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Achievements and trends of solid oxide fuel cells in clean energy field: a perspective review

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Abstract The main concerns in the world today, especially in the energy field, are subjected to clean, efficient, and durable sources of energy. These three aspects are the main goals that scientist are paying attention to. However, the various types of energy resources include fossil and sustainable ones, but still some challenges are chasing these kinds from energy conversion, storage, and efficiency. Hence, the most reliable and considered energy resource nowadays is the utilized one which is as highly efficient, clean, and everlasting as possible. So, in this review, an attempt is made to highlight one of the promising types as a clean and efficient energy resource. Solid oxide fuel cell (SOFC) is the most efficient type of the fuel cell types involved with hydrogen and hydrocarbon-based fuels, especially when it works with combined heat and power (CHP). The importance of this type is due to its nature of work as conversion tool from chemical to electrical for generation of power without noise, pollution, and can be safely handled.

Keywords solid oxide fuel cells (SOFCs), clean energy, design, micro-scale, nano-scale, performance

1 Introduction

The massive increase of the total population in the world resulted in a huge consumption from various energy resources [1]. This quick progress made scientists pay an intensive interest in developing new energy resources. Through the enhancement of the materials utilized, it may give an advantage over the usage of fossil fuels and overcome its problems. Moreover, the environmental issues such as the global warming problem are ongoing right now. Hence, researchers should have the liability in finding a reliable solution and decrease the use of the fossil fuel, which will help to confront the run-out problems in the future [1,2]. Thereby, proposing alternative ones [1] can achieve this duty considering the safe manipulations. Accordingly, the utilization of fuel cells has rapidly increased. Based on reports from Fuel Cell Today (FCT), and Fuel Cells 2000 (FC2000), fuel cells (FCs) can offer clean, efficient, and reliable power generation to almost any electrical power device [2]. Besides, widespread use of fuel cells in portable, stationary, and transport applications are planned. Thus, offering novel and efficient materials that are able to participate in overcoming the current serious challenges considered here in this review, specifically for solid oxide fuel cells (SOFCs). Meanwhile, the components of SOFCs (electrodes, electrolytes and inter-connects) have to be actively investigated and developed to be fitted with the industrial and human needs [3,4]. Moreover, drawing the specifications of the applied materials conducted in SOFCs devices by optimum characterization and reliable analysis will provide a superior efficiency in various applications. These goals could be clearly identified through exploring new materials with high proton or electronic conduction and photo catalytic activity that can serve as gas sensors or components SOFCs ($\text{LnBaMn}_2\text{O}_{5+\delta}$, $\text{Ln} = \text{Sm, Pr, Nd}$,

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Gd, etc for electrode and BCZYM, $M = \text{Zn, Sm, Yb, Mg}$, etc for electrolyte); through developing low-cost, easily-sinterable, perovskite-based materials (Ni, Fe, Cu, Al, Sr); and through developing a solid state ceramic anode or cathode for SOFCs applications at different scales (macro to nano-scale).

Therefore, in this review, sequential steps about the development of fuel cells, as renewable energy resources passing through the history of these types are presented. Then, the focus will be on SOFC and its development along the past decades in addition to its significance in the clean energy sector. Basically, the configuration of SOFCs mainly includes porous electrodes (anode and cathode) detached by a dense electrolyte. All materials used are from hard ceramics instead of liquids. For the fuel feeding sources in SOFCs, the supply of hydrogen and hydrocarbon-based fuels are fed to the anode side, while the air is supplied to the cathode side. The operational conditions can be up to 1000°C (about 1273 K and 1832°F). The basic idea of electrochemical reactions in SOFCs depends on the oxygen ions O^{2-} migrating through the crystal lattice, while the positively charged hydrogen ions H^{+} are flowing over the anode when the oxygen are passing through the electrolyte for oxidizing the fuel at the cathode part. Hence, the electrical power generated, as a result from the electrons, travels from the anode to the cathode in the circuit.

2 Fossil fuel and alternative energy resources

The consideration of fossil fuel (oil, coal, and natural gas) as a long-term source of fuel is becoming difficult to ratify.

Furthermore, the realistic problems that the world is facing in the current time are associated with burning of these fuels to get energy. Carbon dioxide, nitrous oxide, and greenhouse gases are major contributors to global warming. In addition, the rapid increase in world population makes the need of energy an essential source. The estimation of that power amounts to almost two-thirds of our electricity and virtually all of our transportation [3]. Furthermore, these kinds of resources are not sustainable and will vanish someday.

The consumption of energy in the world, specifically in the USA is shown in Fig. 1. For the world, a total of 472 Quads is dominated by oil, with all fossil fuels accounting for 79% of the total. For the USA, a total of 71 Quads is dominated by coal, with fossil fuels accounting for 86% of the total. Renewable energy, mainly from wind, solar and biomass amounted in 2006 to only 1.3% of the total in the world and 5.5% in the USA. According to the last five decades, it can be seen that the world's annual consumption of energy from various sources is rapidly increasing. Figure 2 depicts the average rate of increase from 1970 to 2002 and from 2002 to 2006 [4].

It is necessary to estimate the consumption of energy in the future that world needs, and then make the necessary forecasting and expectations considering the minimum and maximum values (see Fig. 3). Hence, these kinds of expectations can reduce the risks that might happen in the future.

On the other hand, it is very crucial to consider the use of alternative sources as renewable and sustainable ones. Moreover, these renewable sources are able to satisfy the human needs. And hence, small sustainable farms can help to reduce the nation's dependence on fossil fuels through the widespread use of this technology within different

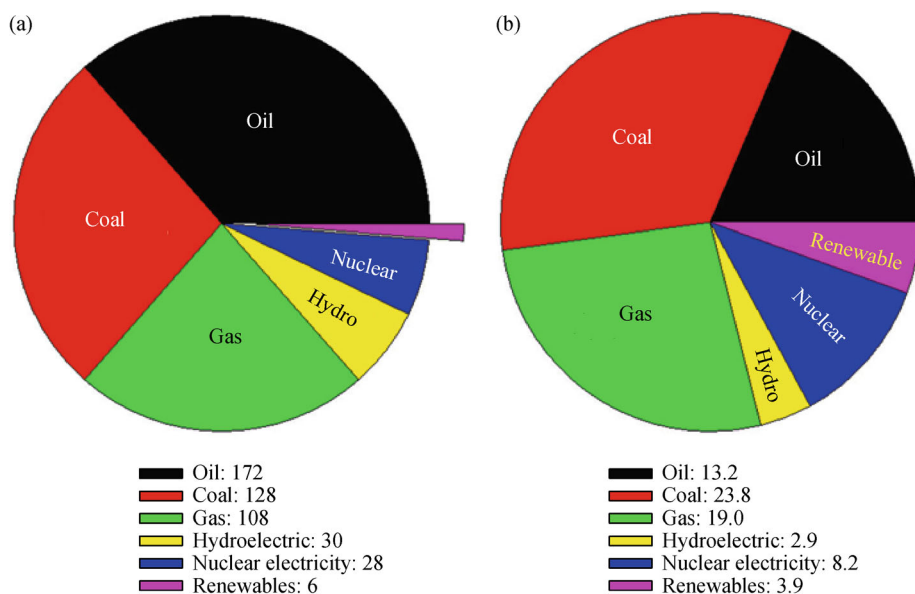


Fig. 1 Sources of energy consumed

(a) The world; (b) the USA (Data are for 2006 and are in units of Quads per year. Adapted with permission from Ref. [4])

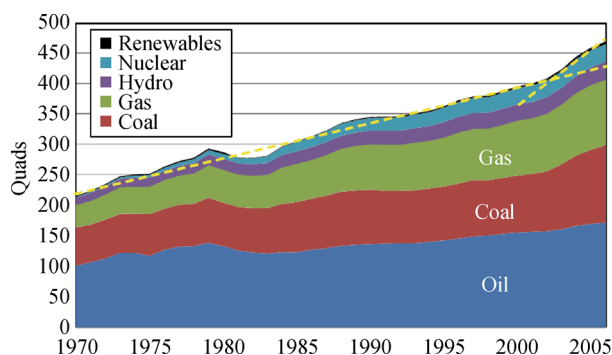


Fig. 2 Previous five decade's history of the world's annual consumption of energy from various sources including fossil and renewable energy (Adapted with permission from Ref. [4])

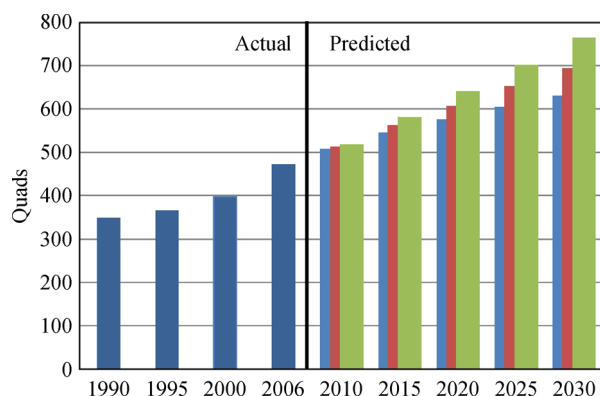


Fig. 3 Predictions of the world's annual energy needs up to 2030 (The triple bars show the minimum, average, and maximum values. Adapted with permission from Ref. [4])

scales. Therefore, working with fuel cell types [5–12] presents a promising future for this source of energy, because of its durability, clean, and safe usage.

Thus, the key benefits that highlights the important role of SOFCs are a very high efficiency from 60% to 90% in electrical, hybrid fuel cell/turbine, and with combined heat and power (CHP); a reduction of CO₂ emissions from 90% to 35% (CHP system and light duty vehicles); a reduction of fossil fuel use from >80% to 90% for FCEVs; a reduction of air pollution of 90% for CHP systems; and a flexibility of the fuel (clean fuel, hydrogen, and conventional fuels (including methane, electrolysis, and natural gas) [13]. In addition, the role of SOFCs among fuel cell types can be noticed (see Fig. 4) precisely as a clean and efficient energy source.

Moreover, SOFCs utilization starts from macro-scale to nano-scales in various applications because of their outstanding characteristics in electrical production with hydrogen fuels when feeding as clean sources of fuel. But, still some challenges are confronting this technology and more developments and investigations are needed.

3 Fuel cells

Generally, fuel cells have advantages over other energy sources in obtaining energy, because of the electrochemical reactions that occur through the supply of hydrogen and an oxygen source (usually air) that is very efficient. As a result, the electrochemical oxidation of hydrogen as a fuel can be accomplished with a high performance. The most important factor for influencing fuel cell performance is the material used as a catalyst, which helps to speed up the reactions at both anode and cathode. There are several types of fuel cells which are mainly classified relying upon the nature of the applied electrolyte. Each type of fuel cell requires specific materials and fuels for different applications. These types include proton exchange membrane fuel cells (PEMFCs), direct methanol fuel cells (DMFCs), phosphoric acid fuel cells (PAFCs), alkaline fuel cells (AFCs), molten carbonate fuel cells (MCFCs), and solid oxide fuel cells (SOFCs). SOFCs have many advantages for a wide range of applications because of their theoretical efficiency, potential to use natural gas, biogas or methane as a fuel, fuel flexibility, and high performance [8]. Many researchers have cited that fuel cells are important because of their modular and distributed nature in addition to the lack of noise and pollution [8–12].

Although many electrode materials for SOFCs have been developed over the past three decades, there still remain some challenges because of their cost and limited durability [9]. Therefore, great effort is being expended to overcome these challenges through design of new materials, which might lead to a superior enhancement of the SOFC performance which is able to fulfil all human energy needs. Furthermore, many attempts to develop anode and cathode materials for SOFCs have been made over the past 20 years. However, some materials, especially Ni/yttria-stabilized zirconia (YSZ), are favored as anodes in SOFCs because of their high electrochemical activity for hydrogen oxidation and high stability under SOFC operating conditions. Besides, current research on SOFCs development has focused on temperatures below 1000°C (usually 500°C–800°C) with the aim of decreasing material cost and improving their stability [14–19].

3.1 History of fuel cell and achievements

Since fuel cells were used as a source of power when scientists began to search for alternative sources of fossil fuels, no one has been expecting that these fuel cells will be promising energy sources until the 21st century. The first fuel cell was made by Sir William Robert Grove (1811–1896) when he developed an improved wet-cell battery in 1838 [20]. Moreover, the main idea of his research is that electrolysis uses electricity to split water into hydrogen and oxygen during reactions, and that the opposite reaction must be capable of producing electricity. Thus, Grove

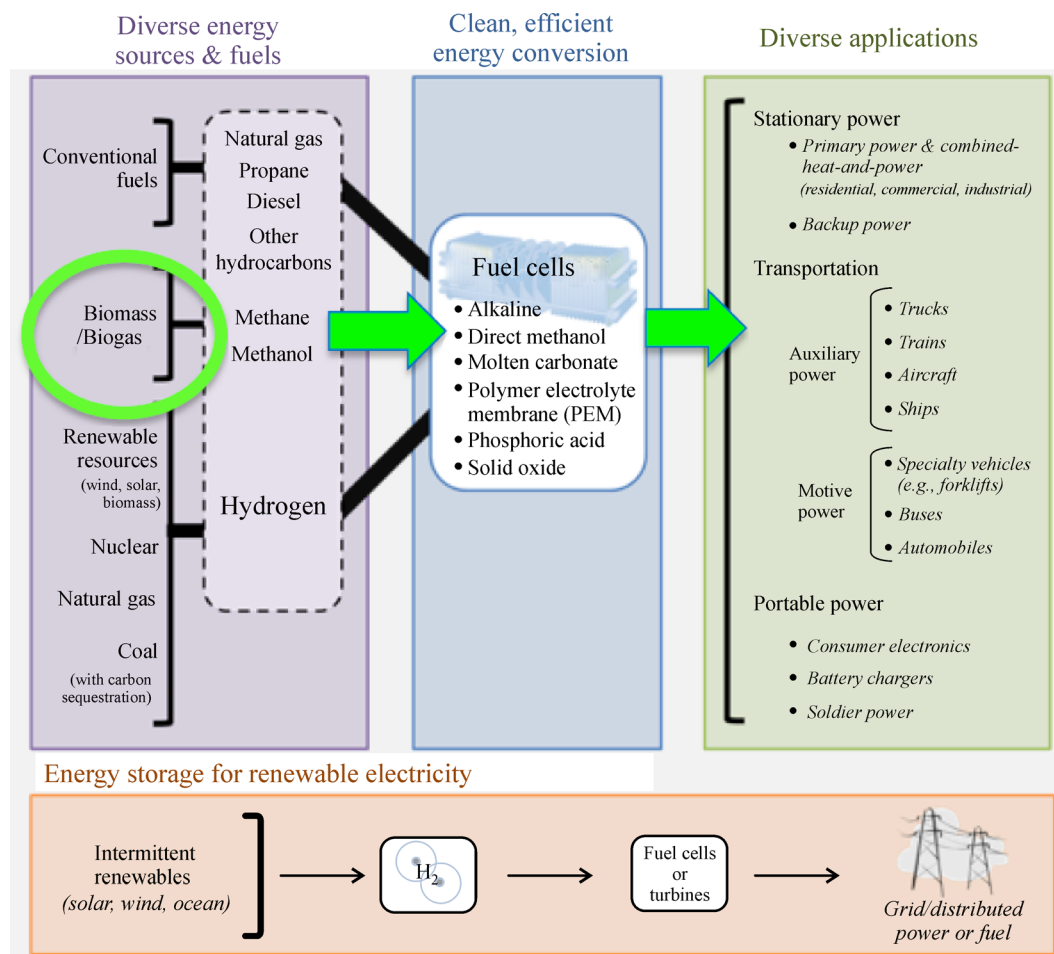


Fig. 4 Role of fuel cell types as a clean source of energy resource (Adapted with permission from Ref. [13])

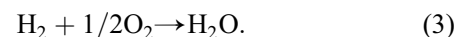
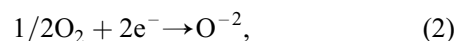
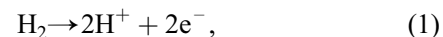
developed the first fuel cell based on the combination of hydrogen and oxygen to produce electricity. Ludwig Mond and Carl Langer (1839–1909) [20] conducted experiments with a hydrogen fuel cell that produced 6 A per square foot at 0.73 V. In addition, Friedrich Wilhelm Ostwald (1853–1932) [20], the founder of physical chemistry, derived the relationship between the different components of the fuel cell including the electrodes, electrolyte, and oxidising and reducing agents (anions and cations) from his experimental investigations. Francis Thomas Bacon (1904–1992) [20] then made substantial developments with high-pressure fuel cells; he succeeded in using nickel gauze electrodes in cells that operated at pressures up to 3000 Pa. In the 1960s, International Fuel Cells (IFC) in Windsor, Connecticut developed a fuel cell power plant for the Apollo spacecraft. In the 1970s, IFC developed a more powerful alkaline fuel cell for NASA's space shuttle Orbiter [20,21]. Table 1 lists the most important achievements since the advent of fuel cells.

3.2 How SOFCs works

The operation of a fuel cell mainly depends on the

transportation process in electrochemical reactions, which convert the chemical energy of a fuel and oxidant into electrical energy represented by load through the three main components (anode, electrolyte and cathode). As shown in Fig. 5, the main components of SOFC include porous electrodes detached by a dense electrolyte.

The main reactions of SOFCs [26,27] depend on the hydrogen fed to the anode, the oxygen fed to the cathode, and the hole transportation process, as shown in Eqs. (1)–(3).



The reactions occurred on both anode and cathode can be noticed from Eqs. (4)–(6).

For the anode,

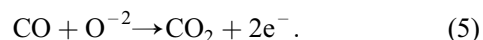
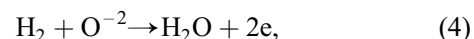
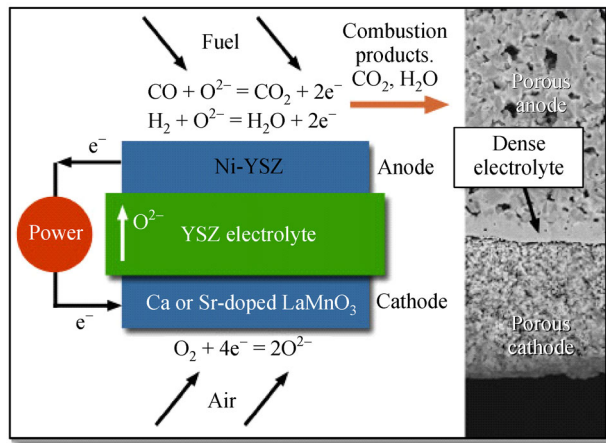
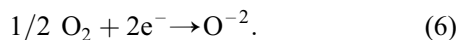


Table 1 Summary of initial achievements in the field of fuel cells [21]

Scientists	Year	Achievements	Ref.
Nicolas and Carlisle	1800	Described the electrolysis of water	[21]
Grove	1838	Created the first gas battery	[22–24]
Monde and Langer	1889	Conducted experiments on hydrogen fuel cells	[22]
Ostwald	1893	Described theoretical performance of fuel cells	[22,23]
Jacque	1896	Developed first fuel cell	[22]
Buar and Preis	1921	Experimented with high-temperature solid oxide electrodes	[22]
Bacon	1939	Researched alkaline fuel cells	[22]
DuPont, Parkersburg, West Virginia	1950	Teflon is used in membranes	[22,23,25]
Grubb	1955	Developed a sulfonated PEMFC	[22,23]
Brores and Ketelar	1958	Built a molten carbonate fuel cell	[22]
Central Technical Institute	1959	Researched SOFCs	[22]
IFC, Windsor Connecticut	1960	Developed a fuel cell power plant for the Apollo spacecraft	[22]
Elmore and Tanner	1961	Phosphoric acid fuel cell	[22]
IFC, Windsor Connecticut	1970	Oil crises, and developed a more powerful alkaline fuel cell for NASA's space shuttle Orbiter	[22,25]
NASA jet propulsion	1990	First direct methanol fuel cell	[22,23]
Bauch up power	2007	Fuel cell being to be commercially sold as APU & stationary equipment's power generation	[22,25]
Honda	2008	Announced first mass production of fuel cell cars FCX clarity	[25]
Portable fuel cell chargers	2009	Residential micro fuel cell-CHP become commercially available in Japan	[25]

**Fig. 5** Schematic diagram of cell arrangement and transportation processes in an SOFC (Adapted with permission from Ref. [23])

(Significantly slower than H_2 conversion)
For the cathode,



The theory of this process has been well explained by Tesfai and John [26].

Optimization of the efficiency and performance of solid oxide fuel cells can be controlled by improving the materials used as fuel cell components, which is currently

the subject of continuous investigation. For example, the use of lanthanum cobaltate as a cathode [28] and lanthanum manganite as an anode [28,29], and Ytria Stabilized Zirconia (YSZ) as electrolytes. Through the following subtitles, synthesis, design and characterization of different materials used in SOFCs will be illustrated.

Typically, many experimental studies on different types of solid oxide fuel cells have been reported, and the methodology of any work should be going through the following steps:

- Selection of the SOFCs compounds materials being tested.
- Determination of the specific amount (stoichiometric/non-stoichiometric) of each component to be synthesized.
- Starting preparation and synthesis of the selected materials (dry or wet route) until calcination stages finish.
- Examination of the material composition by X-ray powder diffraction (XRD) or Neutron powder diffractions (NPD) to identify and confirm the structural phase of the compound.
- Identification of the material phase and continuation of the other different characterization procedures (physical characterizations).
- Final testing through focusing on the electrochemical performance tests (conductivity and power density).

Once the previous steps are achieved for the selected material, it is easy to repeat again for another series of new material compounds.

3.3 Fuel cells types, applications, and advantages

The main features of common types of fuel cells according to their different requirements and applications can be observed from Fig. 6. Besides, the functional parameters of FCs based on fuel, material used, reforming, and operational temperature ranges are listed in Table 2 [29].

4 Geometrical design of SOFCs

SOFC design types [41] including planar, tubular [42] monolithic [43,44], and roller [45] structures are shown in Figs. 7–10. All primary types of SOFCs are fabricated based on the type of cell design, the required performance, and the economical manufacture (effective cost) [44], as listed in Table 3.

4.1 Planar design

The primary structure of a unit cell consists of two porous layers (anode and cathode) separated by a dense layer (electrolyte). In case of many cells assembling (Stack), interconnect is necessary and sealant is another optional component for planner type of SOFC to prevent mixing of fuel and air [42].

4.2 Monolithic design

This type also considers a primary structure design SOFC and it is similar to the heat exchanger design. The main structure consists of a thin cell which includes both anode and cathode detached by the dense electrolyte, in addition to interconnect and current collectors compacted together into a corrugated structure. There are two different configurations for this design, gas co-flow and gas cross-flow configurations [34].

4.3 Tubular design

This configuration basically depends on elimination of sealant and it includes a tubular support tube covered with the cathode in the core, then the anode in the outside cell and in between the electrolyte is located. The oxidant is introduced through the core of the support tube, whereas the fuel flows at the outside of this support tube [42].

4.4 SOFC roll design

The arrangement and configuration in this type is prepared by using a tape casting process; each component of the fuel cell is cast separately as an easily manipulated flexible tape. The anode, electrolyte, and cathode components are laminated together and structured to give the desired geometry. The fuel supply is inserted in both anode and cathode (core) through stainless steel tubes [45].

5 Material components of SOFCs

5.1 Anode

The importance of developing an anode material as the main part of the fuel cell components is that the material being used in this part accounts for nearly 95% [46] of the material used in the electrolyte supported cell [47]. Also, the fuel oxidation-reaction taking place at the anode catalyzes the reaction of the fuel with oxygen [48] as shown previously in Eq. (4) and in Fig. 11. To maintain the highest performance of the anode material, the anode should be a highly (ionic, electronic) conductive, chemically compatible, thermally stable, highly porous structure, and fine particle size with an organized structure. However, in the meantime, common anode materials are traditional materials that have been used for a long time despite

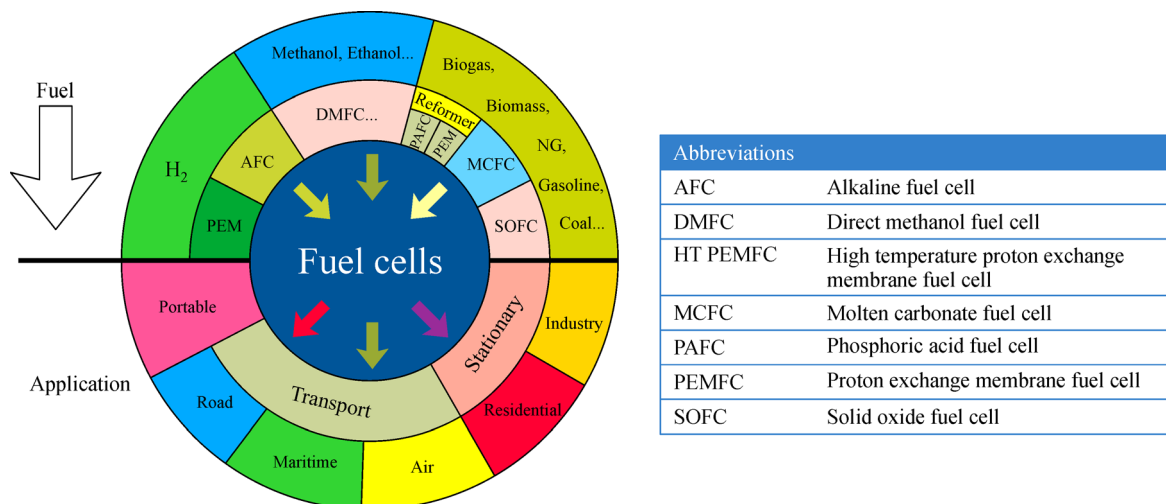


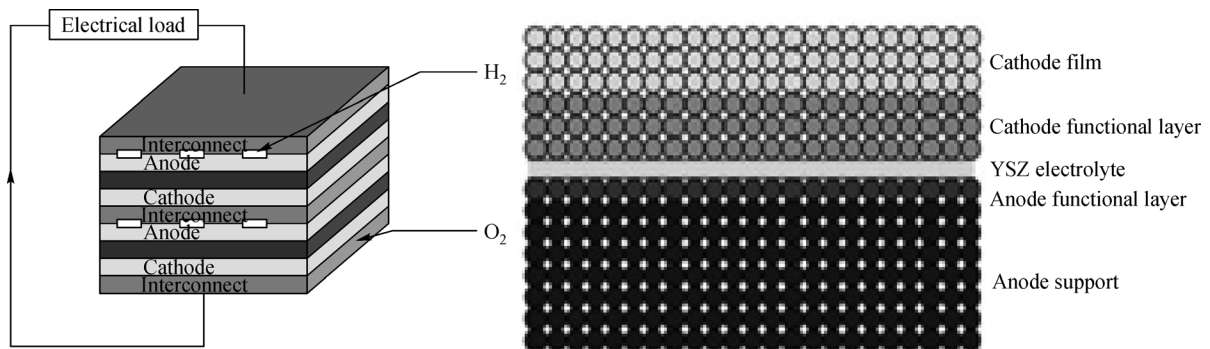
Fig. 6 Fuel cell types and its abbreviations (Adapted with permission from Ref. [30])

Table 2 Important advances in different kinds of fuel cells

Parameters	Type of fuel cell					Ref.
	PEMFC	AFC	PAFC	MCFC	SOFC	
Electrolyte	Hydrated polymeric ion exchange membranes	Mobilised or immobilized potassium hydroxide in asbestos matrix	Immobilised liquid phosphoric acid in SiC	Immobilised liquid molten carbonate in LiAlO_2	Perovskites (ceramics)	[25,31]
Electrodes	Carbon	Transition metals	Carbon	Nickel and nickel oxide	Perovskite and perovskite/metal cermet	[25,32]
Catalyst	Platinum	Platinum	Platinum	Electrode material	Electrode material	[33–36]
Interconnect	Carbon or metal	Metal	Graphite	Stainless steel or nickel	Nickel, ceramic, or steel	[25,37]
Operating temperature/ $^{\circ}\text{C}$	40–80	65–220	205	650	600–1000	[25,31]
Charge carrier	H^+	OH^-	H^+	CO_3^{2-}	O^{2-}	[25,38]
External reformer for hydrocarbon fuels	Yes	Yes	Yes	No, for some fuels	No, for some fuels and cell designs	[25,39]
External shift conversion of CO to hydrogen	Yes + purification to remove trace CO	Yes + purification to remove CO and CO_2	Yes	No	No	[38,40]
Prime cell components	Carbon-based	Carbon-based	Graphite-based	Stainless-based	Ceramic	[25,31]
Product water management	Evaporative	Evaporative	Evaporative	Gaseous product	Gaseous product	[25,31]
Product heat management	Process gas + liquid cooling medium	Process gas + electrolyte circulation	Process gas + liquid cooling medium or steam generation	Internal reforming + process gas	Internal reforming + process gas	[25,31]

Table 3 Fabrication methods for the various types of fuel cell concepts and their components [44]

Design	Fabrication method		
	Electrolyte	Electrodes	Interconnect
Tubular concept	CVD/EVD, plasma spraying	Slurry coating, plasma spraying, CVD/EVD	EVD, plasma spraying
Monolithic	Calender rolling, laminating, co-sintering	Calender rolling, laminating, co-sintering	Calender rolling, laminating, co-sintering
Planar	Tape casting, calender rolling	Screen printing, slurry coating	Ceramic or metal processing
Roller	Tape casting/co-sintering	Tape casting/co-sintering	Tape casting/co-sintering

**Fig. 7** Planar type SOFC (Adapted with permission from Ref. [42])

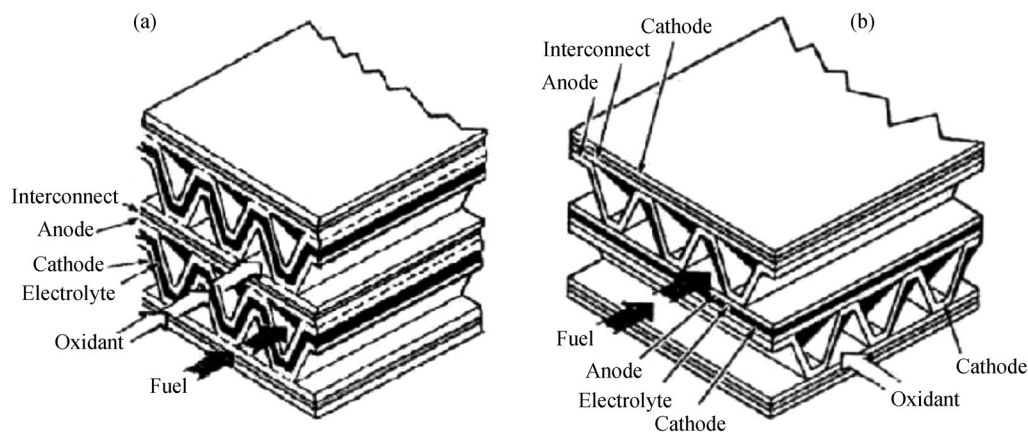


Fig. 8 Monolithic SOFC design
(a) Gas co-flow; (b) gas cross-flow (Adapted with permission from Ref. [44])

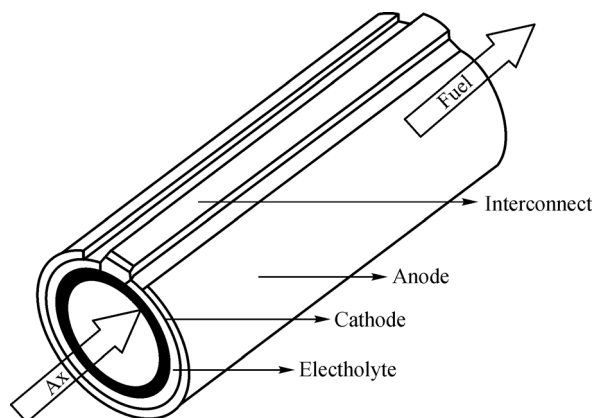


Fig. 9 Tubular design SOFC (Adapted with permission from Refs. [42,44])

exhibiting poor performance.

In the past decades, improvements concerning anode materials properties have been reported by selecting new synthesis and design of materials, and Table 4 represents some of the most important materials that are used recently with reported conductivity performance values [50].

5.2 Electrolyte and interconnects

In an SOFC, electrolyte may be an anode-supported fuel cell or electrolyte-supported fuel cell [9,48,64] and in both cases, the role of electrolyte is essential as it must possess a high ionic or proton conductivity, chemically and mechanically compatible with the other components of the cell. The main feature of this electrolyte is that it should be a fully dense ceramic layer in the structure and it is preferable to be very thin in order to reduce internal cell resistance in electrochemical reactions [5,12]. These oxide ions pass through the electrolyte and react with the fuel (e.g., hydrogen and carbon monoxide molecules), which diffuse into the anode side, at the anode and electrolyte interface, which can be described by Eq. (5). For the material used in electrolyte, yttria stabilized zirconia (YSZ) and cerium oxide (CeO_2) stabilized by Gd or Sm are the most common and main materials considered for electrolyte applications [65]. So, to increase the ionic conductivity, Y is doped with Zr which increases the concentration of oxygen vacancies. On the other hand, cerium oxide has been considered as a good electrolyte material when it is doped with Gadolinium (GDC), because of its high ionic

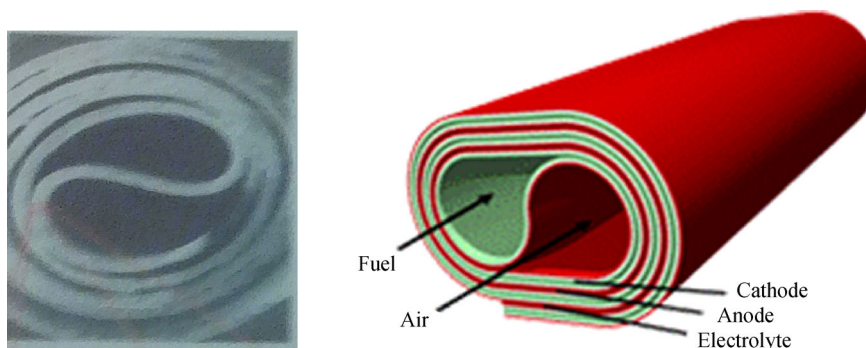


Fig. 10 Roll design SOFC (Adapted with permission from Ref. [45])

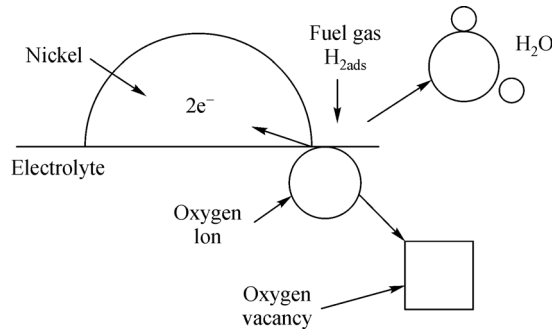


Fig. 11 An example showing a schematic mechanism for anode reaction with H_2 fuel (Adapted with permission from Ref. [49])

conductivity than YSZ, and it also allows the operation at lower temperatures [57]. For this type of electrolyte GDC, it is preferable on single-chamber fuel cell testing [61] because of the porosity percentage. Another type, which is proton conducting electrolyte, basically has been used because of the essential role it plays in hydrogen technology. For instance, BCZY is one of the promising electrolytes that has been used in SOFCs and has shown a superior performance when it is utilized [66].

Typically in SOFCs, the proper way to connect between anode and cathode electrically can be achieved by interconnect. Moreover, the interconnect represents the physical barrier between the oxidant and the reducing fuel atmosphere. Therefore, the interconnect must be a dense material as well as the electrolyte which has a good electronic conductor and oxide-ion insulator, chemically stable in both oxidizing and reducing atmospheres, thermally matched to the neighboring cathode and anode, and physically gas tight [67,68]. For all previous requirements, the selection of the interconnecting materials must be constrained by the targeted operating temperature

of the cell and mainly determined by its performance in the active application. However, some essential factors must be considered in the selection of interconnecting materials including oxygen kinetics, electrical properties, chemical compatibility, and mechanical stability as well. At an earlier stage of SOFCs development, the high operating temperature ($\sim 1000^\circ\text{C}$) restricts the use of metals as interconnects. The only suitable material for high-temperature SOFCs was alkaline-earth doped LaCrO_3 or other Cr-containing perovskites. After the emergence of high-performance anode-supported SOFCs, the operating temperature of an SOFC was significantly lowered to the range where cost-effective, commercially available, and high-temperature metallic alloys are suitable for use [68,69]. Despite of the fact that metallic interconnects have the advance and preferable over ceramic LaCrO_3 -based ones, they are truly electronic conductors and oxide-ion insulators. Besides, their cost is lower and fabrication is reliable compared to the ceramic ones. Additionally, thermal stability is efficient, specifically with the modern planar SOFC design where a metallic interconnect is typically used as the mechanical support of a thin assembly of each component in the fuel cell.

5.3 Cathode

Cathode is described as a contact layer with the electrolyte exposed to the fuel (air/oxygen) [70–72]. The importance of this electrode can be explained by the functional work in the cell operation through the cathode and oxygen reactions, which works as a carrier to electrons from the external circuit to oxygen location giving ions and transportation of oxygen ions to electrolyte interface [67]. The selection of the cathode materials requires some distinct properties such as the commonly perovskite materials with a lanthanum manganite composition doped

Table 4 Conductivities of materials developed as anodes for SOFCs

Materials	DC conductivity/($\text{S} \cdot \text{cm}^{-1}$)	Advantage/disadvantage	Ref.
$\text{Sc}_{0.1}\text{Y}_{0.1}\text{Zr}_{0.6}\text{Ti}_{0.2}\text{O}_{1.9}$	0.14	Operate at high temperature	[51]
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{0.8}\text{Cr}_{0.2}\text{O}_3$	0.5	Low conductivity	[52]
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.95}\text{Ru}_{0.05}\text{O}_3$	0.6	Expensive	[8,53]
$(\text{La}_{0.7}\text{Sr}_{0.3})_{1-x}\text{Ce}_x\text{Cr}_{1-x}\text{Ni}_x\text{O}_3$	5.03	Carbon deposition	[54]
$\text{Sr}_{0.88}\text{Y}_{0.08}\text{TiO}_3$	64	High operating temperature	[55]
CrTi_2O_5	177	Expensive	[8,56]
Ni-YSZ	250	High operating temperature	[57]
$\text{Ti}_{0.34}\text{Nb}_{0.66}\text{O}_2$	340	Very expensive	[58]
LaSrTiO_2	360	No compatibility	[59]
Ni-SDC	573	Coke formation	[8,60]
Ni-GDC	1070	Coke formation, and electronic performance degradation	[8,61]
Cu-CeO_2	5200	Improved electronic conductivity	[8,62]
$\text{Cu-GDCCrTi}_2\text{O}_5$	8500	Good thermal expansion, and electronic performance	[8,63]

with rare earth elements [73,74] such as Co, Ce or Sr [70,75]. These materials have an important advantage that gives a good matching in thermo-mechanical performance with the electrolyte and, moreover, they are mixed ionic and electrical conductors. The whole efforts were made regarding the synthesis of material composition in the cathode part concentrating on the controlling of oxygen non-stoichiometry and defect aspects can enhance the ionic and electronic conductivities used in SOFCs, in addition to the catalytic properties. For any material used in SOFCs as cathode, first, it should be a highly electronic conductive; secondly, it should be chemically compatible, and thermally stable to match with the other component of the fuel cell; third, the microstructure should be in high percentages of porosity for oxidation reactions cathode/electrolyte interface; fourth, it should give a high catalytic activity for the oxygen reduction reaction; and finally, it should be easy in processing and reliable cost manufacturing [76–78]. Moreover, the results obtained from the literature and proper selection of the cathode materials mainly depend on the electrolyte materials used and specifically focusing on the thermal expansion coefficient matching in the whole cell [79]. Table 5 tabulates the cathode materials commonly used [70].

Therefore, materials selected for SOFCs mainly depend on their functionality in the specific applications, and they must be matched altogether in the cell. Meanwhile, Wincewicz and Cooper [80] have presented a schematic block diagram which lists the materials commonly used and manufacturing alternatives for SOFCs as shown in Fig. 12.

6 SOFCs material structures

Material behavior is mainly identified from its properties and through its microstructure levels basically allowed by quantum mechanics that explained atoms and solids characteristics in the early of 1930s. The combination of physics, chemistry and mechanics of material is focusing on the relationship between the properties of a material within microstructure levels. The enhancement of the materials used in the energy field leads to an ideal performance in the functional applications. Furthermore, among the common classifications of material, ceramics plays an essential role in modern technology. Ceramics materials (electrodes and electrolytes) have proven their great enhancement in SOFCs applications as shown from the pervious and current research work. Therefore, the coming sections will show some ceramic structure types, (see Table 6 broader range of chemical composition than metals with more complicated structures). However, the great concern from scientific research are around specific types (see Fig. 13), but here the main focus was on perovskites and fluorite structure as commonly utilized materials for SOFCs.

Table 5 Conductivities of materials developed as a cathode for SOFCs [70]

Composition	TEC $\times 10^{-6}/\text{K}^{-1}$	$T/^{\circ}\text{C}$	$\sigma_e/(\text{S}\cdot\text{cm}^{-1})$
$\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$	11.8	900	300
$\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$	11.7	800	240
$\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$	13	800	130
$\text{Pr}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$	12	950	220
$\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$	19.1	800	1220
$\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$	20.5	800	1600
$\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$	12.2	750	150
$\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$	-	550	352
	-	800	369
$\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$	16.3	800	129
$\text{Pr}_{0.5}\text{Sr}_{0.2}\text{FeO}_3$	13.2	550	300
$\text{Pr}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$	12.1	800	78
$\text{La}_{0.7}\text{Sr}_{0.3}\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_3$	13.7	750	290
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$	20.1	600	1050
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.8}\text{O}_3$	15.4	600	125
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_3$	18.1	500	1400
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$	21.4	800	269
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$	15.3	600	330
$\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$	16.8	600	
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$	14.8	800	87
$\text{La}_{0.2}\text{Sr}_{0.8}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$	19.3	800	1000
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_3$	19.2	700	1400
$\text{Pr}_{0.8}\text{Sr}_{0.3}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$	12.8	800	76
$\text{Pr}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$	11.1	800	200
$\text{Pr}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$	19.69	550	950
$\text{Pr}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$	21.33	550	600
$\text{Pr}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_3$	-	700	1236
$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$	20	500	30
$\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$	20.5	700–900	> 1000
$\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_3$	11.4	800	580
$\text{Sr}_{0.9}\text{Ce}_{0.1}\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_3$	18.9	800	87

6.1 Perovskites structures

Perovskites take their name from the mineral, which was first discovered in the Ural mountains of Russia by Gustav Rose in 1839 and was named after Russian mineralogist L. A. Perovskit (1792–1856) [82]. Besides, many of the complex oxides that display interesting physical, chemical, mechanical and electrical properties are based on perovskite crystal structure. From the chemistry side, perovskite compounds are identified by the general formula ABX_3 , where ‘A’ and ‘B’ are two cations of very different sizes, and X is an anion that bonds to both (oxygen). The ‘A’ atoms are larger than the ‘B’ atoms. The

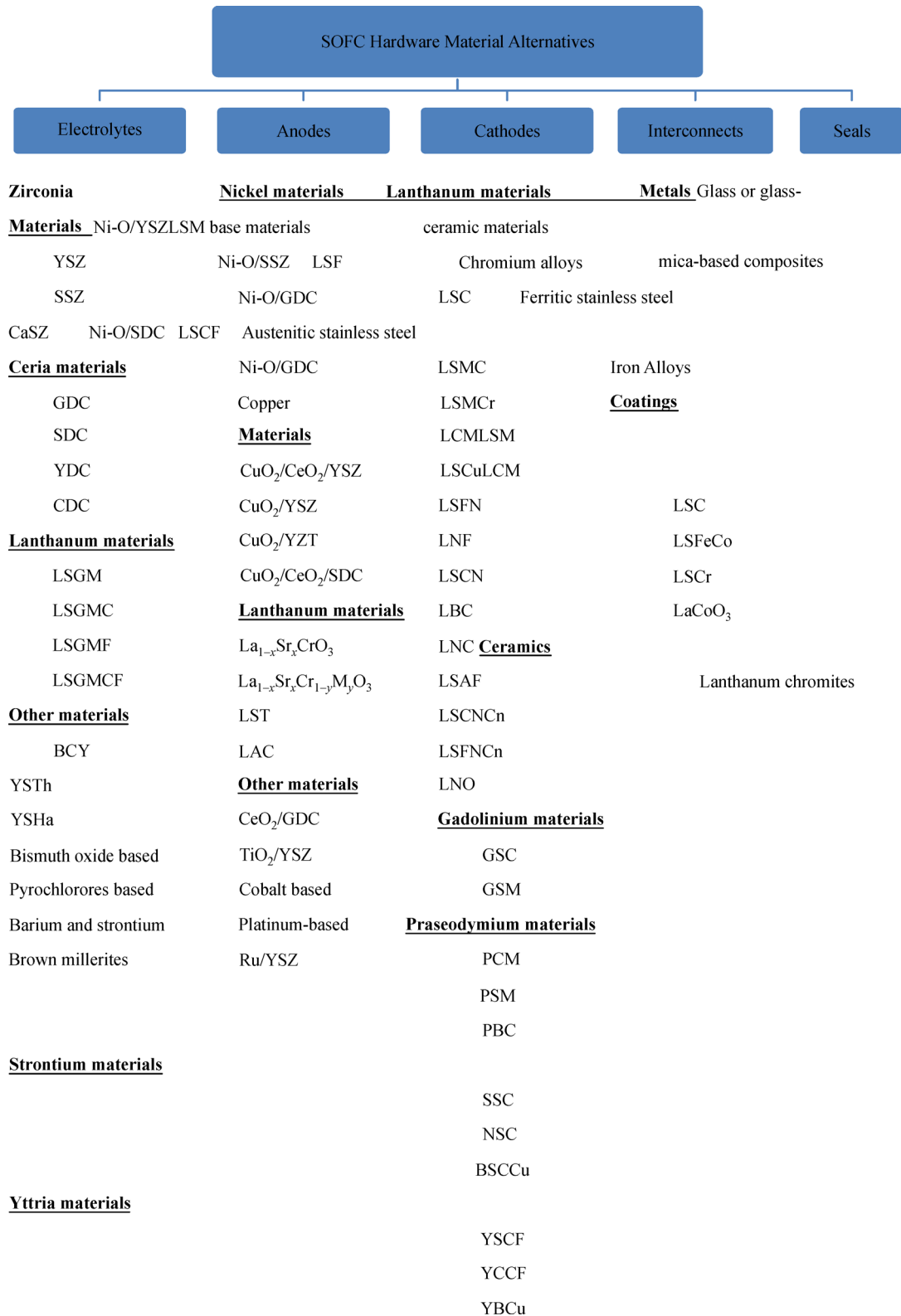


Fig. 12 Taxonomy of example SOFC material alternatives (Adapted with permission from Ref. [80])

Table 6 Common ceramic structural materials [81]

Structure	Lattice	Chemical formula
Caesiumchloride	SC	AX
Rock salt	FCC	AX
Fluorite	FCC	AX ₂
Silicates	FCC	AX ₂
Corundum	Hexagonal	A ₂ X ₃
Perovskites	SC	ABX ₃ -A ₂ B ₂ X ₆
Spinel	FCC	AB ₂ X ₄
Diamond	FCC	
Graphite	Hexagonal	

ideal cubic-symmetry structure has the B cation in 6-fold coordination, surrounded by an octahedron of anions, and the A cation in 12-fold cub-octahedral coordination [83]. Perovskites containing these cations which have an ability to create alkaline anticorrosive pigments, can be once from possible compensations [84].

However, in spite of the big lists of main ternary crystal structures, many scientists reported that among these structures there are only a specific numbers of structures which can be counted as world useful ceramics. Both spinel and perovskite are the most important structures among this list. Moreover, and through the chemical manipulation of Perovskite ABX₃ there is a possibility to produce an incredibly array of phases with a variety of functions, as shown in Fig. 14 [85].

6.1.1 Single perovskites

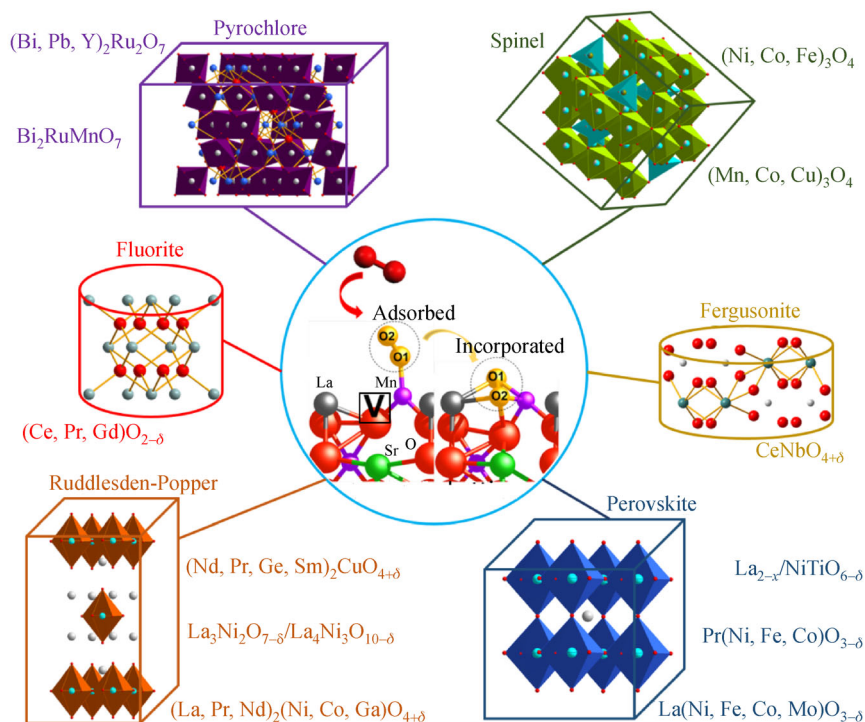
In the case of a single perovskite, it can be noticed in the ideal perovskite structure (see Fig. 15) that the oxygen ions form a cubic close packed lattice (ccp) with the metal ion in octahedral interstitials.

In this single perovskite structure, the A-sites are typically occupied by trivalent or divalent cations such as the Lanthanides (La, Sm, Nd, Pr...) or alkaline earth (Ba, Sr, Ca...). The B-sites are occupied by transition metals such as (Mn, Cu, Fe, Cr, Al, W...) usually taking valence 3 + or 4 + to electronically balance the compounds.

6.1.2 Double perovskites

Double perovskites studies were started in the early 1950s, and expanded in the late 1950s, but it was not widespread until the 1980s because high flux Newton sources, and crystallography of large class of these compounds were uniquely defined [87]. So the double perovskite structure is basically chemically manipulated by replacing the ion B-sites to be BB' positions which can be explained by the basic double perovskite structure-formula A₂BB'O₆ [88] (see Fig. 16).

The fact is that A₂BB'O₆ double perovskite structure exhibits intriguing properties, such as half-metallicity, high temperature ferrimagnetism, and a rich variety of magnetic interactions, that cannot be realized in simpler materials. However, these structurally and chemically complex

**Fig. 13** Most concerned structures in SOFCs research field (Adapted with permission from Ref. [17])

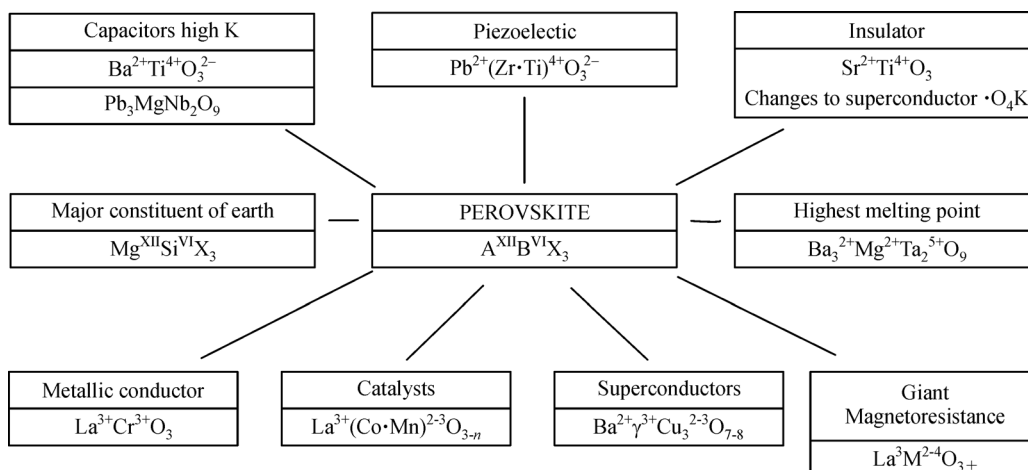


Fig. 14 Perovskite – the maximum multifunctional structure (Adapted with permission from Ref. [85])

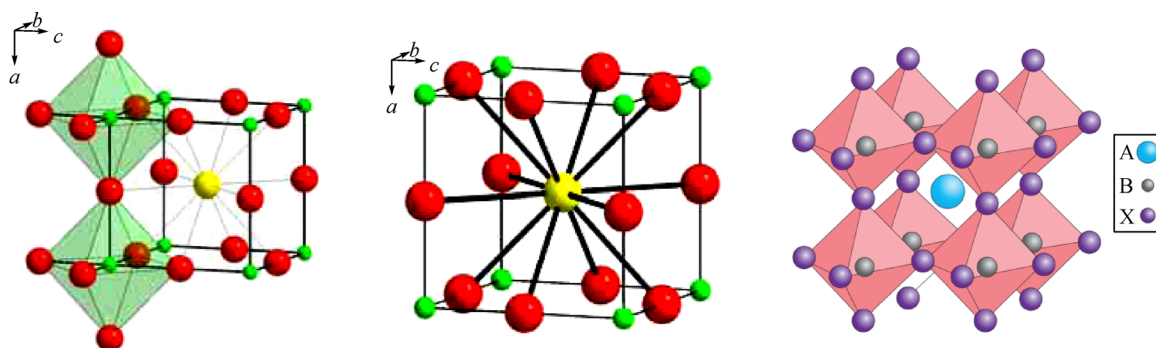


Fig. 15 ABX_3 ideal perovskite structure showing oxygen octahedron containing the B ion linked through corners to form a three-dimensional cubic lattice (Adapted with permission from Ref. [86])

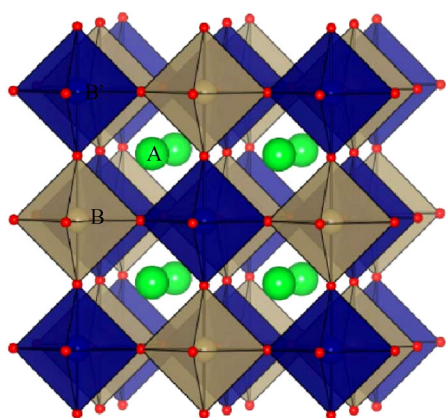


Fig. 16 Structure of an ordered double perovskite $A_2BB'O_6$ (Adapted with permission from Ref. [91])

materials present challenges extending from synthesis of high quality materials for characterization and theoretical understanding of their properties, so they have been

relatively unexplored [89]. That has led to a large focus on double perovskite since the discovery of the Sr_2FeMoO_6 in 1998 and exhibit a good electrochemical and physical effects at a temperature above room temperature [90]. It was the first step to open the way for the synthesis of double perovskite compounds and use it as electrode materials in solid oxide fuel cell applications due to the proton conducting properties and thermal stability as well [88].

The structural arrangement of atoms in the unit cell (ordering) of B-sites and A-sites, and especially the electronic configuration has considered the main inside infrastructures of complex oxides unit cell. Therefore, the double perovskite structure [91] displays different amounts and forms of B-site ordering. However, B-site cations order more readily than A-site cations. Since both A-site and B-site cations ordering can be realized, it results in differences by means of order. So with reference to the ordering of the double perovskite compounds, it can follow the rock salt ordering of B/B' cations and it is preferable in $A_2BB'X_6$ perovskites in addition to the appearance of the layered perovskite ordering of A/A' cations which is also

avored in $AA'B_2X_6$ and $AA'BB'X_6$ perovskites, as shown in Fig. 17 [92].

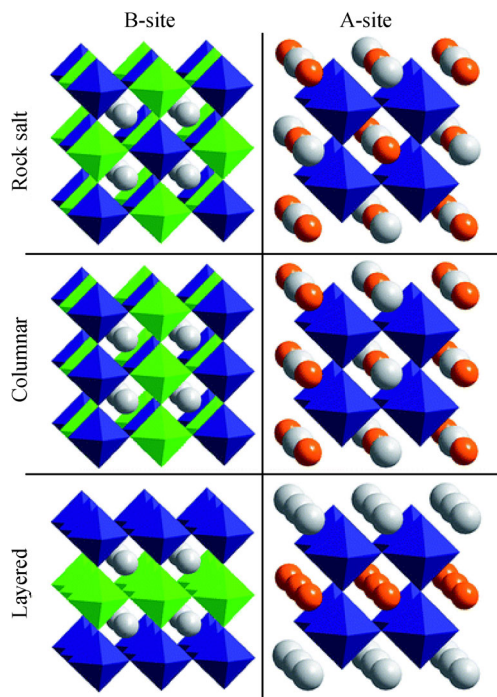


Fig. 17 Ordering schemes in perovskites, for B-site ordering in $A_2BB'X_6$ perovskites and for A-site ordering in $AA'B_2X_6$ perovskites (Adapted with permission from Ref. [92])

7 SOFCs trend from macro to nano-structured level

Excessive and rapidly consumption of natural energy resources (fossil fuels) has triggered a global energy challenge from both environmental and industrial sides [93–95]. Furthermore, the increasing demand of clean energy use in the whole world obligates scientists to find out alternatives to overcome and confront the problems appeared [93,96,97]. Consequently, and from the many types of sustainable energy sources, SOFCs devices with involvement of hydrogen fuel have shown high performances, efficiencies, and clean power-generation in the technology applied [97,98]. Otherwise, its role to be a very good candidate to sustainable and renewable energy field is maintained by introducing fast increase in power requirements and to minimize the impact of the increased power consumption on the environment [8,74–100].

These SOFCs types have been developed over the 100 years from the conventional types to nano-scale types to fulfill the requirement in different scales starting with remote village to the portable smart devices [101]. Figure 18 briefly summerizes the pathway of fuel cells/SOFCs from macro to nano-scale [101,102].

The most essential consideration in the development of

SOFCs is the durability of such devices in the specified applications through characterization of the cell, quantification of degradation process, and design of the working conditions (especially fuel composition and air composition) [103–106], in addition to the expected superior performance on the long-term that matches with workable scale.

Although SOFCs have proven to be a highly and promising resource of energy since 1938 and even today in the extent of different temperatures, yet the need for improvement of performance in terms of efficiency and design committed researchers to develop the structural levels (conventional to nanoscale). For example, different research has been conducted in the development of SOFCs devices through the enhancement of the material used [3–29,40–55].

Boder and Dittmeyer [107] have developed a technique to improve the catalytic activities of conventional SOFC anodes for direct internal reforming of natural gas. The results obtained suggests that it is possible to improve the performance of SOFCs with direct internal reforming of hydrocarbons with electrochemical performance comparable to that of standard cells. Meanwhile, Weber and Ivers-Tiffée [108] in their work and through the material concepts have proposed for the optimum selection. They refer to the stack design as a significant issue for handling the technology of fuel cell. In addition, the highlight of microstructure level has become essentially requested for getting highly efficient SOFCs operating in different temperature ranges. The micro-solid oxide fuel cell after it was first developed in 1999 [109] has shown a big potential in the application of portable electronic devices [109,110] with a noticeable good performance at temperature ranges from 700°C to 300°C. With regard to this enhancement of the cell efficiency [111,112] in micro-scale levels through the synthesis and preparation of some different materials, Table 7 illustrates the material used in micro-SOFCs.

Since Morse et al. [109] has shown the approach for the fabrication and assembly of micro-SOFCs with remarkable efficiency, in addition to the acceptable ranges of LT-SOFC and IT-SOFC from the literature, this progress with micro-scale has given the ignition of nano-scale level investigations from electrochemical energy conversion and storage devices as an alternative energy resource emerging in the 21st century [124]. This development in nano-scale level will enable the enhancement of materials commonly used in SOFCs. Through doping of mixed ionic and electronic conductors like Ce^{4+} [125] and with the interface spacing, it is expected to have an effect on conductivity behavior compared to the width of the space charge carrying grains in the composite of comparatively large crystals [126]. Therefore, some attempts have been made to investigate the nano-structured SOFCs with different materials as shown in Table 8.

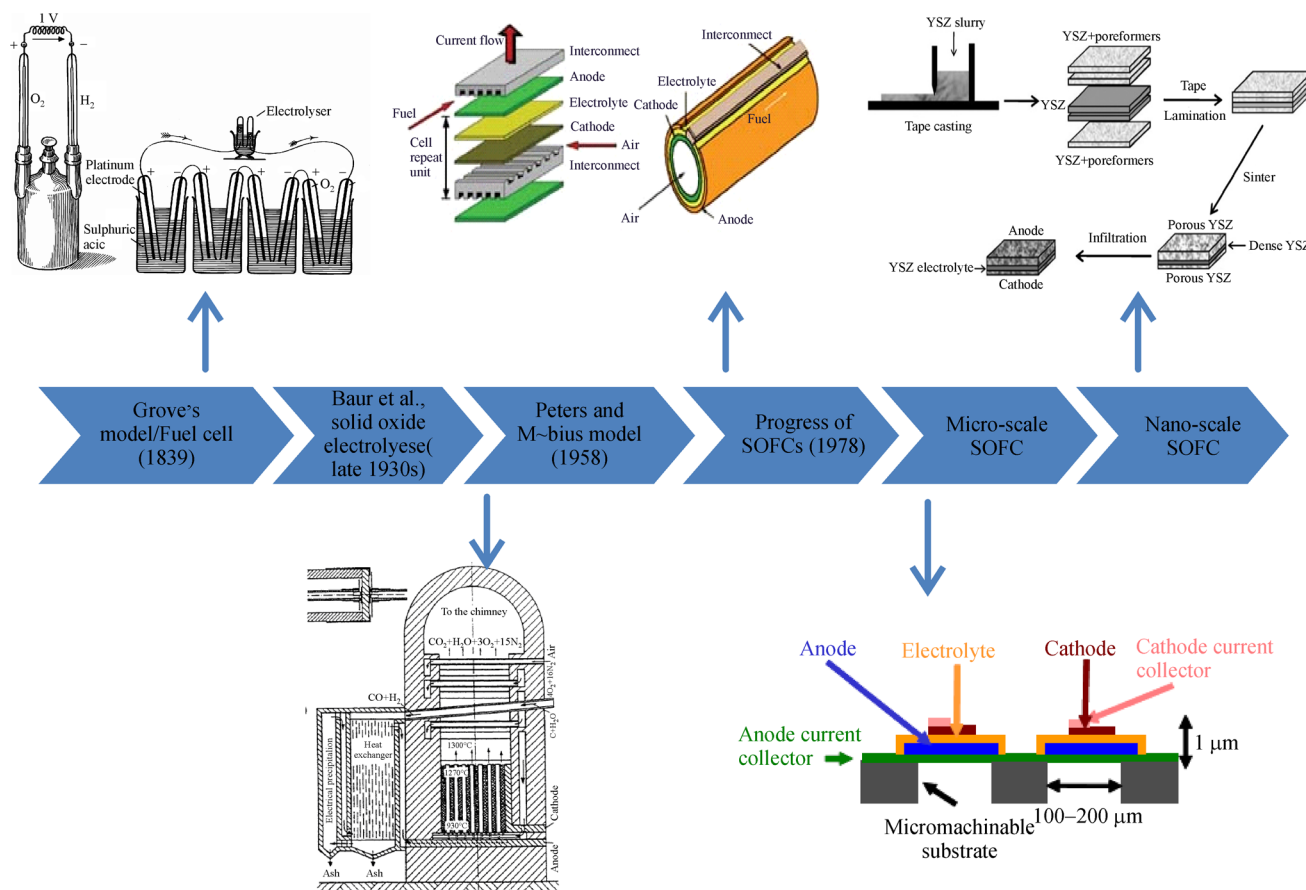


Fig. 18 Trend of fuel cell/SOFCs development from conventional to nano-scale (Adapted with permission from Refs. [102–105])

Table 7 Some materials used in micro-scale SOFCs

Anode	Cathode	Electrolyte	Substrate	Temperature/°C	Ref.
Pt	Pt	8YSZ	Foturan, silicon wafer	450–550	[103]
Ni	LSCF	GDC	-	450–550	[113]
Ni	LSM	8YSZ	-	400–700	[114]
Pt	Pt, LSCF	8YSZ	Foturan, glass-ceramic	400–600	[115]
Pt	Pt	8YSZ	Silicon wafer, SiO ₂	500	[116]
Pt	Pt	8YSZ	Silicon wafer, Si ₃ N ₄	350–400	[117]
Pt	Pt	8YSZ, CGO	Silicon wafer, Si ₃ N ₄	350	[118]
Ru	Pt	8YSZ	Silicon wafer, Si ₃ N ₄	265–350	[119]
Pt	Pt	8YSZ	Silicon wafer, Si ₃ N ₄	400–450	[120]
Ni	Pt, LSCF	CGO	Ni plate	450	[121]
Ni	Pt	8YSZ	Porous Ni	370–400	[122]
Ni + SDC	BSCF + SDC	SDC	-	500–600	[123]

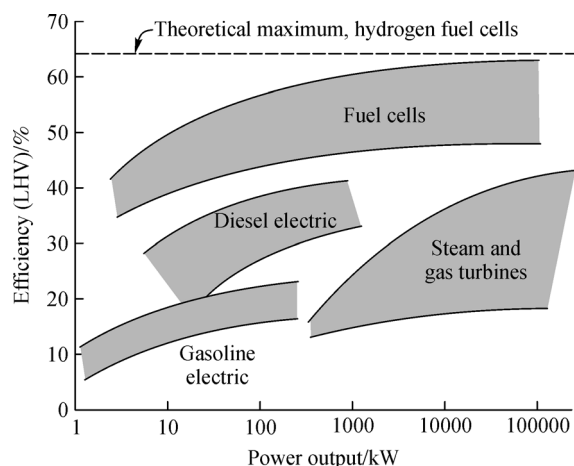
8 SOFCs performance and efficiency

Fuel cell performance can be obtained from the electrochemical impedance spectroscopy (EIS), DC conductivity measurements, I - V curves and related power density,

photocatalytic activities, and binding energy measurements using X-ray photoelectronic spectroscopy (XPS) in addition to magnetic measurements and its effect on electrical properties. Otherwise, the performance of a fuel cell is measured by identifying and calculating the losses that

Table 8 Some materials used in nano-scale SOFCs

Anode	Cathode	Electrolyte	Substrate	Temperature/°C	Ref.
Ni	-	GDC(LiNa)C ₃	-	450–550	[127]
Ni	LSM-YSZ	ScSZ	-	700	[128]
-	LSCF-GDC	GDC	-	650–850	[129]
Pt	LSCF	YSZ	Silicon wafer, Si ₃ N ₄	450–500	[130]
Ni-SDC	SSC	ScSZ	-	600–700	[131]
Ru	Pt	CGO-YSZ	-	470–520	[132]
Pt	Pt	YSZ	-	350–500	[133]
Ni	Pt	YSZ	-	600	[134]

**Fig. 19** Comparison of obtained efficiency against output power of different fuel resources (Adapted with permission from Ref. [136])

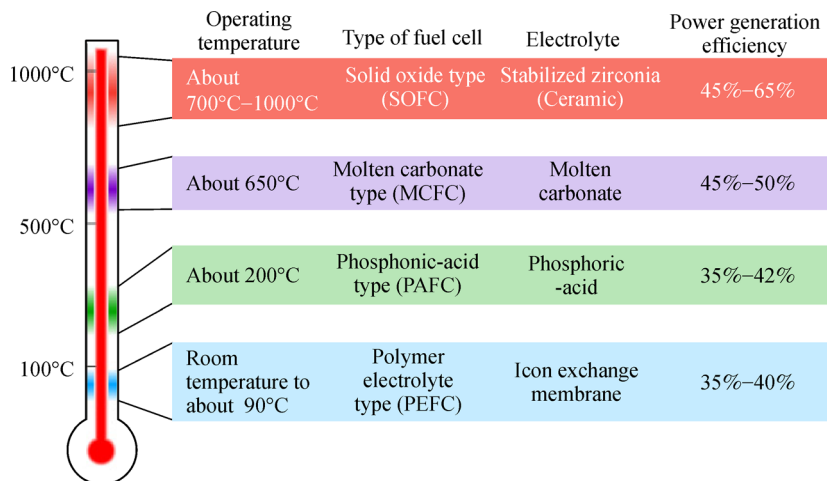
lower the potential from the thermodynamics ideal case. Therefore, the main objective in fuel test is to minimize these losses when building the reactors, considering the general losses [135].

$$V = E_{\text{thermo}} - \eta_{\text{act}} - \eta_{\text{Ohmic}} - \eta_{\text{conc}}, \quad (7)$$

where V is the operating voltage, E_{thermo} is the thermodynamic predicted voltage, η_{act} is the activation losses due to reaction kinetics, η_{Ohmic} are the ohmic losses from ionic and electronic losses, and η_{conc} are the concentration losses due to mass transport.

Hence, the great benefits of SOFCs devices are their excellent performance and highly efficient service at a wide variety of applications (large scales hybrid SOFC/turbine as well as the electronic portable ones). This widespread technology is competing with other types of energy resources as a renewable and sustainable energy resource, because of its superior efficiency as standpoint in all rated power ranges. Hence, fuel cell research works (see Fig. 19) have placed this impressive technology in the first place compared to different types of energy resources in terms of efficiency against power. On the other hand, Fig. 20 illustrates the advantages of SOFCs over other fuel cell types. SOFCs show the potential at temperature ranges from 700°C to 1000°C and the efficiency as well from 40% to 65%.

However, the environmental requirements [94,95] set the characteristics for the energy used in the meantime due

**Fig. 20** SOFCs superior advantages over other types of fuel cells (Adapted with permission from Ref. [137])

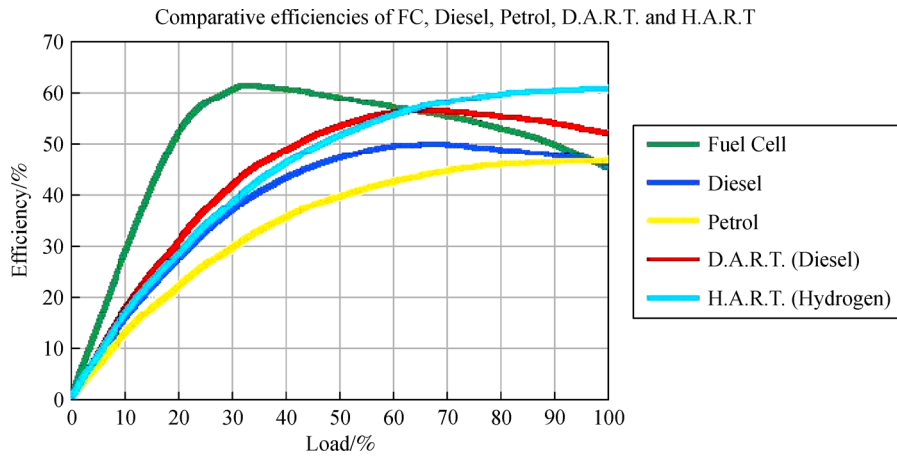


Fig. 21 Comparison of different fuel resources (Adapted with permission from Ref. [138])

to the rapid technology and its unexpected results like climate changes. But the technology of fuel cell is able to face these challenges by introducing almost a cleaner and more efficient energy compared to other ones as shown in Fig. 21.

The operation principles of SOFCs are simply subjected to the materials used [139] which require an accurate identification of its properties through reliable characterization. Meanwhile, the ongoing research every day reports the new findings due to the development of the materials used and its impact on the performance through the investigation of the power density. The recent reported performance was measured by Vibhu et al. [140] who succeeded in obtaining a high power density of 1.6 W/cm^2 as shown in Fig. 22. This value is among the highest obtained as can be observed from Fig. 23 that represents the highest peak power of SOFCs [140–153].

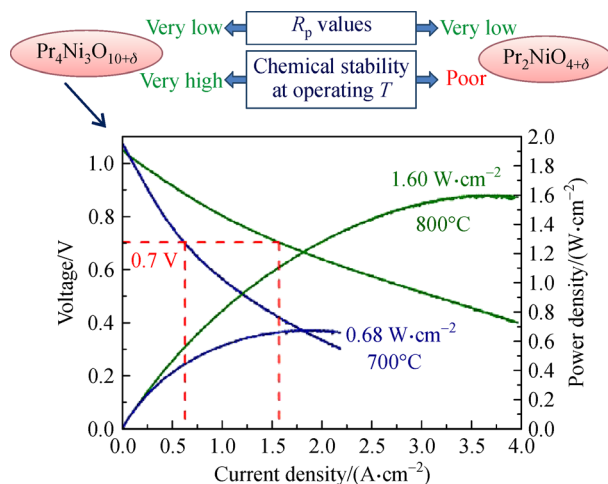


Fig. 22 Highest performance reported by Vibhu et al. (Adapted with permission from Ref. [140])

9 SOFCs power optimization in engineering applications

Generally, any power generation system involving SOFC includes three essential parts: reforming tool for hydrocarbon fuels to hydrogen gas, the SOFC unit/stack (see Figs. 7 to 10), and a converter from DC power to AC power [44]. The control and optimization of an energy conversion system in SOFCs mainly depends on the fuel concentration fed to the cell stack, and hence a high efficiency could be exhibited. Accordingly, the operational temperatures are very important to control and the thermal impact (hate waste) in cell power station should be considered. Some important engineering applications related to SOFC utilization like combined heat and power (SOFC-CHP), gas turbine (SOFC-GT) in the chemical production approach require a well-controlled process to achieve the highest, reliable and less economic impact in addition to everlasting as possible. References [153–157] were focusing on optimization analysis of power and energy systems, using recuperates in SOFC energy conversion systems.

10 SOFCs research progress

Among the different types of fuel cells that can be used and because of their potential in applications at different scales, SOFCs have emerged as a sort of chemical fuel. According to the energy source and Fig. 24, SOFCs play an important role in fuel cell technology in our daily life. For SOFCs, it is very important to be aware of the enhancement of surface properties, the interface between the material and the atmosphere. These factors are giving the indications of the overall device performance [44].

However, the chemical reaction occurred involving oxygen kinetics such as oxygen (surface change rates, ion

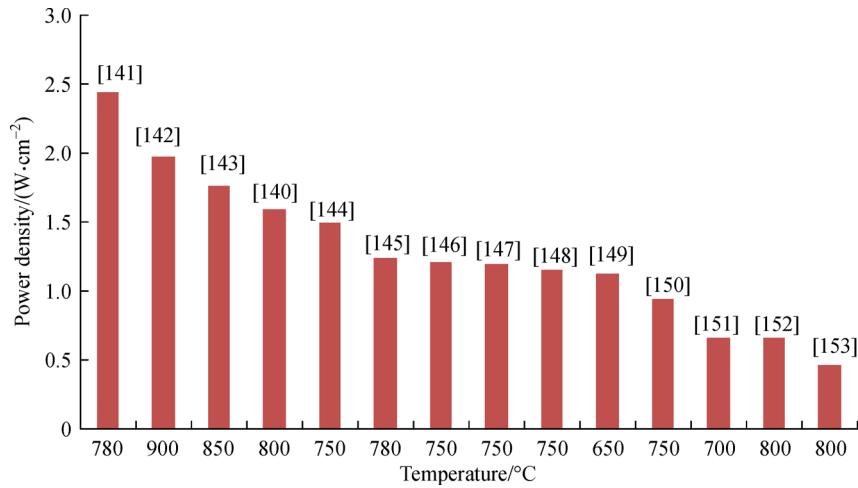


Fig. 23 Representation of high power densities against temperature

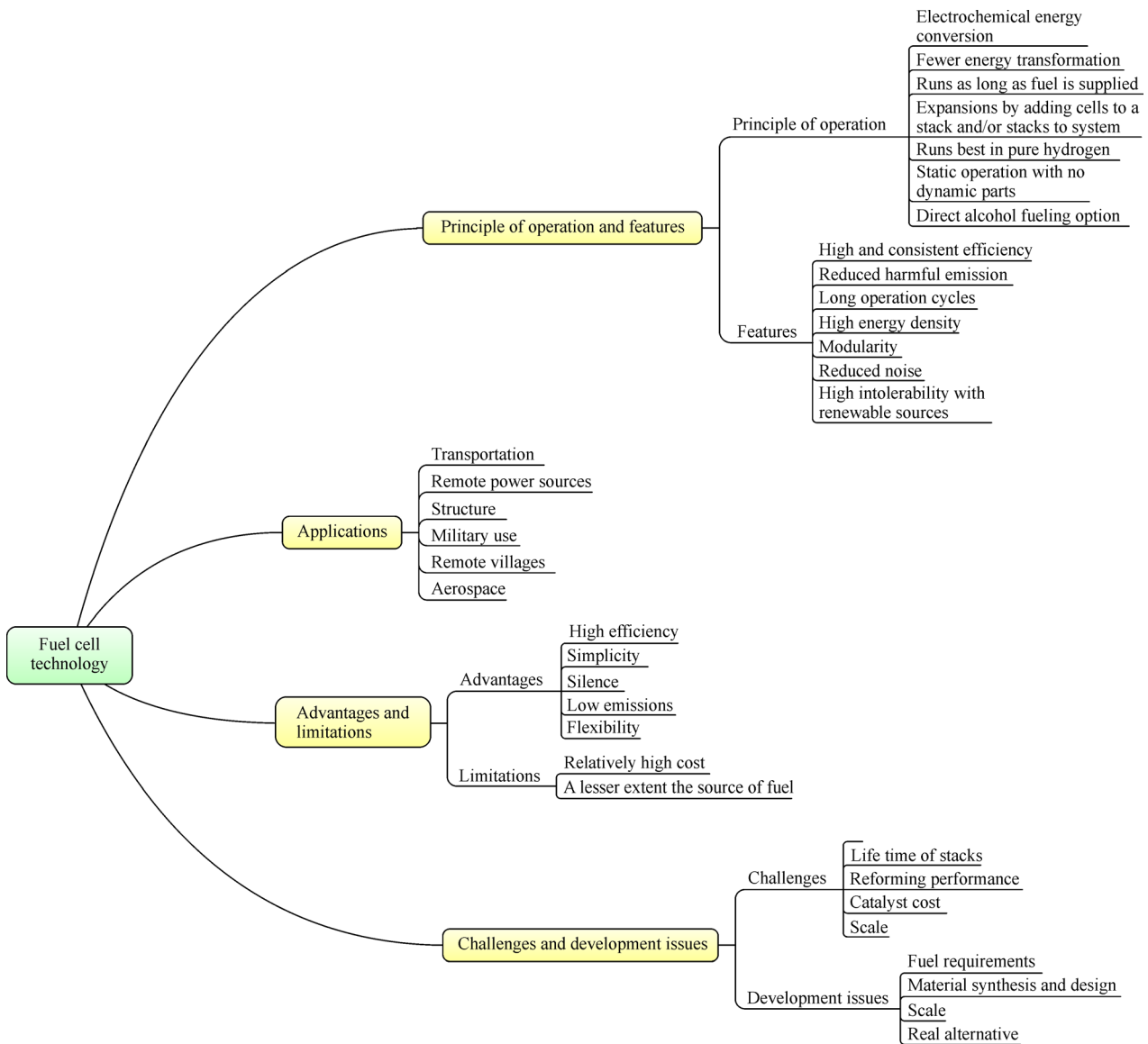


Fig. 24 Outlines of fuel cell technology

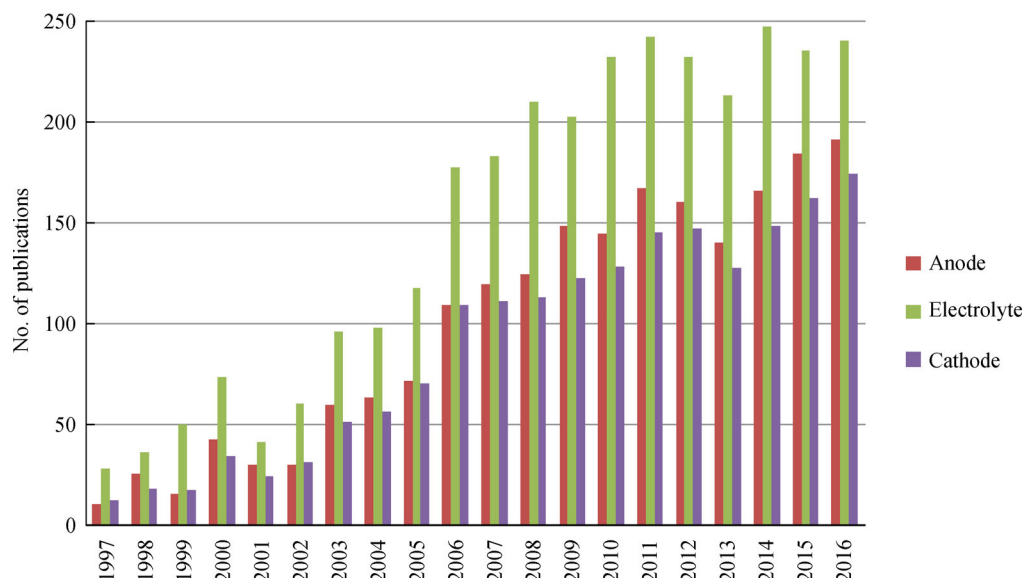


Fig. 25 Research progress in SOFCs components

diffusivity), electronic conduction, and electrocatalytic activity are getting great interest in SOFCs systems within the variety of high and low temperature electrochemical applications. Furthermore, all reactions depend on oxygen kinetics (oxygen thermodynamics and stoichiometry) [158–160]. In some cases, doping of an additive material, for example Sr, can result in the increase of vacancy concentration and delocalization, leading to a maximum electronic transport by controlling both the degree of dopant segregation and grain size [158,159]. The importance of SOFCs research obligates scientists to concentrate on the development and enhancement of the components of SOFCs. Figure 25 shows the progress rate of research from 1997 until now.

Based upon what have mentioned in the earlier sections, it can be summarized that SOFCs are one of the best solutions today and in the future. Table 9 summarizes the essential aspects with the basic parameters of any SOFC that should be achieved. Also, this is simply a brief analysis of the main requirements: strength, weakness, opportunity, and technical (SWOT) that should be considered when working with SOFCs.

11 Conclusions

Accordingly, and with reference to what have been mentioned previously in this review, an attempt was made to present a series of the common and newly synthesized materials after physical, chemical, and electrochemical characterizations. These materials have shown an advancement when they are applied in the SOFCs field. With more improvement, they will become promising in the clean energy sector. The most essential observation

Table 9 Essential aspects with the basic parameters of any SOFC device

SOFCs parameters	Merits/ strength	Limitation/ weakness	Opportunity/ availability	Threat/ handling
Cost		*		*
Efficiency	*			
Power density	*			
Fuel utilization		*		*
Degradation rate		*		
Materials	*	*	*	*
Design	*	*	*	*
Manufacturability		*	*	
Durability	*		*	*
Environmental impact	*		*	*
Modularity	*			*
Scalability	*			
Economic entitlement	*		*	
Applications	*	*	*	*
Transportation and storage	*			*
Technological developments	*		*	*
Life time		*		*

here about SOFCs is their various geometrical types which can be adaptable to the related applications. Some advantages and disadvantages can be observed which briefly include merits/strengths such as efficient, scalable, and friendly to the environment; limitations/weaknesses such as cost and complex manufacturing; opportunities/

availabilities such as materials and designs; and threat/handling such as fuel utilization and storage. The progress of SOFCs and investigations into materials related are increasing rapidly due to the essential needs of this highly efficient source in the clean energy sector.

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