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Study Of Nanometerials (Solids Oxide Fule Cell In Nature) Based On Sofcs At Deferent Scales From Macro To Nanoscales Level At High Temperatures.

Dr. Rakesh Kumar

Assistant Professor, Department of Physics Narain College, Shikohabad, (Firozabad)

Abstract

Solid oxide fuel cells (SOFCs) have emerged as promising candidates for efficient and environmentally friendly energy conversion technologies. Their high energy conversion efficiency and fuel flexibility make them particularly attractive for various applications, ranging from stationary power generation to portable electronic devices. Recently, research has focused on utilizing nanostructured materials to enhance the performance of SOFCs. This comprehensive review summarizes the latest advancements in the design, fabrication, and characterization of nanostructured materials integrated in SOFC. The review begins by elucidating the fundamental principles underlying SOFC operation, emphasizing the critical role of electrode materials, electrolytes, and interfacial interactions in overall cell performance, and the importance of nanostructured materials in addressing key challenges. It provides an in-depth analysis of various types of nanostructures, highlighting their roles in improving the electrochemical performance, stability, and durability of SOFCs. Furthermore, this review delves into the fabrication techniques that enable precise control over nanostructure morphology, composition, and architecture. The influence of nanoscale effects on ionic and electronic transport within the electrolyte and electrodes is thoroughly explored, shedding light on the mechanisms behind enhanced performance. By providing a comprehensive overview of the current state of research on nanostructured materials for SOFCs, this review aims to guide researchers, engineers, and policymakers toward the development of high-performance, cost-effective, and sustainable energy conversion systems.

Keywords: SOFC; **nanostructures**; **nanomaterials**; **electrochemistry**; **energy conversion**; **interfacial reactions**; **durability**

1. Introduction

The global quest for clean, sustainable, and efficient energy sources has gained a lot of attention due to concerns about the depletion of fossil fuels and the urgent need to address climate change. The most important factor influencing fuel cell performance is the material used as a catalyst. Catalysts speed up the reactions at both anode and cathode. There are several types of fuel cells. They are categorised depending on the nature of the electrolyte. Each type of fuel cell requires specific materials and fuels for different applications. Fuel cell 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). Nowadays, researchers focus on SOFCs. SOFCs have many advantages for a wide range of applications because of their electrical efficiency, potential to use natural gas, biogas or CH4 as a fuel and high performance [1,2]. Many researchers mentioned that fuel cells are important for their modularity and distributed nature with lack of noise and pollution [1–4]. SOFC is an important type of fuel cell and it is consists of two porous components (anode and cathode) separated by a highly dense component (electrolyte, such as Yttria-Stabilised Zirconia (YSZ)) or Gadolium doped Ceria (GDC). Although many electrode materials for SOFCs have been developed over the past three decades,challenges of cost and limited durability still exist [5]. Therefore, great effort is being made to overcome these challenges through synthesis and design of new materials, at a nano-scale level, which may lead to improved SOFC performance in different applications at reduced temperatures. Furthermore, many attempts were made to develop electrode materials for SOFCs over the last 30 years. Some materials, especially Ni/YSZ, are favored as SOFC anodes because of their high electrochemical activity for H2 oxidation and high stability under SOFC operating conditions. The use of La0.75Sr0.25MnO3 (LSM) cathode material has been proven to have a high performance for application in SOFCs [2]. Current research on SOFC development has focused on temperatures below 1000 °C (usually 400–700 °C) with the aim of decreasing material cost and improving stability [1,4,6–8]. The consideration of fossil fuels (oil, coal, and natural gas) as a long term energy source is becoming difficult to justify. Specifically, carbon dioxide, nitrous oxides and green houses emissions are considered the major contributors to global warming. In ddition the rapid increases of the world population makes the need

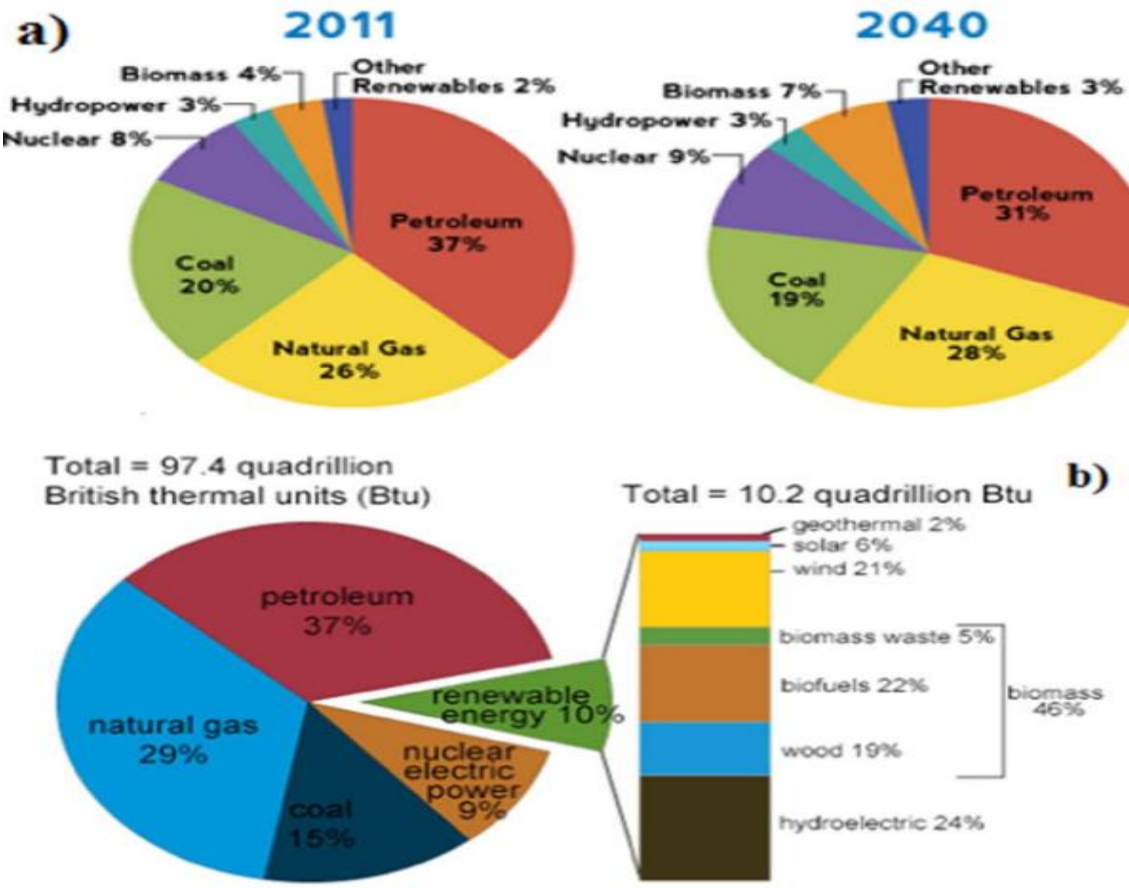


Fig. 1. Multiple sources of energy consumption in (a) Worldwide by 2040 and in (b) USA in 2017. Data are in units of Quads per year [1,12].

The estimation of energy powers almost two-thirds of our electricity and virtually all of our transportation [9–12]. Moreover, these kinds of resources are not sustainable and will finish someday. The total consumption of energy worldwide and in USA are shown in Fig. 1. For the total world consumption, the total amount of 600 Quads is dominated by oil (37%), with all fossil fuels accounting for 83% of the total until 2011 and will be 78% by 2040 because of more usage of renewable energy resources. On the other hand, for the USA, the total of 97.4 Quads is dominated by oil and natural gasses, with fossil fuels accounting for 81% of the total by 2016. Basically renewable energy, mainly from wind, solar, biomass, geothermal and nuclear amounted in 2016 to only 17% of the total in the world and 19% in the USA. According to the past three decades, we can see that the world's annual consumption of renewable energy is rapidly increases and Fig. 2 below is showing the average rate of increase from 1990 to date and the expectations until 2040 [11,12]. The needs of energy in future in the world makes it very essential to estimate and expect the consumptions of the used energy (see Fig. 3). By considering the minimum and maximum values this is guaranteed that these kinds of expectations can reduce the risks which might be happened in the future. It is very crucial to consider the usage of alternatives sources renewable and sustainable ones. And it can be able to stand with the human needs and the most obvious way that small sustainable farms can help in reducing the nation's dependence on fossil fuels(oil, coal and natural gas) can be done by widespread this technology in different scales. Therefore, working with fuel cell types [1–8] presents a promising future for this source of energy, because of its durability, clean and safe usage.

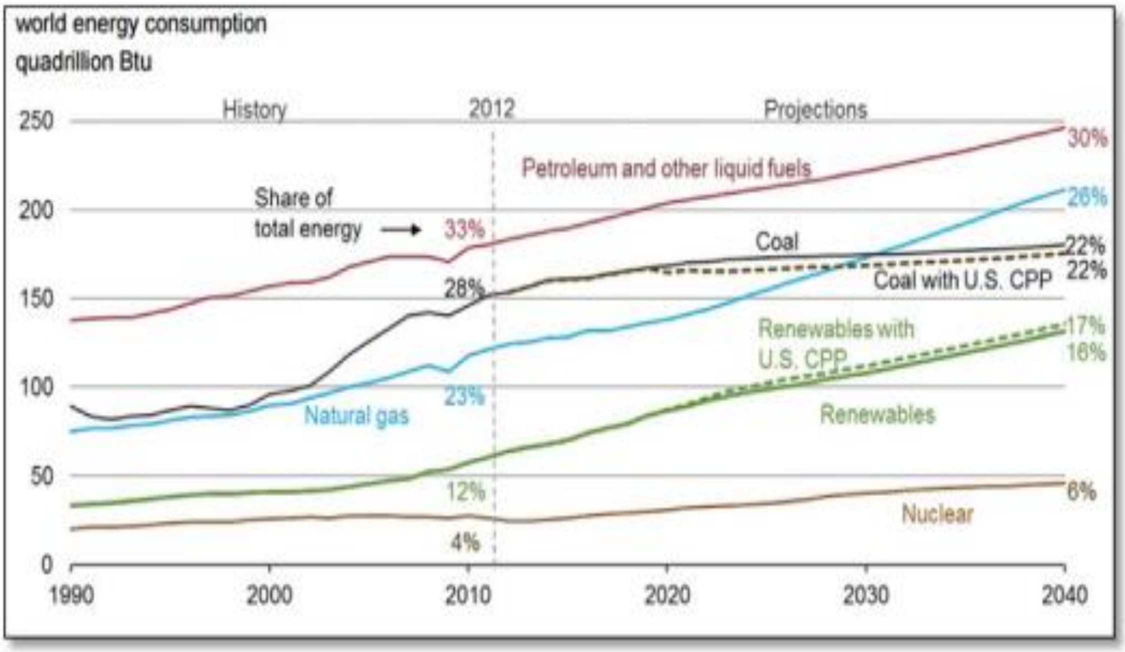


Fig. 2. Previous three decade's history trend to the world's annual consumption of total energy and the expected quads amounts by 2040 from various sources including fossil fuels and renewable energy [13].

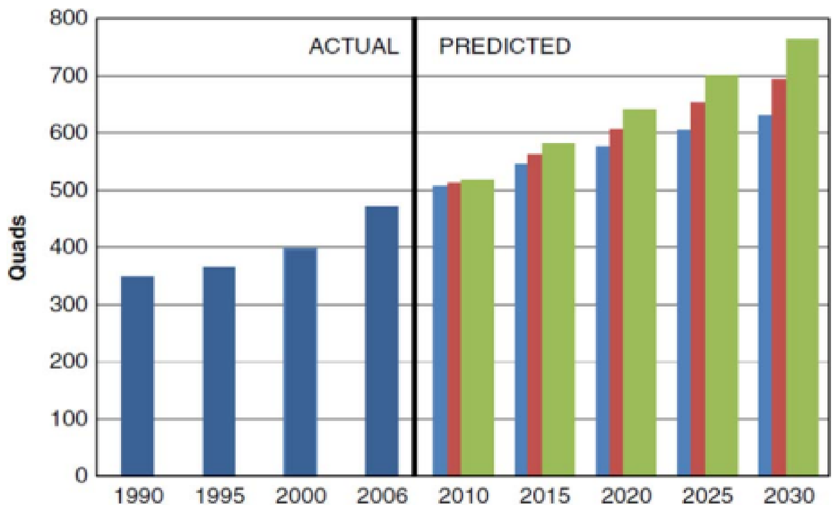


Fig. 3. Bar charts of the actual world's annual energy demands from 1990 to date. The triple bars show the prediction of minimum average and maximum values in the world by 2030 [10].

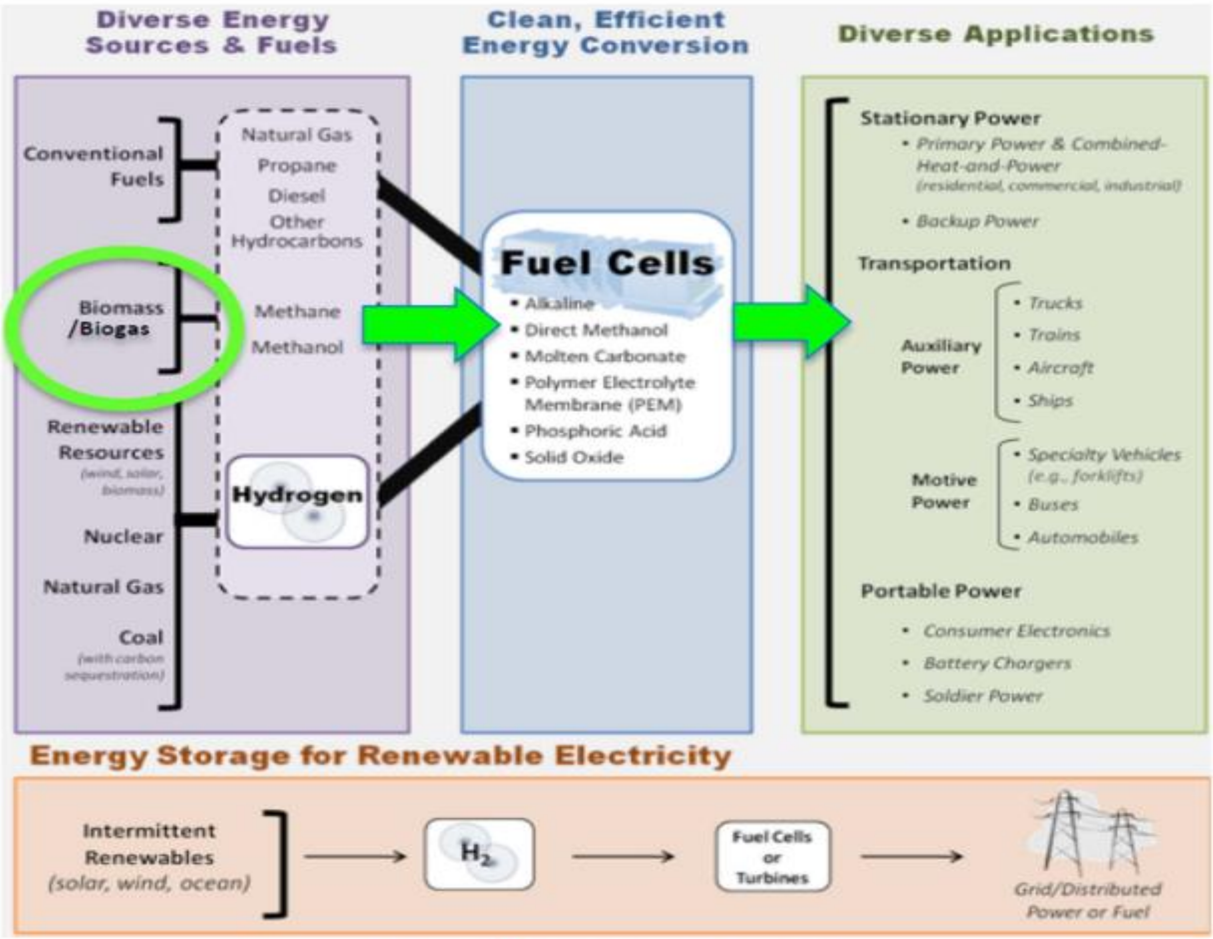


Fig. 4. Role of fuel cells as renewable energy resource [14].

The key benefits that highlights the important role of SOFCs are [14]; a) very high efficiency from 60% to 85% in (electrical, hybrid fuel cell/turbine, and with combined heat and power (CHP), b) reduction of CO2 emissions from 90% to 35% (CHP system and light duty vehicles), c) reduction of fossil fuel usage from > 80% to 90% for Fuel Cell and Electric Vehicles (FCEVs), d) reduction of air pollution 90% for CHP systems, e) flexibility of the fuel (clean fuel, hydrogen, and conventional fuels (including methane, electrolysis, and natural gas)). Also the role of fuel cells can be clearly noticed (see Fig. 4) as a renewable energy source. As the SOFC is considered one of the best sustainable resources that can be used and applied from macro-scale to nano-scales for their superior enhancement in the efficiency. Also nanostructured materials are now well desired especially at low temperatures and for portable smart devices. But there are still some challenges confront this technology will be drawn in the up coming discussion. This review work will cover through the historical and achievement of SOFCs until nearest future and the research progress in SOFCs. Then it will continue by addressing the main approaches of SOFCs and its related components that are main challanges. Afterwareds, the trends of development and performance in SOFCs when utilizing the nanostructured materials and their mertits will be discussed and finally, some recommendations for future studies in nano-SOFCs.

2. History of fuel cell and achievements

Fuel cells have been used as a source of power long time ago, and it was initially started since scientists began searching for an alternative sources to overcome fossil fuels ran out. However, no one might not expected that these fuel cells would be an essential and promising energy source until the 21st century. The first FC device was made by Sir William Robert Grove (1811–1896) by his introducing and developing a wet-cell battery in 1838 [15,16]. Moreover, the main idea of his research was depended on electrolysis reactions and uses electricity to split water into hydrogen H+ and oxygen O- during reactions, and that the opposite reaction must be capable of producing electricity. Thus, W. Grove developed the first fuel based on the combination of hydrogen and oxygen to produce electricity. Ludwig Mond (1839–1909) and Carl Langer conducted experiments with a hydrogen fuel cell that produced 6 Amp/ft2 at 0.73 V. In addition, Friedrich Wilhelm Ostwald (1853–1932), the founder of physical chemistry, derived the relationship between the different components of the fuel cell including the electrodes, electrolyte, oxidizing and reduucing agents (anions and cations) from his experimental investigations. Francis Thomas Bacon (1904–1992) then made substantial developments with high-pressure fuel cells; he succeeded to introduce an efficient nickel gauze electrodes in cells that operated at pressure up to 3000 psi. In the earlier time of 1960s, the International Fuel Cells (IFC) in Windsor, Connecticut, USA developed a fuel cell power plant for the Apollo spacecraft. In the 1970s, IFC had developed more powerful alkaline fuel cell unit for NASA's space shuttle Orbiter [17,18]. Table 1 listed the most important achievements since the advent of fuel cells until the implementation of nanomaterial in SOFCs through the addition of nanoparticles of Ni/GDC anode and developing of electrolyte thin film as well [24–29].

Table 1
Summary of initial and recent achievements in the field of fuel cells and nano-SOFCs [19–29].

Scientist (s)	Year	achievement	Ref.
W. Nicolas and A Carlisle	1800	Described the electrolysis of water	[19]
Sir W. Grove	1838	Created the first gas battery	[20–22]
L. Monde and C. Langer	1889	Conducted experiments on H_2 fuel cells	[20]
F. W. Ostwald	1893	Described theoretical performance of fuel cells	[20,21]
W. Jacquse	1896	Developed first fuel cell	[20]
E. Buar and H. Preis	1921	Experimented with high-temperature solid oxide electrodes	[20]
F. T. Bacon	1939	Researched alkaline fuel cells	[20]
DuPont, Parkersburg, West Virginia	1950	Teflon was used in membranes	[20–23]
T. Grubb	1955	Developed a sulfonated PEMFC	[20,21]
G. H. J. Brores and J. A. Ketelar	1958	Built a molten carbonate fuel cell	[20]
Central Technical Institute	1959	Researched SOFCs	[20]
IFC, Windsor Connecticut	1960	Developed a fuel cell power plant for the Apollo spacecraft	[20]
G. V. Elmore and H. A. Tanner	1961	Phosphoric acid fuel cell	[20]
IFC, Windsor Connecticut	1970	Oil crises, and developed a more powerful alkaline fuel cell for NASA's space shuttle Orbiter	[20,23]
NASA jet propulsion	1990	First direct methanol fuel cell	[20,21]
Bauch up power	2007	Fuel cell being to be commercially sold as APU & stationary equipment's power generation.	[20,23]
Honda manufacturing	2008	Announced first mass production of fuel cell cars FCX clarity	[23]
Portable fuel cell chargers	2009	Residential micro fuel cell-CHP become commercially available in Japan	[23]
Feng Han et al., institute of energy research Germany	2010	Development of nano-structured YSZ electrolyte layers for SOFC applications	[24]
Masaru Tsuchiya et al., USA	2011	Scalable nanostructured membranes for solid-oxide fuel cells	[25]
NIST centre for neutron research, USA	2012	Nanotechnology for fuel cell catalysts (carbon nanotube)	[26]
Advanced Industrial Science and Technology (AIST) in Japan	2013	Portable fuel cell system with nanostructured electrodes	[27]
Tatsumi Ishihara, Japan	2016	Nanomaterials for Advanced Electrode of Low Temperature Solid Oxide Fuel Cells (SOFCs)	[28]
Research Council of Norway, NTNU, SINTEF and the University of Oslo	2017	FOXCET (Functional Oxide for Clean Energy Technologies: fuel cells, gas separation membranes and electrolysers through the implementation of nanomaterials.	[29]

3. SOFCs research and progress

Among the different types of the fuel cells that can be used and because of their potential application at different scales, SOFCs have emerged as sort of chemical fuel as its energy source and according to Fig. 5, it represents the role of fuel cell technology in our daily life. For SOFCs, it is important to be aware of the enhancement in the properties of surface, the interface between the material and the atmosphere are the indications of the overall device performance [30]. However, the chemical reaction process occurred involving oxygen kinetics such as oxygen (surface change rates and ion diffusivity), electronic conduction and electrocatalytic activity are paying great interest to SOFCs systems within the variety of high- and low-temperature electrochemical applications. Furthermore, all dependent oxygen kinetics (oxygen thermodynamics and stoichiometry) [31,32]. In some cases, doing of an additive material for example Sr, can result in the increase of vacancy concentration and delocalization, leading to maximum electronic transport by controlling both the degree of dopant segregation and grain size [30,31]. Because of the importance of SOFCs research focus was clearly noticed and the scientists give lots of concentration on the developing and enhancement of the SOFCs materials components (anode, electrolyte, and cathode) as can be observed from Fig. 6 the progress rate of research since 1997 until today. The utilization of nanoscience in energy sector, specifically in fuel cell technology can be cleary noticed from Fig. 7 and how it is rapidly increasing within the previous decades.

Fig. 5. Outlines of fuel cell technology.

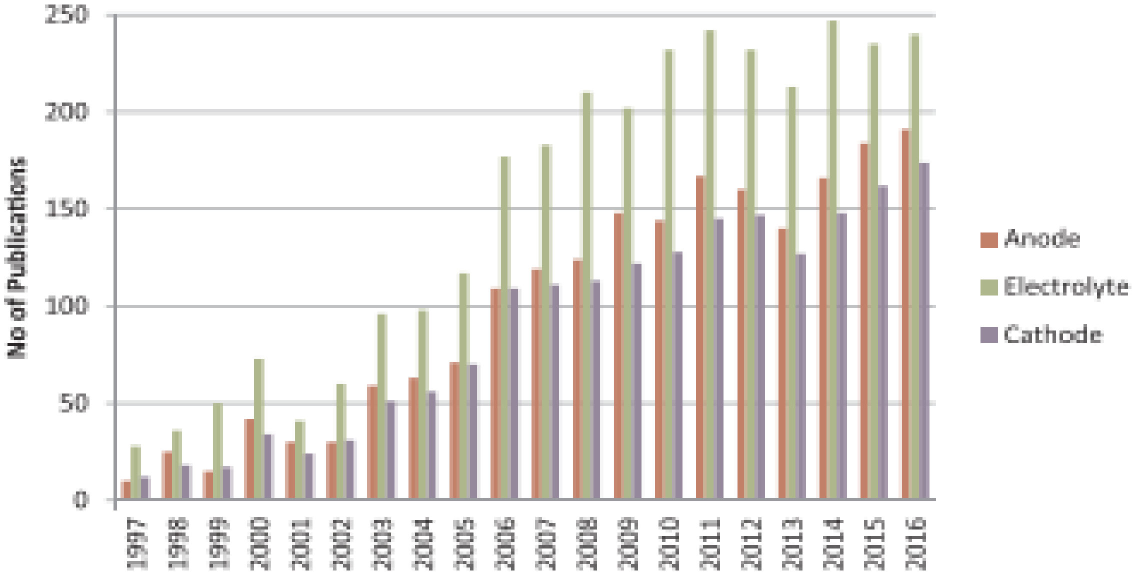


Fig. 6. Research progress on SOFCs materials components according to the web of science

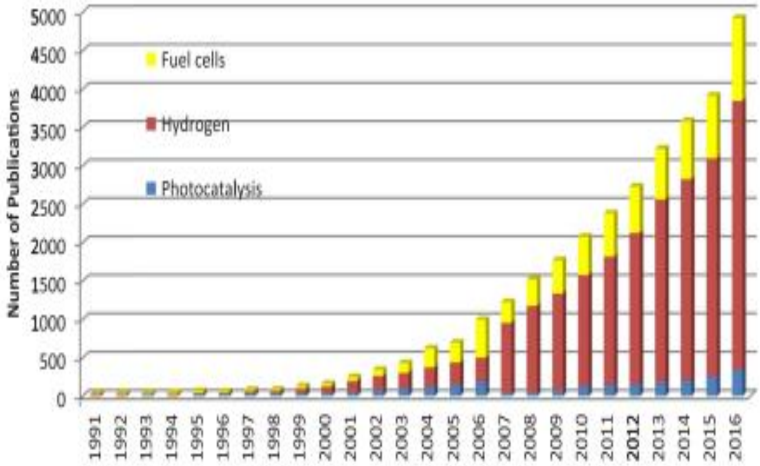


Fig. 7. Nano-science and nanotechnology- number of publications and research spot in energy sector according to few selected areas; the data are obtained from ISI web of science.

4. Main operational approach of SOFCs

Typically the functional operation of the SOFCs is mainly depending on the transportation process by means of H+ and O− in the electrochemical reactions. Converting the chemical energy of a fuel and oxidant into electrical energy is represented by the load through the three main components [33–46]. A dense electrolyte contained in anode and cathode (porous supporting structure) as shown in Fig. 8. The main function is based on the charge carrier oxygen ion (O2−) results from air split to oxygen ions and electrons (e−). Then, resultant ions are undertaken through the dense electrolyte to consolidate with hydrogen (H+) at the anode and liberates electrons. The electric power (load) obtained by the released electrons traveled to an external circuit, in addition to exhausted heat. The main reactions of an SOFC [44,45] rely on anode fedding by H2, the cathode fedding by O2, and the whole transportation process as clearly presented in the following equations. The theory of this process was well explained by Tesfai et al. [44]. H He → +∓ − 2 2 2 (1) O eO + →− − 1/2 2 2 2 (2) H O HO 2 22 + → 1/2 (3) And for the reactions occurred on both anode and cathode can be noticed from the following: +→ + − For the anode H O H O 2 2 2 2 (4) CO 2 CO2 2 +→ + O e (5) (Significantly slower than H2 conversion) + →− − For the cathode O e O 1/2 2 2 2 (6) Optimisation of the efficiency and performance of fuel cells by improving the materials (nanostructured) used as fuel cell components is currently the subject of continuous investigation. For example, the use of lanthanum manganite as a cathode part such as Cobalt, Co [5] and some other materials with different compositions used as anodes depending on the B-site in the perovskites manipulations like Manganese, Mn [46,47] and electrolytes thin films utilization.

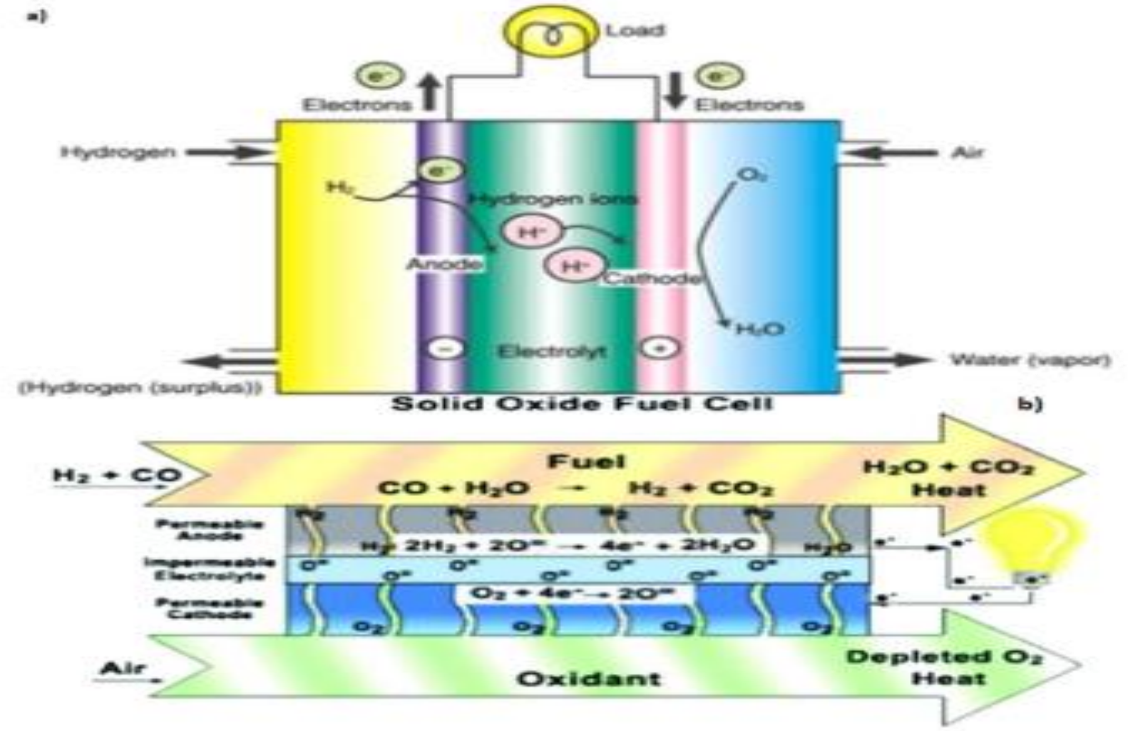


Fig. 8. Schematic diagram of a) proton ion and b) oxygen ion transport processes in an SOFC

5. Investigated materials for SOFCs components

Several materials and their different combinations have been improved to fulfill the requirements of SOFCs [48]. However, for versatile materials for applications in SOFC devices need more developments and investigations and each component in the cell with superior enhanced properties. These are mainly depends on the performance of the materials within scale level. So, the main components of the fuel cell stack (electrolyte, the anode, cathode and the interconnect) require a deep understanding in science of this process to match. [49]. However, the great technological challenges along with this development of SOFCs are directly related to materials science, and can be noticed for instance; material challenges concerning the electrolyte conductors in terms of both cost and fabrication process. Moreover, any material properties improvements in SOFCs are mainly covered electrical conductivity, catalytic activity, chemical compatibility and thermal stability. In addition to, the common features of these components must implicate the following; first, both electrolyte and interconnect must be highly dense to prevent gas mixing. Secondly, both anode and cathode must be sufficiently porous and structurally organized to let the gas transport in the reaction sites in addition to the highest ionic and electronic conductivity of both electrodes [44–50]. Furthermore, from the electrochemical point of view, the electrolyte should be strictly an ionic conductor and interconnects should be an electronic conductor as well as electrodes. The upcoming subtopics are highlighting the commonly used cell components in SOFC device.

5.1. Anode materials

The importance of developing anode material as the main part of the fuel cell components because of the percentage of material being used in this part nearly around 95% [48] of the used material in the cell in anode supported cells [49]. Also the fuel oxidation-reaction take place at the anode and catalyse the reaction of the fuel with oxygen [50] as shown in Eq. (4) and as in Fig. 9. In order to maintain the highest performance of anode material, it 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 exhibiting poor performance. In the past three decades, improvements concerning anode materials properties have been reported by selecting new synthesis and design of materials especially in the nanostructured levels [24,25]. Table 2 shows some of the most important anode materials are recently used with their performance, advantages and disadvantages as well [51].

Table 2
Conductivities of some selected materials developed as anodes for SOFCs [51].

Materials	DC Conductivity ($S\ cm^{-1}$)	Advantage/disadvantage
$Sc_{0.1}Y_{0.1}Zr_{0.6}Ti_{0.2}O_{1.9}$	0.14	Operate at high temperature
$La_{0.8}Sr_{0.2}Fe_{0.8}Cr_{0.2}O_3$	0.5	Low conductivity
$La_{0.8}Sr_{0.2}Cr_{0.95}Ru_{0.05}O_3$	0.6	Expensive
$(La_{0.7}Sr_{0.3})_{1-x}Ce_xCr_{1-x}Ni_xO_3$	5.03	Carbon deposition
$Sr_{0.88}Y_{0.08}TiO_3$	64	High operating temperature
$CrTi_2O_5$	177	Expensive
Ni-YSZ	250	High operating temperature
$Ti_{0.34}Nb_{0.66}O_2$	340	Very expensive
$LaSrTiO_2$	360	No compatibility
Ni-SDC	573	Coke formation
Ni-GDC	1070	Coke formation, and electronic performance degradation
Cu-CeO_2	5200	Improved electronic conductivity
Cu-GDCCrTi_2O_5	8500	Good thermal expansion, and electronic performance

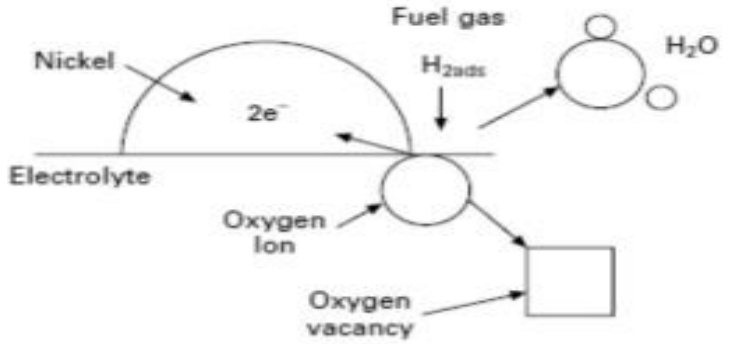


Fig. 9. An example showing a schematic mechanism for anode reaction with H_2 fuel [50].

5.2. Electrolytes and interconnecting materials

In an SOFC, it may be an anode-supported fuel cell or electrolytesupported fuel cell [49,50], both cases the role of electrolyte is essential as it must possess high ionic conductivity, chemically and mechanically compatible with the other components of the cell. The main feature of this electrolyte that it should be a highly dense and are preferable to be very thin to minimize the internal cell resistance during electrochemical reactions [1,52]. 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. For the used materials as electrolyte includes; yttria stabilized zirconia (YSZ) and Gadolinium doped ceria (GDC). GDC are the most common and main materials considered in SOFC devices [53]. So, increasing the ionic conductivity, yttria is doped to zirconia which increases the concentration of oxygen vacancies and achieved high stability. On the other hand, cerium oxide has been considered as a good electrolyte material because of its high ionic conductivity than YSZ, and it allow the operation at lower temperatures especially when applies in single chamber SOFCs. Typically in SOFCs, the proper way to connect between anode and cathode electrically can be achieved by the interconnect. Moreover, it represents the physical barrier between the oxidant and the reducing fuel atmospheres. Therefore, the interconnect must be a dense material like the electrolyte which is 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 finally it should be physically gas tight [54,55]. For all previous requirements, the selection of interconnect materials must constrained by the target operating temperature of the cell and mainly determined by its performance in the active application. However, the main selection of the interconnecting materials required some essential factors to be considered includes; oxygen kinetics, electrical properties, chemical compatibility and mechanical stability. Since an earlier stage of SOFCs development, the high operating temperature was ~1000 °C restricted the use of metals as interconnects. The only suitable material for high-temperature SOFCs was alkalineearth doped LaCrO3 or other Cr-containing perovskites. After the emergence of high-performance anode-supported SOFCs, the operating temperature of SOFC was significantly lowered to the range where costeffectiveness, commercially available of high-temperature metallic alloys were suitablely used [55,56]. Metallic interconnects also have the advantage over ceramic LaCrO3-based ones because the metallic interconnects are truly electronic conductors and oxide-ion insulators; their cost and fabrication are reliable compared to the ceramic ones. Additionally, thermal stability is excellent 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 materials

The second major component in fuel cell is the cathode part which has a contact layer with the electrolyte and exposed to the air/oxygen [57–59]. The importance of this electrode part 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 [54]. The selection of the cathode materials requires some distinct properties such as high porosity and stability in oxygen atmosphere. Lanthanum manganite composition doped with rare earth elements [60, 61] such as Co, Ce or Sr [57,62] showed good performance as cathode in SOFCs. These materials should have important properties to make good thermo-mechanical matching with the electrolyte and to have mixed ionic and electrical conduction. The synthesis of materials for cathode part concentrate to control oxygen non-stoichiometry and defect which can achieve an enhancement of the ionic and/or electronic conductivities and catalytic properties. For any material used in SOFCs as cathode, firstly it should be a highly electronic conductor; secondly it should be chemically compatible, and thermally stable matching with the other components of the fuel cell unit; thirdly the microstructure should be in high percentages of porosity for oxidation reactions at cathode/electrolyte interface; fourthly it should offer highly catalytic activities for O- during the reducing reaction, and finally it should be easy in processing and reliable cost effective manufacturing [63–65]. From the literatures, the proper selection of the cathode materials mainly depends on the used electrolyte materials and specifically focusing on the thermal expansion coefficient matching in the whole cell [66]. Table 3 below shows some commonly used cathode materials [57]. Therefore, selected materials for SOFCs mainly depend on their functionality in specific applications. The materials must match altogether in the cell. Keegan et al. [67] presented a schematic block diagram which lists the most commonly used materials and manufacturing alternatives for SOFCs as shown in Fig. 10.

6. Challenges and limitations of SOFCs

The main target of any highly efficient electricity generators is concerned and depends on the flexibility and tolerance to the impurities of fuel inlet [68]. Therefore, SOFCs have owned these important features among the several types of fuel cells. In addition to the merit of operational temperatures at high levels (800–1000 °C), there still some challenges and limitations for the operating temperature through the durability of the used materials at elevated temperatuers with fixed properties [69,70]. The major challenges and limitations in SOFC devices are the proper selection of material based on its properties can be clearly identified through the following: a) the hazard of poisoning due to coke and sulfur deposition, surface diffusion, distortion of charge transfer in anode, b) restrain of O^{-2} migration that is responsible for electrochemical reactions occurrence in solid electrolyte, c) cathode multiple rate determining factors; like, over potential existence in addition to geometry of active surface, d) total mismatching of coefficient of thermal expansion (CTE) for the whole cell components, e) chemical instability and incompatibility in the oxidizing and reducing environments, and finally f) isolation process of the fuel and oxidizing gases during the matching process of (CTE) for the cell components using the sealant [71]. The requirements of SOFCs devices with proper functional operation in terms of high performance, and get the ultimate goal as presented in Fig. 11, there must be a proper selection of materials with effective cost [48,72] through showing low electronic resistance of electrodes, catalysts, sealants and interconnects, and low ionic resistance of electrolytes. Briefly, these challenges can be overcome by [7,74] i) extended startup of fuel burning, hence start-up times for SOFC operation are prolonged; ii) sealing problems can be solved by the relative CTE of adjoining materials that does not react with joining parts; and iii) the induced thermal stresses at electrolyte-electrode interfaces, which causes interdiffusion between cell components can be controlled by keeping it under wraps during SOFC operation [75].

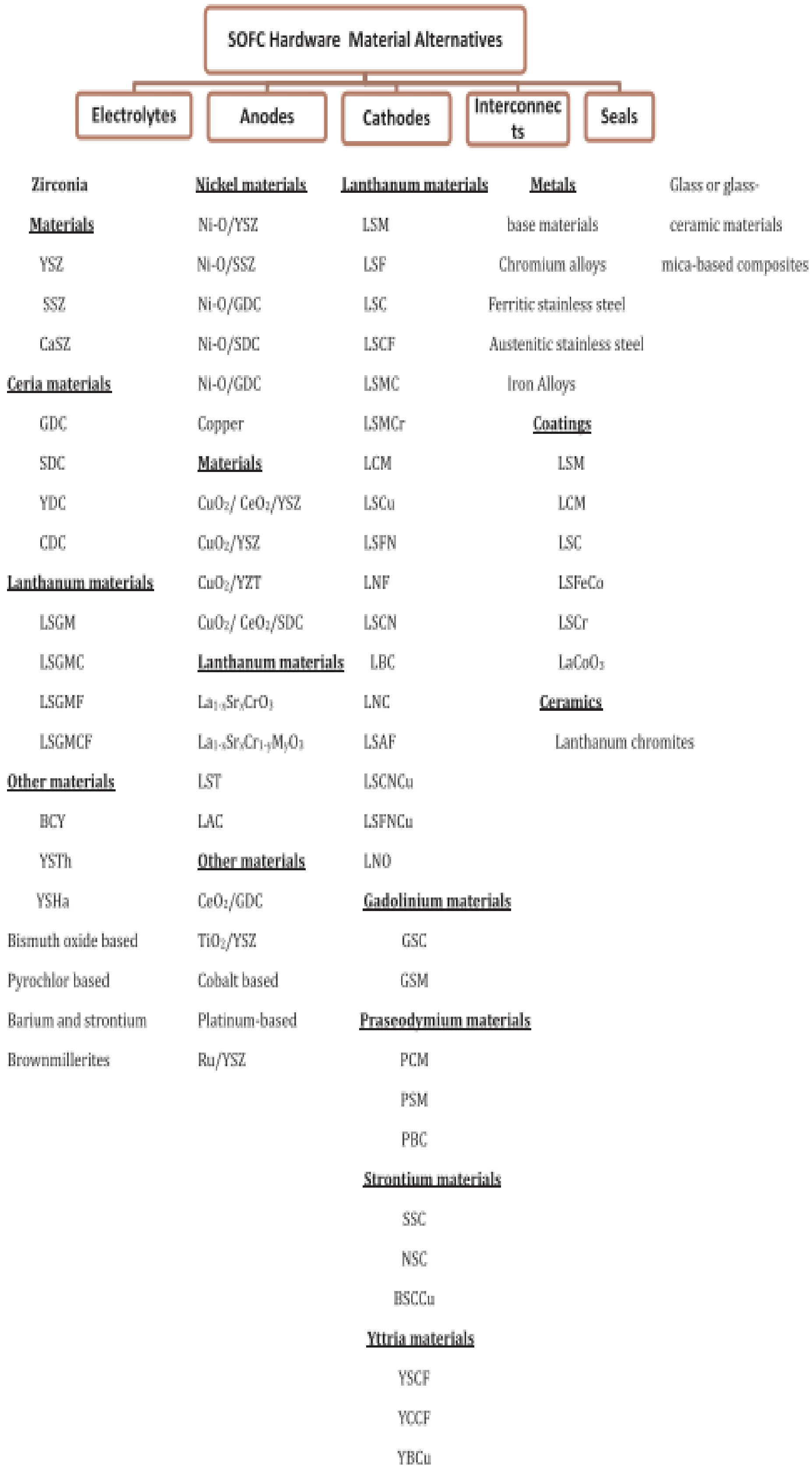


Fig. 10. Taxonomy of SOFCs materials alternatives [67].

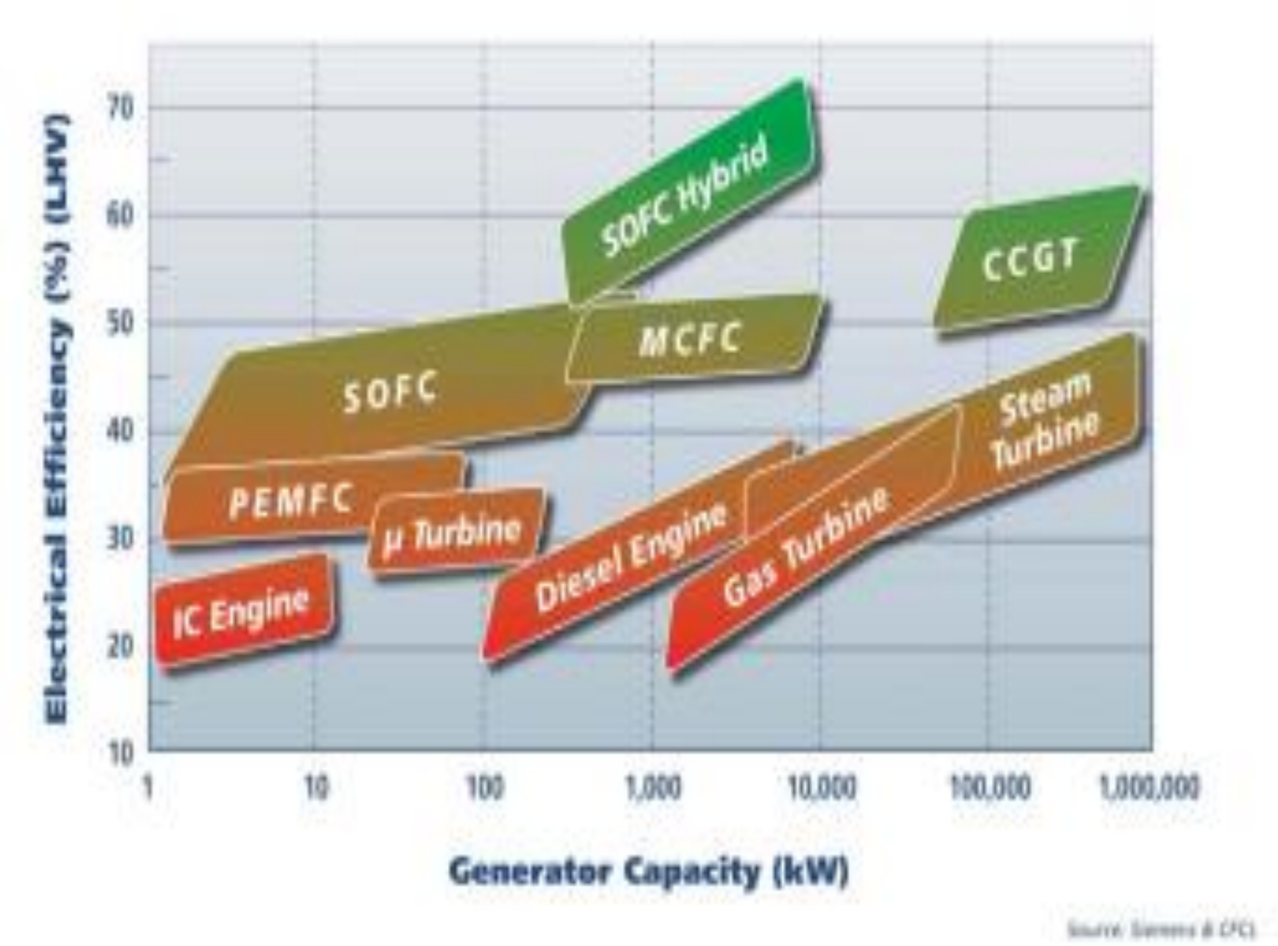


Fig. 11. Schematic representation of fuel resources device to obtain electrical efficiency [73].

7. SOFCs trend from macro to nano-structured level

Excessive and rapid consumption of natural energy resources (fossil fuels) has triggered a global energy challenges from both environmental and industrial sides [9,10,19]. Furthermore, the increasing demand of energy usage in the world obligates scientists to find out alternatives to overcome and confront the appeared problems [9,34,35]. Consequently, among many types of sustainable energy sources, SOFC devices have proved the high performance, the most efficient, and the clean power-generating in the applied technology [36–38]. The role of SOFC is very good in sustainable and renewable energy field by introducing fast increase in power requirements and to minimize the impact of the increased power consumption on the environment [10,39]. The progress of the SOFCs have been developed over the 100 years from the conventional types to nano-scale types to fulfill the requirements in different scales starting with remote village to the portable smart devices [15]. Since nanotechnology application in the beginning of 19th century in energy sector, it played a very important role in the improvement and development of electrocatalytic properties for REDOX reactions and hence has a great impact on the fuel cell device costs. Many nanostructured materials were applied in fuel cell devices to enhance the efficiency and minimize the catalyst loading [76]. The main reason that make nanomaterials essential for SOFCs is to lower the cell operational temperature from 900 °C to 300–400 °C [77]. The more interesting about nanomaterials utilization in SOFCs, are their possibility to offering high thermal stability with accepted electrochemical conductivity values (0.25 W/cm2 and 0.1 S/cm per single cell). Moreover, they showed ability of sulfur tolerance and lack of carbon deposition on the anode side with hydrocarbon fuel feeding [78,79]. The nanostructured array can also concurrent a well-connected pores and work as contact points for triple phase boundaries isolation in electrode components [76,78]. Thus, achieving all the previous aspects make the nanomaterials selection for the cell components are very compatible to each others and have the required chemical, mechanical and thermal stability as well [77–81]. The interesting findings made the choice of nanomaterials in SOFC are essential because these nanostructured arrays can offer the required performance values with less effort. Many attempts were done to investigate and offer the highest output power can be obtained from SOFCs in various applications at low temperature ranges [76–85].

8. Fundamental concepts of macro, micro and nano- structured SOFCs

The enhancement of SOFC devices from macro to nano-scale have the potential to surpass current SOFCs technology in terms of cost, robustness, reliability and endurance [86]. But the main considerations and concepts of this technology must be deeply clarified to investigate precisely. Hence, the main requirements of SOFCs (mechanical, chemical, electrical and fabrications) will be able to be controlled through the employment of new architectures or material sets over imitative designs with highest volumetric power density [87]. According to the main fundamental of the SOFCs designs (shown in Fig. 12), it is required from the cell to provide some merits are not exist in the conventional ones as previously shown in Table 4. Basically, the conversion system should provide [88] highest efficiency, flexibility, modularity and lowest level of poisoning of NOx and SOx emissions. As well as it should be electrochemically and mechanically stable, quiet and vibration-free operation. The basic concepts in all levels (macro and nano) is the same and the transportation process during the reactions is governed by oxygen handling [90]. This process is mainly depends on the oxidizer which is required to oxidize the unreacted fuels. The reason is to design the distribution way for H2 or CO2 are subjected to purity limitations and some other contaminations. Adams et al. [90] mentioned that “the Kinder Morgan, Weyburn, Sleipner and (proposed) Dynamics CO2 pipelines have maximum concentration restrictions for total hydrocarbons (i.e., unspent fuel) of 2–5%, maximum N2 concentrations of 300 ppm, maximum O2 concentration of 10–50 ppm, and minimum CO2 concentration limits of 93–96%. Therefore, high quality oxygen is better. Ferreira et al. [91] presented a very efficient way to obtain high purity O2 (95%) for gasification and other purposes. This technique helps in providing O2 for post anode oxidation as well. But the most important factors that offer high electrochemical stability and good enhancement [92] are the mobility of an ion and microstructural control as illustrated in Fig. 13 that was explained by interface conduction mechanism [93–95]. The main concepts of nanostructured materials from bulk to nanoparticles/ nanotubes/ nanofilm (atoms) preparation needs proper selection of the synthesise methods that covers Chemical Precipitation Method, Heat Assisted Chemical Reaction Method, Chemical Reaction Method (colloidal solution), Chemical Precipitation from Homogeneous Solution Method, Sol-gel Method, Hydrothermal Method, Ultrasonic Assisted Method, Reaction via Microemulsion Method, Electrochemical Processing Method, Preparation within Matrix/Templet, Nanocrystalline Thin Film using Physical Vapour Deposition or Sputtering Method, Laser Ablation Method and Microwave-assisted Solvothermal Method[34,39]. The characterizations of these nanomaterials are the same as conventional SOFCs methods. The two basic concepts (synthesis and characterization) of nanostructured materials achieved the technological breakthrough in the SOFCs with a fully developed, controlled and applicability to clean and sustainable energy resources [68,78].

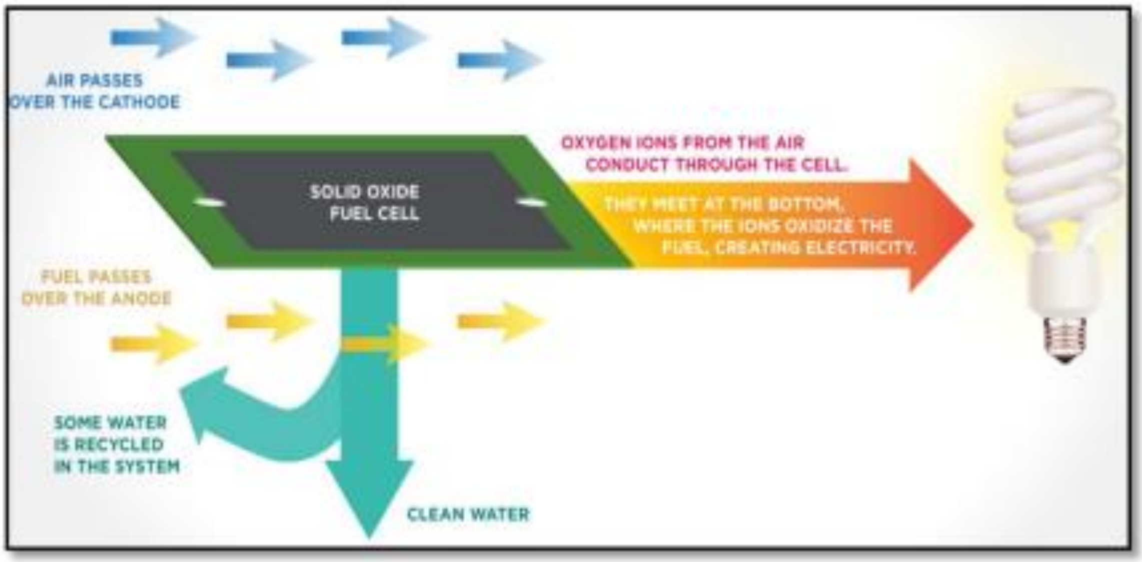


Fig. 12 The basic concept of SOFC [89].

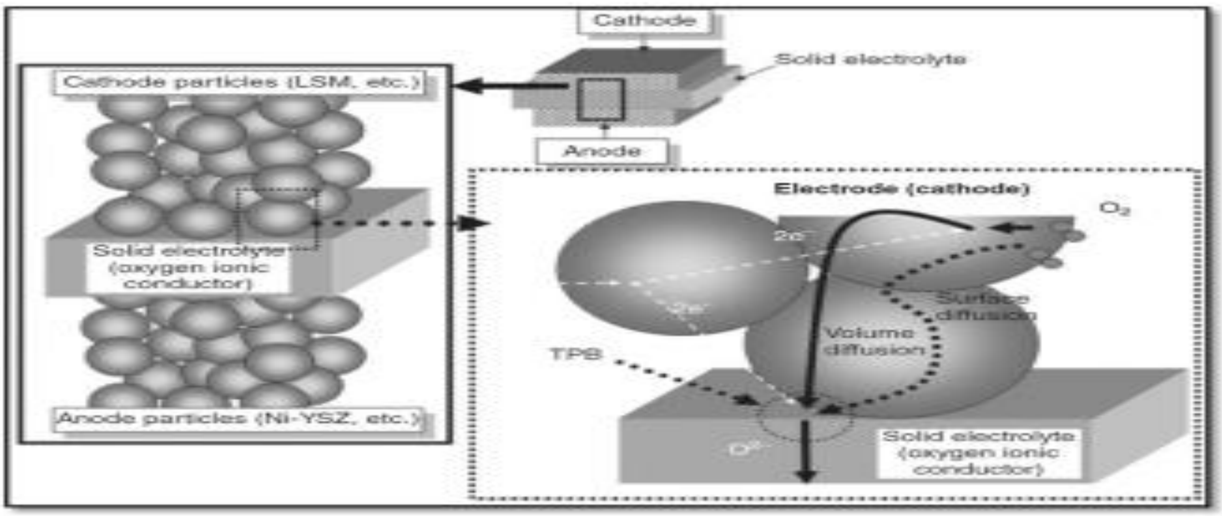


Fig. 13 Schematic representation of molecules to ions at the triple – phase boundary. [92.]

8.1 Classification

Typically any materials using in SOFC devices can be obtained and synthesis through different techniques. These techniques are wet chemistry or dry chemistry- target are to get the desired macro/micro/ nanostructure [96]. Then the materials are classified from the structural level by studying of atomic level [97]. The characterizations of SOFC materials can be done by different techniques such as X-ray powder diffraction(XRD), neutron diffraction (ND), X-ray photoelectron spectroscopy(XPS), Raman spectroscopy(RS) and energy dispersive spectroscopy (EDS). For the microstructural analysis, it includes scanning electron microscopy (SEM), transmission electron microscopy (TEM), and chromatography analysis, etc. These characterizations give the proper identification from macro-scale to nano-scale (various levels) as shown in Fig. 14. The material properties are not only depending on the observation of physical properties by naked eye at the macroscopic level but also rely on the complex interaction mechanisms on the small level microscale or nano-scale [1,19,23,100,101]. Moreover, the significant impact on SOCF material performance is subjected to their structure identification [7,39,102–104] which leads to the proper assessment of its mechanical properties, photocatalytic behaviour, electro-magnetic properties, chemical properties and electrochemical performance. With the rapid spread of smart technology nowadays, it is important to develop SOFCs with multiscale. Therefore, it requires accurate identification with reliable predictions by exploring the mechanisms of work along the macro/micro/nano-structured level. Although, SOFCs research work have proven highly promising resource of energy since 1938, the need for improvement its performance in terms of efficiency and design committed researchers to develop the structural levels (conventional to nanoscale). Different research work has been performed in the development of SOFC devices through the enhancement of materials [1–10,15–25,30–64]. Boder et al. [105] have developed a technique to improve the catalytic activities of conventional SOFC anodes for direct internal reforming of natural gas. They reported that it is possible to improve the performance of SOFCs with direct internal reforming of hydrocarbons with electrochemical performance comparable to that of the standard cells. André Weber et al. [106] has proposed for the optimum selection of materials. They refer to the stack design as a significant issue for handling the technology of fuel cell. In addition, the highlights of microstructure has become essentially required for getting highly efficient SOFCs operating in different temperatures. Micro-solid oxide fuel cell (developed in 1999) [107], has shown big potential in the application of portable electronic devices [108,109] with a noticeable good performance at ranges of temperature from 700 °C to 300 °C. With regard to this enhancement of the cell efficiency [109] in micro-scale levels through the synthesis and preparation, different materials have been developed. Table 4 illustrates the used material in micro-SOFCs. Jeffrey et al.[107] has shown the approach for the fabrication and assembly of micro-SOFCs with remarkable efficiency in 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 for 21st century [104]. Through the doping of mixed ionic electron conductors like Ce+3 [119] interface spacing is expected to affect on conductivity behaviour compare to the width of the space charge carrying grains in the composite in comparatively large crystals [120]. Some attempts were made to investigate the microSOFCs with different materials which are shown in

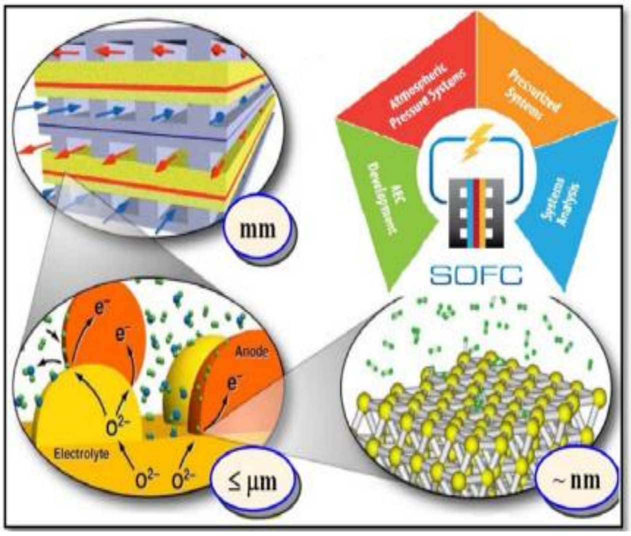


Fig. 14. The trend of material structure form macro to nano-scale [98,99].

Table - 4

List of different materials used in micro-SOFCs.

Anode	Cathode	Electrolyte	Substrate	Temperature (°C)	Ref.
Pt	Pt	8YSZ	Foturan, silicon wafer	450–550	[41]
Ni	LSCF	GDC	–	450–550	[87]
Ni	LSM	8YSZ	–	400–700	[93]
Pt	Pt, LSCF	8YSZ	Foturan, glass-ceramic	400–600	[110]
Pt	Pt	8YSZ	Silicon wafer, SiO_2	500	[111]
Pt	Pt	8YSZ	Silicon wafer, Si_3N_4	350–400	[112]
Pt	Pt	8YSZ, CGO	Silicon wafer, Si_3N_4	350	[113]
Ru	Pt	8YSZ	Silicon wafer, Si_3N_4	265–350	[114]
Pt	Pt	8YSZ	Silicon wafer, Si_3N_4	400–450	[115]
Ni	Pt, LSCF	CGO	Ni plate	450	[116]
Ni	Pt	8YSZ	Porous Ni	370–400	[117]
Ni + SDC	BSCF + SDC	SDC	–	500–600	[118]

Table- 5

Selected nano-materials for SOFCs.

Anode	Cathode	Electrolyte	Substrate	Temperature (°C)	Ref.
Ni	–	GDC	–	450–550	[121]
Ni	LSM-YSZ	ScSZ	–	700	[122]
–	LSCF-GDC	GDC	–	650–850	[123]
Pt	LSCF	YSZ	Silicon wafer, Si_3N_4	450–500	[124]
Ni-SDC	SSC	ScSZ	–	600–700	[125]
Ru	Pt	CGO-YSZ	–	470–520	[126]
Pt	Pt	YSZ		350–500	[127]
Ni	Pt	YSZ	–	600	[128]
Pt	LSCF	YSZ	–	400–500	[25]
Pt- ZrO_2	LSM	YSZ	–	650–800	[80]
LSCF	LSCF	CGO	–	700	[82]
PSM	PSM	YSZ	–	500–800	[83]
SSC-NiO-YSZ	SSC-LSF-GDC	YSZ	–	700–800	[129]
LSM-YSZ	LSM-YSZ	YSZ	–	600–800	[130]
LSM-YSZ	LSM-YSZ	YSZ		650–850	[131]
NiO-YSZ	LSF-YSZ	YSZ		700–800	[132]
NiO-YSZ	LSM-GD	YSZ		750	[133]
LSM-YSZ	LSM-YSZ	YSZ		650–800	[134]

Table 4.A list of nano-materials used in SOFCs are presented in Table 5.

8.2. Performance and efficiency of SOFC

The great benefits of SOFC devices is their excellent performance and highly efficient service at a wide variety of applications (large scales hybrid SOFC/turbine as well as the portable electronics). This widespread technology is competing with other type of energy resources such as renewable and sustainable type, because of its superior efficiency as standpoint in all rated power ranges. Hence, from fuel cell research work (shown in Fig. 16) placed this impressive technology in the first place compared to different types of energy resources in terms of efficiency against power. Fig. 16 illustrates the comparison of energy efficiency between fuel cells and other energy generation techniques. Fuel cells shows the highest potential with efficiency from 40% to 65%. Similarly, Fig. 17 shows the superiority of SOFCs over other types of fuel cells. However, the environmental requirements [10, 23] for the energy technologies are important and Fuel cells show the most promising among all other energy techniques. The technology of fuel cell able to face the environmental challenges by introducing most clean and efficient techniques (see Fig. 18). The operation principles of SOFCs are related to the used materials [138] which require an accurate identification of its properties through reliable characterization as mentioned. The electrochemical behaviour of ions and cations through the reaction process can be expected from the structural analysis using XRD or ND as shown in Fig. 19. The precise expectation of transportation reactions can be obtained through theoretical analysis [141–143] or modelling and simulations [73,144–146] which participates in the investigation of the transport of species on the surfaces of SOFCs electrodes (nanoscale level). Also, the control of the system can be achieved (macroscale level) [147] with time scale as presented in Fig. 20. Then, the obtained results in terms of performance within parallel to the experimental will draw the specification of the efficiency and performance for SOFCs at different scales (from macro to nano). Additionally, it will be able to provide a sufficient environment for renewable fuels. The performance of SOFCs at different scales can be understood through power density (shown in Fig. 21) is the key to wide industrial applications. The efficiency measurements of the cell normally are due to materials properties and their standing with different ranges of operational temperatures. Therefore, the investigations occurred at different scales and the target is the enhancement of the output performance with effective cost gives SOFCs the superior to be the most efficient type of fuel cell technology. Thus, the merits of 65% performance from SOFC devices with continuous modification enables this technology to be applied from remote power villages to the smart portable electronic devices.

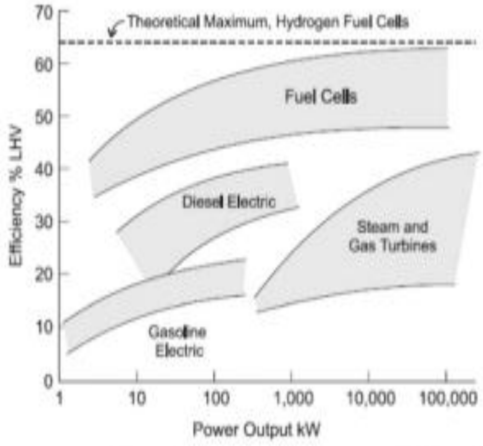


Fig. 16. Comparison of obtained efficiency against output power of different fuel resources [135].

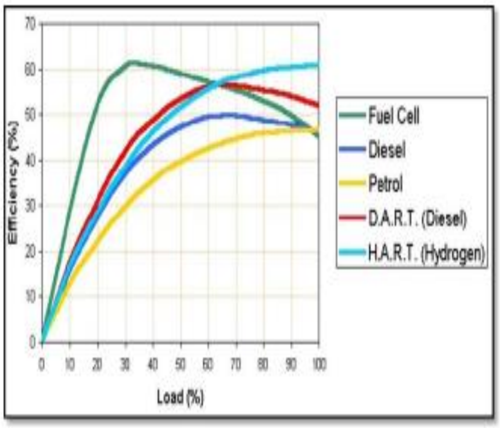
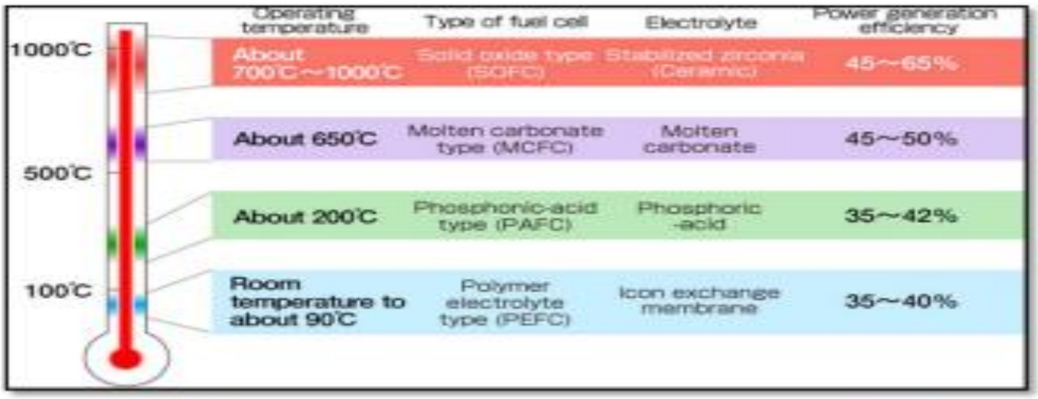


Fig. 18. Comparison of different fuel resources efficiency [137].



Operating temperature	Type of fuel cell	Electrolyte	Power generation efficiency
About 700℃~1000℃	Solid oxide type (SOFC)	Stabilized zirconia (Ceramic)	45~65%
About 650℃	Molten carbonate type (MCFC)	Molten carbonate	45~50%
About 200℃	Phosphoric-acid type (PAFC)	Phosphoric-acid	35~42%
Room temperature to about 90℃	Polymer electrolyte type (PEFC)	Icon exchange membrane	35~40%

Fig. 17. The superior advantages of SOFCs over other types [136].

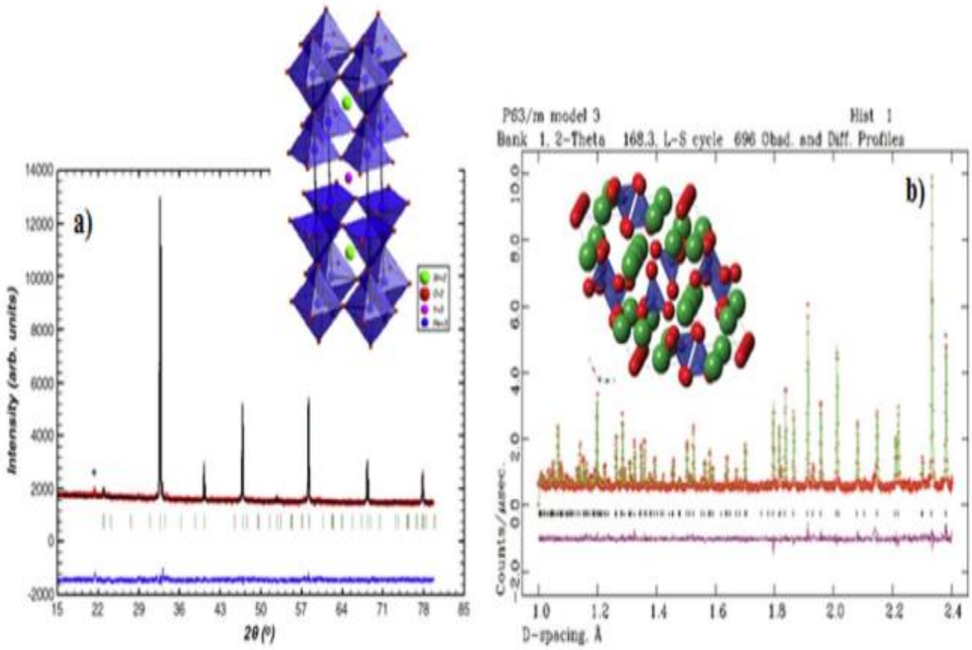


Fig. 19. Identification of material structure through a) XRD and b) ND [139,140].

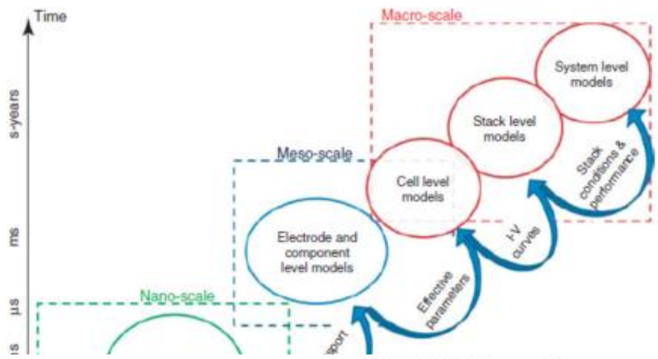


Fig. 20. Time and length scales involved in theoretical SOFCs [117].

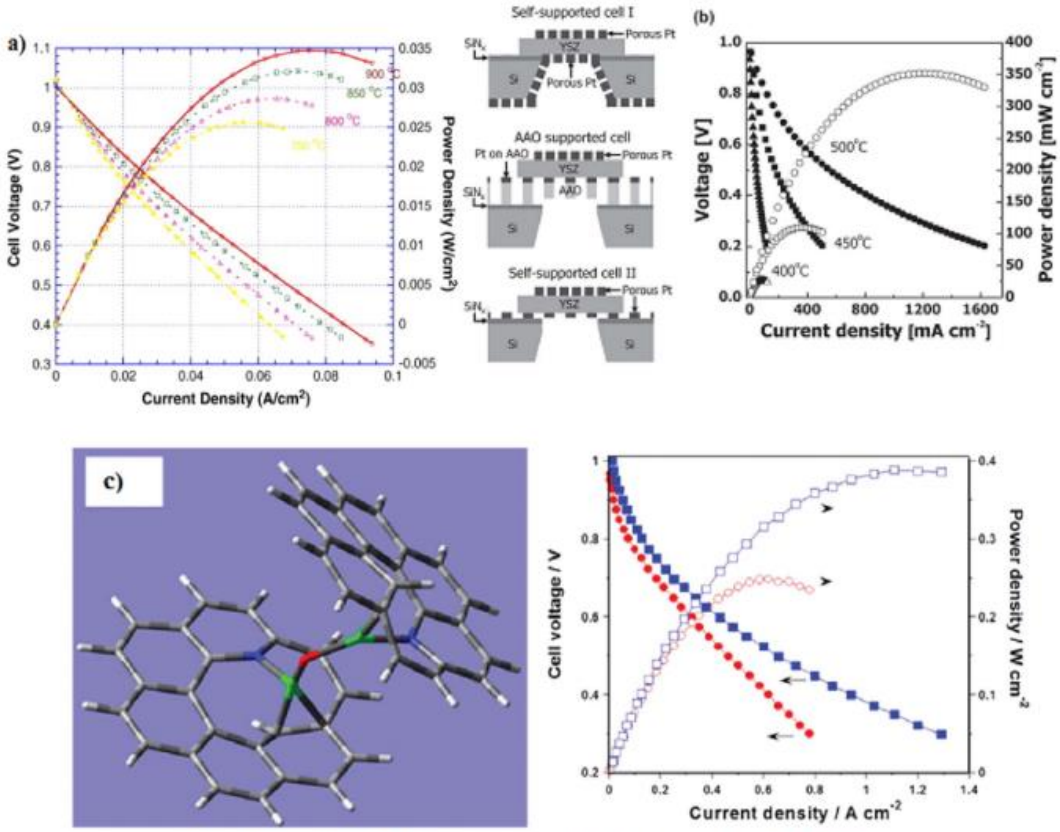


Fig. 21. Performance of SOFCs at different scales a) macro-scale, b) micro-scale and c) nano-scale [139,148,149].

9. Advantages of nano-materials in SOFC

Nano-scale materials have found their vital role in the scientific community. In recent decades they have been emerging in developing novel highly desirable properties that are absent in bulk phases, hence the development of these levels of materials are highly required. The advance of SOFC in lowering its operating temperature has opened up new prospects for the application of both micro and nano materials. This can be clearly observed from the merits driven by micro/nanoSOFC from the performance of the used materials at intermediate temperature ranges. For instance, the Ni/YSZ/Pt [128] has been investigated at 600 °C for 10 h with dry H2 and air, the obtained power density was 23.3 mW/cm2 . On the other hands, by using Pt/YSZ/Pt [41] power output of 150 mW/cm2 at 550 °C were observed at humidified H2:N2 (1:4). Nowadays, the highest performance in a small size is the main target for the smart technology applications.

10. Recommendations of nanotechnology for SOFCs

Over the past three decades, nanotechnolgy utilization in energy sectors has shown a great development and enhancement in the power and efficiency. The most promising issues dealt with carbon-based metal-free catalysts for energy conversion and storage. The reason to use carbon based materials is for their high mechanical, thermal, and chemical stabilities. They show superior performance in electrical and electrochemical properties, in addition to their reasonable cost and availability [150]. The nanomaterial graft in the synthesized metallopolymers has modified for the catalytic activities. It is also a resultant nanocomposites which significantly enhanced the open circuit potential of the related devices with light harvesting metallopolymer [151]. Other interesting findings have been presented through the metallic nanocatalysts when used to tune activity and selectivity for O2, CO2 reduction and oxidation of ethanol in energy sector (conversion and storage). The most essential part in these applications were related to nanopores that provide low-coordinated sites for the electrochemical reactions and hence can alter the selectivity and controlled time span [152]. The fuel cells higher cost, durability and lifetime challenges were the most impacting factors that made the utilization of nanomaterials well desired in their devices and related applications. Also the environmental and sustainability issues makes the selection of nanostructured material are crucial. Very recent studies were done on the improvement of cathodes, anodes and electrolytes in SOFCs, but they are very limited and needed to be expanded. The utilization of nanotechnology will attribute some promising nanostructured materials for SOFCs components and catalyst supports [153]. Based on these observations, it will be more beneficial to apply nanostructured array experimentally with carbon based materials or graphene materials in SOFCs related components. This will show a promising achievement in the electrochemical and electrical properties in the energy field and will have a very positive impact on the environmental and sustainable sides.

11. Conclusions

Investigations of SOFCs at different scales from macro-scale to nanoscale level have done for their merits and advances. High energy conversion efficiency, high fuel flexibility, environmental safety issues at different scales and the possibility to convert exhaust heat (outcomes during reactions) to another usage makes SOFCs superior to other renewable energy resources. The world's energy demand is rapidly increasing and the reserve of natural fossil fuels are deplaying, so urgent production of energy from other alternatives are required. SOFCs are one of the most efficient and promising energy generation techniques to solve these issues. The important issue which controls the whole process mainly depends on the material performance during operational temperatures. This can be easily developed and enhanced with nanostructured materials and applied to SOFCs devices. Different characterizations and analyses such as XRD, ND, SEM, TEM, TGA, EIS and electrical performance measurements for the cell components were considered and drawn the specifications for each scale. Some theoretical works have been performed but it must be sufficiently detailed to predict results that can help to increase the performance. Such investigations at different scale levels (from macro-scale to nano-scale) will help theoretically and experimentally to extend lifetime, make it cost-effective and achieve high performance at low temperatuers for various applications. The recommendations of nanomaterials with integration of carbon or graphene may change the map of SOFCs and will offer more efficient devices with high power and performance in various applications.

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