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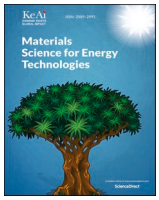

Constraints in sustainable electrode materials development for solid oxide fuel cell: A brief review

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ABSTRACT

Solid oxide fuel cells (SOFCs) are efficient electrochemical energy device that converts the chemical energy of fuels directly into electricity. It has a high power and energy density and a sustainable source of energy. The electrode (cathode and anode) materials are essential for the efficient operation of SOFCs. Several electrode materials have been studied in the last two decades, mainly perovskite materials. The investigated materials have resulted in improved electrochemical performance of SOFCs, increased commercial viability, and reduced operational costs. However, the sustainability of most of the material compositions (heteroatoms) used as electrodes in SOFCs has never been investigated. The present study examines the recent progress, challenges, and constraints associated with electrode material development in SOFCs from a sustainable perspective. Heteroatoms majorly employed for doping in electrode materials' long-term availability on the earth's surface was established. The study also provides an overview on the current state of electrode materials development for symmetrical solid oxide fuel cells. This is intended to address the complexities of different materials development for the anode and cathode.

1. Introduction

Overreliance on fossil fuels as the primary source of energy poses a significant challenge to the environment. This form of energy is unsustainable in the long term and has adverse effects on the climate, resulting in the depletion of ozone layers. Among the drawbacks associated with fossil fuels are CO_2 emissions, greenhouse gas effects, the release of nitrogen oxides, and particulates. Energy experts are of the view that there is a need for increased use of sustainable energy-generating technologies [1,2], as it will increase the amount of clean energy available to the global community. Currently, there are several clean energy technologies, including sunlight energy harvesting devices (solar collectors and photovoltaic collectors), biomass, hydrothermal, wind turbines, and fuel cells [3–5]. Most of these technologies are limited by environmental constraints, such as overcast days, intermittency, and low energy conversion rates. However, fuel cell has proven to have high energy conversion rates (around 60 %), less environmental dependence, and cost-effective compared to other sustainable energy-generating devices. Without the requirement for direct combustion as an intermediate step, fuel cells electrochemically convert chemical energy into electrical energy and heat, resulting in higher conversion efficiency than those of conventional clean energy technologies. The absence of the combustion chamber in fuel cells makes it eco-environmental friendliness [6,7]. Various types of fuel cell technologies exist, including polymer electrolyte membrane fuel cell (PEMFC), solid oxide fuel cell (SOFC), direct methanol fuel cell (DMFC), alkaline

Abbreviations: LNO, lanthanum nickelate; SDC, Samarium doped ceria; LSM, Lanthanum strontium manganite; GDC, Gadolinium-doped ceria; YSZ, Yttria stabilized zirconia; ORR, Oxygen reduction reaction; LSC, Lanthanum strontium cobaltite; LSCM, Lanthanum strontium chromium manganite; SOFC, Solid oxide fuel cell; SSOFC, Symmetrical solid oxide fuel cell.

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fuel cell (AFC), phosphoric acid fuel cells (PAFC), and molten carbonate fuel cell (MCFC). However, SOFC have shown excellent properties due to its durability and flexibility with fuels, high energy and power densities compared to other electrochemical energy conversion devices.

The three main components of the SOFC are the cathode, electrolyte, and anode. Anode (negative electrode) in fuel cells is responsible for oxidizing hydrogen, releasing electrons and producing protons. The protons then travel via an electrolyte to the cathode (positive electrode), where they combine with oxygen to produce water, releasing more electrons in the process. Electrical current is produced as the electrons flow through an external circuit. Accelerating the oxidation and reduction reactions taking place at the electrodes with electrocatalyst materials such as platinum and other transition metals, ensures the effective conversion of chemical energy to electrical energy [8–10]. However, platinum catalysts are expensive and their electrocatalytic properties tend to decrease after prolonged use in SOFC. This can be attributed to the high operating temperatures of traditional SOFC. Fig. 1 provides an overview of the conventional SOFC and its various components.

The performance and durability of SOFCs is mainly influenced by the selection and optimization of electrode materials. Advancements in electrode materials development have been a major focal point for the past few decades. The present study aims to examine the recent progress in electrode material development for SOFC from a sustainable perspective, while highlighting its limitations. Electrode materials development for symmetrical solid oxide fuel cell were also investigated. Various materials employed in electrode synthesis were analysed, including perovskites, composites, cermet materials, and mixed ionic-electronic conductors. This group of materials was mainly analysed due to their high conductivity, stability at high temperatures, and compatibility with oxygen reduction and fuel oxidation reactions. Although several review studies have been published in the past decade, none was devoted to the sustainability of electrode materials development in SOFC, particularly the long-term availability of heteroatoms. In order to provide an overview of recent advancements in the application of electrode materials in SOFCs, a brief literature review was conducted. To gather relevant literature, three bibliographic databases (ScienceDirect, Web of Science, and Google Scholar) were searched using keywords such as “fuel cell,” “solid oxide fuel cells,” and “electrode materials”. Fig. 2 provides an overview of how the literature was sourced. Similar techniques have been adopted by other researchers in their review studies [11–13].

Most previous related review studies focused on new materials development, optimizations, and future research trends [14–23]. The availability of the heteroatoms used in electrode materials doping, and it’s sustainability on the long term has never been investigated. The review study by Bello et al. [24] on proton conducting SOFC (P-SOFC) provide valuable insight on its effectiveness compared to oxygen conducting SOFC (O-SOFC) in terms of none-dilution of fuels at anode, better theoretical efficiency and optimal performance at low working temperature. However, electrode materials sustainability and availability on the long-term were never investigated. Thus, the main goal of the present study is to provide a brief overview of electrode materials development from a sustainable point of view, focusing mainly on the availability of heteroatoms in the periodic table on the long term. The flowchart in Fig. 3 provides an overview on the topics addressed in the present review study.

2. SOFC electrode materials

2.1. Anode materials

The anode of SOFCs is typically made of porous ceramic materials. These ceramic materials can either be nickel-cermet or lanthanum chromite ($LaCrO_3$) [25,26]. Anodic material must possess high electronic conductivity, robust stability, and effective thermal compatibility with other cell components. It should also possess considerable electrocatalytic efficiency to facilitate oxidation reactions and possess optimal porosity for the effective transport of carrier gases in the high temperature. Several doped perovskite materials have been developed over the past few years as possible anode materials. Nickel anode-based materials are mainly employed in SOFC due its cost-effectiveness and ease of synthesis. To maintain the required porosity and prevent the sintering of nickel particles at high operating temperatures, the anode materials are dispersed with solid electrolyte materials to form cermet [27,28]. This provides compatible thermal expansion coefficients with the solid electrolyte, preventing any issues associated with adhesion during operation. Solid electrolyte plays a critical role as supporting material for anode, which can impact the anode’s catalytic properties. $Ce_{0.9}Sr_{0.1}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ (CSCMn) was synthesized via the gel combustion method, and investigated as a potential anode for SOFC using $Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC) electrolyte [29]. The CSCMn demonstrated excellent chemical compatibility with SDC in N_2 environment, but showed structural changes and sulfide formation after exposure to 5 % H_2S-N_2 at 800 °C. The effect of sulfide formation on the electrochemical performance of the material needs to be investigated. Further experiments are needed to analyse the changes induced by the new phase.

In recent years, efforts have been centred on investigating electrical conducting oxides as potential alternatives to Ni-based anode materials [30,31]. These oxides have demonstrated good stability under oxidizing and reducing conditions. The use of oxides as anode in SOFC presents an

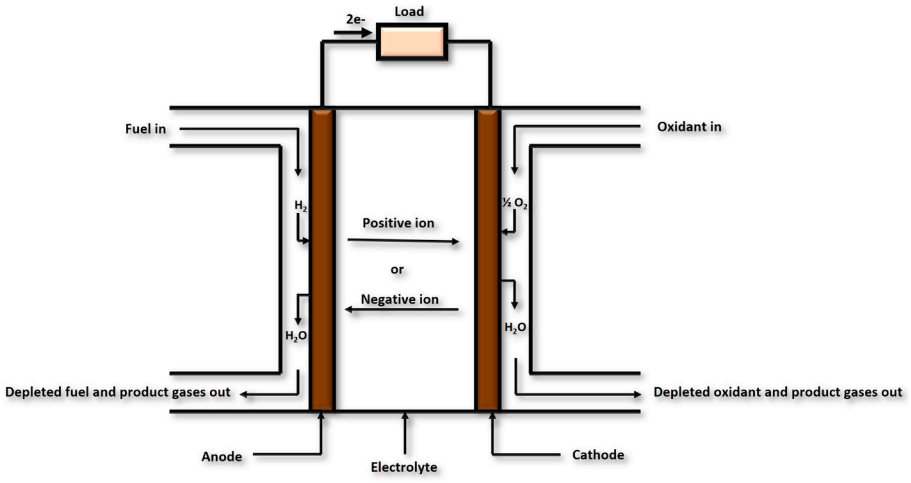

Fig. 1. Schematic diagram of a generalized solid oxide fuel cell.

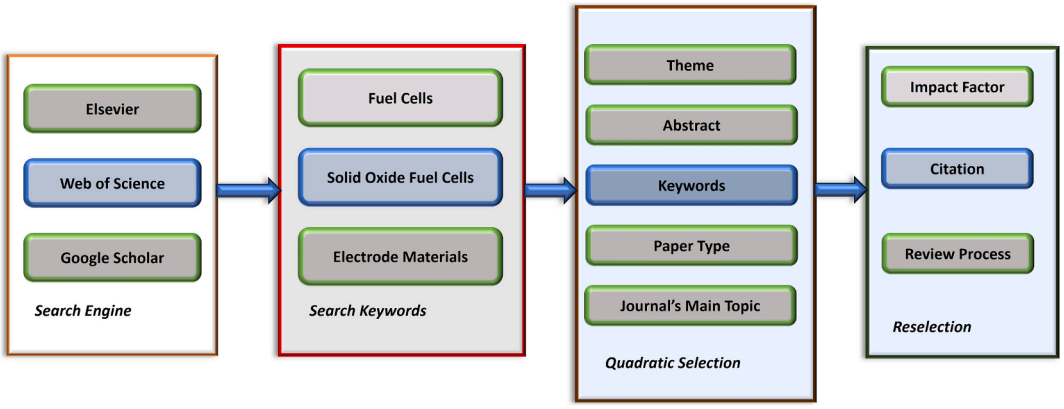

Fig. 2. Methodology adopted in the present study.

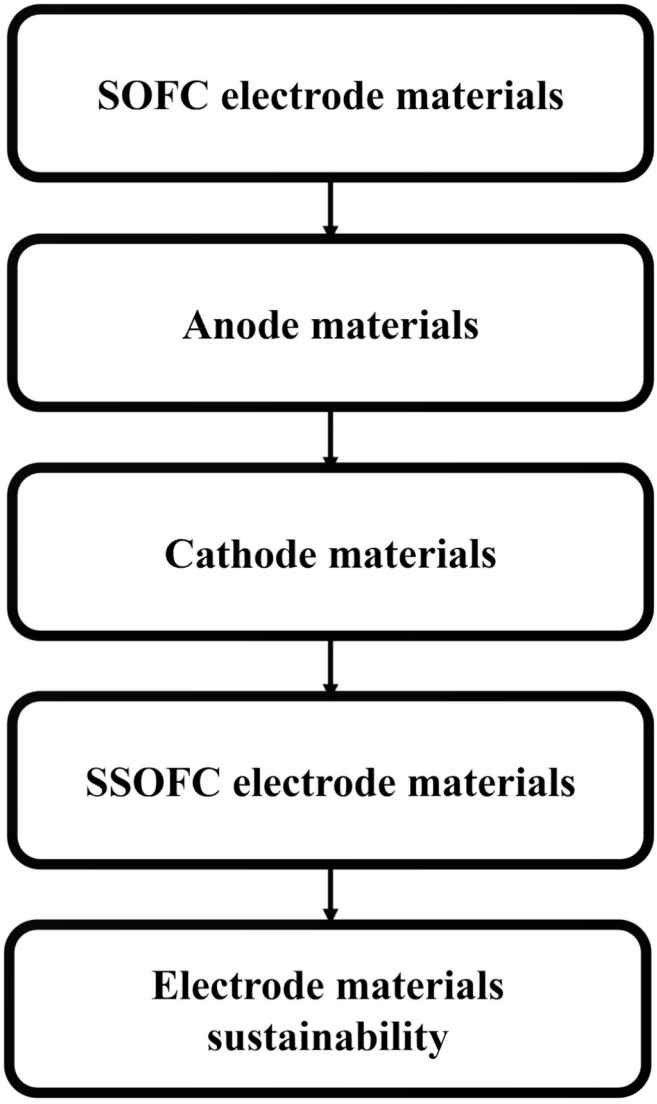

Fig. 3. Overview of the topics addressed in the present study.

exciting solution to the various challenges associated with nickel cermet anodes, including carbon deposition, sulphur poisoning, sintering, and the potential formation of nickel oxide under an oxidizing environment. Oxides showing promise as potential anode materials include lanthanum chromite ($LaCrO_3$) and strontium titanate ($SrTiO_3$), both of which have been extensively investigated along with various doping of A and B sites [32–34]. $La_{0.7}Sr_{0.3}Cr_{0.8}Ti_{0.2}O_3$ has been analysed as possible replacement for $LaCrO_3$ (lanthanum chromite) series [35,36]. While strontium titanate has also been investigated with niobium and lanthanum substitutions, such as $Sr_{0.6}Ti_{0.2}Nb_{0.8}O_3$ and $La_{0.4}Sr_{0.6}TiO_3$ [37]. Among the new series of perovskite anode materials that were recently synthesised, those belonging to $LaCrO_3$ demonstrated good anodic properties, low polarization resistance and low thermal expansion coefficient. Furthermore, mixed-conducting oxides such as terbia- and titania-doped YSZ, with yttria-doped ceria, have demonstrated potential to be an excellent anode material since it can significantly reduce overpotential losses at the anode. Fig. 4 illustrates the good polarisation resistance in $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ (LSCM) anode material series with CGO electrolyte. The maximum values of polarisation resistance reported for this group of materials are less than 0.3 Ω/cm^2 [38,39]. This facilitates the exchange of charges between the anode-electrolyte interface. Despite the exceptional properties of these materials, pure LSCM demonstrated limited activity in the oxidation of H_2S-free fuels. Nevertheless, it displayed a superior balance between high chemical stability in a sulfur/carbon environment and adequate electrical conductivity compared to other anode materials [40]. Thus, LSCM could be a suitable anode matrix, with its properties further optimized depending on the chosen fuel. The sustainability of this group of materials needs to be investigated, as lanthanum-based materials have been heavily used in materials development for energy conversion devices. Its continued availability in the long term and level of depletion are currently unknown. Hence, a comprehensive study is needed to establish its exact reserve on the earth's surface.

A recent investigation identified alternative anode materials that show significant potential for enabling the direct electrocatalytic oxidation of hydrocarbon fuel through the utilization of electrochemically pumped oxygen ions, thus negating the necessity for any additional co-fed oxidant [42–44]. Some of the new anode materials investigated consist of copper-based materials, with substantial amounts of ceria incorporated in addition to YSZ [45,46]. While other options include the addition of yttria-doped ceria to nickel and YSZ. The practicality of using such anodes for direct hydrocarbon oxidation remains uncertain due to the extremely harsh synthesis conditions required. Their long-term performance is also a major concern, as deactivation caused by carbon deposition will likely occur. The development of these anodes is currently an active field of research. Table 1 summarises previous studies on anode materials used for SOFC applications.

Comparative analysis of Table 1 shows that $La_{0.43}Ca_{0.37}Ni_{0.06}Ti_{0.94}O_{3-\delta}$ has the highest power density of 0.94 W/cm^2 at 900 °C. This indicates that low doping with La yielded better power density compared to high doping of composite $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$-$Ce_{0.8}Gd_{0.2}O_{1.9}$ at 800 °C. Generally, materials with La composition exhibit favourable electrochemical performance and are often

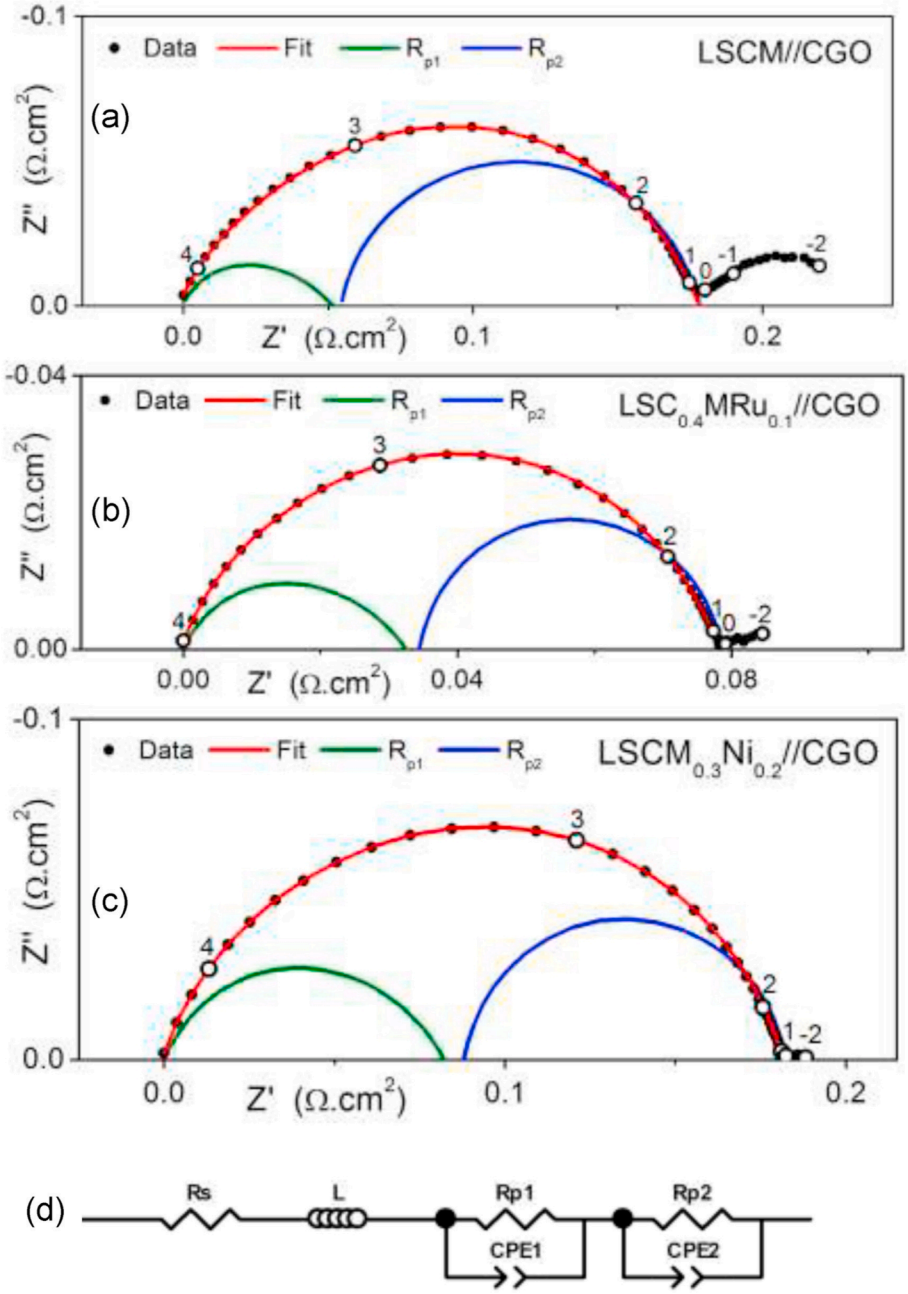

Fig. 4. EIS Nyquist plot obtained at 600 °C under wet Ar/H_2 (5 %) for (a) LSCM-, (b) $LSC_{0.4}MRu_{0.1}$- and (c) $LSCM_{0.3}Ni_{0.2}$-based symmetrical cell, fitted with the equivalent circuit (d) proposed and subtracted from Rs [41].

compatible with commonly used SOFC electrolyte (YSZ/GDC). This compatibility ensures an optimal interfacial contact and minimal interface resistance between the anode and electrolyte, which are crucial for efficient ion transport in SOFCs. However, this group of materials are susceptible to poisoning by certain impurities present in the fuel or atmosphere, such as sulfur compounds. This poisoning can lead to degradation of the anode performance over time and necessitate frequent cleaning or regeneration steps to maintain optimal operation.

2.2. Cathode materials

The cathode materials used in solid oxide fuel cell should have excellent thermal compatibility with electrolyte to avoid delamination during high operating temperatures. It should possess high electronic conductivity, good ionic conductivity and have a porous structure [63–66]. The cathode plays an important role in SOFC performance, as it is responsible for facilitating the oxygen reduction reaction. To achieve these goals, cathode materials must exhibit low polarization resistance, and good stability. Some of the most used cathode materials in SOFCs include lanthanum strontium manganite (LSM), lanthanum strontium cobaltite (LSC), and lanthanum nickelate (LNO) [67–69]. Other materials such as samarium-doped ceria (SDC) and gadolinium-doped ceria (GDC) can also be used as cathode materials in SOFCs in certain conditions.

In SOFCs, it is a common practice to use cathode with two layers [70]. The initial layer comprises mixed LSM and yttria-stabilized zirconia, which are similar to NiO/YSZ cermet used as anode. This methodology improves the thermal matching between the cathode and zirconia electrolytes, resulting in increased porosity and enhanced resistance to sintering, while preserving the electronic conductivity

Table 1
Various Anode materials investigated for SOFC applications.

Compositions	Temperature (°C)	Maximum power density (W/cm^2)	Ref.
$PrBaMn_{1.8}Co_{0.2}O_5$ (PBMCo)	900	0.12	[47]
Fe–Co/$PrBa_{0.8}Sr_{0.2}Mn_2O_5$	800	0.68	[48]
$(LaSr)_{0.9}Fe_{0.9}Cu_{0.1}O_4$ (LSFCu)	800	0.40	[49]
$Ce_{0.2}Sr_{0.8}Fe_{0.95}Ni_{0.05}O_3$	800	0.58	[50]
$SV_{0.5}Mo_{0.5}Ni_{0.1}O_{4-\delta}$	800	0.22	[51]
$Sm_{0.5}Ba_{0.5}MnO_{3-\delta}$	800	0.30	[52]
Ag-$(La_{0.60}Sr_{0.40})_{0.95}Co_{0.20}Fe_{0.80}O_{3-x}$	800	0.07	[53]
Ni-$Ce_{0.6}Mn_{0.3}Fe_{0.1}O_2$	750	0.49	[54]
$(PrBa)_{0.95}Fe_{1.4}Cu_{0.4}Nb_{0.2}O_{5+\delta}$	750	0.27	[55]
CuO-ZnO-SDC	700	0.13	[56]
$La_{0.75}Sr_{0.25}Co_{0.5}Mn_{0.5}O_{3-\delta}$	800	0.36	[40]
$Ca_2Fe_2O_5$-$Ca_2Co_2O_5$	800	0.16	[57]
$Ba_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$	800	0.908	[58]
$SmBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+\delta}$	825	0.032	[59]
$La_{0.43}Ca_{0.37}Ni_{0.06}Ti_{0.94}O_{3-\delta}$	900	0.94	[60]
$La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$-$Ce_{0.8}Gd_{0.2}O_{1.9}$	800	0.221	[61]
$SrMo_{0.8}Al_{0.2}O_{3-\delta}$	850	0.633	[62]

[71]. The second layer known as the current collection layer is entirely composed of LSM. Integrating platinum into LSM cathodes has demonstrated efficacy in improving cell performance through the reduction of electrical resistance at the interface between the cathode and the current collector [72–74]. However, the high cost of platinum should be taken into account when utilizing this technique.

Fig. 5 illustrates the thermogravimetry differential thermal analysis (TG-DTA) of an LSM group of perovskites. The TG-DTA profile shows a weight loss at approximately 401 °C, which can be attributed to the evaporation of moisture from the sample and the formation of oxygen vacancies. LSM has some limitations in terms of its electrochemical compatibility with zirconia electrolyte, which usually limits sintering temperatures to below 1300 °C. At temperatures exceeding 1300 °C, manganese has been observed to undergo diffusion into the zirconia electrolyte, resulting in adverse effects on both the cathode and electrolyte components [75]. Despite the high operating temperatures of SOFCs, the extent of manganese diffusion remains minimal, and extensive long-term studies demonstrate no deterioration in the cathode resulting from the interplay between LSM and the zirconia electrolyte [68,76]. Several investigations have demonstrated that up to a temperature of 1200 °C, there is no evident reaction between LSM and zirconia. However, at temperatures exceeding 1200 °C, the formation of $La_2Zr_2O_7$ and $SrZrO_3$ occurs, particularly with increased levels of strontium [77]. The electrical conductivity of $La_2Zr_2O_7$ is over 100 times less than that of zirconia. Fig. 6 shows the morphology analysis of highly porous LSM series of cathode materials.

Doped lanthanum cobaltite ($LaCoO_3$) has been extensively explored as a cathode material in SOFCs owing to its inherent p-type conductivity and the notable oxygen deficit it exhibits at elevated temperatures [79]. The substitution of divalent cation, especially strontium on the lanthanum site can increase its conductivity, and further performance enhancements can be achieved by replacing iron on the cobalt site [80]. $LaCoO_3$ exhibits superior electrical conductivity compared to $LaMnO_3$ under similar conditions [81]. However, its use as cathode material in zirconia-based SOFCs is generally limited due to its reactivity towards zirconia and its ability to undergo reduction at high temperatures. Moreover, $LaCoO_3$ exhibits a substantially larger thermal expansion coefficient than $LaMnO_3$, which already surpasses that of yttria-stabilized zirconia [82]. To address these issues, researchers have attempted to enhance the linear thermal elongation of $LaCoO_3$ to better match that of YSZ electrolyte by mixing $LaCoO_3$ with $LaMnO_3$ [83,84]. While primary findings on composite $LaCoO_3$-$LaMnO_3$ is interesting, its low polarization resistance at intermediate-temperature requires further optimization.

LSCF has a higher electrical conductivity compared to LSM, which makes it the preferred cathode material for IT-SOFC that uses gadolinia-doped ceria or lanthanum gallate electrolytes [85]. The performance of LSM cathodes is inadequate at low operating temperatures, and significantly restricts the overall SOFCs performance. Currently, there is a considerable emphasis on developing cathode materials that exhibit superior performance at low temperatures (<500 °C). The use of composite cathodes has demonstrated some potential in achieving this goal. Researchers continue to investigate new cathode materials that can improve SOFC performance, such materials must have higher ORR and good thermal coefficient at high temperature. Advancements in cathode materials could lead to more efficient, cost-effective SOFC with broader applications in energy generation. Table 2 gives an overview of previously investigated cathode materials for SOFC application.

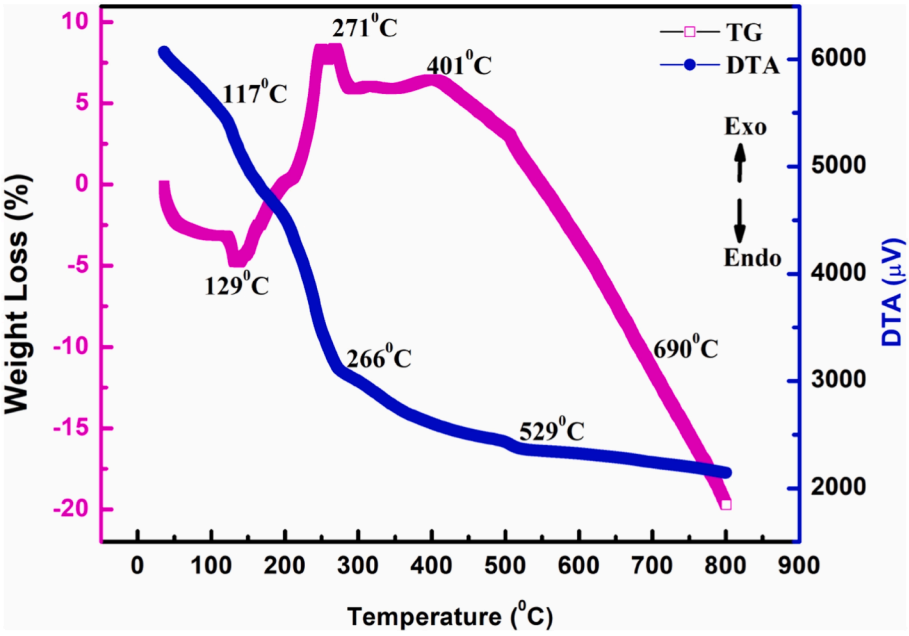

Fig. 5. TG-DTA profile of LSMN7382 dry gel at a temperature of 40–800 °C [78].

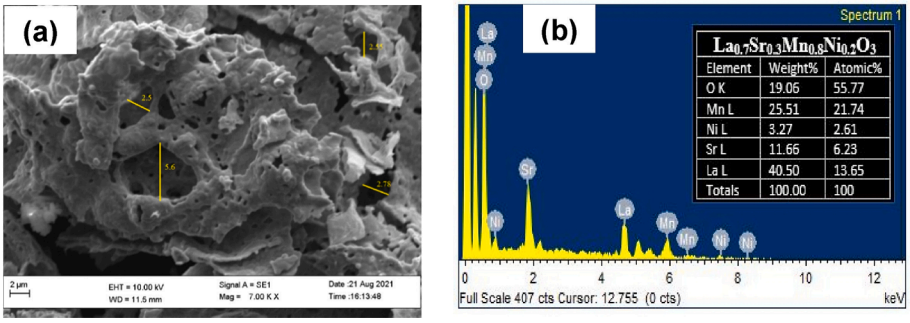

Fig. 6. (a) Scanning electron microscope (SEM) of LSMN7382 nanopowder and (b) corresponding elemental analysis (EDAX) [78].

Table 2
Previous studies on cathode materials for SOFCs application.

Compositions	Temperature (°C)	Polarization resistance (Ohm/cm^2)	Ref
$Nd_{0.5}Ba_{0.5}Zr_{0.5}Fe_{0.2}O_{3+\delta}$	800	0.206	[86]
$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$-$Sm_{0.2}Ce_{0.8}O_{1.9}$	600	0.45	[87]
$CuBi_2O_4$	700	0.58	[88]
$PrBaFe_{1.9}Mo_{0.1}O_{5+\delta}$	800	0.092	[89]
$NdBaCo_{1.5}Cu_{0.5}O_{5+\delta}$	700	0.67	[90]
$BaZr_{0.125}Y_{0.125}Fe_{0.75}O_3$	600	0.18	[91]
$40CuFe_2O_4$-60GDC	800	1.17	[92]
$PrBaCo_2O_{5+\delta}$	800	0.181	[93]
$La_{0.7}Sr_{0.3}Co_{0.25}Fe_{0.25}Ni_{0.25}Mn_{0.25}O_{3-\delta}$	600	5.24	[94]
$PrBa_{0.8}Ca_{0.2}Co_2O_{5+\delta}$	700	0.166	[95]
$La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_{3-\delta}$@$Gd_{0.2}Ce_{0.8}O_{1.9}$	750	0.16	[96]
$Sr_2Fe_{1.5}Sc_{0.5}O_{6-\delta}$	700	0.043	[97]
$Sm_{0.5}Sr_{0.5}CoO_3$	700	0.5	[98]
$Sr_2Fe_{1.5}Mo_{0.4}In_{0.1}O_{6-\delta}$	800	0.046	[99]
$Ba_{0.5}Sr_{0.5}(Co_{0.8}Fe_{0.2})_{0.96}Zn_{0.04}O_{3-\delta}$	600	0.23	[100]
$Nd_{1.5}Ba_{1.5}CoFeMnO_{9-\delta}$	700	1.1273	[101]
$La_{0.8}Ba_{0.1}Bi_{0.1}FeO_3$	550	0.33	[102]
$Ba(Co_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1})_{0.95}Ni_{0.05}O_{3-\delta}$	550	0.607	[103]

In Table 2, $Sr_2Fe_{1.5}Sc_{0.5}O_{6-\delta}$ has a polarization resistance of 0.043 Ohm/cm^2 at 700 °C, followed by cobalt-containing materials, with $Ba_{0.5}Sr_{0.5}(Co_{0.8}Fe_{0.2})_{0.96}Zn_{0.04}O_{3-\delta}$ having a polarization resistance of 0.23 Ohm/cm^2 at 600 °C. A critical overview of Table 2 also showed that cobalt-containing cathode materials has better R_p at low temperatures compared to cobalt-free cathode materials. Cobalt-containing oxides possess a balanced combination of electronic and ionic conductivity, which is crucial for efficient charge transport in SOFC cathodes. This balanced conductivity enables rapid oxygen ion diffusion through the cathode material, facilitating oxygen reduction and minimizing polarization losses. However, cobalt-containing perovskite cathodes may react with impurities present in the fuel or air streams, leading to the formation of secondary phases or surface contaminants. These reactions can alter the cathode's surface chemistry, decrease catalytic activity, and increase polarization resistance, ultimately compromising cell performance and durability. High polarization resistance in SOFC electrode materials reduces cell efficiency, and causes voltage loss, lower power output, incomplete fuel utilization, and material degradation. Mitigation strategies include developing advanced materials, doping, optimizing microstructures, and adjusting operating conditions. Furthermore, cobalt is relatively expensive and sensitive material, with concerns about its supply chain sustainability and environmental impacts. High cost of cobalt can significantly affect the overall cost of SOFCs and limit their widespread commercialization, prompting study on cobalt-free cathode materials.

2.3. Symmetrical solid oxide fuel cell electrode materials

Symmetrical solid oxide fuel cell (SSOFC) offers enhanced thermo-mechanical compatibility between the electrolyte and electrode, cost-effective fabrication, and increased resistance to coking and sulfur poisoning. Initially restricted to electrode materials with stable phase structures in both reducing and oxidizing environments. However, ongoing investigations are exploring novel electrode materials that can undergo beneficial phase transitions or reductions in reducing atmospheres. Meng et al. [104] developed SOFC with tri-layer porous/dense/porous $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) structures and nanoscale $SrFe_{0.75}Mo_{0.25}O_{3-\delta}$ (SFMO) catalysts. They observed exceptionally high-power density of 0.97 W/cm^2 at 800 °C with hydrogen fuel. Impedance measurements showed higher polarization resistances in hydrogen compared to air (0.22 vs 0.04 Ω/cm^2 at 800 °C). The adsorption of hydrogen on SFMO catalysts and charge transfer at SFMO/LSGM interfaces was identified as rate-limiting steps for hydrogen oxidation at high and low temperatures. Additionally, the composites achieved excellent carbon resistance in *iso*-octane fuels, reaching a power density of 0.39 W/cm^2 at 800 °C. Although the results are remarkable, the polarization resistance of 0.22 Ωcm^2 at 800 °C in a hydrogen environment is too high for effective oxidation of fuel. Gao et al. [105] infiltrated Pr_2NiO_4 (PNO) with SDC to develop a bi-electrode for symmetrical SOFC. In-situ exsolution of Ni nanoparticles on PNO after H_2 reduction increased hydrogen oxidation at the anode. SDC infiltration improved ORR performance at the cathode. The symmetrical cell achieved a maximum power density of 375 mW/cm^2 at 800 °C with H_2 and air. PNO-40SDC/SDC/PNO-40SDC cells demonstrated no degradation after 168 h at 750 °C and demonstrated stability during H_2/air cycling, suggesting PNO as a promising electro-catalyst for SOFC. However, nickel-based materials faced significant challenges of carbon deposition, leading to a decline in cell performance.

The doping of Ca on the A-site significantly enhances the catalytic efficiency of anodic–cathodic reactions, and improves CO_2 tolerance [106]. Ca-doped $Pr_{0.5}Ba_{0.5}FeO_3$-(Ca–PBF) electrode exhibits excellent redox resistance, electrochemical activity, and durability. At 700 °C, the polarization resistance was reduced for both cathode and anode, compared to PBF (without Ca-doping). The optimal power density reached 480 mW/cm^2 with H_2 fuel, indicating Ca–PBF as a suitable electrode material for symmetrical solid oxide fuel cell due to its excellent stability and catalytic activity. In Fig. 7, the electrochemical impedance spectra of PBF/Ca–PBF measured in wet H_2 (3 % H_2) is shown. Zhang et al. [107] investigated the doping effect of Ni, Cu, and Co on the B-site of $Sr_2FeNi_{0.2}Cu_{0.2}Co_{0.1}Mo_{0.5}O_6$ (SFNCCM). The materials possess good structural stability, excellent thermal compatibility with GDC, and a maximum electrical conductivity of 21.7 S/cm at 800 °C. The average TEC for SFNCCM was estimated to be 18.3 × 10^{-6} K^{-1} at 30–1000 °C. SFNCCM has an area specific resistance of 0.046 Ω cm^2 at 800 °C, with an optimal power density of 610 mW/cm^2. However, at high operating temperatures, new phases were formed with increased oxygen vacancies affecting material stability, suggesting

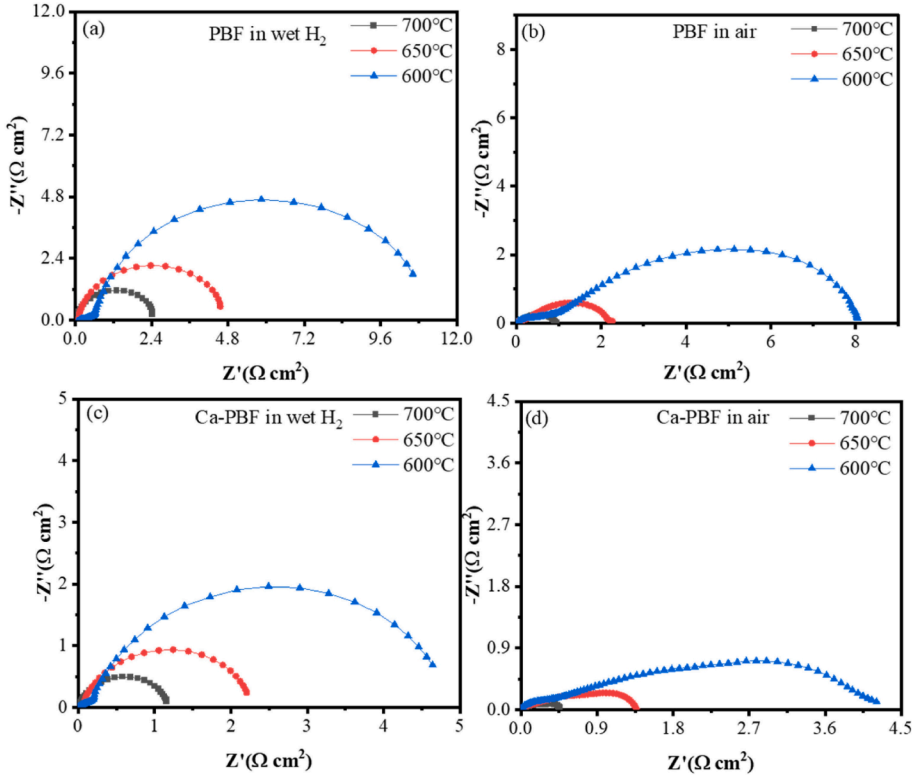

Fig. 7. Electrochemical impedance profile of PBF and Ca–PBF measured in wet H_2 (a, c) and air (b, d) [106].

potential improvement by doping with high-valent or high-bond energy metals. Thus, further studies are needed to improve the stability of this material at high temperatures. Sr and Ge-doped $PrBa_{0.5}Sr_{0.5}Fe_{1.9}Ge_{0.1}O_{5+\delta}$ (PBSFG) shows promise compared to $PrBaFe_2O_{5+\delta}$ (PBF) as electrode material in SSOFC and CO_2 electrolysis [108]. In SSOFC mode, a stable 1.05 W/cm^2 power density was achieved at 800 °C. For CO_2 electrolysis, stable mode was attained at 850 °C and 1.5 V. PBSFG shows a high current density of 825 mA/cm^2 compared to 370 mA/cm^2 for PBF. The DRT, Tafel slope, XPS, and ECR tests demonstrated improved catalytic activity and improved electrochemical reactions. The high cell performance is attributed to improved oxygen-ion-vacancy concentration and charge-transfer rate, particularly in fuel electrode reactions like CO_2 adsorption and dissociation, suggesting Sr and Ge-doped PBF as a favourable candidate for electrodes in SSOFCs. Table 3 summarises recent findings in symmetrical solid oxide fuel electrode materials development.

Based on the data presented in Table 3, $Sr_{0.9}Fe_{0.8}Sc_{0.1}Co_{0.1}O_{3-\delta}$ exhibits the lowest polarization resistance of 0.117 Ohm/cm^2 at 850 °C, suggesting its potential as electrode material in SSOFC. Pt@C–$Ni_{0.8}Co_{0.15}Al_{0.05}LiO_{2-\delta}$, operating at a lower temperature of 550 °C, exhibits a higher polarization resistance of 0.24 Ohm/cm^2, despite the high polarization resistance this material could still be viable for SSOFC electrode if composite YSZ-Pt@C–$Ni_{0.8}Co_{0.15}Al_{0.05}LiO_{2-\delta}$/GDC/Pt@C–$Ni_{0.8}Co_{0.15}Al_{0.05}LiO_{2-\delta}$ are used. Generally, low polarization resistance in electrode materials is desirable for SOFC applications. It enhances performance and efficiency by minimizing voltage losses, improving power output, ensuring better fuel utilization, and reducing heat generation and material degradation. The study on symmetrical solid oxide fuel cell is still an active area of research, and more investigations are needed to gain full insight into electrode materials that can provide excellent electrochemical performance as anode and cathode.

Table 3
Symmetrical solid oxide fuel cell electrode materials.

Material compositions	Temperature (°C)	Polarization resistance (Ohm/cm^2)	Ref.
$Sr_{0.9}Fe_{0.8}Sc_{0.1}Co_{0.1}O_{3-\delta}$	850	0.117	[109]
Pt@C–$Ni_{0.8}Co_{0.15}Al_{0.05}LiO_{2-\delta}$	550	0.24	[110]
$La_{0.6}Ba_{0.4}Ni_{0.2}Fe_{0.7}Ti_{0.1}O_{3-\delta}$	800	0.153	[111]
$Nd_{0.9}Ce_{0.1}BaCoFeO_{5+\delta}$	700	0.078	[112]
$Gd_2SrCo_{0.8}Fe_{1.2}O_{7-\delta}$	800	0.106	[113]
$Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$	700	0.62	[114]

2.4. Sustainable electrode development in solid oxide fuel cell

Heteroatoms play a crucial role in improving ionic conductivity, catalytic activity, and overall performance of SOFC. However, their environmental impact and the search for alternative materials are important considerations in the advancement of SOFC technology. Some of the commonly used heteroatoms include nickel, cobalt, lanthanum, yttrium, and cerium, each with associated environmental challenges in extraction and processing. Sustainable strategies involve exploring alternative materials like copper, iron, and bismuth oxide, improving recycling processes, and adopting green synthesis methods. Sustainable electrode materials development for SOFCs involves enhancing performance while reducing costs and environmental impact. The use of novel nanostructured materials, such as perovskites and ceria-based composites, to improve electrochemical activity and stability has endangered some groups of elements in the periodic table. Some elements are rarely used due to issues such as limited availability, toxicity, and challenges in waste management [115,116]. Notably, elements like cobalt (Co) and nickel (Ni), despite their favourable electrochemical properties, present challenges such as scarcity, environmental impact from mining, and difficulties in end-of-life disposal. Nevertheless, recent studies have focused on the development of cobalt-free cathode materials and nickel-free anode materials. Fig. 7 provides an overview on the sustainability profiles of the elements used in electrode materials compositions for SOFCs. The elements not coloured do not have a verified sustainability profile. Current knowledge on their exact reserve is limited, thus urgent

studies are needed to explore and understand their estimated remaining deposit. Gold (Au) is highlighted in red in the sustainability ranking, indicating limited availability and emphasising the need for its cautious utilization. Based on verified known reserves, Au has 5–20 years before its known reserves get depleted. However, Au is hardly used in electrode material preparation in SOFC but is mainly employed as current collectors in electrochemical analysis due to its high melting point compared to silver wires.

Several initiatives have been taken to recuperate and recycle metals used in SOFC electrode materials. However, the development of efficient recycling systems remains challenging. The intricate process of separating and recycling mixed-metal electrodes, which often include a variety of elements, presents technical obstacles. Although some metal recovery processes have proven successful, broader implementation is hindered by the complexity of the recovery technique and high cost. There is a growing inclination towards utilizing elements characterized as "green" in Fig. 8 due to their favourable environmental properties, sustainability, and abundant availability. Elements such as manganese (Mn), cobalt (Co), and strontium (Sr) emerge as alternatives to the green elements owing to their minimal toxicity and potential for effective recycling [118]. It is imperative to recognize that achieving complete sustainability in electrode materials development for SOFC may require performance trade-offs. The harmonization of electrochemical efficiency with sustainability criteria remains a persistent challenge in the field of energy materials development. Nonetheless, advancements in green chemistry principles and sustainable practices continue to drive innovation towards more eco-friendliness SOFC electrode materials development.

3. Future research direction on sustainable electrode materials development for SOFC

The high energy conversion rate of SOFC (around 60 %) makes it one of the most effective clean energy technologies. Sustainable electrodes are not only crucial for the long-term survival of SOFC, but also aid in attaining the world objective of a near net-zero emissions by 2050 [119,120]. Hence future research directions must focus on the following:

- Nanostructured composite electrodes have shown excellent electrochemical performance in air and H_2 environments. Hence this set of electrode materials should be prioritised for further investigations in symmetrical SOFC configuration.
- New catalyst materials and integration techniques should be utilized to enhance the mechanism of oxygen reduction and fuel oxidation reactions. The expensive nature of Pt, Co and Ni, means that other novel materials must be investigated.
- Ba, Sr, and Ca have mainly been used as dopants to enhance the thermal stability of electrodes with YSZ and GDC electrolytes. However, the use of Sc as a dopant in $Sr_{0.9}Fe_{0.8}Sc_{0.1}Co_{0.1}O_{3-\delta}$ as reported in this study aids in mitigating the thermal degradation of electrodes at high temperature. Future studies need to focus on the use of Sc as a dopant with other series of perovskite materials.
- Developing cost-effective and abundant materials without compromising performance needs to be studied.
- More investigation is needed to understand the exact mechanism for electrode–electrolyte interface optimization for ion and electron transport, reducing polarization losses and improving overall cell efficiency.
- Several investigations have relied on the use of metal oxides as electrode materials, thereby endangering some vital elements in the periodic table. Future studies must be carried out on the possibility of using agricultural waste, and other sustainable means of electrode materials development. However, there specific chemical composition must be investigated, as some of the agricultural waste contains some of the endangered elements in the periodic table.
- Based on the sustainability profile, elements in green should be favoured for future investigations on SOFC electrode materials development. However, highlighted in green colour also include expensive and rare metals like Sc and some lanthanoids, toxic Cr, but doesn't include Fe, hence performance trade-off must be looked into critically over long-term availability in the selection of some specific heteroatoms.
- It is necessary to develop and acceptable methods to determine what are the specific criteria for sustainable electrodes in SOFC. Several gaps remain, and complete knowledge on SOFC sustainable electrodes are limited.

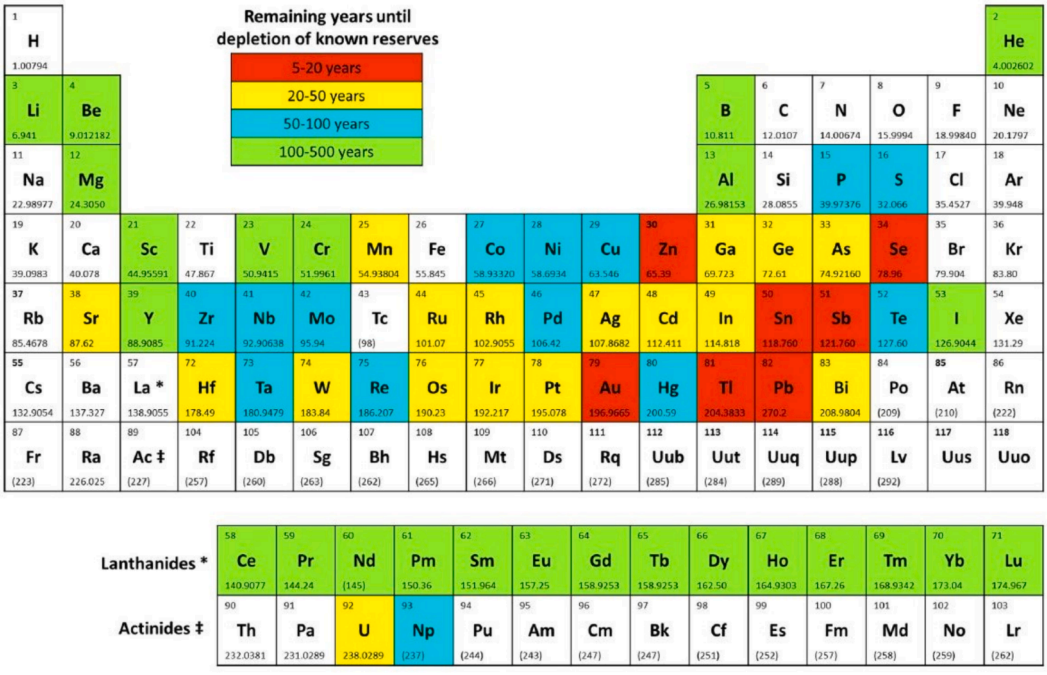

Fig. 8. Sustainable profile of elements in the periodic table [117].

4. Conclusions

Sustainable electrode materials are crucial for enhancing the efficiency, durability, and commercial viability of solid oxide fuel cell. This mini review highlights several key constraints and challenges faced in the development of sustainable electrode materials for SOFCs, paying close attention to the availability of heteroatoms in the long term. The high operating temperatures of SOFCs present a fundamental constraint, limiting the selection of suitable electrode materials to those with excellent thermal stability and conductivity. This has resulted in a continuous search for new materials that can maintain good electrochemical performance and structural integrity under high operating temperatures. The requirement for high electrochemical activity and catalytic efficiency further complicates the search for ideal electrode materials. Several promising materials exhibit insufficient electrochemical performance or suffer from poor chemical stability, hindering their practical application. Strategies to enhance the intrinsic activity and stability of electrode materials, such as nanostructuring, doping, and surface modification, have been investigated but often come with their own set of challenges and limitations. The most efficient electrode material compositions, such as rare earth elements and precious metals are expensive. Furthermore, the environmental impact associated with the extraction, processing, and disposal of these materials raises concerns about the overall sustainability of SOFC technology. The long-term sustainability of heteroatoms, as illustrated in Fig. 7, is also of great concern. Despite these challenges, significant progress has been made in recent years towards the development of sustainable electrode materials for SOFCs. Future studies must investigate the possibility of developing green electrodes, where sustainable materials are given priority.

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CRediT authorship contribution statement

Lukman Ahmed Omeiza: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Asset Kabyshev:** Visualization, Funding acquisition, Conceptualization. **Kenzhebatyr Bekmyrza:** Resources, Investigation, Funding acquisition, Formal analysis. **Kairat A. Kuterbekov:** Visualization, Supervision, Resources, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Marzhan Kubenova:** Visualization, Validation, Project administration, Funding acquisition, Formal analysis, Data curation. **Zhuldyz A. Zhumadilova:** Validation, Methodology, Funding acquisition, Data curation. **Yathavan Subramanian:** Visualization, Validation, Investigation, Funding acquisition, Data curation. **Muhammed Ali:** Writing – review & editing, Validation, Supervision, Formal analysis, Conceptualization. **Nursultan Aidarbekov:** Supervision, Validation, Writing – review & editing. **Abul Kalam Azad:** Writing – original draft, Visualization, Validation, Supervision, Conceptualization.

Declaration of competing interest

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

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