A Review on Improvement of Composite anode Structures for Solid Oxide Fuels of Low-Temperature

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Abstract : The high energy efficiency and improved fuel durability of the solid oxide (SOFC) platform are very appealing. It is more environmentally friendly than traditional power plants. Recently the mid-to-low-temperature solid oxide fuel cells that run at 400e800 C are attracting greater exposure. Reducing its operating temperature may make the SOFC more competitive and marketably more market-friendly with the other types of fuel cells and portable energy storage (EES) systems for a variety of applications (for example: transport, portable, stationary). For the use of low temperatures (400e600 kWC) high-performance composite anode requirements require microstructural and chemical stability , high electronic conductivity and good electrochemical perforation. The actual Ni-YSZ (nickel-yttrian zirconia) high-temperature anode is usually reported at low temperatures with high interfocial resistance. This analysis reveals a variety of potential composite anode materials (Ni-based and Ni-free) for low-temperature SOFCs produced in the last 10 years. The study shows that most of these anodes still have relatively high resistance to polarization. The emphasis is also put on raising the resistance to polarization in order to retain cell strength. The common approaches in literature to improve anodes are I the selection of high-performance electrolytes, (ii) the utilization of proper nanopowder linkage and (iii) the addition of noble metals as electrocatalysts.

Introduction

Global energy needs are expected to rise annually by 1.2 percent in 2035 as urbanization and overcrowding accelerate dramatically. The new power generation method, which primarily targets declining fossil fuels, commonly known as greenhouse gases as a by-product, can not meet this demand. The planet is moving more and more towards integrated renewable energy systems. Fuel cells are currently known as the largest new energy storage system with limited effects on the environment. Form and working temperature can be defined as electrolyte cells. Types of fuel cells include the ex-membrane fossil fuel cell (PEMFC), fuel cell phosphoric acid, fuel cell alkaline, carbonate mold fuel cell and solid fuel cell oxide (SOFC). (SOFC) As an electrolyte, SOFCs use a dense ceramic oxide conduction material.

SOFCs are stationary electrical devices, which convert fuel directly from chemical products into energy with almost null emissions. Owing to higher choices in power , low noise, eco-friendly , high performance (approximately 60%) and other fuel cell types, the SOFCs are gaining significant attention as renewables. In relation to traditional power generation (coal, inter-nal engines) systems; The Carnot process is not exclusive to the SOFC. SOFC serves in a range of applications including (1) domestic and commercial household energy generation systems, including combined heater (CHC) and micro combined heat (m-CHP). Generally SOFC devices are generated using different watt to megawatt outputs and are very scalable.

Table 1 e Targeted markets and applications of SOFC [2,9].

Targeted markets	Targeted applications	Companies	Countries
Portable (<250 W)	Portable power generation Portable military Equipment	Acumentrics/Altrex Protonex Ultra Electronics AMI Hitachi Ceres Power Samsung	United States Japan United Kingdom South Korea
Stationary (from 1 kW to 1 MW)	Combined heat and Power (CHP) Micro-combined heat and power (m-CHP) Remote-area power supply	Acumentrics/Altrex Bloom Energy FuelCell Energy Protonex	United States

|		
	(RAPS)	Mitsubishi	Japan
	Commercial distributed power generation (power grid)	Toyota	
		Samsung	South Korea
		Siemens	Germany
		DDI Energy	Canada
		Ceres Power	United Kingdom
		Topsoe Fuel Cell	Denmark
		Hexis	Switzerland
		SOFCpower	Italy
		Convion	Finland
		Ceramic Fuel Cells	Australia
Transportation (about 5 kW)	Auxiliary power unit (APU) Ship/marine Propulsion	Dephi Protonex	United States
		Ultra Electronics AMI	
		Hitachi	Japan
		Mitsubishi	
		Toyota	
		Siemens	Germany
		DDI Energy	Canada
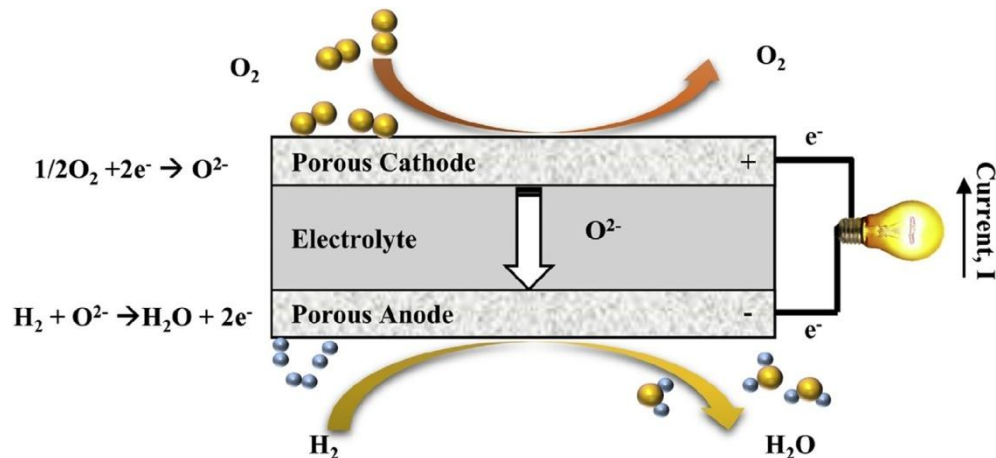
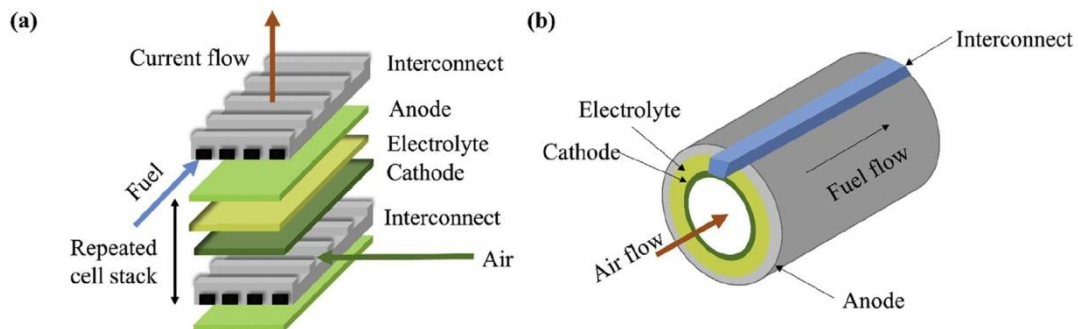Fig. 1 e Schematic diagram of the basic principle of SOFC.

Fig. 2 e Cell geometries of (a) planar and (b) tubular SOFC.

In and out of the pipe. Planar SOFC provides less resistance to ohms, more capacity per unit and lower production costs than its tubular equivalents, and more specifically anode-supported cells. Of example, the cell design that is expected to use a thick layer of anode of electrolytes and cathodes is favored by most researchers. The anode carries electrons of fuel oxidation (interconnection) to the collector. Anode materials have to follow many stringent requirements in order to achieve consistent anode efficiency.

The early development of SOFC anode materials in a single electronic conducting process. Much of the metals used were transion tions, namely Pt, Pd, Ru, Co, Fe and graphite. These materials, however, like Fe and graphite, are corrosive, extremely unstable and expensive in reducing atmosphere. Ni has the highest hydrogen oxidation catalytic activity and relatively low costs for most transition metals. Ni is currently the most frequently preferred material for a candi-date anode.

However, Ni cannot be used alone because of its high susceptibility to self-sintering and its higher thermal expansion coefficients than other electrolytes, which greatly decreases porosity. Such inconveniences can cause a poor anodeelectrolyte and TPB interface, which eventually affect electrochemical performance. A Ni-based composite anode can be developed by combining an electro-conductive material (NiO) and an ionic conductor material (electrolyte), to address these limitations. This process increases the effectiveness of the TPB. TPB is the only region where electrolyte oxide conduction, metal conductive electron (Ni) and gas react. The transfer of charges can therefore be done as shown. The hydrogen fuel passes through the porous anode network and interacts with oxide ions, and it is possible to produce water or electron.
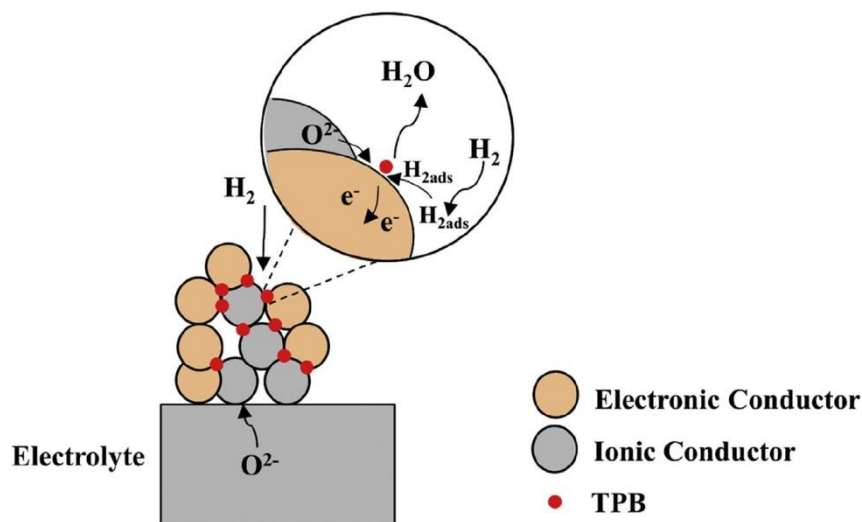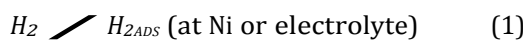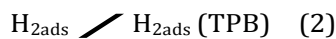

Fig. 3 e TPB of composite anode material

Dissociation and Adsorption of H_2

Hydrogen gas (H_{2ads}) adsorption occurs at the surface of Ni or electrolyte.

$H_2 \nearrow H_{2ADS}$ (at Ni or electrolyte)   (1)

H_{2ads} diffusion into and adsorption H_{2ads} onto the TPB

H_{2ads} diffuses on the surface of Ni or electrolyte and ad-sorbs onto the TPB region.

$H_{2ads} \nearrow H_{2ads}$ (TPB)   (2)

Anodic electrochemical reaction

Electrochemical reaction occurs as the electrolyte oxygen ion reacts to hydrogen and forms an electrolyte oxygen (OX), oxygen void (VO). In neighboring neuronal ions, electrons pass to complete the process when water ($H2O$) forms the end of the reaction.

The composite anodes also have the advantage of improving the length of the TPB and thus increasing electro-chemical performance. External elements in anode materials add an electrolyte step decreases their thermal

expansion failure with the electrolyte which protects the Ni from auto sintering. In order for strong electron conductivity > 100 S / cm, compound anode must be at least 30 Vol. percent nitrogen content. In order to achieve a rapid ion transfer, the electrolyte is however heat-activated and this result was hard to achieve, in particular at lower temperatures. Therefore, for lower-temperature operations it is important to choose high-performance ionic conduction electrolytes.

Apparently, the SOFC materials used in the composite anode, such as NieY2O3-stabilized ZrO2(YSZ) are strongly tempered (~1000 AC) to ensure that the optimal conductivity of oxygen ion (~0.1 S / cm) is attained. The operation at high temperature induces a range of technical challenges such as the misplacement of thermal expansion, the coarsening of electrodes, chemical reactions, and high cost which prevent the use of SOFCs. Lowering SOFC working temperatures under 600 µC helps to preserve the techno-economic void of cells. This will increase the choice and duration of cheap SOFC components and improve stability and shorten start-up and shut-down times. Unhappiness also leads to po-larisation, which is primarily associated with weak electrolytes and electrodes kinetics, as worked at low temperatures.

The ministation of SOFCs (micro-SOFCs) devices will benefit more efficiently from low operating temperatures than PEMFCs and electricity (EES) systems, such as batteries and supercapacitors. In stationary or handheld devices, this strategy should improve market competitivity. The aim of improving cell longevity and the stability of the anode portion has led to the development of low-temperature SOFCs (LTeSOFCs), which could function at 400 $^{\circ}$Ce600 $^{\circ}$C. However, the anode polarization resistance.

Composite anode materials for LT-SOFC

Numerous anode materials have been produced during the last decade. Despite our best, not all results, in particular data on conductivity, have been gathered successfully. Therefore, region-specific resistive density or power density is used throughout the next debate. The material of anodis can be classified as Ni-based or Ni-free anodes. Nickel-based anodes usually contain a minimum of 30% Ni content to have a adequate electrical conductivity (> 100 S / cm).

Over the last decade, a number of Ni-based cer-mets have been produced using a simple ball-milling process, exhibited promising cell efficiency. For example, by simple milling and heat treatment at 800 ^{o} C for 4 h, Raza et al. developed NieSDC(Na^2CO^3). The thermal treatment permits an encapsulation of the carbonate layer on the composite. In addition to using NiOs as an electrocatalyst, several au-thors have begun to add secondary phases such as ZnO. Rasse et al.

Also investigated the ZnO/NiOeSDC (Na_2CO_3) composite anode prepared via ball-milling which exhibited a power density range of 840e1257 mW/cm^2 at 480 $^{\circ}$Ce520 $^{\circ}$C. This method is expected to encourage electrocatalytic activity, extend the effective zone of TPB and thereby boost electrochemical efficiency. Another composite anode has also been made, such as NieLSGM (strontium and magnesium doped lanthanum gallate). However, NieLSGM was limited in chemical compatibility, such that an extra thin layer of NieLDC ($La_{0.4}Ce_{0.6}O_{2-d}$) is required to prevent the diffusion of Ni and La from the LSGM electrolyte. The cell production process may be complicated by this extra thin layer created using a physical vapor deposition method.

Performance enhancement approaches

Other factors like powder properties and improvement method may be improved in addition to the anode material. Electro-chemical performance is controlled by the microstructural aspects of an anode, which is generally determined by the pulver properties such as particle size and surface. In order to ensure efficient operation at low temperatures, the choice of the composite anode for electrolytes is also important. This section examines: (1) ceria carbonate electrolyte is used, (2) nanopowder extraction is applied and (3) electrocatalytic treatment is used.

Using ceria carbonate electrolyte

The electrolyte is a dense oxide conducting material which is sandwiched between the cathode and the anode, which prevents the gas from crossing and internal circuits. To guarantee low ohmic losses, the electromagnets

require fast and strong ionic conductions of approx. 0.1 S/cm. The ceria-based electrolytes including SDC and GDC have mostly been studied at intermediate temperature in the past decade (600 o Ce800 o C). Several limits have been established that prohibit the ceria-based electrolytes from further decreasing temperatures (< 600 o c).

Exploiting nanopowders

The powder properties of the TPB, porosity, and particulate diffusion are known to increase directly, ultimately influencing electrochemicals. Nano-to submicron composite anode powders may also be added to reduce sensitive resistance to polarization at lower temperatures. In recent years, this notion has become the priority. Techniques like ball frying or synthesis, for example, pudder prepa- ration,

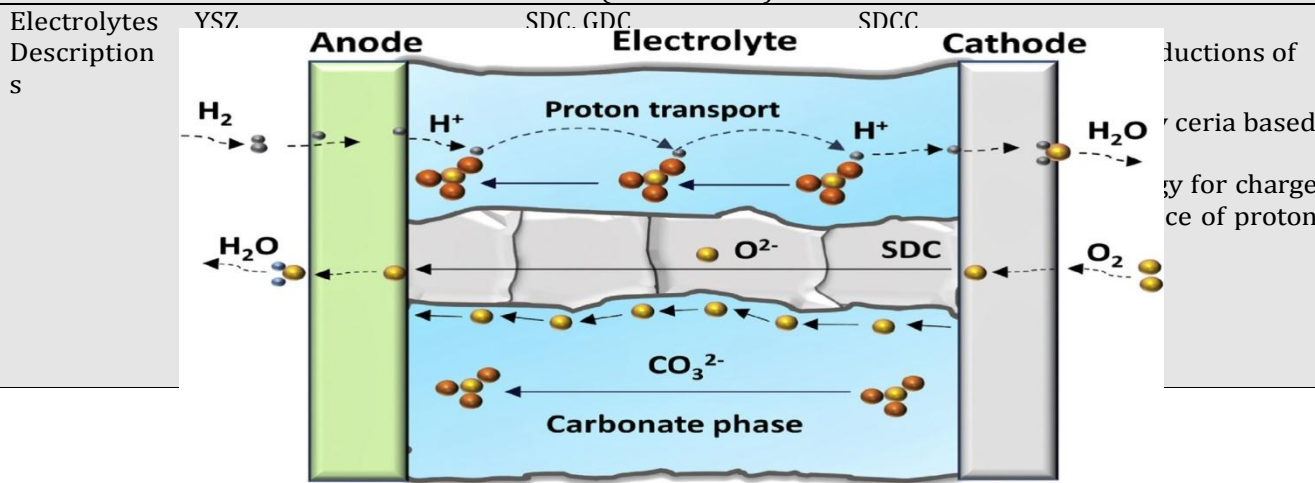| Table 3 e Description of common electrolytes based on their working temperature [37,70e72]			
Operational temperature	High temperature (800e1000 $^\circ$C)	Intermediate temperature (600e800 $^\circ$C)	Low temperature (<600 $^\circ$C)
Electrolytes Descriptions	YSZ,	SDC, GDC	SDCC,

Fig. 4 e Simplified schematic diagram of the ionic and proton conductions adapted from Fan et al. and Xia et al.

Significant in intimate powder growth, the impact on area-specific resistance of the par-taicle dimensions is shown by anodic microstructures. Tornik et al. showed the impact on NieGDC composite anodes' po-larization resistance of particle size reduction. NIOeGDC composite anode poweders were compared and yielded mean particle sizes respectively of 2.37 and 0.55 mm in tight comparison with conventional ball friction and high-energy ball friction.

For a high-energy ball framing process a fine anode microstructure was obtained that reduced the area-specific resistance (0.64Ucm2) by 35 per cent, and the activation energy at 600 ᵒC by 20 per cent compared to the conventional ball milling process. Macedo et al. have reported two methods of preparing NiOeGDC anodiums, namely commercial NiO and GDC powder milling and sol-gel routing using hexahydrate, gadolinium hexahydrate and nickel nitrate as the starting precursor. All processes developed microstructure homogeneous anode. But the method of sol gel

Table 4 e Influence of particle size on area-specific resistance.

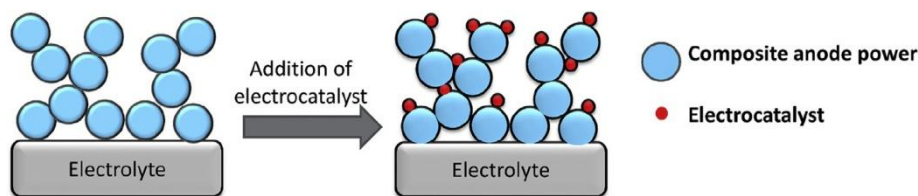| Material	Preparation method	Particle size	Operating Temperature ($^\circ$C)	Area Specific Resistance (U cm^2)
NieGDC (Synthesis) [81]	Ball milling	1 mm	650	6.28
	Sol gel	50 nm	650	1.22
NieGDC (Powder refinement) [57]	Low speed ball-milling (200 rpm)	2.37 mm	600	0.98
	High speed ball-milling (500 rpm)	0.55 mm	600	0.64
Cu$_{0.2}$Zn$_{0.8}$eNSDC (Synthesis) [61]	Solid state	20 nm	550	0.43

Fig. 5 e Schematic diagram of discrete metallic electrocatalyst on composite anode substrate

performance of 500 mW/cm² at 550 $^\circ$C. Use nano-scaling powder on the basis of these experiments, anode electrochemical behaviour changes can be made.

Usage of metallic electrocatalyst

At a low working temperature, the resistance to polarisation is still difficult. Anode polarizing resistances may be as critical as the cathode, which add up to 60% of the overall cellular polarization tance. The anodyic electric shake-ups need to be strengthened at reduced temperature. In the com-position anode, the addition of a metal electrocatalyst can boost electrochemical behavior of the anode. In addition, it is typically used in cathodes with wide temperature range with the use of noble metal such as Pt and Palladium, as metallic catalysts. Using noble metals in electrodes the length of the TPB has improved and the charging transition accelerates, which greatly reduces resistance to polarization. Metallic electrocatalysts were inserted into the electrode in various methods, such as mechanical mixing, liquid penetration and other chemical deposition, as listed in brief below. These techniques are presented with strengths and disadvantages

Mechanical blending/mixing

In this process composite anode powder is simply mixed with metallic electro-catalysers by means of balls. The dynamic chemical cycle is not taken into consideration and only single-stage sintering is used. The metal electrocatalysts are normally ductile, which ensures that the material can be closely combined without drastically affecting particle size. Unless the mixing criteria such as ball count and high speed were wrongly chosen, distorted configurations of metallic particles would be broken and the microstructure would deteriorate.

Liquid infiltration

The process of liquid penetration also soaks or lowers the substratum in a metal-nitrate or chloride Premix solution along with a surfactant and solvent. The premix is placed in a sintered porous (anode or electrolyte) substrate with a syringe. The infiltrated layer would then be arranged in a slightly lower temperature for sintering process, which is ideal for breaking down nitrate and organic compounds. Numerous scholars are extensively interested in the process of liquid infiltration. This eliminates metal accumulation, uniformity and electrode densification problems and thus increases the stability of the microstructure. While porous substrates may achieve a standardized distribution of electrocatalyst, an infiltration cycle can take a long time because of capillary effects and increased viscosity of solution with increased metal load. This influence usually impedes the completion of the process of penetration to achieve the desired metal charge on the porous substratum. The pro-cess infiltration can also be limited by large areas of infiltration.

Table 5 e Strengths and drawbacks of several metallic electrocatalyst incorporation techniques [86e90].		
Incorporation techniques	Strengths	Drawbacks
Mechanical mixing/blending	Single processing step	Particle reduction is not achievable due to ductility of metallic electrocatalyst
	Complex chemical processes are avoided	
	Set up cost is inexpensive	
Liquid Infiltration	Reduces sintering temperature	Low microstructural control
	Good microstructural control	Repeated infiltrating cycle
	Reduces the amount of electrocatalyst	Low adhesion force poses difficulties during infiltration process
Deposition	Reduces sintering temperature	Not suitable for substrate with large surface areas
	Good microstructural control	Long processing
		Complex chemical process
		Various processing parameters and process limiting factors
		Set up cost is relatively expensive

An electric current encouraged. While the tar-geted porous layer, both the cathode and anode are immersed into an aqueous electrolyte solution of metallic electro catalyst ions. The cathode ions are picked at and the anode dissolves in the aqueous solution of the electrolyte. Therefore, guided metal ions are absorbed mainly during electrodeposition. Electrodeposition calls for a lower sintering temperature to ensure a minimum thermal mismatch with others. Micro-structural characteristics (poral length) and processing factors such as potential electrolyte decrease, electromagnetic temperature, current density and applied voltage affect the operation. Electroless deposition, on the other hand , requires chemical deposition without electrical control. A sintered pore substratum is immersed in a bath of so-called metal nitrate. The auto-catalytic chemical reaction, leading to the formation on the surface of the porous base with a thin metallic sheet, is then added into the water. A reducing agent, namely hydrazine and form aldehyde. To obtain a bimetallic base, electrical deposition should be combined with electro deposition. A conductive surface is laid by electro-less deposition in this combination process on a Porous substrate prior to the electrodeposition of the metallic electrocatalyst. A variety of factors, such as metal cation concentrations and the reduction agent, as well como the bath temperature, can influence the electroless deposit rate. Electrical and electrodeposition methods for microstructural control are highly flexible.

The lowest area-specific resistance of 0.16 U cm² among others tested (Pd-CGO [11.86 U cm²], Ru-CGO [18.09 U cm²], Ni-CGO [0.96 U cm²]), and electrocatalyst free STN anode (352 U cm²) was tested at 600 °C. The increase in region resistance is due to the electrocatalyst 's elevated catalytic behaviours. Within the same research, the use of ternary electrocatalysts has also shown increased region specific resistance. The processing of NiePteCGO Ternary Electrocatalysts for STN was due to the synergist effects from NI and Pt on the improved charge transfer cycle, with a lowest area-specific resistance of 0,10 U cm2 at600 ºC.

Conclusions

Several components and improvement methods were explored for composite anodis at low temperatures. In view of the past studies, most composite anodes have been formed with ceria-based electrolytes. The polarization resistance remains high despite the development of the ma-terials, particularly in low-temperature areas. Improvements were then required. Because of the strong ionic conduction properties at lower temperatures, SDCC electrolyte integrated the most composite anodes discussed. With the use of nanocomposite powders, the region-specific resistance decreased significantly, while electrocatalytics also helped to decrease resistance to laration. Many works succeed in improving electrical catalysts integrated in anodes. However, long-term stability and durability studies in the resulting cells remain insufficient and are urgently needed to speed up the future maturity of LTeSOFCs, notably in the low working temperature.

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