourier transform infrared spectroscopy
MS	Mass spectrometry
SELWOR	StaTiFea-Maa-Oca
SNCE	$SrNh_{0.1}Co_{0.0}$ Fe $O_{0.0}$
SNO	$S_{11} S_{0,1} S_{0,0} S_{1} S_{1}$
BES	$B_{2}Ee_{2} = Sn_{2} = O_{2}$
XDS	Σ_{rrav} nhotoelectron spectroscopy
	Atomic layer denosition
	Acomic alfer deposition

NAP-XPS	Near ambient pressure-XPS
NEDO	New Energy and Industrial Technology Development
	Organization of Japan
SEM	Scanning electron microscopy
SE DCE	Secondary electron
DSE ISCrM	LasSraCra -Mna -Oa -
AFI.	Anode functional laver
NBSCF	NdBa ₀ $_{5}$ Sr ₀ $_{5}$ Co ₁ $_{5}$ Fe ₀ $_{5}$ O ₅ $_{8}$
BSCF	$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$
WDCM	Wet and dry cycling mode
AFM	Atomic force microscopy
FIB-SEM	Focused ion beam-SEM
TGA	Thermogravimetric analysis
DSC	Differential scanning calorimetry
DFI	Density functional theory
CALDHA	Pidac0 $_{2}$ 0 $_{5+\delta}$
ESB	$B_1 \in Er_{0,4}O_2$
icn-LSME	LSB <i>in-situ</i> co-assembled nanocomposite LSM-Bi _{1.6} Er _{0.4} O ₃
LCaF	La _{0.65} Ca _{0.35} FeO _{3-δ}
FCC	face-centered cubic
LPG	liquid petroleum gas
LSCFM	$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.7}Mo_{0.1}O_{3\!-\!\delta}$
Ce-GSCF	$Gd_{0.65}Sr_{0.35}(Co_{0.25}Fe_{0.75})_{0.9}Ce_{0.1}O_{3-\delta}$
BSF	BaCo _{0.7} Fe _{0.3} O _{3-δ}
EC _x BC	$Eu_{1-x}Ca_xBaCo_2O_{5+\delta}$
SFINI BCEZV	SIFe _{0.8} ND _{0.1} Ta _{0.1} O _{3-δ} Base Case Cose Fee 7r V O
SC	$SrCoO_{0.5}$
PBC	$PrBa_{0.94}C_{0.2}O_{5+8}$
LC	$LaCoO_{3-\delta}$
CFA	Co–Fe alloy
RP-SCFM	Ruddlesden–Popper structured oxide
	$Sr_{3}Co_{0.1}Fe_{1.3}Mo_{0.6}O_{7-\delta}$
NFA	Ni–Fe alloy
RP-PSNF	Ruddlesden-Popper $Pr_{0.32}Sr_{0.48}Ni_{0.2}Fe_{0.8}O_{3-\delta}$
ESB	$Bi_{1.6}Er_{0.4}O_3$
SNC SETD70	$SrND_{0.1}CO_{0.9}O_{3-\delta}$
SEHf	$SrEe_{0.2}Fe_{0.8}Fi_{0.15}Ku_{0.05}O_{3-\delta}$
SFCoM	$Sr_1 \circ Fe_1 4Co_0 1Mo_0 = O_6 s$
SLFC	Single-layer SOFCs
Variables	& constants Definition & Unit
ASR	Area specific resistance, Ω cm ²
P _{SO2}	Partial pressure of SO_2 , Pa
P ₀₂ TEC	Partial pressure of O_2 , Pa Thermal expansion coefficient K^{-1}
I	Current density mA cm^{-2}
Rp	Polarization resistance. Ω
Ro	Ohmic resistance, Ω
R ₁	Charge transport resistance, Ω
R ₂	Catalytic reaction resistance, Ω
Μ	Molar, M
heating r	ate °C/h
wt%	weight percentage
U	applied regime value for stability test $c_{abuse} = 2$
ы Б	Carvanostatic regime for stability test, MA Cm
r T	Temperature °C.
t	Duration, h
- Power de	ensity $W m^{-2}/mW cm^{-2}$
V	Voltage, V
А	Atmosphere

	vol%	volume percent
	Frequent	Chemical Formula Full name
	BaCeO ₃	Barium cerate(IV)
	BaZrO ₃	Barium Zirconate
	Cr	Chromium
	S	Sulfur
	CO_2	Carbon Dioxide
	Cr_2O_3	Chromium Trioxide
	CrO ₂ (OH) ₂ Chromium Dihydroxile
	SO_2	Sulfur Dioxide
	SrSO ₄	Strontium Sulfate
	Sr	Strontium
	Со	Cobalt
	CoFe ₂ O ₄	Cobalt Iron Oxide
	Fe	Iron
	La ₂ O ₂ SO	4 Lanthanum Oxysulfates
	SrCrO ₄	Strontium Chromate
	$SrCO_3$	Strontium Carbonate
	$Sr(OH)_2$	Strontium Hydroxide
	$SrZrO_3$	Strontium Zirconate
	BaCeO ₃	Barium Cerate(IV)
	BaO	Barium Oxide
	Y_2O_3	Yttrium Oxide
	ZrO_2	Zirconium Oxide
	Ni	Nickel
	NiO	Nickel Oxide
	CO	Carbon Monoxide
	Р	Phosphorous
	As	Arsenic
	Se	Selenium
	Cl	Chlorine
	Sb	Antimony
	H_2S	Hydrogen Sulfide
	Ni _x S _y	Nickel Sulfide
	NiP	Nickel Phosphide
	PH_3	Phosphane
	AsH ₃	Arsine
1	NicAsa	Nickel Arsenide (V)

Ni ₁₁ As ₈	Nickel Arsenide (VIII)
NiCl ₂	Nickel Chloride
LaCrO ₃	Lanthanum Chromate
Mn_3O_4	Manganese (II, III) Oxide
La_2O_3	Lanthanum (III) Oxide
Nd_2O_3	Neodymium Oxide
NiFe ₂ O ₄	Nickel Ferrite
Sr ₂ SiO ₄	Strontium Orthosilicate
BaCrO ₄	Barium Chromate
CuMn ₂ O ₄	Copper Manganese Oxide
CH ₄	Methane
Li ⁺	Lithium-ion
Na^+	Sodium-ion
\mathbf{K}^+	Potassium-ion
PrO _x	Praseodymium Oxide
TiS ₂	Titanium Sulfide
FeS ₂	Iron Sulfide
MoS_2	Molybden Sulfide
Sr(OH)2.8	SH ₂ O Strontium Hydroxide
SrNiO ₃	Strontium Nitrate
Pd	Palladium
OH^-	Hydroxide ion
Mn	Manganese
Al_2O_3	Aluminium Oxide
Cr^{+6}	Chromium ion
Rh	Rhodium
Ag	Silver
Pt	Pelatinum
Au	Gold
Nb	Niobium
Та	Tantalum
Sn	Tin
Ca	Calcium
Eu ³⁺	Europium ion
${O_o}^{\times}$	RP-SCFM lattice oxygen
Vo ^{••}	RP-SCFM oxygen vacancy
Hf	Hafnium

[14], they require several properties for their components (cathode, electrolyte, anode, interconnect, sealant), including [7,15–17].

- Appropriate conductivity (Electrolyte must be an electronic insulator and providing a good ionic conductivity, while electrodes should show a promising electronic and ionic conductivity)
- Acceptable stability (Chemical, Thermal, Morphological, Mechanical)
- Good compatibility with other components (Chemically, Thermally, Mechanically)
- Porous structure for electrodes (for adequate gas transportation to reaction sites) and dense electrolyte (for preventing gas mixing)
- High electrical conductivity, perfect gas tightness, and high resistivity against oxidation, sulfation, and carbon deposition for interconnects
- Hermeticity and insulating nature for sealants

Besides, these requirements should be achieved in a cost-effective and easy-to-fabricate way. On account of these prerequisites, different materials are available for the SOFC application. In the case of oxide-ion SOFCs (O–SOFCs), electrolytes are composed of perovskite or fluorite structure with oxygen deficiency to provide oxygen pathways by oxygen vacancies. Zirconia-based (e.g., YSZ), ceria-based (e.g., gadolinia-doped ceria (GDC)), and lanthanum gallate-based (e.g.,

 $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM)) [18] electrolytes are the most common examples for O-SOFCs. On the other hand, proton-conducting SOFCs (H–SOFCs) transport H^+ instead of O^{2-} and there is no generated water molecule at the anode side, which brings several advantages such as high performance at lower operating temperatures and better durability in using hydrocarbon fuels. For this type, BaCeO₃-, BaZrO₃based perovskites, such as $BaCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-\delta}$ (BCZY) [19], are the most popular electrolytes [20]. Cathodes are also different for O-SOFCs and H-SOFCs. O-SOFC cathodes are mainly perovskite- (ABX₃), like $La_{1\text{-}x}Sr_xMnO_3$ (LSM) and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF), and layered perovskite- (AA'B_2O_{5+\delta}), such as NdBa_{1-x}Ca_xCo_2O_{5+\delta} (NBCaCO) [21] based cathodes, where A, A', and B are cations but with different radius and X is an anion (mostly oxide) connected to cations [22]. Cathode function in H–SOFCs requires three charge carriers of O^{2-} , H⁺, and e⁻ to show acceptable performance. Therefore, mixing the proton-conducting oxides with O^{2-} conductors can be the key to provide an effective electrode reaction [22]. $Ba_2YCu_3O_{6+\delta}$ (BYC) [23]. $Ba_{x}Co_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-\delta}$ (BCFZY) [24,25], $BaFe_{0.8}Zn_{0.1}Bi_{0.1}O_{3-\delta}$ (BFZB) [26], $Pr_2NiO_{3.9+\delta}F_{0.1}$ (PNOF) [27], and $PrBaCo_{2-x}Ta_xO_{5+\delta}$ (PBCT) [28] are some of these examples. In terms of conventional anode material, there are generally Ni-, including Ni-YSZ [29], Ni-GDC [30], and Ni-Samarium-doped ceria (SDC)- based [31], and perovskite-based materials, such as Sr₂FeMoO_{6-δ} (SFM) [32], and La_{0.7}Sr_{0.3}Cr_{0.5}Mn_{0.5}O_{3-δ} (LSCM) [33].



Fig. 1. Schematic of a typical SOFC and its working principles. Cathode, the top layer, reduces the Oxygen molecules of the oxidant gas to Oxygen ions. Then, the Oxygen anions (O^{2-}) pass through the electrolyte, the middle layer, to reach the anode, the bottom layer. The O^{2-} ions react with H₂, fed to the anode, and create water and generate electrons. Finally, these generated electrons are transferred to the cathode by the external circuit to complete the discharge process. Reprinted from Jouttijärvi et al. [12] (with minor edition) with permission. Copyright 2018, John Wiley and Sons.

Different companies have already begun the commercialization of SOFC for various purposes. For example, Bloom energy company (USA) has commercialized this technology for large stationary applications, while other companies such as JX Nippon Oil & Energy, Aisin (Japan), and Ceramic Fuel Cells Limited (CFCL) (Europe) have made the same effort on micro Combined Heats and Power (CHP) systems for small stationary applications [34]. In this regard, Ceres company (Europe) reported a degradation rate of $\sim 1\%/1000$ h for its first pre-commercial small scale CHP [35]. However, high capital tariffs and expensive operating costs due to degradation issues are serious challenges for a commercial breakthrough of SOFC technology [36,37]. For instance, SOFC systems for stationary applications demand 40,000-80,000 h of service for market launch [38]. Several country departments, such as the U.S. Department of Energy (DOE), have set targets towards system capital costs and degradation rates to overcome these challenges. The degradation rate, which is the electrical potential lowering rate here [34], for 2020 was targeted at 0.2%/1000 h for SOFC stacks. In this regard, scientists of the field expect the average degradation rates of 0.5%/1000 h, 0.3%/1000 h, and 0.2%/1000 h for 2020, 2035, and 2050, respectively [36].

So far, the longest SOFC operation belongs to F1002-97, a short stack from Forschungszentrum Jülich GmbH, which reached 93,000 h of operation at 700 °C under 0.5 A cm⁻² constant current density with 40% fuel utilization of wet H₂ and compressed air as oxidant [39]. This two-layer short stack consisted of a 500 µm-thick anode support (Ni-8YSZ; 8 mol% YSZ), a 7 µm-thick anode (Ni-8YSZ), a 10 µm-thick 8YSZ electrolyte, a 40 µm-thick LSCF cathode, and a 5 µm-thick GDC barrier layer. It also had a 5.5 mm intermediate temperature metal (ITM) interconnect with a MnO_x protective coating and glass sealants [40]. However, the average voltage degradation rate (0.5%/kh) crossed the given limit for SOFC commercialization [41], mainly due to the chromium (Cr) poisoned cathodes and interconnectors oxidation [42]. Besides, the stack was mostly run at a cell voltage of 0.7 V, which is much below the typical operating voltages for SOFCs [43]. There are also other stacks with long-term operations to study the durability performance of various SOFC components and design along with different working parameters [38], including ~ 40,000 h and 0.5–1%/kh by Mai et al., [44], 6000 h and ~1.4%/kh by Chou et al., [45] 5000 h and 0.75%/kh by Ido et al., [46] and 1000 h without any noticeable degradation by Thaheem et al. [47].

For achieving these durability targets, it is necessary to determine the origins of degradation and clarify the relevant mechanisms from the smallest working unit, which is the cell level. In the present study, we first briefly describe different SOFC configurations to better understand SOFC structures. Then, a comprehensive overview of the most critical degradation mechanisms in the main components of the SOFC, along with the study tools and limitations, are described, all in the cell level and lab scale. Finally, we discuss the most recent progress for enhancing SOFC stability.

2. SOFC structural configurations

Through different cell geometries for SOFC setup, planar and tubular designs are the most common configurations for practical applications, presented in Fig. 2 (a). The tubular cell consists of an array of sandwiched electrolyte and electrodes in a specific length and diameter. The planar design (radial or flat plate) includes a compact assembly of electrolyte and electrodes. The planar design has a simpler and cheaper fabrication procedure, higher power density, and low internal resistance due to its short current path. On the other hand, the tubular cell presents a more solid thermo-cycling performance, and it is easier to seal [48,49]. Both cell designs require sufficient mechanical strength to withstand the operation stresses provided by the support layer. The support layer has the largest thickness, and the thickness of other layers is minimized to avoid high internal resistance, enhance cell efficiency, and reduce costs. Generally, SOFCs have one support layer, and they can be designed as the anode-, cathode-, or electrolyte-supported [50,51], shown in Fig. 2 (b). Planar designs are mostly anode-supported, while tubular ones are fabricated in electrolyte-supported configuration [52]. In the planar SOFCs, the reactant gases diffuse into the porous microstructure from the center to the circumference. Unlike the planar ones, the fuel flow runs outside and the oxidant inside in a cathode-supported tubular cell.



Fig. 2. SOFC geometries: (a) 3D model of the planar and tubular cell, (b) crosssections of electrolyte-, anode-, and cathode-supported cells for both planar and tubular geometry.

For the anode-supported ones, the fuel flow goes inside, and the oxidant circulates outside in the tube during the operation [8,49,53].

Electrolyte-supported SOFCs are the oldest design as YSZ provides a robust support layer and is easier to fabricate. However, a thick electrolyte layer causes higher ohmic losses, which degrades the SOFC power density output. Regarding the electrode-supported cells, an anode-supported design is more favorable than a cathode-supported one, owing to its higher power densities, particularly at lower temperatures. The second generation is the anode-supported cells, with a 200–1500 μ m anode thickness and a thin electrolyte. This design decreases electrolytic resistance and leads to better conductivity at lower temperatures. Since the electrolyte no longer provides mechanical support, other materials with higher ionic conductivity and lower mechanical strength can be replaced with the YSZ to improve the cell's output. Furthermore, anode-supported cells' fabrication process is simpler, and the anode microstructure is more controllable [50,51,54, 55].

Although the industry is more interested in the anode-supported design, both anode- and electrolyte-supported cells are used in laboratory experiments. For instance, electrolyte-support allows for an easier independent analysis of each electrode process in a three-electrode operation, while the anode-support offers better output results [56].

Stacks also consist of several SOFC single cells joined to each other by interconnects. Interconnects act as a physical wall between the anode's reducing and cathode's oxidizing atmospheres. Planar and tubular stack designs are illustrated in Fig. 3. Moreover, planar design stacks require a sealant to avoid leakages or direct mixing of fuel and oxidant. Sealing, on the other hand, is typically not a major issue in tubular SOFCs [7].

It is worth noting that there is another geometry for SOFC stacks, the flat-tubular configuration, providing the features of both planar and tubular SOFCs into a single design, like high power density, good thermal robustness, and ease of sealing [58]. The Siemens-Westinghouse SOFC company invented this design to address the low power density of tubular cells [59–61]. Park et al. [62] reported a 5-cell stack with flat-tubular anode-supported cells without using metallic interconnect plates, showing a degradation rate of 0.69%/kh during 1093 h under a current load of 16 A at 750 °C. However, there are no records of their durability performance on the cell level [62].

3. Detailed degradation mechanisms

The severe working conditions of SOFC have several diverse degradation processes, which arise from each component and their interactions, making it challenging to fulfill the long-term stability requirements. Degradation is commonly characterized as loss of performance, and the degradation rate is generally stated as the voltage loss per 1000 h, especially in stacks. Change in area specific resistance (ASR) is another measure for reporting the degradation of single cells [63]. It should be noted that evaluating the degradation process in SOFC is quite complicated as long-term studies are needed, and the operation factors (temperature, fuel impurities, current density, etc.) affect the procedure [64]. Fig. 4 represents two photographs of degraded SOFCs after the performance. A summary of each cell component's main degradation mechanisms (cathode, electrolyte, anode) and a brief overview of stack elements (interconnects and sealants) is presented below.

3.1. Cathode

Cathode degradation mechanisms can be classified into three main groups [67]:

- Poisoning (by Cr, S, CO₂, Humidity)
- Microstructural deformation
- Chemical and Thermal Strains (Delamination)

The most rigorous degradation in LSCF cathodes is Cr poisoning, caused by the Cr evaporation from the unprotected metallic interconnects. Cr poisoning can happen in two potential ways for SOFC cathodes, chemical and electrochemical. In the chemical one, the volatile Cr species (CrO₃ or other gaseous kinds) directly counter the cathode surface and its segregated ions. Then, the resulted precipitated species not only corrupt the electrical properties but also hinder the gas pathways of the cathode. This mechanism increases the degradation effect of cathode material segregation as well. In the electrochemical mechanism, the triple-phase boundary (TPB) sites are inhibited by the deposition of reduced high valence volatile Cr species. These Cr₂O₃ or other low valence Cr kinds prevent the O₂ reduction at TPBs and O₂ diffusion in the cathode [68]. It is noteworthy that the operating conditions, including temperature, water vapor, and current density, can alter the Cr poisoning intensity. The temperature has the highest impact, and lower temperature causes more severe Cr poisoning. The humidity increase also increases the Cr poisoning effect since the CrO₂(OH)₂ is quite stable in this environment. The cathode degradation rate by this mechanism will rise with the current density increment [17].

Sulfur (S) poisoning in cathodes was first determined by Yukawa et al. [69] with Secondary Ion Mass Spectrometry (SIMS) and is not as well-known as Cr poisoning. They have figured out that the S deposition within cathode material was strongly associated with the cathode high overpotentials. A possible cause of this case is the trace amount of SO_2 in the air that may deposit by interacting with the cathode near the air inlet of cells. While the SO_2 content is just in the ppm scale, it still can affect the cell/stack performance and reduces the SOFC operation length [70]. In LSCF cathodes, S poisoning leads to the fine grain SrSO₄ precipitation in the grain boundaries of the cathode/electrolyte interface [71]. This



Fig. 3. Illustrations of (a) planar, adopted from Grayson, K [57]. with color modification, and (b) tubular design stacks, adopted from Hossain et al., [20] with modifications. Copyright 2017. Elsevier.



Fig. 4. (a) a cracked electrolyte after anodic re-oxidation, Reprinted from Batfalsky et al., [65] with permission. Copyright 2016. Elsevier. (b) Ni-YSZ|YSZ|LSM anode supported button cell after 120 h of operation in 50 ppm H_2S sour fuel. Reprinted from Cao et al., [66]. Copyright 2020. Royal Society of Chemistry.

SrSO₄ deposition can also happen on the cathode surface with a homogenous distribution [72]. Hence, the S poisoning causes Oxygen reduction reaction (ORR) degradation since the Sr and Co components of the cathode material are decreased by the formation of SrSO₄ and precipitation of CoFe₂O₄. The electrochemically active surface area is also reduced due to the formation of secondary phases such as SrSO₄, La₂O₂SO₄, Co oxide, and Co₂Fe₂O₄ among SO₂ adsorption by cathode surface particles. Fig. 5 presents a schematic of S poisoning in LSCF cathodes in dry conditions [73]. Several parameters, including temperature, P_{SO2}, Sr content, and P_{O2}, affect the S poisoning process. It is worth mentioning that S poisoning is more complex than Cr poisoning as in the first case, S oxidation and Co/Fe reduction are happening at the same time, but there is no oxidation reaction in Cr poisoning [70]. Perovskite surface can also adsorb the CO₂, causing carbonate formation on the surface, increased polarization, reduction in O2 adsorption, and ORR activity. The cathode's electrocatalytic properties are also impressed by the competition between O2 and CO2 adsorption on the cathode surface, determining the catalytic efficiency [74].

The change in the cathode morphology is another degradation mechanism that occurs under the cathodic overpotential and alters the cathode microstructure. This phenomenon usually happens when the cathode has cations with much different mobility, leading to component separation, called "Kinetic Demixing" [17]. Sr segregation is a kind of kinetic demixing that can happen in cathode surface and cathode/electrolyte interface LSCF and LSC cathode materials [75-77]. Sr segregation in the surface can change the cathode surface chemistry, affecting the oxygen exchange kinetics and reducing ORR reactions [77, 78]. Furthermore, these Sr species can react with surrounding gaseous phases such as Cr, CO2, and humidity, forming insulating layers of SrCrO₄, SrCO₃, and Sr(OH)₂ [79]. The SrCrO₄ formation also causes Sr deficiency at the A-site, which reduces ORR activity. Further, this Sr reduction in perovskite lattice degrades the electrical conductivity as well [79]. Sr enrichment in the interface can react with YSZ and results in insulating phases such as SrZrO₃, which induces the increment in the

cell's ohmic resistance [75].

Particle coarsening in high-temperature SOFC can also cause performance degradation because the reduced absorbent surface area increases the polarization resistance [80]. The chemical strain is also a degradation mechanism in cathode material due to the oxygen non-stoichiometry. With the formation of oxygen vacancies in the lattice, the B-site cations' overall valance number reduces. This reduction enlarges the B-site ionic radius and causes lattice expansion, resulting in a thermal expansion coefficient (TEC) mismatch between the cathode and the electrolyte. If the mismatch becomes too large, the electrolyte will be broken by bending [17]. Besides, this difference in TEC can induce the applied thermal stress during the operation and results in component delamination. Delamination makes severe issues due to the prolonged current pathway, hindering charge conduction, and destruction of reaction sites. When delamination happens, the current is localized in an intact area. This current localization contributes to higher cathode loss of activation, and higher ohmic loss of electrolyte as well [81].

Surface engineering is a functional and economical technique to deal with cathode poisoning, using a protection layer against Cr diffusion. Doping is another strategy to address this issue, enhancing the chemical and structural stability of the cathode material towards poisonous species. These techniques are already discussed in the state-of-the-art section in detail. Operation conditions are essential in controlling and inhibiting the degradation process in cathodes as well. It is suggested to run the cell at moderate temperature and at low polarization to prevent any major over-potential and further deterioration of the cathode [67]. A functional interlayer such as $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ (CGO) can slow down the Sr diffusion from the cathode through the electrolyte if the barrier is dense enough [82]. In the case of S poisoning, there are several ways to address this issue and enhance SOFC lifetime. S content can be reduced by applying a chemical filter for the air inlet of the SOFC system. Moreover, a trapping layer on the cathode surface can catch the SO₂ and prevents degradation. Some additives such as $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ (SSC)



Fig. 5. Schematic of S poisoning mechanism and formation of SrSO₄ and CoFe₂O₄ secondary phases. Reprinted from Budiman et al., [73] with permission. Copyright 2019. IOP Publishing.

nanofibers, BaCeO₃ and BaO, modify the cathode by surface engineering and become more resistant to S poisoning [83–86].

3.2. Electrolyte

The main degradation mechanisms in the SOFC electrolyte can be listed as [37]:

- Phase Transition, impurities, and dopant diffusion

- Mechanical failures

During the SOFC operation at high temperatures and harsh atmosphere, a phase change in the electrolyte layer can affect the SOFC performance by reducing the ionic conductivity and phase stability, which eventually causes degradation. YSZ, as the most common electrolyte for SOFC, presents a competitive ion conductivity over a broad range of partial oxygen pressure, good stability under harsh operating conditions, and satisfying mechanical properties under elevated temperatures. However, several microstructural changes due to the long exposure at 1000 °C degrade the electrolyte conductivity and SOFC performance. The most notable phenomenon is the phase transformation from cubic to tetragonal zirconia, which strongly depends on the Y_2O_3 concentration in ZrO_2 [87,88]. Due to Hatturi et al. [89] research, 9.5YSZ was the optimized electrolyte because of its high conductivity and excellent stability compared with 8, 8.5, 9, 10YSZ electrolytes [89]. Ionic conductivity faced a decreasing trend with higher dopant content, as the emerging of point defects lowers the defect mobility [16]. Phase transition is also a challenge in Sc₂O₃-stabilized ZrO₂ (ScSZ) electrolyte, a proper candidate for low-to-intermediate temperatures operation, which experiences a cubic-rhombohedral-cubic phase transformation at lower temperatures [16,90]. As the rhombohedral phase has a weaker ionic conductivity, the cell faces an increase in the ASR, causing lower performance [16]. This transition causes unwanted residual stress in the SOFC stack as well [91].

Furthermore, chemical interactions between the electrolyte and its contacted components, especially cathode, are another source of degradation. The chemical interactions give rise to the formation interface and insulating secondary phases [92,93]. In the LSCF/YSZ systems, both the high-temperature sintering process and cathodic polarization cause Sr segregation and SrZrO₃ formation, which is undesirable for the SOFC performance and durability. In the case of LSCF/GDC systems, the Sr segregation rate is much slower and less destructive than the one in YSZ. However, limited and isolated Co accumulation happens here, which, of course, is not as damaging as Sr segregation. Fig. 6 (a) and (b) compare the interface reaction in both LSCF/YSZ and LSCF/GDC systems, respectively [92]. Due to the better chemical stability of GDC, a barrier layer from this material may enhance the stability and electrochemical properties of the YSZ-based systems. Still, a highly resistive Ce-Zr solid solution phase forms at the GDC/YSZ interface in elevated sintering temperature above 1300 °C, inducing a severe degradation in SOFC [94]. It should be mentioned that

the ceria-based electrolytes may suffer from chemical stability and introducing electronic conduction as Ce^{4+} reduces to Ce^{3+} at low oxygen partial pressure, making an electrical short-circuit at once with dropping the overall efficiency and decreasing the open circuit voltage (OCV) [16, 95]. The reaction between the LSGM electrolyte and cathode material is not similar to the one in YSZ or GCD electrolytes and generally takes place through the interdiffusion of cations rather than forming a secondary phase [96]. Considering the beneficial role of Co, Fe, and Ni interdiffusions for electrolyte performance, this small amount of interdiffusion is not detrimental.

Nevertheless, extreme interdiffusion will cause degradation in both cathode and electrolyte performance. Therefore, applying a ceria protection layer between the LSGM electrolyte and LSC cathode may stop the Co interdiffusion. But then again, the formation of an insulating phase can cause degradation [16]. Electrolyte/anode chemical reactions are less severe than electrolyte/cathode ones. Ni-YSZ, as the most common anode material, has no problems with the YSZ electrolyte. Nonetheless, the formation of a resistive layer may occur between LSGM and Ni-based anodes and causes SOFC degradation [16].

The last degradation mechanism in the SOFC electrolyte is mechanical failures resulting from thermal and chemical stresses. SOFCs are almost stress-free at high working temperatures, but the cooling down to room temperature causes residual stresses due to the difference in TECs of cathode/electrolyte or anode/electrolyte [93]. This residual stress introduces the crack initiation or delamination, which eventually leads to mechanical failure [97]. Fig. 7 illustrates an SEM micrograph of a partially delaminated YSZ electrolyte and NiO/YSZ anode [98]. Phase



Fig. 7. Delamination SEM image of a partially delaminated anode layer on YSZ electrolyte. Reprinted from Selcuk et al., [98] with permission. Copyright 2001. Springer Nature.



Fig. 6. Schemes of the surface segregation and interface reaction in (a) LSCF/YSZ and (b) LSCF/GDC cells. The red arrow indicates the Sr segregation, diffusion, and reaction direction. Reprinted from Sun et al., [92] with permission. Copyright 2021. Elsevier.

transformations are also responsible for residual stresses, like the phase changes of ScSZ that experiences a partial cubic to rhombohedral and back to cubic transformation through the heating range of 300–500 $^{\circ}$ C [91]. The difference in TEC between YSZ and GDC layers is also another example of delamination and mechanical degradation [94].

Another source of mechanical failure in the SOFC electrolyte is chemical stress induced by the chemical environment of the SOFC operation. The oxidation of Ni-based anodes and the resulted volume change is probably the most crucial example of chemical stress. The penetration of unwanted oxygen to the anode, either due to system leakage or uncontrolled fuel utilization, causes irreversible expansion of Ni-based anodes. Since there is a significant difference between the Ni and NiO volumes, this oxidization creates internal stress, tension in the electrolyte, crack formation, and eventually the system failure. The gas permeation through these cracks also speeds up the other degradation mechanism [93,99]. GDC reduction is another major cause of chemical stress as the GDC experiences a volume expansion and eventual cracking, along with the TEC mismatching between the other components [91,100,101].

3.3. Anode

Anode degradation mechanisms can be divided into three main categories:

- Microstructural changes
- Coking and Poisoning
- Delamination

The most common microstructural changes in Ni-based anodes are Ni coarsening, Ni migration, and Ni depletion, which are somehow connected to each other [102]. Ni coarsening is known as the most detrimental degradation mechanism in SOFC anode electrodes. The primary reason is surface diffusion along with the interface and is generally related to a kind of "Ostwald ripening" mechanism [103]. This coarsening arises from the tendency to lower the chemical potential by smoothing the particle surface and reducing the curvatures since the higher curvatures result in higher chemical potential [99,104]. Ni particle growth reduces both TBP sites (Fig. 8) and electrical conductivity, which weakens both performance and stability of the SOFC. Besides, the catalytic activity of the Ni decreases due to the loss of specific surface area in larger particles. Moreover, this mechanism deteriorates the Ni-YSZ contact and eventually causes the delamination of Ni from YSZ [105–107]. Ni coarsening can also result in Ni migration to the anode surface by evaporation/condensation process and diffusion. In the SOFC operating conditions, high temperature and water pressure, Ni, O2, and H₂O react together and form Ni(OH)₂, taking place near the TPB region. Since Ni(OH)₂ has a lower melting point than the operation temperature, it would be evaporated, transferred to the surface, and then condensates to Ni atomic form. This Ni migration to the surface brings inconsistency in the Ni content of the anode and causes Ni depletion around the electrolyte/anode interface. This redistribution may affect the TPB length, particle size distribution, porosity, tortuosity and

eventually causes the SOFC degradation. Further, Ni coarsening is responsible for Ni depletion, as the larger particles adsorb the smaller ones [67,102,108].

As previously mentioned, fuel flexibility is one of the advantages of SOFCs as they can internally reform the hydrocarbon fuels at elevated operating temperatures. However, there is the risk of anode coking as the produced Carbon Monoxide (CO) during the reforming process continues to react, referring to the Boudourd reaction [109–112]. This CO reacts with H₂ as well and results in more carbon formation. Several factors influence the coking rate, including steam/carbon ratio, anode composition, operation temperature, and current density. For instance, carbon deposition is inversely related to the steam/carbon ratio and applied current density. Anode coking covers the surface and blocks the TPBs and gas channels, and causes mechanical and electrochemical degradation. As the carbon deposition increases, so much pressure is created that can lead to the anode fraction [113]. Fig. 9 (a) and (b) show the SEM micrographs before and after carbon deposition on the surface of a Ni-based anode, respectively [110]. Kan et al. [114] showed that carbon formation occurs at the beginning of the cell operation. After the carbon deposition, amorphous carbon changes to graphitic carbon, damaging the single cell's cohesive structure [114].

Apart from coking, hydrocarbon gaseous fuels are composed of different contaminants, including sulfur (S), phosphorous (P) [115,116], arsenic (As) [117], selenium (Se) [118], chlorine (Cl) [119], and antimony (Sb), may interfere with the anode and degrade the performance and stability of the SOFC [120]. The type and amount of these elements in the hydrocarbon fuel depend on the coal's mine location and their process technique. The S poisoning from the hydrocarbon fuels in the anode is arisen from the interaction of H₂S anode, creating H₂ and elemental S. Ni particles have a strong tendency to adsorb this elemental S, which causes Nickel Sulfide (Ni_xS_v) deposition and blockage of active sites along with the redistribution of Ni at the interface [121]. Fig. 10 (a) illustrates S poisoning's effect on Ni-based anode, taking place at two main steps [122]. Temperature, polarization, cell configuration among the H₂S concentration impact the degree of S poisoning [123]. P traces in coal lead to Nickel Phosphide's development at the anode/electrolyte interface and brings irreversible performance loss to SOFC as these species hinder the active sites [124]. In addition to performance failure, the formation of NiP causes stress, resulted in the originating of microcracks in the Ni-free YSZ matrix and mechanical degradation in the anode, as in Fig. 10 (b) [115].

As is one of the especially concerned anode contaminants, as it is commonly spread in coals, easily reacts with H_2 to form arsine (AsH₃), and even small traces (10 ppb or less) are detrimental for SOFCs. Furthermore, this element is a notable poison for Ni catalysts due to its strong tendency to react with Ni. The formation of Ni₅As₂ and Ni₁₁As₈, determined by temperature, As concentration, flow rate, and exposure time, causes Ni coarsening and Ni migration to the anode surface. These processes induce the loss of electrical connectivity in the anode support and, finally, result in sudden failure. Before the failure, there is almost no sign of electrochemical degradation of the cell [126,127]. Se, another toxic impurity with higher volatility, is distributed in different coals in different concentrations. Se poisoning, which is quite like S poisoning,



Fig. 8. Change in the TPB site caused by Ni coarsening. Reprinted from Khan et al., [103] with permission. Copyright 2018. Elsevier.



Fig. 9. SEM images of Ni-based anode surface (a) before and (b) after carbon deposition. Reprinted from Subotic et al., [110] with permission. Copyright 2016. Elsevier.



Fig. 10. (a) S poisoning effect on Ni-based anode upon exposure to H_2S , Reprinted from Cheng et al., [125] with permission. Copyright 2011. Royal Society of Chemistry; RSC Publishing. (b) Schematic diagram of the reaction of the Ni/YSZ anode with phosphorus in coal gas. Nickel phosphide phases form in outer portions of the anode support as illustrated by an SEM image of the anode-supported cell after 470 h operation on coal gas with 5 ppm PH₃ at 800 °C in the upper left corner. Surface diffusion of phosphorus to the active interface occurs as well, responsible for initial performance losses. Reprinted from Marina et al., [115] with permission. Copyright 2010. Elsevier.

originates from Se by Ni's surface adsorption and formation of Ni₃Se₂ at the anode/electrolyte interface. This solid phase inhibits the accessibility to active sites and causes SOFC degradation [118,126]. Cl poisoning is also a severe case since the SOFC practical fuels, like biofuels, contain Cl compounds in high concentrations. The presence of Cl, an electronegative species, can prevent the H₂ adsorption on the Ni surface, blocking the TBP region and limiting the electrochemical performance of SOFC [128]. This adsorption-desorption mechanism is found out to be a reversible process. Haga et al. [129] studied the microstructural change of Ni–Sc stabilized Zr anode by Cl poisoning. There was a considerable change in the microstructure after conducting the poisoning test by wet H₂ - 5 ppm Cl₂. Ni reaction with Cl₂ caused the NiCl₂ sublimation, which led to the continuous Ni depletion in the anode. The degradation rate of this test was 3%/1000 h, showing the importance of Cl poisoning [129].

Sb is another coal impurity with a wide application as a passivating agent for Ni catalysts in refineries. Cell degradation from Sb poisoning results from two processes, depending on the exposure length, Sb concentration, and applied current density. Ni surface adsorbs Sb, and the electrocatalytic activity of anode diminishes at the initial step, same as S and Se poisoning. This adsorption mechanism is reversible, and early reaction products only exist on the adsorption layer's surface. With a longer exposure duration, the late stage of the degradation, the severe one, begins with the broad formation of solid reaction products, especially NiSb. These products obstruct the electrical conduction pathways between particles (Percolation Loss), which irreversibly induces ohmic resistance. Furthermore, Sb poisoning leads to Ni coarsening, consumption, and migration to the surface, which are also unfavorable for anode performance [120,130].

Anode delamination is mainly due to oxidation cycling and thermal cycling. The first case causes volume changes in the anode, and the second one is because of the mismatch in TEC of the anode and the electrolyte [131]. Delamination is less common in anode than cathode

due to the similar TEC of anode and electrolyte, but it still exists [81]. It should be noted that the Ni coarsening induces delamination because when the Ni particles grow bigger, the contact area with the electrolyte becomes smaller. Furthermore, delamination causes TPB reduction, which is one of the leading causes of degradation in SOFC [132].

3.4. Interconnects

The three degradation modes of interconnects are as follows:

- Corrosion
- Cr vaporization
- Mechanical failures

Interconnects are a fundamental element in SOFC stacks as they provide electrically conductive pathways among the single cells and aid in separating one cell's anode side fuel from the cathode side air of the next cell in the stack [82]. High-temperature SOFCs use ceramic interconnects developed from the semiconductor oxides. The most common of them are LaCrO3-based interconnects, which are p-type semiconductor oxides. However, their application is restricted due to their challenging fabrication method, high price, and inadequate flexural strength [7]. Current SOFCs with lower operating temperatures (500-800 °C) use metallic interconnects instead of former ceramic ones owing to their lower cost, better electrical conductivity, and more straightforward fabrication processes [133]. Metal alloys such as Fe-Cr alloys, Cr alloys, Ni(Fe)-Cr-based heat resistant alloys, and austenitic and ferritic stainless steels (SS) are widely utilized as metallic interconnects. However, most metals are affected by oxygen, which causes corrosion. The corrosion not only weakens the mechanical stability of the interconnect but also reduces its electrical conductivity due to the emergence of insulating oxide phases like Cr₂O₃ and (Mn,Cr)₃O₄ [7,134, 135]. Moreover, the simultaneous exposure of SOFC to fuel at one side

and air at the other side in ferritic SSs is another cause of the corrosion, called the "dual atmosphere effect" [136]. This degradation is due to the different scale growth caused by the hydrogen transfer through the steel, accelerating the iron transfer and increasing its activity in growing iron oxides phases [137]. "Metal dusting" phenomenon, a serious kind of corrosion in metals and alloys in the carbon-supersaturated gaseous atmosphere at high temperatures, is another hazard to the metallic interconnectors while using carbon-containing fuel gases [138]. Metal dusting results in forming fine metal carbide or pure metal and carbon dust, causing a brittle structure and reducing the interconnector's mechanical strength [82,139].

Cr vaporization from interconnects causes Cr poisoning to the cathodes, one of the most severe degradation mechanisms in SOFCs responsible for a significant decrement in electrical conductivity by blocking the electrode's active TBP sites [7,140]. Furthermore, this Cr vaporization induces the Cr depletion in the interconnect, and this depletion below a specific threshold threatens its mechanical strength and structural integrity through the oxidation break-away [135,141]. Compared to other metallic interconnects, superalloys such as Ni–Cr- or Ni–Fe–Cr-base alloys provide a lower scale growth rate, leading to higher oxidation resistance behavior. Nevertheless, Ni-base alloys with enough Cr to obtain a high oxidation resistance show a high TEC, bringing the TEC mismatch between the other SOFC components and results in mechanical failure [7,142].

The Cr vaporization issue can be addressed by modifying whether the alloy composition [143,144] or surface conditions [141]. Stanislowski et al. [145] showed that the surface modification is more favorable due to Cr release results from different common Ni-, Cr-, and Fe-based alloys. These results presented that the Cr-dominant oxide generators need to be protected by protective coatings to become free of Cr evaporation [141]. Generally, 3 types of coating materials are available for SOFC interconnects, including reactive element oxides (e.g., La₂O₃, Nd₂O₃, Y₂O₃) [133,146], rare earth perovskites (e.g., LSM [147], La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O₃₋₆ (LSCM) [148]), and composite spinel oxides (e.g., Mn–Co-based [149–153], NiFe₂O₄ [154–156], Cu-based [157, 158]). So far, composite spinel oxides found out to be the most potential coating to save the interconnect from the Cr vaporization, enhance the electrical conductivity, and lower the TEC at the same time [149,153, 159,160].

3.5. Sealant

In general, sealants face the following modes of degradation:

- mechanical failure and leakage
- corrosion
- poisoning

Bonding or rigid sealants, e.g., glass ceramics, are sensitive to thermo-mechanical stress during the thermal cycles. This susceptibility causes non-linear behavior in thermal properties, including TEC, viscosity, and porosity, and changes over time, leading to TEC mismatch between the sealant and other stack components, mechanical failure, and eventually leakage [161–163]. Typically, leakage indicates that the anode receives less fuel than planned, which increases the stack's fuel consumption, causing fuel shortage, operating limitations, performance loss, and anode oxidation [164]. Hence, quantifying any changes in the stack leakages throughout the operation is valuable to identify them from other causes of stack voltage degradation, like increase in contact resistance, S poisoning, or measurement faults [165]. To lower the risk of mechanical failure and leakage rate, using non-crystallizing sealants, such as SiO2-Al2O3-CaO-Na2O-ZrO2-Y2O3 systems, can be helpful since they are resistive to the considerable change in the TEC of material [161,166]. Another solution can be hybrid sealants to develop a seal that takes mechanical characteristics from the compressible core but, unlike typical compressive seals, has meager interfacial leak rates due to the

compliant surface coating [167,168]. Fig. 11(a-d) illustrates the difference between a simple compressive seal and different types of hybrid seals. Fig. 11 (a) represents a regular mica-based compressive seal, which the most common cause of the leakage is the contact between the mica and the metal or ceramic. Using a compliant layer from binding sealants at the surface of the mica layer (shown in Fig. 11 (b)) can enhance the gas-tightness behavior by making a hybrid seal. Moreover, Fig. 11 (c) depicts another technique for creating a hybrid seal with mica and metal sealants by setting the mica powder in the interspace of a corrugated metal sealant. Also, it is possible to develop the sealant performance through the infiltration of the mica with a bonding sealant phase to enhance mica particle-to-mica-particle adhesion, as outlined in Fig. 11 (d) [164]. In this regard, Rautanen et al. [162] developed a hybrid sealant, glass powder-coated Thermiculite 866, with leakage rates of 0.1–0.3 mL m min $^{-1}$, 60–90% less than the uncoated sealant. This decreased leak rate was due to the conformability of the glass coating that covered the Thermiculite 866 surface defects and blockage of interfacial leak paths by the adjacent elements [162].

Although glass-based sealants show a better leakage resistivity, their impurities, like Si, can be poisonous to cathode and anode and hinder their surface reactions, causing performance degradation in the SOFC stack. In Si poisoning, Si deposits on the TPBs and cathode surface, inhibiting the oxygen reduction reaction [139]. Moreover, deposited Si can react with the cathode surface and change the surface composition by forming insulating phases. In fact, this form of poisoning is most commonly seen in Sr-containing perovskites at high temperatures, forming stable silicates (e.g., Sr₂SiO₄) and blocking the active surface sites [139,169]. In addition to impurities, their constructive cations, such as Ba²⁺ and Zr⁴⁺, can become deleterious for the long-term performance of the SOFC. Ba²⁺ has a strong tendency to react with Cr from the ferritic interconnects and create unwanted and insulating BaCrO₄ [170]. On the other hand, Zr^{4+} leans to form bulk crystallization in the glass or glass-ceramic sealants, causing the growth of microcracks and weak mechanical stability in long-term performance [171]. Also, the presence of alkali cations (Li⁺, Na⁺, K⁺) in the glass- and glass-ceramic-based sealants makes them more likely to react with other cell components. They can induce cathode Cr poisoning by speeding the Cr vaporization of interconnects [139,172,173].

There are several techniques to control the sealants corrosion, such as lowering the Si content, making Ba²⁺-, alkaline- and alkaline earth metals-free sealants, and controlling the Zr⁴⁺ amount [82,170,171]. In this regard, Kiebach et al. [170] from DTU developed a CaO and ZnO-rich glass composed of 50 mol% CaO, 20 mol% ZnO, 20 mol% B₂O3, and 10 mol% SiO₂, named CZBS. This CZBS glass showed no degradation or sealant-related leakage for over 400 h under dual-phase atmospheres (Air/H₂) at 750 °C (for first 100 h) and 850 °C for the rest of the operation.

4. Characterization techniques

The advancement of SOFCs to fulfill the durability targets needs a developed understanding of material properties and their interactions. Using different characterization methods to study the SOFC materials and how they behave before and after operations helps in advancing this field. Furthermore, this requirement leads to the development of various types of state-of-the-art characterization equipment, which are adaptable to the extreme operating conditions of SOFCs. These advanced methods, known as *in-situ* techniques, help us study the materials while operating as a SOFC. In-situ TEM, in-situ Raman spectroscopy, and infrared imaging are in this category [174]. In addition to characterization techniques, numerical modeling is a leading approach to study and investigate the SOFC behavior for optimizing, controlling, and enhancing energy efficiency and durability performance [175,176]. This section will cover the different structural and electrochemical characterization techniques along with the numerical modeling for studying and developing SOFC durability and stability performance. A summary



Fig. 11. (a) a simple compressive mica sealant, (b) hybrid sealant with ceramic/metal compliant layer and mica. (c) hybrid sealant with corrugated metal and mica powder. (d) hybrid seal with infiltrated mica and ceramic/metal compliant layer. Reprinted from Jeffrey W. Fergus, [164] with permission. Copyright 2005. Elsevier.

of these characterization techniques is given in Table 1.

4.1. Electrochemical characterization

Electrochemical characterization is an essential tool for the degradation evaluation of SOFC. The most common techniques for this purpose are current-voltage (I–V) measurements, electrochemical impedance spectroscopy (EIS), and long-term galvanostatic or potentiostatic stability tests. These measurements are carried out in a fuel cell reactor with the desired operating temperature, fuel, and oxidant [177]. The degradation study in the I–V and C–V measurements and EIS is usually based on the comparison of the SOFC performance before and after the durability test under the current conditions and atmospheres [178]. Furthermore, these techniques demonstrate the effectiveness of a method to prevent degradation by comparing the SOFC performance before and after applying that specific method, such as coating and doping.

4.1.1. Current-voltage measurement

The current-voltage (I–V) measurement technique evaluates the SOFC performance by applying a direct current (DC) sweep through the SOFC from 0 to a given current density, and a potentiostat/galvanostat device measures the resulting DC potential. In the I–V curve, the irreversible losses, including reaction rate, resistance, and gas transport, decrease the voltage output from its theoretical value [176]. The degradation rate is calculated by comparing the initial results and the results obtained after the operation of the SOFC. For instance, Wang et al. [179] used the I–V measurements to study the effect of porous and dense CuMn₂O₄ coating for the interconnect on the Cr poisoning. Fig. 12 presents the I–V curves and the corresponding power density of three different anode-supported cells of LSM|LSM-8YSZ|Ni-8YSZ at 0 h and 48 h after cell performance at 800 °C in dry air. The results indicated that the cell with the dense spinel coating had the highest power density and lower voltage loss, owing to Cr-poisoning prevention.

4.1.2. Electrochemical impedance spectroscopy

In the electrochemical impedance spectroscopy (EIS) measurements, the cell is subjected to a low magnitude alternating signal, calculating the impedance as a function of the alternating current (AC) source. In general, a Nyquist plot demonstrates the Impedance spectra by showing the imaginary part on the Y-axis and the real part on the X-axis at different frequencies. The intercept on the real axis at higher frequencies (>1 kHz) represents the cell's ohmic resistance, including interconnect and wires. At the lower frequencies (<1 kHz), this interception corresponds to the total cell resistance, which is the sum of the ohmic and electrode polarization resistances. This relationship is applicable in studying the dynamic electrode process, ORR activity, double layer capacitance, grain diffusion, and other similar phenomenons [180–182]. The electrode polarization resistance, which includes the charge- and mass-transfers, can reflect the degradation behavior of the

SOFC by comparing the polarization resistance values before and after the cell performance under different operation terms. The EIS measurements can be performed both in Open Circuit Voltage (OCV) and under load conditions [183].

Li et al. [182] studied the effect of a dense La₂NiO_{4+ δ} (LN) coating on the Cr tolerance of the PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+ δ} (PBSCF) double perovskite by EIS. Fig. 13 (a) and (b) exhibit the Nyquist plots of pure and coated cathodes at 400 mA cm⁻² at 750 °C for 1200 min, respectively. There is a significant reduction of low-frequency resistance (R_L) after applying the LN coating, indicating that LN coating will effectively facilitate the cathode's oxygen surface function due to its superior oxygen surface exchange property. Fig. 13 (c) and (d) represent the rise of the Polarization resistance (R_P) and Ohmic resistance (R_Q) as a function of aging time at 750 °C under a cathodic polarized current of 400 mA cm⁻² for 1200 min. There is a parabolic mode in the R_P increment of PBSCF cathode, demonstrating that the Cr deposition takes place at the beginning of the polarization. Moreover, R_P's ascending trend for the coated cathode is much slower than the pure one, showing the cathode's enhanced Cr toleration [182].

Wei et al. [184] examined the role of reduced $La_{0.6}Sr_{0.2}Cr_{0.85}Ni_{0.15}O_3$ containing exsolved Ni nanoparticles with GDC (LSCrN@Ni-GDC) (Fig. 14 (a)) in the prevention of carbon formation by EIS measurement. The EIS was performed on Ni–GDC anode-supported cells with and without the LSCrN@Ni-GDC catalyst layer at 750 °C using 50% CO₂–50%CH₄ as fuel. The Nyquist plot (Fig. 14 (b)) demonstrates a smaller anode polarization resistance for the LSCrN@Ni-GDC cell, owing to the LSCrN@Ni-GDC CH₄ pre-reforming characteristic, which prevented carbon formation and saved the gas pathways from blockage [185].

In another work, EIS was used to investigate the degradation phenomena of the Sm_{0.5}Sr_{0.5}CoO_{3- $\delta}$} (SSC) fibrous cathode with encapsulated Sm_{0.2}Ce_{0.8}O_{1.9} (SDC) particles (SSC-SDC). To do this, researchers compared the EIS data of SSC-SDC half-cell before and after applying a cathodic polarization (500 mA cm⁻², 700 °C, 120 h). The results revealed that charge transport (R₁) and surface catalytic reaction (R₂) resistances increased from 0.034 Ω to 0.076 Ω –0.090 Ω and 0.134 Ω , respectively. This degradation was due to the Sr enrichment and Co deficiency on the surface, which insulated the fibers. Moreover, particle coarsening and grain growth reduced the TPB areas and caused unfavorable performance [186].

4.1.3. Calendar life test

The calendar life test performs the durability test under constant operating conditions, such as voltage or current density [189]. For instance, Xu et al. [74] performed a durability test for an anode-supported flat-tube cell with 30 cm² of cathode effective are for almost 400 h under a 16 A cell current at 750 °C to test the CO₂-tolerance of a Ga-doped perovskite cathode $Sr_2Fe_{1.3}Ga_{0.2}Mo_{0.5}O_{6-\delta}$ (SFGM). First, the anode-supported single cell of SFGM cathode was operated in pure air for 97 h. Then, a 5% CO₂-containing air purged in, and the operation

A summary of characterization techniques in the evaluation of SOFC's durability and stability.

Characterization Tool	In- situ/ ex-	Result	Adv.	Disadv.
	situ			
Electrochemical				
I–V measurements	In- situ	Power density	Conclusive performance metric	Intrinsically nonspecific, Lack of information in the degradation
EIS	In- situ	Resistance of cell components	Transport properties and role of each component in	Lack of information in the degradation process
Calendar life test	In- situ	Current/ Voltage changes during the time	onmic losses Degradation rate	Lack of information in the degradation process
Chemical (Spectroso Raman	copy tech Both	niques) Electrical	Degradation	Limited
Spectroscopy	Dom	conductivity, doping, phase, and compositional information of materials and adsorbates	processes such as phase separation, coking, and S poisoning	sampling area [174]
XRD	Both	Changes in the crystal structure	Phase changes, poisoning, and formation of secondary phases	Limited sampling area
FT-IR	Ex- situ	Surface chemistry of components	Adsorbed species and surface reactions [187]	Experimentally challenging
XPS	Both	Material chemistry and structure	Impurity analysis	Providing elemental information instead of molecular
SIMS	Ex- situ	Detailed surface chemistry	Sensitive impurity analysis (1–1000 ppm) [188]	Locally destructive, Lack of quantitative results
Structural (Macrosc	opy tech	niques)	Structuro1	Lask of
194/096	situ	decomposition of component	stability	information in the degradation process
Dilatometry	Ex- situ	Thermal expansion	Structural stability	Lack of information in the degradation process
Tensile test	Ex- situ	Tensile strength	Structural stability	Lack of information in the degradation process
Bending test	Ex- situ	Flexural strength	Structural stability	Lack of information in the degradation process
Structural (Microsco SEM and EDS	py techr Ex-	nques) Morphological	Formation of	Unable to detect
JEWI AHU EDO	situ	and elemental details	secondary phases, poisoning	impurities in ppm

Table 1 (continued)

Characterization Tool	In- situ/ ex- situ	Result	Adv.	Disadv.
TEM	Ex- situ	Diffraction patterns and crystal structure	Structural changes	Challenges in sample preparation
AFM	Ex- situ	Surface roughness	Poisoning and formation of secondary phases	Single scan image size

continued for 291 h. There was a small reduction in the cell voltage after switching to CO₂-containing air as CO₂ filled the ORR actives sites and decreased the discharge performance (Fig. 15 (a)). Even after this voltage reduction, SFGM performance was stable during the next 291 h. This excellent CO₂ resistivity was due to the weaker affinity of SFGM towards the chemical adsorption of CO₂. Fig. 15 (b) compares the competitive adsorption of CO₂ and O₂ on the surface of SFGM [74].

In another study, researchers demonstrated the superior contaminant tolerance of a novel hybrid catalyst of $PrNi_{0.5}Mn_{0.5}O_3$ (PNM) with exsoluted PrO_x nanoparticles for the LSCF cathode (Fig. 16 (a)) by conducting a long term-stability test. Fig. 16 (b) compares the durability performance of three different single cells of bare LSCF, 0.1 M, and 0.3 M hybrid-LSCF under 7 V at 750 °C for 600 h wet H₂ and direct Crofer contact. The results represented an exceptional durability behavior in the 0.3 M hybrid catalyst coating (0.04%/h as degradation rate) along with the enhanced power density. The improved durability performance against Cr poisoning and moisture was due to the presence of the dense conformal PNM coating, while the PrO_x nanoparticles accelerated ORR kinetics and boosted the power density [79].

4.2. Chemical and structural characterizations

Chemical and structural characterizations are valuable methods for understanding the origin of the degradation behavior of SOFC. There are multiple analytical techniques useful to characterize the "postmortem" status of different SOFC elements when the cell has been cooled down to room temperature and disassembled, called *ex-situ* characterization [190]. On the other hand, *in-situ* characterization methods study the samples during the electrochemical operation at elevated temperatures with the desired atmosphere. These *in-situ* techniques connect the phase transitions, composition changes, and other physical transformations to the performance degradation of SOFC, evaluated by voltammetry and EIS [190,191]. This section will cover the role of these spectroscopic techniques, such as Raman spectroscopy, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and mass spectrometry (MS), in studying the degradation of SOFCs' performance.

4.2.1. Chemical characterization (Spectroscopy techniques)

4.2.1.1. Raman spectroscopy. Raman spectroscopy is a unique tool for studying SOFC degradation behavior. It is not an electron-based technique and so does not need a vacuum environment, allowing the *in-situ* studies of samples under the harsh operating conditions of SOFC. There are several studies on using *in-situ* Raman spectroscopy for detecting coking [192–197]. Kirtley et al. [196] used the *in-situ* Raman spectroscopy to evaluate the carbon formation rate on Ni/YSZ anodes, which there were exposed to dry CH₄ for 10 min under OCV at 730 °C. The Raman Spectra of Ni cermets in Fig. 17 (a) shows no peak from 1200 to 1700 cm⁻¹ before the exposure. After a few seconds of CH₄ initiation, a vibrational band at 1556 cm⁻¹ occurs in the Raman spectrum, attributed to the "G" peak of highly ordered graphite. This graphite signal proceeds to increase during the next ~7–8 min before hitting an asymptotic limit (Fig. 17 (b)). Other phenomena, including the formation of the surface



Fig. 12. I-V curves and the corresponding power density of LSM/LSM-8YSZ/Ni-8YSZ anode-supported cells (a) before and (b) after 48 h cell performance at 800 °C in dry air to study the effect of CuMn₂O₄ spinel coating on the Cr poisoning. Reprinted from Wang et al., [179] with permission. Copyright 2018. Elsevier.



Fig. 13. EIS results of cathodes with a current density of 400 mA cm⁻² at 750 °C for 1200 min in the presence of SUS430 interconnect for Cr-poisoning evaluation: (a, c) PBSCF and (b, d) LN-coated PBSCF. Reprinted from Li et al., [182] with permission. Copyright 2018. Elsevier.

layer in electrolytes [198,199], S [200–202], and Cr poisoning [79,203], are discoverable using *in-situ* Raman spectroscopy. Fig. 17 (c) illustrates a schematic of the *in-situ* Raman spectroscopy arrangements [125].

Ex-situ Raman spectroscopy is a practical technique to study the phase stability, oxidation degrees, degradation of different SOFC elements, species migration through the SOFC structure, and poisoning [174,203], mostly for coking and S poisoning [205–207]. Niu et al. [204] used the *ex-situ* Raman spectroscopy to investigate the coking and S poisoning resistance of double perovskite $Sr_2TiFe_{0.5}Mo_{0.5}O_{6-8}$ (SFTM05) anode. As it is obvious in the anode's Raman spectra (Fig. 17 (d)), there are no signs of S poisoning due to the absence of 460, 622, 1001 cm⁻¹ peaks for SrSO₄, 335, and 380 cm⁻¹ peaks for TiS₂, 340, and 370 cm⁻¹ peaks for FeS₂, and 380 and 410 cm⁻¹ peaks for MoS₂. Moreover, the Raman spectrum indicates no carbon deposition as carbon's three primary peaks are not detected in the spectrum [204].

4.2.1.2. Fourier-transform infrared spectroscopy. Fourier-transform infrared (FT-IR) spectroscopy is another spectroscopic method to study the SOFC degradation by providing direct analysis of adsorbate molecules and adsorbent solid surfaces, which leads to a complete estimation of surface structure changes in SOFC components, like S [208], Cl [209], CO₂ [210,211], and humidity [212] poisonings [208]. For instance, Zhu et al. [213] studied the CO₂ resistivity of SrNb_{0.1}CO_{0.9-x}Fe_xO_{3-δ} ($0 \le x \le 0.9$) (SNCF_x) with the FT-IR technique by exposing the powders to high purity CO₂ (99.999%) at 600 °C for 1 h. Fig. 18 (a) and (b) present the FT-IR spectra of SNCF_x powders before and after CO₂ exposure, respectively. Comparing the intensity of 1440 cm⁻¹ and 860 cm⁻¹ peaks, which are the characteristic vibrational bands of carbonate groups, provides a CO₂-resistive behavior for SNC, SNCF0.5, and SNF.

4.2.1.3. X-ray diffraction. X-ray diffraction (XRD) is an effective



Fig. 14. (a) Schematic diagram of LSCrN@Ni-GDC in an anode-supported oxide-conducting SOFC, (b) EIS data of GDC anode-supported cell with and without LSCrN@Ni-GDC catalyst layer at 750 °C with 50%CO₂-50%CH₄ as fuel. Reprinted from Wei et al., [184] with permission. Copyright 2021. Elsevier.



Fig. 15. (a) Durability test of an anode-supported single cell of SFGM cathode, (b) Schematic illustration of competitive chemical adsorption of CO₂ and O₂ on the surface of SFGM cathode. Reprinted from Xu et al., [74] with permission. Copyright 2020. Elsevier.



Fig. 16. (a) Schematic of the hybrid catalyst of PrNi0.5Mn0.5O3 (PNM) with exsoluted PrO_x nanoparticles for the LSCF cathode, (b) long-term durability test for three different single cells of bare LSCF, 0.1 M, and 0.3 M hybrid-LSCF under 7 V at 750 °C for 600 h with wet H₂ and direct Crofer contact. Reprinted from Chen et al., [79] with permission. Copyright 2018. Elsevier.

technique to examine the changes in the crystal structure of electrochemical cell materials, available in both *ex-situ* and *in-situ* modes [214]. XRD is practical for studying the chemical stability and compatibility of SOFC different components [204,215,216]. Furthermore, unit cell growth and changes in TEC [217], phase changes and impurities [215], poisoning [182,218], and formation of secondary phases such as Sr segregation [219] are observable via this mode. Niu et al. [204] used the *ex-situ* XRD to study the chemical compatibility of the Sr₂TiFe_{0.5}Mo_{0.5}O₆₋₆ (STFM05) anode with LSGM and SDC electrolytes. The SFTM05-LSGM and SFTM05-SDC were first calcinated at 1000 °C for 10 h in 5% H₂/Ar atmosphere. XRD patterns in Fig. 19 (a) revealed no noticeable peaks other than the SFTM05, LSGM, and SDC peaks. These peaks did not face any shifts, indicating no significant chemical reactions between the components and the chemical compatibility of the SFTM05 anode with LSGM and SDC electrolytes. This specification is essential to preserve the long and stable operation of the SOFC. In another study, [219] researchers investigated the effect of humidity on the process of Sr segregation in Sr₉Ni₇O₂₁ (SNO) cathode via *ex-situ* XRD technique over time. At first, the XRD test was carried out on the as-synthesized SNO powder. Then, the sample powder was placed in a humid environment for 1 week. The XRD patterns of the as-synthesized and moisturized samples are depicted in Fig. 19 (b,c). As it is obvious in



Fig. 18. FT-IR spectra of different SNCF powders (a) before and (b) after exposure to CO₂ at 600 for 1 h. Reprinted from Zhu et al., [213] with permission. Copyright 2015. Elsevier.



Fig. 19. (a) Room-temperature XRD patterns of the STFM05 sample after sintering at 1200 °C for 10 h in 5% H_2 /Ar, [204]. Reprinted from Niu et al., [204] Copyright 2018. Elsevier. XRD patterns of (b) as-synthesized SNO (Sr:Ni ratio of 35:65); (c) the SNO placed in the humid environment for 1 week [219]. Reprinted from Hong et al., [219]. Copyright 2019. Electrochemical Society.

Fig. 19 (c), two new peaks of $Sr(OH)_2.8H_2O$ and $SrNiO_3$ are emerged, implying the Sr segregation from SNO due to the presence of moisture and formation of $Sr(OH)_2.8H_2O$ [219].

In-situ XRD, also called high-temperature XRD measurements, is a valuable technique for observing the crystal structure transformations with temperature and studying the structure stability of the SOFC component in the working temperature [220]. For instance, Dong et al. [221] studied the structural stability of the BaFe_{0.95}Sn_{0.05}O_{3- δ} (BFS) cathode at higher temperatures. The *in-situ* XRD measurement results collected in the temperature range of 100–800 °C are shown in Fig. 20. There is a multiple-to-single phase transition, which occurs around 500 °C due to Fe ions' thermal reduction. Subsequently, this single phase shows proper stability for further heating up to 800 °C, demonstrating a thermodynamically stable state within the cell activity's temperature range [221].

4.2.1.4. X-ray photoelectron spectroscopy. X-ray photoelectron spectroscopy (XPS) is another important tool to examine the surface chemistry of the SOFC components, which is critical to governing the stability and can be performed in both *ex-situ* and *in-situ* modes. This characterization method is suitable for studying the Sr segregation [222–224], carbon deposition [225,226], the formation of secondary phases [227, 228], and chemical stability [229,230]. Jang et al. [226] used the XPS *ex-situ* analysis to show the effect of Pd nanoparticles on the coke resistivity of Ni anode. The XPS analysis was conducted on a bare and a Pd-coated Ni anode after the methanol cell test. As shown in XPS spectra in Fig. 21 (a,b), the amount of carbon considerably decreased after applying 600 cycles of Pd nanoparticles coating by the atomic layer deposition (ALD) method [226].

In another study [231], the transformation of the surface structure of the La_{0.6}Sr_{0.4}CoO_{3- δ} electrodes was characterized by near-ambient pressure (NAP)-XPS at high temperatures while running impedance spectroscopy to measure the surface activity of the material at the same time. To collect the *in-situ* XPS spectra during the EIS measurements, 0.5 mbar O₂ was added into the NAP-XPS chamber, and the temperature was raised to 780 °C stepwise. The XPS results revealed the Sr segregation and formation of a secondary Sr-rich oxide phase at the surface at 450–500 °C due to the emergence of a third species in both Sr 3d and O 1s spectra (Fig. 22). This Sr oxide phase covered the electrochemically active sites of the Co surface, causing LSC degradation [231].

4.2.1.5. Secondary Ion Mass Spectrometry. The Secondary Ion Mass Spectrometry (SIMS) technique is able to detect the concentration distribution of contaminations, including poisoning (such as S and Cr) [73,



Fig. 20. In-situ XRD patterns of BFS over the temperature range between 100 and 800 °C in the air. Reprinted from Dong et al., [221]. Copyright 2016. Elsevier.

232] and secondary phases [223,233,234], in a high-sensitivity depth direction for studying the poisoning resistivity properties of SOFC components. New Energy and Industrial Technology Development Organization of Japan (NEDO) is among the first groups to use SIMS to detect cathode S poisoning for their SOFC durability project [70]. Develos-Bagarinao et al. [235] research is an example of using ex-situ SIMS to clarify the physical origin of the cathode/interlayer of interfacial resistances of how GDC cathode/interlayer microstructure affects long-term durability. First, they carried out the SIMS elemental depth profiling on as-grown LSC thin film deposited on GDC-buffered (100)and (111)-oriented YSZ, shown in Fig. 23 (a) and (b), respectively. Then, additional SIMS analysis was performed on the similar samples after annealing at 600 °C for \sim 160 h, represented in Fig. 23 (c) and (d) for LSC/GDC/YSZ(100) and LSC/GDC/YSZ(111), respectively. The profiles demonstrated a wide cation (Zr and Y) diffusion across the LSC/GDC interface on the YSZ(100) substrate after the annealing due to the nanocolumnar microstructure of the GDC interlayer. This cation interdiffusion caused the formation of the yttrium-doped SrZrO₃ (SZY) secondary phase with a blocking effect in the interface. In contrast, LSC/GDC/YSZ(111) before and after profiles are almost identical without any prominent Y or Zr peaks, indicating no SZY formation as the GDC layer is dense and prevents the interdiffusion [235].

4.2.2. Structural characterization (Microscopy techniques)

Microstructural changes have a significant role in affecting the degradation process of SOFCs; hence, microscopy techniques are valuable for a detailed study of SOFC microstructure by providing both 2D and 3D images of the component structure [12,236]. Researchers use microscopic analyses, including AFM, SEM, and TEM, in pre- and post-test as well as *in-situ* modes to perform a comprehensive study on degradation mechanisms.

In general, electron microscopy studies, including scanning electron microscopy (SEM) and Transmission electron microscopy (TEM), are conducted by directing a high-energy focused electron beam on the sample surface, which generates different electron signals with different energies to providing a 2D image. Fig. 24 illustrates the interaction of the electron beam with the sample. Secondary electron (SE) and back-scattered electron (BSE) signals are widely used in the SEM.

4.2.2.1. Scanning electron microscopy. Secondary electrons (SEs) present information about the surface characteristics as they are low-energy electrons (< 50 eV) and the scanning electron microscopy (SEM) detector can only find them if they are emitted close enough to the sample's surface. Different degradation mechanisms like Cr [237] and S poisoning [238], coking [239], Ni agglomeration [240,241], Sr segregation are detectable using SE - SEM. Fig. 25(a-g) shows the SE - SEM images of various SOFC components deteriorated by the mentioned mechanisms after long-term operation. Fig. 25 (a) and (b) demonstrate the fresh LSM cathode, and Cr poisoned LSM cathode after a potentiostatically operation at 0.7 V for 1217 h operation at 700 °C. The LSM cathode catalyst has a porous structure with fine particles. However, after the long-term operation, the particles become much denser due to Cr poisoning, visible as light grey angular crystals on the LSM surface [237]. In Fig. 25 (c) and (d), which are the SE - SEM images of La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-δ} (LSCrM) anode, S poisoning roughened the smooth surface of the electrode after $\sim 5~h$ of H_2S poisoning process at 850 °C in H₂-50 ppm H₂S atmosphere [242]. In the case of coking, Lee et al. [239] exposed the Ni-coated GDC electrolyte to CH₄ for 3 h at 610 °C in order to investigate the susceptibility of Ni surfaces to carbon formations. As shown in Fig. 25 (e), carbon deposition appeared on the exposed Ni surfaces [239]. Moreover, Ni agglomeration, as one of the degradation mechanisms for SOFC anode, is observable in the SE-SEM cross-sections of the anode-electrolyte interfaces for a pristine and degraded cell in Fig. 25 (f) and (g), respectively. The degraded cell, operated by a constant power around 4.5 W at 700 °C with a fuel



Fig. 21. (a) Chemical states of carbon on the surface after cell operation with methanol at 450 °C for the bare Ni anode, and (b) A-Pd 600 samples with the fitting of C–C, C–O, and O–C–O groups. Reprinted from Jang et al., [226] with permission. Copyright 2020. American Chemical Society.



Fig. 22. XPS spectra of the virgin's surface state, water-treated sample directly after introduction into UHV system (a) at room temperature, and (b) the initial state at 400 °C in 0.5 mbar O₂. For both O 1s and Sr 3d, the green line corresponds to the perovskite bulk signal of LSC. The blue line represents the surface signal of the perovskite. The further red peaks of the degraded state result from a third Sr-oxide compound forming on the surface. Before heating, surface hydroxyls were observed—see component at ca. 533 eV in O 1s spectra before heating (yellow line in (a)). Reprinted from Optiz et al., [231] with permission. Copyright 2018. Springer Nature.

utilization of 60%, went through a severe power-drop (to 450 mW) after 237 h. This performance loss was due to Ni oxidation and agglomeration, which caused Ni expansion and eventually induced the anode/e-lectrolyte delamination and depletion of percolation pathways [243].

In BSE, primary electrons interact elastically with the objective surface and scatter to a large angle towards 1 µm depth in the sample. BSEs energy is more than 50 eV, and the resulted image provides an accurate composition contrast; a higher atomic number leads to a brighter image [12,244]. BSE-SEM is another tool for investigating Ni agglomeration [103,245], secondary phase formation, and other common degradations. For instance, Khan et al. [103] evaluated the morphological changes of a Ni-SSZ anode functional layer (AFL) during accelerated aging by performing a long-term operation at 900 °C for 1000 h in an H₂–3%H₂O atmosphere with a single anode-supported flat-tubular SOFC. Fig. 26 (a) and (b) demonstrate how Ni particles expanded after 1000 h of operation [103]. In another study using

BSE-SEM, Lee et al. [246] studied the durability of double perovskite structured NdBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5- δ} (NBSCF) cathode in comparison with the single perovskite structures Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3- δ} (BSCF). They performed the durability test in the wet and dry cycling mode (WDCM), which consisted of supplying dry air for 12 h and afterward switched to wet air (10 vol% H₂O) for 10 h in a galvanostatic mode under 0.18 A cm⁻² at 650 °C. Fig. 26(c–d) and (e-f) illustrate the fresh and post-mortem BSE-SEM images of BSCF and NBSCF cathodes, respectively. Despite the well-durable behavior of NBSCF, there was a serious agglomeration in the BSCF cathode due to the particle growth and presence of Sr enriched phases [246].

4.2.2.2. Transmission electron microscopy. Unlike the SEM technique, the electron beam passes through the sample in the transmission electron microscopy (TEM) as the sample is ultrathin and electron transparent. TEM provides a higher resolution and the ability to study the crystal structure of the specimen. In this regard, Chen et al. [247] used the TEM to examine the effect of gas humidity on LSM/YSZ cathodes' degradation. Fig. 27 (a) and (b) represent the unoperated and the operated cells in H₂-20% H₂O atmosphere at 800 °C for 120 h in a constant current density of 0.75 A cm⁻², respectively. Before the operation, there was no sign of nanoscale MnO_x, SrO_x, or La₂O₃ secondary phases, and the TBP area remained intact. However, after the process, TBPs hosted the nano-voids, propagating inward along the LSM/YSZ interface. Moreover, amorphous material filled the voids region due to the formation of secondary phases originating from the mobile OH⁻ and Mn ion species [247].

4.2.2.3. Atomic force microscopy. Atomic force microscopy (AFM) is another essential tool in evaluating surface roughness and morphology to examine the degradation process at the components' surface, such as Si poisoning, Sr segregation, and formation of secondary phases like SrZrO_{3.} [223,248,249]. He et al. [75] used the AFM technique to study the LSCF/YSZ interfaces before and after polarization at 750 °C and 1000 mA cm⁻². Fig. 28 (a) illustrates the interface after 1 h polarization, without any marks on the YSZ electrolyte surface. However, a considerable amount of crater-shape marks was observable after 12 h of polarization Fig. 28 (b). These marks became deeper and larger after 100 h of polarization in Fig. 28 (c), which indicated the formation of the SrZrO₃ phase on the YSZ electrolyte surface [75].

4.2.2.4. Focused ion beam-scanning electron microscopy. In addition to the 2D images, it is essential to have 3D images for studying the degradation of SOFCs. The focused ion beam-scanning electron microscopy (FIB-SEM), a cut-and-image technique, provides flawless volumetric data and opens the doors for generating 3D images of SOFC



Fig. 23. SIMS elemental depth profiles showing the normalized intensities of the metal cations (primary y-axis) and the corrected fraction of the 18O isotope tracer (secondary y-axis) for (a) as-grown LSC/GDC/YSZ (100), and (b) as-grown LSC/GDC/YSZ (111). (c) and (d) depict the corresponding SIMS elemental depth profiles after annealing in air at 600 °C for 161 h. Arrows indicate peaks located at interfaces. Reprinted from Develos-Bagarinao et al., [235] with permission. Copyright 2020. Elsevier.



Fig. 24. Interactions between the electron beam and the sample. Scanning electron microscopy (SEM) analyses secondary and backscattered electrons, whereas transmission electron microscopy (TEM) focuses on transmitted electrons. Reprinted from Jouttijärvi et al., [12] with permission. Copyright 2018. John Wiley and Sons.

microstructure. There is a schematic configuration of FIB-SEM and a low-magnification image of a SOFC with a trench in Fig. 29(a–b) [250]. Several studies used this 3D reconstruction technique to examine the Sr segregation [251], Ni agglomeration [105,252], S poisoning [253], and other deterioration processes in the SOFCs [12,250]. For example, Wankmuller et al. [254] studied the formation of insulating SrZrO₃ phase for GDC/YSZ electrolyte. They combined the 2D FIB-SEM images of primary and secondary phases at 1100, 1200, 1300, and 1400 °C with

a 3D FIB-SEM reconstruction (1300 $^{\circ}$ C). Fig. 29(c–d) demonstrates the direct contact between the pore phase and SrZrO₃. This direct contact caused the SrZrO₃ formation at the interface due to Sr gas diffusion during the cathode sintering [254].

4.2.3. Structural characterization (Macroscopy techniques)

4.2.3.1. Thermogravimetric analysis and differential scanning calorimetry. A different technique from spectroscopic ones to estimate the structural stability and formation of secondary phases caused by different degradation mechanisms, such as Cr poisoning and Sr segregation, is Thermogravimetric analysis (TGA) [219,255,256]. This analysis can be performed in different atmospheres to provide the desired condition for testing the stability and durability of a SOFC component. For instance, a lump of fused Cr_2O_3 can bring the required conditions to study cathode's Cr poisoning behavior [257]. After setting the desired parameters, the stability and poisoning resistivity can be estimated by analyzing the weight changes of the component [258,259]. The differential scanning calorimetry (DSC) is also helpful in examining the degradation, such as the formation of Sr phases, by showing the phase transition endothermic/exothermic peaks [260,261].

4.2.3.2. Dilatometry. Thermal expansion behavior is one of the key factors in SOFC's long-term durability to ensure the TEC compatibility of SOFC components as well as structural thermal stability. Dilatometry measurement is a functional tool to analyze the linear thermal expansion dynamic of the SOFC components at high temperatures [262,263]. Niu et al. [204] used the dilatometry measurements in the H₂ atmosphere to choose the most thermally compatible anode for LSGM electrolyte in cell fabrication [204]. In another work, Khan et al. [264] studied the effect of thermal cycling on the SOFC cathode degradation by dilatometry technique. A palette of LSCF-GDC cathode was analyzed with a dilatometer in the temperature range of 400–800 °C and a heating rate of 200 °C/h for 10 thermal cycles. The dilatometry data illustrated a decreasing trend in the cathode TEC as the thermal cycling proceeded, suggesting an irreversible deformation and eventually causing



Fig. 25. SE - SEM micrographs of (a) and (b) Cr poisoning in LSM cathode, Reprinted from Tucker et al., [237] with permission. Copyright 2017. Elsevier. (c) and (d) S poisoning in LSCrM anode, Reprinted from Li et al., [242] with permission. Copyright 2017. Elsevier. (e) carbon formation in Ni electrodes after the performance test in CH₃, Reprinted from Lee et al., [239] with permission. Copyright 2016. Elsevier. and (f) and (g) Ni agglomeration in anode/electrolyte interface. Reprinted from Torrell et al., [243] with permission. Copyright 2017. Elsevier.

delamination and cell degradation [264].

4.2.3.3. Tensile strength measurement. Studying mechanical stability is one of the major concerns in SOFCs since poor mechanical strength in the electrolyte, interconnects, or sealants cause gas leakage and mechanical failure [67]. One of the most common methods to estimate the bonding strength is the tensile test [265]. As an example, Li et al. [266] evaluated the effect of Al2O3 fibers on the mechanical properties of compressive seals. Fig. 30 (a) depicts the tensile curves of pure (F0), 20 wt% fiber (F20), and 50% wt% fiber (F50) sealants, which F0 and F50 showed the highest tensile strength and ductility, respectively. Tensile strength clearly dropped, while flexibility improved as fiber content increased for fiber-reinforced seals [266]. In another research, the tensile test examined the mechanical properties of 3YSZ electrolyte with 75 μ m thickness. Fig. 30 (b) exhibits the photos of the samples after the tensile test. Results revealed that the mechanical stability of a 75 μ m thickness of a 3YSZ electrolyte is comparable with a 150 µm-8YSZ electrolyte [267].

4.2.3.4. Flexural strength measurement. Another essential mechanical feature of SOFC components is flexural strength, which defines their ability to withstand bending loads by a three- or four-point bending test. Fig. 31 (a) presents a schematic of a three-point bending test in which d, D, and L are the diameter of the loading tool, the diameter of the identical support cylinders, and the distance between the centers of the cylinders, respectively [268]. Morales et al. [269] used the three-point bending test to determine the effect of using AFLs (NiO-SDC) on anode-supported microtubular SOFCs by conducting a three-point bending test. The results of mechanical and electrochemical tests (shown in Fig. 31 (b)) of three cell configurations with different numbers of AFLs revealed that the cell with a single-layer AFL of 50:50 wt% NiO: SDC and a thickness of 12 µm performed best (0.52 W cm⁻²) at 650 °C with hydrogen as fuel and air as oxidant [269].

4.3. Modeling

As a cost-effective method, modeling is a notable way to better

understand the SOFC performance, which leads to optimizing and controlling the SOFC efficiency and lifespan. A 4xn optimization matrix, in respect to electrolyte, anode, cathode, and interconnect, defines the SOFC performance to obtain desirable properties, including proper chemical compatibility, prominent electrical conductivity and catalytic activity, as well as thermal and mechanical stability [139,270-273]. Moreover, a complete study of the SOFCs' phenomena demands a multidisciplinary methodology. Chemical processes, electrical conduction, ionic conduction, gas-phase mass movement, and heat transfer all occur at the same time and are intimately coupled. Hence, implementing conservation and constitutive laws and the kinetics of the chemical reactions is essential. Besides, it is consequential to consider the different factors of degradation mechanisms to adopt the modeling strategy in SOFC deterioration issues, such as microstructural changes, poisoning, formation of secondary phases, etc. [274,275]. Table 2 summarizes some of the different modeling techniques for investigating the SOFC failure mechanisms.

There are several numerical studies for optimizing the SOFC components' microstructure to enhance durability [103,278,288,289]. Various computational methods, such as two particle method, finite element model, phase-field model, etc., are available to study the Ni coarsening process [290]. For instance, Zhu et al. [276] studied how microstructure transformations of Ni-YSZ anode and YSZ electrolyte affect the SOFC degradation behavior by a Multiphysics model with the coupling of gas transports, electrochemical reactions, and electrical current conductions. They found that Ni coarsening causes more than 1%/1000 h degradation rate in the long-term cell performance. They also recognized a reduction in YSZ conductivity, from 5.45 S m⁻¹ to 4.30 S m^{-1} in the first 500 h of SOFC performance due to its cubic-to-tetragonal phase transformation [276]. Another detrimental microstructural change is the formation of secondary phases and cation segregation in cathodes. In this regard, Choi et al. [223] used the density functional theory (DFT), which enables the prediction and analysis of material properties using quantum mechanical principles, to calculate the charge distribution and Oxygen vacancy formation energies to minimize the Sr segregation in SSC cathode. Similarly, a combined DFT and molecular-based theoretical technique was applied to calculate the



Fig. 26. BSE-SEM images of (a–b) Ni agglomeration in Ni-SSZ anode AFL before and after 1000 h of aging, Reprinted from Khan et al., [103] with permission. Copyright 2018. Elsevier. (c–d) Sr segregation in BSCF cathode, and (e–f) resistivity to Sr segregation in NBSC cathode. Reprinted from Lee et al., [246] with permission. Copyright 2016. Elsevier.



Fig. 27. Representative TEM image of (a) the original TPB region and the LSM/YSZ interface in the fresh cell and (b) the active layer of cell operated for 120 h. The interfacial defects initiate from the original TPBs, while the LSM/YSZ interface and YSZ/YSZ grain boundaries initially remain intact. Reprinted from Chen et al., [247] with permission. Copyright 2019. Elsevier.

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Fig. 28. AFM micrographs of the YSZ electrolyte surface in contact with directly assembled LSCF electrode after polarization at 750 $^{\circ}$ C and 1000 mA cm⁻² for (a) 1 h, (b) 12 h, and (c) 100 h. LSCF electrode was removed by acid treatment. Reprinted from He et al., [75] with permission. Copyright 2018. IOP Publishing.



Fig. 29. (a) schematic of FIB-SEM analysis, (b) The fuel cell was first cut and polished, leaving a crosssectional surface with the anode, electrolyte, and cathode exposed. The FIB was then used to mill a rectangular trench into this surface in the anode's vicinity. A series of SEM images were acquired from one of the trench sidewalls as the FIB 'shaved' away material from this surface. Reprinted from Wilson et al., [250] with permission. Copyright 2006. Springer Nature. Visualization of reconstructed 3D structure (GDC sintering temperature of 1300 °C). (c) Representation of the whole structure (10.7 imes 14.7 imes1.4 μ m³) showing the gain in information achieved by the presented method. (d) LSCF, pore phase, SZO, ID, and YSZ revealing direct contact between the pore phase and SZO. The contact between SZO and the pores shows that a Sr gas diffusion through the pores during cathode sintering leads to SZO formation at the interface. There is no contact between the pore phase and ID or YSZ, revealing that SZO is formed during sintering developing a layer between pore and ID. Reprinted from Wankmuller et al., [254] with permission. Copyright 2017. Elsevier.



Fig. 30. (a) The tensile curves of pure and Al_2O_3 fiber-reinforced sealants. Reprinted from Li et al., [266] with permission. Copyright 2019. Elsevier [266]. (b) Photograph of 3YSZ samples after conducting the tensile test. Reprinted from Celic et al., [267] with permission. Copyright 2015. Elsevier [267].

energetics for oxygen vacancy formation in PrBaCo₂O₅₊₈ (PBCO) cathode for a better understanding of Ba segregation [277]. Furthermore, modeling and numerical studies are also used to determine carbon resistivity [278,291,292], S [122,279,280,291,293], and Cr poisoning [279], along with the thermal stress [281–283] and mechanical strength [294]. Darvish et al. [295] studied the Cr poisoning effects in a humidified atmosphere on the phase stability of the LSM/YSZ system by the CALPHAD (calculation of phase diagrams) approach. Thermodynamic simulation results demonstrated the destructive effect of Cr-containing humidified air on the perovskite phase stability and electronic conductivity. This detrimental impact is due to the diffusion of volatile Cr^{+6} species, CrO_3 and $CrO_2(OH)_2$, into the perovskite structure and substitute at B-sites, causing a decrease in Mn concentration and formation of Mn oxides secondary phases on the TBPs of LSM



Fig. 31. (a) schematic of three-point bending test. Reprinted from Timurkutluk et al., [268] with permission. Copyright 2018. Elsevier [268]. (b) mechanical and electrochemical results of three cells with different numbers and compositions of anode functional layers. Reprinted from Morales et al., [269] with permission. Copyright 2018. American Chemical Society [269].

A summary of different modeling techniques to study degradation mechanisms in SOFCs.

Study case	Modeling Method	Degradation Mechanism	Ref.
microstructural evaluation of Ni-YSZ anode, YSZ electrolyte, and SS430 interconnect	Multiphysics modeling	Ni coarsening (anode), phase transformation (electrolyte), and oxidation (interconnect)	[276]
double perovskite PBCO cathode	DM and DFT simulation	cation segregation (Ba ²⁺)	[277]
GDC/SSC cathode	DFT	cation segregation (Sr ²⁺)	[223]
porosity optimization of porous GDC electrolyte	finite element and Multiphysics modeling	carbon deposition	[278]
anode supported SOFC with Ni-cermet anode	lumped volume model	S poisoning	[122]
LSM cathode	CALPHAD method	combined Cr and S poisoning	[279]
LSCF	CALPHAD method	secondary phase formation and S poisoning	[280]
planar anode-supported cell	finite element method and Multiphysics modeling	mechanical failure	[281]
planar anode-supported SOFC with functionally graded electrodes	Multiphysics model	thermal stress and mechanical failure	[282]
2D functionally graded electrodes	Multiphysics model (COMSOL software)	thermal stress and mechanical failure	[283]
Ni catalyst with transition metal doping (Cu, Rh, Pd, Ag, Pt, Au)	DFT	S poisoning	[284]
Full-stack SOFC	Multiphysics modeling (FLUENT software)	creep strain and mechanical failure	[285]
Full-stack SOFC	Multiphysics modeling (COMSOL software)	Ni coarsening in the anode, Cr poisoning in the cathode, and corrosion in the interconnect	[286]
Glass composite sealant/ Crofer 22APU interconnect diffusion couple.	Multiphysics modeling (COMSOL software)	Thermal stress and leakage	[287]

cathode [295]. In another report, Hwang et al. [284] studied the thermodynamic stability of the Ni-based alloys against S poisoning by DFT. They examined the doping role of transition metals (Cu, Rh, Pd, Ag, Pt, and Au) into a Ni catalyst on adsorption of S compounds and H₂S decomposition. Multiphysics modeling is also a valuable method to evaluate the mechanical performance of SOFCs. Guo et al. [285] conducted a thermo-mechanical analysis using a multiphysics model to study the impact of creep on the mechanical degradation of all SOFC components during 10,000 h. The results showed that the creep strain is minor for electrolyte/cathode, so it is possible not to consider it for mechanical assessments [285]. In another work, Rizvandi et al. [286] developed a 3D multiscale full-stack model considering Ni particle coarsening in the anode, Cr poisoning in the cathode, and corrosion in the interconnect as deterioration phenomena. The model can assess the operation of 38,000 h within 1.4 h, and it is verified by the experimental data for a steady-state functioning of an 18-cell Jülich Mark-F stack [285].

5. Durability, the state-of-the-art

Many efforts have been made to improve SOFC performance, but only a few attempts reached exceptional results in both power density and stability, simultaneously [295–298]. Most of the state-of-the-art published literature on SOFC with high power densities over 2 W cm⁻² in the temperature range of 650–800 °C did not address the stability issues or only reported a short-term durability test, without any harsh conditions that causing degradation [295,298–303], listed in Table 3. To date, many review papers had discussed the high performance of solid oxide fuel cells in the power density area. However, there is no comprehensive review covering the recent developments in SOFC stability. Therefore, this section reviews the most recent attempts to enhance SOFC stability. Table 4 presents some of the most recent literature in the field of SOFC stability improvement.

Perovskite oxides are one of the attractive materials for SOFC research due to their mixed ionic and electronic conductivity and high catalytic activities [304]. Their ABX₃ mixed structure contains rare earth and alkaline earth metals at the A-site and transition metals at the B-sites, where A-site cations are bigger in size than B-site cations and have the same size as X-site anions, shown in Fig. 32 [305]. In general, the ideal perovskite has a face-centered cubic (FCC) structure at room temperature. However, this structure can become distorted as a result of the formation of oxygen/cationic vacancies formation and angles readjustment between cations and oxygen. A-sites deficiencies result in cationic vacancies, which give rise to a better ionic conductivity for keeping the overall charge of the structure neutral. On the other hand,

A summary of published literature of high power density SOFCs without significant durability. U, T, t, and G represent the applied regime value, temperature, duration, and Galvanostatic regime.

Cell design (anode electrolyte cathode)	Test condition oxidant/ fuel	Conductors	Temperature (°C)	Power density (W cm ⁻²)	Stability regime/U/T/t	Ref.
SDCN40* SCSZ** PrOx	oxygen/H ₂	0^{2}	700	2.00	-	[300]
NI-YSZ YSZ/ESB**** NI-YSZ YSZ icn-LSMESB****	dry air/wet H ₂	0 0 ²⁻	700 750	2.08	-	[302]
Ni-YSZ YSZ GDC LSC-GDC	air/H ₂	0 ²⁻	650	3.01	G/300 mA cm ⁻² /650 °C/ 25 h	[299]
anodized aluminum oxide Ni-YSZ YSZ GDC LSCF-YSZ	air/H ₂	O ²⁻	650	2.5	G/200 mA cm ⁻² /600 °C/ 5.5 h	[301]
NiO-YSZ YSZ GDC LCaF****-GDC	synthetic air/wet H ₂	0 ²⁻	800	4.4	-	[303]

*Ni and Sm-doped ceria, ** SCSZ: Sc₂O₃ stabilized zirconia, *** ESB: Bi_{1.6}Er_{0.4}O₃, **** icn-LSMESB: in situ co-assembled nanocomposite LSM-Bi_{1.6}Er_{0.4}O₃, ***** La_{0.65}Ca_{0.35}FeO_{3.6}.

multivalent elements for the B-site are selected according to their potential for redox reactions, based on oxygen/anion partial pressure over the SOFCs operation [304,306–308].

Incorporation of high valance transition metals, such as Mo, Nb, Co [309], and Ta [310–312], on the B-site of perovskite electrodes, leads to a stable cubic structure. This feature can be considered as one of the answers to the perovskites' stability issues, including inferior chemical stability and considerable volume changes [308], especially in the symmetric design of solid oxide fuel cells [310,313,314]. To point out, BSCF is a high potential cathode material at low temperatures, owing to its high energy output and oxygen diffusion rate. Substitution of Mo in the cubic structure of BSCF can enhance its stability in reducing atmospheres and make it a suitable electrode for both anode and cathode in a symmetrical solid oxide fuel cell. A long-term stability test in a constant voltage of 0.7 V at 700 °C revealed no change in the power density after 115 h in a humidified H_2 atmosphere, and it remained at 418 mW cm⁻² [254]. Mo doping is also used for the LSCF symmetrical electrode to develop both structural stability and catalytic activity [315]. Moreover, this Mo substitution with Fe reduced the TEC from 16.6 to $12.9 \times ~10^{-6}$ K⁻¹ and made it more compatible with LSGM electrolyte. A stability test of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.7}Mo_{0.1}O_{3-\delta}$ (LSCFM) single cell was performed under a constant 0.05 A at 850 °C in liquid petroleum gas (LPG) for 40 h, and the voltage output (~ 0.9 V) was almost steady during that time. Hence, this LSCFM electrode can tolerate carbon deposition and S poisoning as well [316].

Another approach to enhance the redox stability of SOFC is Ce doping. HTXRD analysis from RT to 1000 °C confirmed the promising thermal stability of the hybrid $Gd_{0.65}Sr_{0.35}(Co_{0.25}Fe_{0.75})_{0.9}Ce_{0.1}O_{3-\delta}$ (Ce-GSCF) electrode when no other phases emerged in the results. Furthermore, Ce doping decreases the GSCF TEC and enhances the thermomechanical stability of the electrode. The Ce-GSCF symmetrical single cell showed no degradation after 180 h operation at 0.7 V in 700 °C and humidified H₂, proving the GSCF perovskite material's improved stability [228].

A third method is to use Sn as a metal dopant in BaCo_{0.7}Fe_{0.3}O_{3-δ} (BCF) oxide to preserve its cubic structure and provide strong exchange surface properties and oxygen bulk diffusion [317,318]. Xia et al. [319] investigated the long-term stability of a novel BSF cathode-Sn doped $(Bi_{0.5}Si_{0.5}Fe_{0.9}Sn_{0.1}O_{3-\delta})$ material. After the 100 h of continuous testing at 0.6 V and 650 °C, the degradation rate was 1%, from 468 mW cm⁻² to 463 mW cm⁻². The SEM images after the stability tests showed no cracks or delamination. This stable morphology resulted from compatible cathode TEC (12.9 \times $10^{-6}~\text{K}^{-1})$ with the CGO (13.2 \times $10^{-6}~\text{K}^{-1})$ electrolyte. Sn doping increased the average binding energy of BSF and led to a smaller TEC than the conventional BSF [319]. Likewise, TEC can be optimized through Ca doping as well. A study by Xiang et al. [320] reported that a layered perovskite $Eu_{1-x}Ca_xBaCo_2O_{5+\delta}$ (EC_xBC) could show a low TEC with a 0.2 Ca fraction. By introducing Ca^{2+} ions into the Eu³⁺ sites, the oxidation states of cobalt ions can increase to preserve electrical neutrality, raising the polarization force of the cobalt ions. This

increased polarization force weakened the ionicity of Co–O bonds, leading to reducing the TEC ($16.9 \times 10^{-6} \text{ K}^{-1}$) and making it more compatible with the electrolyte. The slow degradation of power output (2.3%) in 0.5 V and 700 °C for 100 h had arisen from the TEC compatibility of the components, which prevented the thermomechanical strains [320].

The doping technique can also be used for enhancing CO₂ tolerance in cathodes. The selected dopants should have (1) high acidity, (2) high valence state, and (3) high average bonding energy [321]. In research by Zhang et al. [322], Hf was used to improve the stability of SrFeO_{3- δ}. The cathode was exposed to 1% vol CO₂ for 60 h for the evaluation of CO₂ tolerance. The ASR polarization values barely increased during the process, indicating that the CO₂ adsorption occurred without perovskite's surface structural destruction. Additionally, the ASR polarization returned quickly to the original value after the CO₂ flow switched off, showing that the CO₂ adsorption is reversible at active ORR sites. This improved chemical stability was due to the doping of redox-inactive Hf cation at the Fe site of SF [322]. This strategy was used with alkaline metals by Rehman et al. [323] for SrFe_{0.8}Nb_{0.1}Ta_{0.1}O₃₋₆ (SFNT) cathode, resulting in the in-situ formation of alkali metal carbonates at the surface with the highest performance cobalt-free single-phase cathode that has been published to date (0.12 Ω cm² ASR at 600 °C). The stability test evaluated the CO₂ tolerance of the SFNT-Li doped cathode in 10% CO_2 at 600 $^\circ\text{C}$ for 50 h. The degradation rate was \sim -8.1 \times 10 $^{-12}$ W cm $^{-2}$ h^{-1} , making this cathode a promising component in the CO₂ environment. This boosted performance has arisen from the O2 released during alkaline metal carbonation, increasing the oxygen partial pressure and forming an Oxygen cloud at the cathode surface. This cloud facilitated the surface exchange process towards CO2 and protected the cathode surface [323].

Moreover, Ga-doping can contribute to improving the structural stability of Fe-based perovskite cathodes [324]. Recently, a Ga-doped SFM cathode was reported that possessed an acceptable CO_2 tolerance. In this cathode, B-site Fe was substituted by Ga, which reduced the SFGM affinity towards CO_2 chemical adsorption. The durability test was performed under 16A at 750 °C, 97 h in air, and 291 h in 5% CO_2 . Regardless of the slight decrease in output voltage, results indicated a promising stable performance [73].

Ca doping can also improve CO_2 tolerance by partially replacing it with Ba in Ba-containing cathodes. This replacement results in stabilizing the perovskite structure and lowering the Ba enrichment at the cathode surface. The output voltage of Ca-containing Ba_{0.95}Ca_{0.05}Co_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-δ} (BCFZY) cathode decreased slightly after switching from air to air-1% CO₂ and maintained steady for 30 h under 400 mA cm⁻² at 700 °C [325].

In addition to perovskite material, doping can improve the spinelbased SOFCs as well. In a recent work by Thaheem et al. [297], a Cu doped (Mn, Co)₃O₄ spinel cathode achieved a significant power density (2 W cm⁻² at 800 °C) and excellent stability performance at the same time. The output voltage stayed steady during 300 h of the test under

Some of the most recent research in improving the durability and stability of SOFC's components. G and P regimes represent galvanostatic and potentiostatic test modes, respectively. Moreover, U, T, t, and A represent the applied regime value, temperature, duration, and atmosphere.

Cell Design (Anode Electrolyte Cathode)	Test Condition Regime/U/	Stability Evaluation			Conductor	Degradation/Solution	Ref.
	T/t/A	Performance Parameter	Initial Value	Final Value			
NiO-GDC GDC Sm_{0.5}Sr_{0.5}CoO_{3-\delta}	G/600 mA cm ⁻² /600 °C/ 250 h	Voltage output (V)	0.728	0.721	0 ²⁻	Delamination of Cathode Materials/Core-shell structure	[336]
	H ₂	Power Density $(mW \ cm^{-2})$	1130	1127			
BSCFM GDC YSZ GDC BSCFM	P/0.7 V/700 °C/115 h $\rm H_2$	Current Density Output (mA cm ⁻²)	170	~ 170	0 ²⁻	Carbon Deposition/Mo doping	[254]
		Power Density (mW cm ⁻²)	418	418			
$\begin{array}{l} SSFTR7020 SDC SSFTR7020 \\ (Sm_{0.7}Sr_{0.2}Fe_{0.8}Ti_{0\cdot 15}Ru_{0\cdot 05}O_{3\cdot\delta}) \end{array}$	G/0.43 mA cm ⁻² /800 °C/ 200 h	Voltage Output (V)	0.65	~ 0.68		Ni Coarsening/Surface modification with Ru	[331]
	H ₂	Power Density (mW cm ⁻²)	~ 400	\sim 476	0 ²⁻		
$\begin{array}{l} \text{NiO-YSZ} \text{YSZ} \text{GDC} \\ \text{Sr}_{2}\text{Fe}_{1.3}\text{Ga}_{0.2}\text{Mo}_{0.5}\text{O}_{6\cdot\delta} \end{array}$	G/16 A/750 °C/388 h (97 h in air and 291 h in 5 vol%	Voltage Output (V)	~ 0.7	~ 0.7	2	CO ₂ Poisoning/Ga doping at Fe sites	[73]
	CO ₂)	Power Density (mW)	12000	12000	02-		
NiO-YSZ YSZ LSM-nanoYSZ	G/0.25 A cm ⁻² /750 °C/230 h	Total Resistance (Ω cm ²)	0.460	0.468		Ni Coarsening/Surface Modification with nanoYSZ	[337]
	H ₂	Voltage Output (V)	0.904	0.909	02-		
		Power Density (mW cm ⁻²)	628	614			
NiO-BZCYYb-1711 BZCYYb-4411 BCaCFZY	G/400 mA cm ⁻² at 700 °C/ 35 h (oxidant: air + 1 vol% CO ₂)	Voltage Output (V)	0.8	~ 0.8	H^+	CO ₂ Poisoning/Ca doping	[344]
$\begin{array}{l} SSFTR72 SDC SSFTR72 \\ (Sm_{0.8}Sr_{0.2}Fe_{0.8}Ti_{0.15}Ru_{0.05}O_{3-\delta}) \end{array}$	G/300 mA cm ⁻² /800 °C/ 240 h H ₂	Voltage Output (V)	~ 0.72	~ 0.72	0 ²⁻	Mismatching TEC and Delamination/Surface modification with Ru Exsolution	[332]
LSCFM SDC LSGM SDC LSCFM (Lab δ Sto δ Coo δ Feo 2 Moo $1O2\delta$)	G/0.025 V/700 °C/25 h Liquid Petroleum Gas	Voltage Output	~ 0.75	~ 0.75	0 ²⁻	S Poisoning/Mo doping	[316]
SFHf SDC SFHf (SrFe _{0.9} Hf _{0.1} O _{$3-\delta$})	Polarization/600 °C/60 h air \pm 60 h in 1 vol% CO ₂	ASR (Ω cm ²)	0.193	0.356	0 ²⁻	CO ₂ Poisoning/Hf doping	[322]
NiO-YSZ NiO-YSZ YSZ LSCD PrO _x -PNM (PrNi _{0.5} Mn _{0.5} O ₃)	$P/0.7 V/750 \circ C/600 h$ $H_2+3\% H_2O + direct Crofer contact$	Power Density (mW cm ⁻²)	460	459.73	0 ²⁻	Cr Poisoning and SrCrO ₄ formation/Surface modification with protection	[78]
$\begin{array}{l} Ni\text{-}YSZ YSZ CGO SPN\text{-}A\text{-}PBC\\ (PrBa_{0.94}Co_2O_{5+\delta}) \end{array}$	P/0.6 V/700 °C/120 h H ₂	Current Density Output (mA cm ⁻²)	~ 1700	~ 1700		Cathode Decomposition/ Surface engineering by Exsolution	[333]
		Power Density (mW cm ⁻²)	1100	~ 1100	0 ²⁻		
$\begin{array}{l} SFCoM LSGM GDC LSCF\\ (Sr_{1.95}Fe_{1.4}Co_{0.1}Mo_{0.5}O_{6\cdot\delta})\end{array}$	G/0.85 A cm ⁻² /750 °C/200 h	Voltage Output (V)	0.75	0.75	0 ²⁻	Carbon deposition/Co doping	[345]
NiO-YSZ YSZ GDC La, Pr, Nd, Sm, and Sr -LSM	$H_2+C_3H_8$ 50 sccm P/0.7 V/700 °C/100 h H_2	ASR (Ω cm ²) Current Density Output (mA	0.278 ~ 0.46	$\sim 0.278 \ \sim 0.46$	0 ²⁻	Sr segregation/Multi doping with La, Pr, Nd, Sm, and Sr	[346]
$\begin{array}{l} Ni\text{-}SDC YSZ PBSCF\\ (PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+\delta})\end{array}$	G/0.254 A cm ⁻² /650 °C/ 120 h	cm -) Voltage Output (V)	0.73	~ 0.73	0 ²⁻	Carbon deposition/Surface modification by infiltrating	[347]
$\begin{array}{l} \text{NiO-YSZ} \text{YSZ} \text{CGO} \\ \text{PBCaC} \left(\text{Pr}_{0.94}\text{Ba}_{0.7}\text{Ca}_{0.3}\text{Co}_2\text{O}_{5+\delta} \right) \end{array}$	9/ vol% CH4 + 3 vol% H2O P/0.6 V/120 h/650 °C/ H ₂ +3% H ₂ O	Current Density Output (mA cm ⁻²)	~ 1350	~ 1350	0 ²⁻	Mismatching TEC in cathode/ Ca dopant	[348]
		Power Density (mW cm $^{-2}$)	~ 800	~ 800			
$\label{eq:linear} \begin{split} NiO\text{-}BZCYYb BZCYYb LBCCF\text{-}BZCYYb \\ (La_{0.5}(Ba_{0.75}Ca_{0.25})_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}) \end{split}$	G/400 mA cm ^{-2} /650 °C/ 100 h/humidified H ₂ and dry air with 80 mL min ^{-1}	Voltage Output (V)	0.76	0.76	H^+	Sr segregation/Ca doping	[349]
Ni–CeZr Ni-YSZ YSZ YSZ-LSM YSZ	P/0.6 V/850 °C/100 h/ humidified H ₂ (for the first 20 h) and N ₂ + \sim 17% Ethanol	Current Density Output (mA cm ⁻²)	~ 100	~ 100	O ²⁻	Carbon deposition/Zr doping for ceria in Ni-ceria anode	[350]
Co@SFCoM LSGM GDC LSCF	G/850 mA cm $^{-2}$ /750 $^{\circ}$ C/ 200 h/C_3H_8 with 50 sccm	Voltage Output (V)	0.75	0.75	0 ²⁻	Carbon deposition/Surface modification of anode with Co exsolution	[345]
Ni-YSZ/YSZ/GDC/BFP05	G/500 mA cm $^{-2}$ /750 °C/50 h/H ₂ with 100 mL min $^{-1}$ and air $+$ 2% CO ₂	Voltage Output (V)	0.7	~ 0.7	0 ^{2.}	CO ₂ poisoning/Pr doping	[11]



Fig. 32. Simple Perovskite structure with ABX₃ formula. Reprinted from Green et al. [305] with permission. Copyright 2014, Springer Nature.

constant 150 mA cm⁻² at 750 °C [297]. The co-doping approach can also be a propitious approach for developing SOFC performance. Yun et al. [296] achieved one of the remarkable results by introducing both Dy and Y to B_2O_3 and combining it with conventional LSM, with a peak power density of 2.23 W cm⁻² at 700 °C. The cell's output voltage was stable under 1 A cm⁻² for 100 h at 700 °C, resulting from the cathode's stabilized structure [296]. Using co-doping in the SrCoO₃₋₆ (SC) cathode also reveals good resistance against CO₂ with a peak power density of 1563 W cm⁻² at 650 °C. The co-doping was carried out by introducing Nd⁺³ to A-site and Nb⁺⁵ to B-site. The ASR values of N_{0.2}SNC before (0.08 Ω cm²) and after (0.20 Ω cm²) placing in 5% CO₂-air flow for 300 min showed a proper CO₂ tolerance performance, resulting from the relatively low oxygen vacancy concentration of N_{0.2}SNC that prevented the cathode from the carbonate formation on the surface by CO₂ [255].

Dopants can improve anode stability as well. A novel perovskite material was prepaid via introducing Ta on the B-sites of LSF, leading to a good stability performance after a 55 h test under constant 0.4 A cm⁻² with H₂-50 ppm H₂S at 800 °C. Since Ta doping stabilizes the LSF lattice against decomposition in a reducing atmosphere, LSFT_{0.5} would be secure from S poisoning and coking [310].

A different method to develop solid oxide fuel cell stability is surface engineering and microstructure optimization [326,327]. Exsolution is a surface modification approach by forming a solid solution incorporating catalytically active metal into the host lattice matrix under an oxidizing atmosphere. Later in the reducing conditions, the metal particles are exsolved on the surface of the host material [328]. This method prevents nanoparticles' agglomeration on the surface and provides a better surface distribution than conventional techniques [329,330]. Researchers discovered that surface engineering by a thin film conformal coating of a perovskite material with distinct nanoparticles in LSCF cathodes can hinder the Sr enrichment and segregation; thereby, enhancing the stability performance. A conformal coating of PNM with exsoluted PrO_x nanoparticles on a conventional LSCF cathode, designed by Chen et al. [78], showed a degradation rate of 0.04%/h, operating at 0.7 V with humidified H₂ and direct Crofer contact at 750 °C for more than 500 h. This duration is 10 times higher than the bare LSCF. The Sr-free nature of this coating made it less active against Cr contaminants, and at the same time, the PrO_x nanoparticles provided a significant amount of oxygen vacancies to boost the cell performance [78].

Moreover, a symmetrical SOFC is designed using Ru nanoparticles' *in-situ* exsolution with a considerable ASR of 0.11 Ω cm². Due to the stability tests under 0.43 A cm⁻² for 200 h under wet H₂ at 800 °C, this electrode also exhibited perfect durability towards Ni coarsening in the reducing environment by maintaining its output voltage during the test [331,332]. In another report, PrBa_{0.94}Co₂O₅₊₆ (PBC) double perovskite was decorated by the PBC nanorods with good stability properties, and the morphology has not faced any changes during 120 h under 0.6 V at 700 °C [333], as it is represented in Fig. 33.

Surface modification with $\text{PrO}_{2-\delta}$ nanoparticles was also been applied for the LSCF cathode. The enhanced surface activity led to the $Sr_{v}Co_{v}O_{z}$ formation (Fig. 34), and the resulted LSCF/ $Sr_{v}Co_{v}O_{z}/PrO_{2-\delta}$ heterostructure improved the cathode stability against Cr poisoning. This tailored cathode exhibited a competitive stability performance under 0.9 A cm⁻² for 100 h at 600 °C [334]. In another research, Ozmen et al. [335] used the nano-ceria for catalyst infiltration of the LSM-GDC YSZ|NiO-YSZ anode-supported cell via a single step deep-coating method to form a uniform and discrete decoration in the electrodes' active layer, close to the electrolyte interface. The infiltrated cell reached a reduction of up to 33% in the polarization resistance (0.275 Ω cm²) compared to a bare sample (0.405 Ω cm²) after ~300 h of EIS measurement at 750 °C using 300 sccm wet H₂ as fuel and 300 sccm air as oxidant under a constant current of 0.325 A cm⁻². The stability performance is improved as this technique limits infiltration/co-firing processes and minimizes nanocatalysts' morphology changes while maintaining an optimal concentration of catalytically active nanoparticles inside the active electrode region [335].

Core-shell structure cathodes are also a potential method to achieve better SOFC performance. One of the exceptional results belongs to Lee et al. [295], reaching 2 W cm⁻² in power density at 550 °C and outstanding stability performance with a degradation rate of 0.00017 V h⁻¹ at 550 °C under constant 1 A cm⁻² for over 250 h by their core/shell-fiber-structured BSCF-GDC cathode. This outstanding performance was mainly owing to the tailored microstructure of the cathode [295]. Recently, the SSC cathode was optimized with a novel core-shell structure by the *in-situ* growth of homogenous SSC nanoparticles without using the conventional multi-step infiltration technique. The stability studies under a constant current density of 600 mA cm⁻² in 600 °C for 200 h revealed that the voltage output (0.728 V) had



Fig. 33. SEM images of (a) A-PBC precursor composed of many irregular microscale particles, and (b) SPN-A-PBC cathode surface after 120 h stability test under 0.6 V at 700 °C. Reprinted from Lu et al., [333] with permission. Copyright 2019, Elsevier.



Fig. 34. Schematic diagram of the process of tailoring SOFC electrode microstructures by surface modification. Reprinted from Wang et al., [334]. Copyright 2020, American Chemical Society.

not changed during the test. This progress was attributable to the robust and continuous formation of SSC nanoparticles on the SSC backbone [336].

Muhoza et al. [337] used the surface engineering strategy for LSM-YSZ cathode by the infiltration of high surface area YSZ nanoparticles. This cathode's stability study was performed under constant 0.25 A cm⁻² at 750 °C for over 230 h, and the result was 0.23%/100 h in the voltage output. The stable nature of YSZ nanoparticles inhibited the cathode decomposition and prevented YSZ scaffold particle reaction, saving the TPB sites and reducing the degradation rate [337]. SFM Cr resistance was also enhanced by $LaCoO_{3-\delta}$'s (LC) infiltration, which prevented SFM and Cr's direct contact. This cathode's polarization resistance remained steady under 400 mA cm⁻² at 800 $^{\circ}$ C with a Cr source for 220 h [338]. LC was also used to enhance the Cr resistivity of BSCF-GDC with the exact mechanism and showed a stable low resistance under a current density of 400 mA cm $^{-2}$ at 750 °C for 115 h with SUS430 interconnect [339]. Alloy nanoparticles can modify the electrode surfaces as well. A new double perovskite material for both anode and cathode is fabricated with the in-situ exsolution of Co-Fe alloy (CFA) nanoparticles on the surface of RP-SCFM (Ruddlesden-Popper structured oxide $Sr_3Co_{0.1}Fe_{1.3}Mo_{0.6}O_{7-\delta}\mbox{).}$ When performing as the anode under the constant 400 mA cm⁻² at 800 °C for almost 250 h in H₂-50 ppm H₂S, this electrode possessed a high resistance against S poisoning and coking. The S tolerance mechanism of this electrode is described in Fig. 35 (OH) $_{0}^{\circ}$ is generated by the combination of water (from H₂ oxidation (2)) and RP-SCFM lattice oxygen (O_0^{\times}) . Then, the generated $(OH)_0^{\bullet}$ species are stored in the oxygen vacancies $(V_0^{\bullet\bullet})$ of RP-SCFM (3). In the meantime, S species are formed from the adsorbed S on the surface of CFA nanoparticles (4), which can react with $(OH)_0^{\bullet}$ and be converted to S₂ and H₂ at the CFA nanoparticles/RP-SCFM interface (5). Thus, S poisoning would be minimized [340].

In another work, Ni–Fe alloy (NFA) nanoparticles were used to decorate the RP-PSNF (Ruddlesden-Popper $Pr_{0.32}Sr_{0.48}Ni_{0.2}Fe_{0.8}O_{3-\delta}$) electrode. The resulting anode exhibited an enhanced coking resistance under the constant 250 mA cm⁻² at 800 °C in humidified C₃H₈ for 60 h since the output voltage has not changed. There was no carbon deposition on the anode surface after the durability test as well. This performance was due to the protection role of exsolved NFA nanoparticles



Fig. 35. Schematic showing the S tolerance of the RP-SCFM-CFA anode. H_2 -50 ppm H_2S was used as fuel. Reprinted from Qiu et al., [340] with permission. Copyright 2020. American Chemical Society.

anchored on the surface, which prevented the anode from coarsening [341].

Interface engineering between cathode and electrolyte is another interesting technique to improve SOFC stability behavior and power density [342]. In research by Kim et al. [343], GDC/SSC-infiltrated cell showed a high tolerance to thermal degradation after a 200 h test under 0.4 A cm⁻² at 650 °C. The modified cathode/electrolyte interface by forming a thin-film-like GDC interlayer with smaller grains size than that of the GDC matrix was the main reason for this improved stability [343]. This method was also used for tailoring the YSZ interface with Bi_{1.6}Er_{0.4}O₃ (ESB) nanopowder via screen printing technique, resulting in 2.1 W cm⁻² at 700 °C. The stability evaluation resulted in an unchanged output voltage after 150 h of a test under 100 mA $\rm cm^{-2}$ at 700 °C since the interlayer blocks the elemental interdiffusion between layers [298]. One of the most recent strategies in this technique is to use the TEC offset strategy to eliminate the TEC mismatch between the cathode and the electrolyte. In this regard, Zhang et al. [262] made a $SrNb_{0.1}Co_{0.9}O_{3\cdot\delta}$ (SNC) (TEC of 19–24 \times 10^{-6} K^{-1} from room temperature to 800 °C) cathode composite with Y₂W₃O₁₂, which has a negative TEC of 7×10^{-6} K⁻¹ from room temperature to 1100 °C. Furthermore, they induced an interfacial phase reaction between these two phases to provide better adhesion. This procedure not only leads to the development of the SrWO₄ interphase and the exsolution of Sr from the perovskite bulk phase but also creates A-site cation deficiency in the perovskite structure. This composite cathode exhibited an average TEC of 12.9 \times 10 $^{-6}$ K $^{-1}$ at 100–800 $^{\circ}\text{C},$ extremely similar to that of the SDC electrolyte (~12.3 \times 10⁻⁶ K⁻¹) and considerably lower than of the bare SNC (~20.5 \times 10⁻⁶ K⁻¹) and other co-based perovskites. The electrochemical performance of the symmetric cell with the composite cathode and SDC electrolyte from the EIS measurement exhibited impressive stability after 200 h of test with a signal amplitude of 10 mV under open-circuit conditions at 600 °C in air and presented a constant R_p of $0.075 \ \Omega \ cm^2$ during the test. While the bare SNC electrode faced a significant performance degradation by increasing from 0.24 Ω cm² to 0.37 Ω cm². The synergetic effects of the lowered TEC, perovskite phase modification, and thermo-mechanical stability all contribute to the SOFC composite cathode's superior electrochemical performance and indicate a new route for future SOFC electrode design [262].

Apart from the traditional three-layer SOFCs, single-layer SOFCs (SLFC) have been presented as a new class, emerged in 2000 by Chen et al. [351] with Sr doped-LaInO₃ perovskite [352]. A conventional SLFC consists of a composite material composed of an electronic conductor or semiconductor and an ionic conductor. This core component supports both electrode reactions on the cell's opposing edges and enables ion transportation across the cell [353]. There are various material options for SLFC by compositing electronic/semiconductor wide band-gap oxides (e.g., $Li_xNi_yZn_{1-x-y}O$) and ionic conductors (e.g., samarium- or gadolinium-doped ceria and perovskite materials) [354]. SLFCs appear to be promising since they will not face chemical, mechanical, and thermal incompatibility issues as in conventional three-layer SOFCs [355]. However, not much research has been done on

the long-term stability and durability of these SLFCs so far, and most of the stability studies are short-term [352,355-357]. In this regard, Deng et al. [358] investigated the electrochemical durability of double perovskite Sr₂Fe_{1.5}Mo_{0.5}O_{6-δ}-SDC composite as an SLFC at 550 °C in a galvanostatic test mode under 156 mA cm⁻² with H₂ as fuel. This material, which had an 841 mW cm^{-2} as maximum power density at 550 °C, presented a stable output voltage above 0.94 V during 24 h of the test [358]. In another study, Gao et al. [359] performed a galvanostatic durability test at 550 °C for around 70 h under 100 mA $\rm cm^{-2}$ current density to justify the promising performance of $SDC\text{-La}_{0.25}Sr_{0.75}Ti_{1}O_{3+\delta}\text{-Ni}_{0.8}Co_{0.15}Al_{0.05}\text{Li}O_{2\cdot\delta} \ \ composite \ \ with \ \ 222$ mW cm $^{-2}$ power density at 550 °C. This SLFC was maintained in a stable cell voltage for 68 h during the operation as the single component structure prevented delamination caused by a mismatch in thermal expansion coefficients between electrodes and electrolyte [359].

6. Conclusions

Solid oxide fuel cells need to overcome the durability and stability challenges to meet a commercial breakthrough. However, degradation studies are absent as most state-of-the-art publications focus on achieving higher power densities. These efforts on improving the performance will not be practical without optimizing the lifespan of SOFCs through degradation research. This review focused on the degradation mechanisms of the electrodes and electrolyte, the latest progress in durability and stability improvements of SOFCs, how they excel in the degradation, and the different characterization techniques for studying the field. Overall, the electrodes (both anode and cathode) are more vulnerable to degradation as they are more exposed to a stimulating atmosphere which causes poisoning. The most serious poisonings in cathode and anode are Cr poisoning and coking, respectively. They also suffer from microstructural deformations along with chemical and thermal strains. For the electrolyte, the degradation mainly occurs as phase transition, dopant diffusion, and mechanical failure. The most recent reports in advancing the degradation behavior have shown several techniques for this purpose, including using dopants for perovskite and spinel-based electrodes, surface engineering via exsolution, using a coating and infiltration, microstructural optimization (e.g., coreshell structure), and interface modification (like applying a thin film between the electrolyte and cathode).

Furthermore, characterization plays a critical role in better understanding the degradation mechanisms giving new insight to overcome the durability issues. Here, the study tools were categorized into electrochemical, chemical, and structural characterization. The first one contains I–V measurement, EIS, and calendar life tests. The chemical and structural characterization groups include Raman spectroscopy, FT-IR, XRD, XPS, SIMS, TGA, DSC, dilatometry, and microscopy techniques. These techniques are conducted in situ, ex situ, or both modes, depending on the characterization type, to provide the information as detailed as possible. Modeling is also another cost-effective method to understand the SOFC performance better.

It is possible to achieve a better knowledge in degradation of SOFC via modern characterization techniques as there is a lack of in-depth knowledge of degradation mechanisms. Degradation processes in SOFCs are complicated and depend on many parameters simultaneously. For instance, the role of temperature is still undefined. There are several reports about enhancing the durability with increasing temperature, leading to uncertainty about the destructive act of high temperatures [360]. Besides, the short-term behavior cannot be interpolated into long-term behavior as the degradation process is non-linear [361-363]. Furthermore, the absence of proper in-situ characterization tools that can work during the electrochemical process of SOFC at high temperatures hinders deeper understanding of the degradation mechanisms. Another challenge is the limited choice of materials for SOFC components due to the severe working conditions. The difficulty is finding a material with the desired properties the for

cathode/electrolyte/anode (mentioned before) whilst having good compatibility with the SOFC harsh working conditions and other components at the same time [364].

Regardless of these fundamental limitations, the lack of systematic standards to study the durability and stability of the SOFCs is strongly felt. For instance, there is no set of standards for long-term/short-term operation durations or no particular range for the applied study techniques in current density or voltage amplitude in the lab scale. It is necessary to set guidelines and criteria to compare the degradation results accurately.

This review will help overcoming the limitations identified by proposing new materials and using modern fabrication methods for SOFC components.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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