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A review on new cobalt-free cathode materials for reversible solid oxide fuel cells

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Abstract

The exponential growth in the requirement of fuel cells and batteries leads to increased demand for cobalt due to its common use in high-performance Li-ion batteries and high-temperature fuel cells/electrolyzers. This sharp increment in demand raises concern about the availability of limited reserves of cobalt which can impact the price of cobalt. Moreover, the geographic limitations of cobalt resources may endanger the whole supply chain. In addition to all those, huge moral issues of cobalt mining are also another problem. Hence, leading battery, fuel cells and electrolyzer manufacturers are looking for sustainable alternatives to reduce cobalt dependency. A more specific limitation is shown in Solid Oxide Fuel Cells (SOFCs) cathode materials that contain cobalt. Incompatibilities have already been observed between the cathode materials containing cobalt and the electrolytes in terms of the thermal expansion coefficient mismatch during the transition of the operating temperature from high to low. An advantage of low operating temperatures is the reduction of material costs compared to high temperature. Increasing the electrochemical performance of the cell and eliminating thermal expansion coefficient difference problems are in concert aimed at the development of cobalt-free cathode materials. Therefore, cobalt-free cathode materials are vital for the sustainability of SOFCs and green transition of the energy sector since they can be used as cathode and anode material in symmetrical SOFCs which is also known as reversible SOFC (RSOFC). In this review, we comprehensively summarize the recent advances of cobalt-free perovskite cathode materials for intermediate temperature RSOFCs.

1. Introduction

Fossil fuels provide most of the world's energy needs but also have negative effects on the environment. Harmful gases like carbon dioxide, carbon monoxide, nitrogen oxides, methane and sulfur dioxide mostly produced from fossil fuels cause environmental problems such as global warming, climate change and the greenhouse effect. Additionally, fossil fuel reserves are limited and rapidly depleted as a result of ever increasing energy demand [1]. Therefore, the search for alternative clean energy sources has gained importance. Hydrogen is one of the most efficient among alternative fuels due to its highest energy carrier properties [2]. Many regulations to reduce the carbon footprint have been put into effect all over the world such as Fitfor55 and Carbon Border Adjustment Mechanicsm (CBAM). In the past year REPowerEU plan was accepted by EU [3]. The plan responds to the recent disruption in the European energy market to be met by increasing the usage of hydrogen. According to different reports (i.e., IRENA, BNEF, Hydrogen Council) [4-7] hydrogen could contribute at least 10% of the mitigation needed to achieve the 1.5°C Scenario and 12% to 18% of final energy demand. Hence, more than 30 countries and the European Union have published hydrogen roadmaps to promote the use of hydrogen [8].

Hydrogen can be used as a fuel in fuel cells. Unlike conventional power generation systems, fuel cells do not pollute the environment as they do not involve a combustion reaction [9]. Conventional power generation systems require many intermediate processes to convert the chemical energy in the fuel into electrical energy, and their efficiency decreases in each process step. On the contrary, fuel cells are an efficient and environmentally friendly technology, as they can directly convert the chemical energy in the fuel into electrical energy silently without the need for any combustion reaction [10]. Fuel cells consist mainly of three layers (Figure 1(a)): anode (fuel electrode), electrolyte (with good ionic conductivity) and cathode (air electrode). There are many different types of fuel cells named by the electrolyte material (polymer, molten salt, alkaline, acid, carbonate and oxide). Solid oxide fuel cells (SOFC) stand out due to high efficiency, long-term stability, fuel flexibility, low emissions, and relatively low cost. Hence investments in SOFC research have constantly increased over the years. According to reports by Grand View Research [11,12], the global solid oxide fuel cell market size has reached 339.8 million USD in 2021 and is expected to exceed 4.0 billion USD by 2028.

High temperature operation of SOFC (800°C to 1000°C) is among the biggest problems in terms of commercialization. The necessity of using costly materials to produce a gas-tight stack is the primary obstacle against market success. Hence, the operating temperature has been brought down to about 500°C to 700°C to reduce cost at the expense of some electrochemical performance. New set of materials

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have been used in these intermediate temperature SOFCs (IT-SOFCs). Advantages associated with the reduction of operating temperatures are the savings in the cost of the system, the increase in the life of the system, the improved prevention of corrosion, the faster start up and shut down cycle of the system and the stability during operation [13-15]. Lower operating temperatures of SOFCs cause a compromise in the performance of fuel cells. Owing to extensive research on new cathode, electrolyte and anode materials these performance losses have now been minimized. As expected there is always room for improvement.

Depending on the time of the day or season of the year, demand for electricity can be highly variable. Traditional power generation methods like solar and wind energy are by nature intermittent. Sometimes there is surplus energy available, other times a shortage. Therefore, a complementary electric power generation system would be highly useful to keep demand and supply in balance. Reversible solid oxide fuel cell (RSOFC) is a very potent technology to use surplus energy efficiently by converting it into hydrogen gas which can be stored for future use for energy generation [16]. Incidentally, the same cell can be employed to produce electricity and hydrogen back and forth. As expected, RSOFCs have to reach a higher maturity level in cost, lifetime and reliability to ensure complete commercialization. Hence, more research and development (R&D) about RSOFCs need to be carried out.

A symmetrical solid oxide fuel cell (SSOFC) is a type of fuel cell in which the cathode and anode are made of the same material [17]. In a traditional SOFC, the cathode is made of a material that is able to promote the oxygen reduction reaction (ORR), while the anode is made of a material that can promote the hydrogen oxidation reaction (HOR). In a symmetrical SOFC, both the cathode and the anode are made of a material that is able to promote both the ORR and the HOR. Hence, they can be also named as RSOFCs.

In order to improve solid oxide fuel cell technology, studies are carried out on the materials used in the layers of SOFCs, especially on the cathode side which is probably the most important one. The function of the cathode layer in SOFC is to reduce the oxygen gas coming from outside to O^{2-} ion. It is necessary to have regions with high catalytic activity to ensure this. Moreover, the chosen cathode material should show both a good ionic and electronic conductivity in oxidizing medium. In addition, they must have a porous enough structure to allow maximum access to oxygen gas. The performance of cobalt-containing SOFC perovskite cathode materials has been extensively studied in the literature [18-20]. Materials like mixed oxides of La, Sr, Co and Fe for the cathode layer (LSCF) and GDC (Gadolinium Doped Ceria) for the electrolyte layers have been the most common. For instance, although LSCF is one of the most common SOFC cathode materials, the coefficient of thermal expansion (CTE) of LSCF is higher than that of GDC which leads to thermal stresses. Besides, chemical stability under operating conditions is unsatisfactory [21,22]. To increase mechanical and chemical stability, cobalt-free Mixed Ionic Electronic Conducting (MIEC) materials are extensively investigated in the last 10 years. One of the most important advantages of cobalt-free cathodes is to allow the use of cathode and anode at the same time in solid oxide fuel cells (SOFCs) and solid oxide electrolysis cells (SOECs) which are also known as RSOFCs [23,24] (Figure 1). In the recent literature, new kind of innovative cobalt-free cathode materials and their presence in RSOFCs have been increasingly studied (Figure 2).

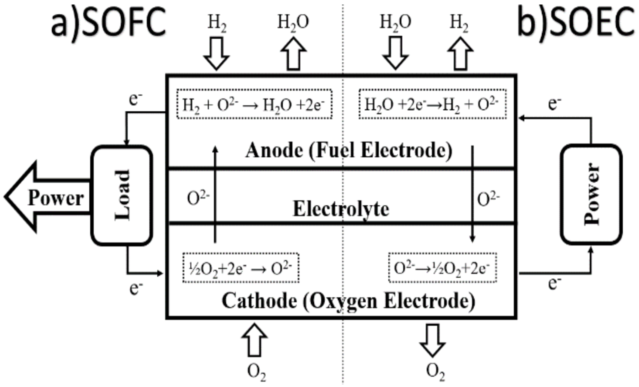

Figure 1. Schematic of (a) SOFC, and (b) SOEC.

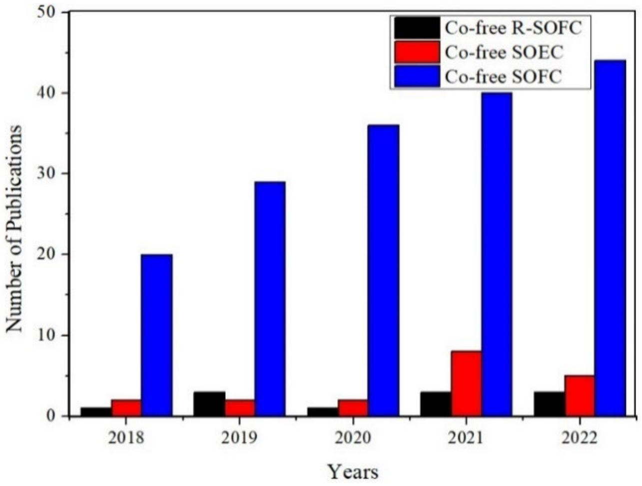

Figure 2. The number of publications for the last five years as a function of time for cobalt-free solid oxide fuel cell, cobalt-free reversible solid oxide fuel cell and cobalt-free solid oxide electrolysis cells [27].

The present review paper is a brief review of various studies on cobalt-free cathode materials which can be used as symmetrical materials in reversible SOFC structures and compositions development. Also a discussion is done about the most important parameters in determining the cathode performance, effective materials synthesis method and electrochemical performance overview. Some reviews about cobalt-free perovskite cathodes used in SOFCs in general are presented by Baharuddin *et al.* [25] and Hashim *et al.* [26]. This review only includes those recent studies on cobalt-free cathode materials aimed for use in RSOFCs. First a discussion is done about why there is a tendency to avoid the use of cobalt. Then the work in the literature about different solution approaches are presented.

2. Problems associated with the use of cobalt in SOFCs

The high coefficient of thermal expansion (CTE) of cobalt-containing perovskite materials is one of the most important disadvantages [21,22,28-32]. In addition, chemical stability of cobalt-containing cathode layers in long-term use is not at a satisfactory level either [33]. Since all these reduce the mechanical stability and cobalt is relatively expensive compared to other rare metals, the search for new cobalt-free cathode materials has begun in the last decade [34-42]. New cathode materials without the use of cobalt help decrease the coefficient of thermal expansion at intermediate temperatures. Replacement of Co by Cr in the cathode layer material brought about a significant reduction in the coefficient of thermal expansion (CTE). Notice that the CTE of LSCF=23.6×10^{-6} K^{-1} at 700°C and the CTE of LSFCr=20.9×10^{-6} K^{-1} at the same temperature [36]. Also, these materials can show high redox stabilities and very good catalytic activities in the oxidation of fuels which further ensures that they can be fabricated as anode and cathode in symmetrical SOFCs. Cobalt-based materials are therefore used in a smaller variety of applications which have led to an increase in the efforts for development of cobalt-free cathode materials.

There are also socioeconomic aspects for replacement of cobalt in SOFC materials. Bamana *et al.* studied cobalt mining in the Democratic Republic of the Congo [43]. They indicated that cobalt mining was accompanied by violence, food and water insecurity, substance abuse, and physical and mental health challenges. Moreover, Congolese people have lost their farmland and homes. Another study [44] showed that people living around the town of Kolwezi had much higher levels of cobalt in their urine and blood than people living in a nearby control area. That study reveals toxic harm to vulnerable communities due to cobalt mining. Although cobalt is a unique base metal used in many applications, its supply is dominated by a single country, the Democratic Republic of Congo (DRC), which produces about 60% of worldwide cobalt with no other country producing more than 6% [45,46]. Due to the high cost and price volatility associated with cobalt, manufacturers investigate alternatives to reduce or eliminate the need for cobalt in applications especially in batteries production [47,48]. For all those reasons, it is obvious that the currently existing cobalt supply chain is not sustainable and the use of cobalt in critical applications for daily life needs to be lowered [44,49].

3. Reversible Solid Oxide Fuel Cells (RSOFCs)

Both electrolysis and electricity generation processes can be performed using the same cell. When such cells are operated in SOFC mode, they produce electricity and heat by combining fuels such as H_2, natural gas, syngas with oxygen. When there is an electrical energy surplus, the device is operated in electrolysis mode and $H_2(g)$ is produced from water as shown in Figure 1. Here the hydrogen gas acts like a temporary energy storage environment. Reversible solid oxide fuel cells (RSOFCs) are a type of fuel cell that can operate in either a fuel cell mode, generating electricity from a fuel and an oxidant, or in an electrolysis mode, producing a fuel from an oxidant and a source of electrons. In fuel cell mode, RSOFCs can be used to generate electricity from a variety of fuels, including hydrocarbons, hydrogen, and alcohols, using oxygen as the oxidant. In electrolysis mode, RSOFCs can be used to produce hydrogen from water or to produce synthesis gases from carbon dioxide and water. It is considered one of their main advantages in renewable energy-based systems.

Symmetrical solid oxide fuel cells (SSOFCs) offer important advantages in terms of manufacturing, thermo-mechanical compatibility with cell components, and operational stability compared to traditional SOFCs which require at least two thermal steps for different electrode materials. This results in high cost and energy consumption so that by using two selected cathode materials as anode material, the fuel cell can be prepared symmetrically.

The most important function of the anode layer is to provide a coherent environment with sufficient catalytic activity for the oxidation of the fuel fed to the cell in SOFCs. In the SOEC anode layer, hydrogen is generated by using electrons fed from an external circuit and water as shown in Figure 1. The anode layer must have high ionic conductivity for the oxygen ions which flow through the electrolyte in the anode/electrolyte interface.

The most important function of the cathode layer in SOFC is to reduce the oxygen gas coming from outside to O^{2-}. In SOEC cathode layer, oxygen gas and electrons form by oxidation of O^{2-} ions which is supplied through the electrolyte originating from the anode layer. The anode and cathode layers of RSOFC have the same requirements: porous structure, higher ion-electron conductivity, chemical stability and thermal expansion compatibility. The electrolyte used in a symmetrical cell should fulfil the same requirements as that of traditional SOFCs. Although both LSFCr and LCFCr as layer materials are reported to perform well in both SOFC and SOEC modes in the literature [34-42], only a few techniques have been tried and still remain open for improvement on the production methods of these materials. Studies involving symmetrical fuel cell materials are recently increasingly published.

In Table 1 the SOFC and SOEC principle of operation mechanism is summarized. In SOFC, H_2 is used as fuel which is oxidized at the fuel electrode (anode) and electron is released. On the opposite side of the cell (cathode), however, oxygen molecule (O_2) is reduced to oxygen ions (O^{2-}). These oxygen ions rapidly pass through the electrolyte to the fuel electrode where they react with the hydrogen to form water vapor. In SOEC, on the other hand, H_2O is used as fuel. It is dissociated to O^{2-} and H_2. Oxygen ion migrates through the electrolyte and are oxidized to O_2 gas. Final water electrolysis products are O_2 and H_2 gases. When SOFC and SOEC are compared according to their efficiency, SOEC shows higher performance.

Kozokaro *et al.* [50] used density functional theory (DFT) to experimentally find suitable catalytic properties of $La_{0.3}Sr_{0.7}Fe_{0.7}Cr_{0.3}O_{3-\delta}$ for SOFCs. Addo *et al.* [51] studied the effect of Ni and/or GDC co-catalysis addition to LSFCr matrix by fabricating three types of symmetrical half cells onto a YSZ electrolyte coated with a GDC buffer layer and electrochemical impedance measurements of the

Table 1. Chemical Mechanism and Differences Between Solid Oxide Fuel Cell (SOFC) and Solid Oxide Electrolysis Cell (SOEC).

	Solid oxide fuel cell	**Solid oxide electrolysis cell**
Anode electrode	$H_2 \rightarrow 2H^+ + 2e^-$	$H_2O + 2e^- \rightarrow O^{2-} + H_2$
Electrolyte	O^{2-} ions migrates	O^{2-} ions migrates
Cathode electrode	$1/2O_2 + 2e^- \rightarrow O^{2-}$	$O^{2-} \rightarrow 1/2O_2 + 2e^-$
Net reaction	$H_2 + 1/2O_2 \rightarrow H_2O$	$H_2O \rightarrow 1/2O_2 + H_2$
Efficiency	50% to 60 %	90%

three types of symmetrical half cells are 1.54 $\Omega\cdot cm^{-2}$, 1.10 $\Omega\cdot cm^{-2}$ and 0.90 $\Omega\cdot cm^{-2}$ at 800°C. $Pr_{0.7}Ca_{0.3}Cr_{1-y}Mn_yO_{3-\delta}$ is a symmetrical electrode which employs Ca in A site. El-Himri *et al.* [52] obtained symmetrical SOFC whose structure is in the form of $PCCM_{0.4}$/ YSZ/$PCCM_{0.4}$ at 950°C in different weather conditions. Freeze-drying method was used to obtain $Pr_{0.7}Ca_{0.3}Cr_{1-y}Mn_yO_{3-\delta}$ (y = 0.2, 0.4, 0.6, 0.8) powder. Recently, Akkurt *et al.* [53], synthesized $La_{0.3}Sr_{0.7}Fe_{0.7}Cr_{0.3}O_{3-\delta}$ (LSFCr) cobalt-free cathode materials via electrospray deposition (ESD) method and Electrochemical Impedance Spectroscopy (EIS) measurements showed favorable ASR values of 0.22 $\Omega\cdot cm^{-2}$ at 700°C. The effects of different coating test conditions on the resulting coating structure and electrochemical performance was investigated.

Tong *et al.* [54], found that hybrid-catalyst-coated cobalt-free $(La_{0.6}Sr_{0.4})_{0.98}FeO_{3-\delta}$ (LSF) electrodes show very low polarization resistance of 0.017 $\Omega\cdot cm^{-2}$ at 750°C. This hybrid nanoengineered catalyst is made of $Ce_{0.85}Gd_{0.15}O_{2-\delta}$ (CGO) and Pr_6O_{11} nanoparticles via co-infiltration method. Another study by Tong and co-workers synthesized cobalt–free iron-based $BaCe_xFe_{1-x}O_{3-\delta}$ (BCF36, x = 0.36, 0.43, and 0.50) powders by sol-gel process [55]. Characterization of BCF36, BCF43 and BCF50 was done and a single cell was produced by a simple spray coating method. The electrochemical analysis was performed for these cathode materials which had different stoichiometric ratios. The polarization resistance values of BCF36 material was found to be 0.060 $\Omega\cdot cm^{-2}$ at 700°C. The reduction of the particle size could affect the electrochemical performance.

For the development of cobalt-free MIEC materials Tarutina *et al.* [56], fabricated a symmetrical membrane based on a $BaFe_{0.7}Zr_{0.2}Y_{0.1}O_{3-\delta}$ composition by a tape calendering method and studied the feasibility of the membrane for oxygen production. Kim *et al.* [57] studied $Ba_{1-x}Nd_xFeO_{3-\delta}$ based cathode material supported with NiO-YSZ anode material to make a cobalt-free perovskite material to be used in RSOFCs. Cathode material was doped with different amount of Nd^{3+} then electrochemical analysis was performed, 3% Nd^{3+} doped BFO was chosen as a good air electrode in RSOFCs. Martinez *et al.* [58] studied mixed ionic–electronic conducting perovskite-based oxides in symmetrical fuel cells (SFCs). The anode and cathode materials were the same as XSCoF ($X_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (X = Ba, La and Sm)) and LSCrM ($La_{0.75}Sr_{0.2}Cr_{0.5}X'_{0.5}O_{3-\delta}$(X′ = Mn, Fe and Al)) in fuel cell. The electrolyte materials were $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$ (LSGM). In symmetric SOFCs, the polarisation resistance (Rp) of the system LSCrM/LSGM/LSCrM was at the highest value of 16.7 $\Omega\cdot cm^2$, while the other system BSCoF/LSGM/LSCrM had the lowest, ~0.12 cm^2 at 1073 K.

Garcie *et al.* [59] studied titanium based nanocomposite symmetric electrode materials which are $(Sr_{0.7}Pr_{0.3})_{0.95}TiO_{3\pm\delta}$–$Ce_{0.9}Gd_{0.1}O_{1.95}$. The spray-pyrolysis method was used for depositing the solution on $Zr_{0.82}Y_{0.16}O_{1.92}$ electrolytes. These nanocomposite electrodes were achieved with polarization resistance near 0.48 $\Omega\cdot cm^2$ in two different atmospheres at 700°C.

The function of cathode and electrolyte materials is to transport charged particles between electrodes continuously and rapidly. Therefore, the development of electrolyte material is also important for RSOFCs at low-temperature. Shao and Haile *et al.* [60] fabricated symmetrical cell of BSCF|SDC($Sm_{0.2}Ce_{0.8}O_{1.9}$)|BSCF for RSOFCs operating at ≤ 500°C and the polarization resistance was 0.6 $\Omega\cdot cm^{-2}$. Zhou W *et al.* [61] reported that the $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) and $LaCoO_3$ (LC) oxide powders could be synthesized and a fuel cell be fabricated. They obtained resistance values for the cathodes at 600°C of 0.21 $\Omega\cdot cm^2$. Ding *et al.* [62] synthesized the $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF)+ Co_3O_4 composite cathode material with different stoichiometric ratios by spray deposition technique. Electrochemical measurements showed that the addition of the Co_3O_4 to the BSCF phase the area specific resistance decreased for this type of IT-SOFCs at 600°C. Lee *et al.*, [63] reported that $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) nanopowder was synthesized by Pechini method then BSCF-ScSZ (Sc_2O_3 stabilized zirconia) nanocomposite materials were fabricated to produce a symmetrical cell of BSCF-ScSZ|YSZ|BSCF-ScSZ. The polarization resistance differences of this nanocomposite symmetrical cell was quite high at 800°C and 850°C. The important aspect of all composite materials is they can exhibit better ionic transfer and stability than simple electrode materials.

Performances of cathode materials can be improved by: A site deficiency creation, A/B site cation substitution on perovskite structure and composite cathodes production.

4. A site deficiency

ABO_3-type perovskite oxides with the general formula ABO_3 (A=alkaline-earth or rare-earth metals and B=transition metals) are used as cathode materials due to their high catalytic activity for ORR and exceptional stability. An efficient method to create oxygen vacancy and change the electronic structure of perovskite is to introduce A-site deficiency which results in improved electrochemical catalytic capability. Every time an oxygen vacancy is produced, the transition metal's valence state and electronic structure change. The surface oxygen vacancies and oxygen migration energy can be altered by the A-site deficiencies in the perovskite materials, which can also reveal more active sites for ORR [64].

Ca element with a smaller ionic radius was added to the Sr element in the A region of the ABO_3 perovskite, thus creating $La_{0.3}Ca_{0.7}Fe_{0.7}Cr_{0.3}O_{2-\delta}$ (LCFCr) and a decrease in the thermal expansion coefficient (12.0 × 10^{-6} K^{-1} at 700°C). The difference between the thermal expansion coefficients of the cathode and GDC becomes smaller and the cells formed with these materials show improved stability in long-term tests. The polarization resistance of the symmetrical cell formed with $La_{0.3}Ca_{0.7}Fe_{0.7}Cr_{0.3}O_{2-\delta}$ (LCFCr) is also determined by both LSCF (0.18 $\Omega\cdot cm^{-2}$ at 800°C) and LSFCr (0.11 $\Omega\cdot cm^{-2}$ at 800°C) was observed to give better results (0.07 $\Omega\cdot cm^{-2}$ at 800°C) [65,66,67]. Chen *et al.* [68] fabricated symmetrical half-cell with $La_{0.3}Sr_{0.7}Fe_{0.7}Cr_{0.3}O_{3-\delta}$ electrode material that has open circuit polarization resistance of 0.25 $\Omega\cdot cm^{-2}$ at 750°C in air. Lü *et al.* [69] studied A-site deficient Fe-based double perovskite oxides $Pr_xBaFe_2O_{5+\delta}$. In that study, Pr-deficiency is shown to be an effective strategy to promote the electrochemical properties of $Pr_xBaFe_2O_{5+\delta}$. Rp values were 0.059, 0.085, 0.133, 0.226 and 0.449 $\Omega\cdot cm^2$ at 800, 750, 700, 650, 600°C, respectively.

$Pr_{0.7}Ca_{0.3}Cr_{1-y}Mn_yO_{3-\delta}$ was also studied as a symmetrical electrode material with Ca in A site. El-Himri *et al.* [52] studied alternative freeze-drying precursor method to achieve polycrystalline powders with 250 $mW\cdot cm^{-2}$ and 160 $mW\cdot cm^{-2}$ (at 950°C) under humidified H_2 and CH_4 gases, respectively. These were obtained with an assembled symmetrical SOFC with $PCCM_{0.4}$/YSZ/$PCCM_{0.4}$ structure.

Fu *et al.* [70] fabricated $Ln_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_{3-\delta}$ (LnSFC) cathode materials that exhibited structural change with increasing radius size of the lanthanide ions from cubic (Ln = PrSFC) to orthorhombic (Ln = NdSFC, SmSFC, and GdSFC) perovskite synthesized by sol-gel method. The LnSFC material and the SDC electrolyte has a good coherence with each other to form this solution screen-printed on dense electrolyte.

5. A/B site cation substitution

Electrical conductivity, catalytic activity, electrode-electrolyte compatibility, or thermal and mechanical stability qualities of materials need to be enhanced and improved that can be crucial for a variety of applications, the A- and/or B-site cations can be partially replaced. Although the fundamental methods for enhancing specific qualities are recognized, further research is still needed to show how physical and chemical properties depend on the elemental composition. A/B site cation substitution is crucial in this situation [71].

Susanto *et al.* [72] investigated that modification of the perovskite structure with the addition of the Cr element in the B side to be a composite cathode of $Sm_{0.5}Sr_{0.5}Fe_{0.8}Cr_{0.2}O_{3-\delta}$ (SSFC) using the solid-state reaction method. At a maximum of 7.32 $S\cdot cm^{-1}$ at 766°C, exceptional conductivity values related to the performance of the SSFC cathode are attained. $BaFeO_{3-\delta}$ (BFO) is popular to be used as cathode material, which has good oxygen ion conductivity and performs well in electrical conductivity due to its high oxygen vacancies for IT-SOFCs [73] because of these properties Wang *et al.* [74] synthesized cobalt–free Nd doped $BaFe_{0.9}Nb_{0.1}O_{3-\delta}$ (BFNb). The Rp values were analysed BFNb cathode on GDC electrolyte were 0.029 $\Omega\cdot cm^{-2}$ and 0.102 $\Omega\cdot cm^{-2}$ at 800°C and 700°C, respectively. Another study showed partial substitution of Fe by Zn to further enhance the electrical conductivity and thermal compatibility of $PrBaFe_2O_{5+\delta}$ (PBF). Zn doping remarkably improved the catalytic activity of the $PrBaFe_{1.9}Zn_{0.1}O_{5+\delta}$ (PBFZ) cathode [75].

In here, SOFC cobalt-free cathode materials were prepared through a sol–gel process such as copper doped $SrFe_{0.9-x}Cu_xMo_{0.1}O_{3-\delta}$ (SFCM, x = 0-0.2), $Pr_xBaFe_2\ O_{5+\delta}$ (Pr_xBF, x = 1.00, 0.97, 0.93, 0.90), $La_{1.5}Ba_{1.5}Cu_3O_{7\pm\delta}$ (LBCu) and $Ln_{0.5}Sr_{0.5}Fe_{0.9}Mo_{0.1}O_{3-\delta}$ (Ln = lanthanide; LnSFM) perovskites [69,76,77,78].

6. Composite cathodes

A composite cathode, which combines an electrolyte material with a cathode material, is one method for improving cathode performance because its electrochemically active area is dispersed throughout its volume, a composite cathode displays low activation polarisation [79]. Composite cathodes are used in solid oxide fuel cells (SOFCs) at moderate temperatures (600°C to 800°C) as the stand-alone normally performing electrodes and electrolytes combined in layersto get much better oxygen reduction reaction (ORR) kinetics. Thus, it is used as an important structure in the development of mixed electronic-ionic conductors and high-performance electrodes [80]. In the literature different cobalt-free composite cathode materials are tested at different temperatures. Abd Aziz *et al.* [81] created a composite cathode, $SrFe_{0.9}Ti_{0.1}O_{3-\delta}$ (SFT) combined with SDC and low area specific resistance (ASR) of 0.12 cm^2 was measured on the 9 layer of SFT, 1 layer of SDC composite cathode, which has a film thickness of 25.60 µm and indicated the cathode's successful operation [81]. As a new Sr and Cobalt-free composite cathode for solid-oxide fuel cells (SOFC), $La_{0.65}Ca_{0.35}FeO_{3-\delta}Gd_{0.2}Ce_{0.8}O_{2-\delta}$ (LCF-GDC) material is analysed at intermediate temperatures, with a low polarization resistance (Rp) value of 0.28 $\Omega\cdot cm^{-2}$ at 750°C [82]. The electrospinning approach was used to create a series of $La_{0.8}Sr_{0.2}Fe_{1-x}Cu_xO_{3-\delta}$ ($LSFCu_x$, x = 0.0-0.3) nanofiber cathodes with Rp is 0.674 $\Omega\cdot cm^{-2}$ at 650°C for intermediate-temperature solid oxide fuel cells (IT-SOFCs) [83]. As observed with these studies, the resistance was increased as the temperature was decreased. This is improved with the usage of different elements effectively. At 700°C, $BaCe_{0.2}Fe_{0.6}Pr_{0.2}O_{3-\delta}$ (BCFP) shows the lowest polarization resistance of 0.057 $\Omega\cdot cm^{-2}$ so that Pr doped $BaCe_{0.2}Fe_{0.8}O_{3-\delta}$ is a promising cobalt-free cathode material [84]. Liu *et al.* synthesized $La_{0.5}Ba_{0.5}Cu_xFe_{1-x}O_{3-\delta}$ ($0 \leq x \leq 1$) perovskite as a cathode via combustion method and used $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (BZCY) electrolyte. Cathode material had a good electrical conductivity and Rp of 0.068 $\Omega\cdot cm^{-2}$ at 700°C [85]. Another similar study is about Sc-doped $Sr_2Fe_{1.5}$-$Mo_{0.5}O_{6-\delta}$ (SFMSc) in which combustion process was used to successfully synthesize the material by partially substituting Mo in $Sr_2Fe_{1.5}$ -$Mo_{0.5}O_{6-\delta}$ (SFM) and also same BZCY electrolyte was used at the end and the cobalt-free cathode material showed good electrochemical performance [86]. Cobalt-free fluorine doped $Bi_{0.7}Sr_{0.3}FeO_{3-\delta-x}F_x$ oxides are synthesized as cathode catalysts. At 600°C, the optimized $Bi_{0.7}Sr_{0.3}FeO_{2.9-\delta}F_{0.10}$ ($BSFF_{0.10}$) cathode possesses a low polarization resistance of 0.12 $\Omega\cdot cm^{-2}$ [87].

Table 2 summarizes the works related to cathode materials production. The sintering temperature is important for the lattice structure of the powder. Cobalt-free cathode materials with different electrochemical performances can be obtained by employing different thermal treatment temperatures.

Table 2. A summary of the information gathered from recent literature about the powder synthesis method, sintering temperature, lattice structure, thermal expansion coefficient (TEC), polarization resistance (Rp) of various cobalt-free perovskite cathodes and electrolytes.

No	**Cathode**	**Powder synthesis method**	**Sintering temperature (°C)**	**Lattice structure**	**Electrolyte**	**Thermal expansion coefficient ($10^{-6}K^{-1}$)**	**Polarization resistance ($\Omega\cdot cm^{-2}$)**	**Power density ($W\cdot cm^{-2}$)**	**Ref.**
1	$La_{0.3}Sr_{0.7}Fe_{0.7}Cr_{0.3}O_{3-\delta}$ (LSFC)	Electrospray deposition	1400	-	$Ce_{0.9}Gd_{0.1}O_{3-\delta}$ (GDC)	-	0.22	-	53
2	($CGO + Pr_6O_{11}$) coated $(La_{0.6}Sr_{0.4})_{0.98}FeO_{3-d}$ (LSF)	Co- infiltration	650	-	$Zr_{0.82}Y_{0.16}O_{1.92}$ (YSZ)	-	0.02 (750°C)	1.57	54

Table 2. (Continued).

No	Cathode	Powder synthesis method	Sintering temperature (°C)	Lattice structure	Electrolyte	Thermal expansion coefficient ($10^{-6}K^{-1}$)	Polarization resistance ($\Omega\cdot cm^{-2}$)	Power density ($W\cdot cm^{-2}$)	Ref.
3	$BaCe_{0.36}Fe_{0.64}O_{3-\delta}$ (BCF36)	Combustion	1000	Cubic and orthorombic perovskite	$BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (BZCY)	-	0.06	1.53	55
4	$Ba_{0.97}Nd_{0.03}FeO_{3-\delta}$	Conventional solid-state reaction	1250	Cubic perovskite	$Zr_{0.82}Y_{0.16}O_{1.92}$ (YSZ)	18.50	0.08	0.44	57
5	$(Sr_{0.3})_{0.95}TiO_{3\pm\delta}-Ce_{0.9}Gd_{0.1}O_{1.95}$	Spray-pyrolysis	800	Cubic perovskite	$Zr_{0.82}Y_{0.16}O_{1.92}$ (YSZ)	-	0.50	0.35	59
6	$La_{0.3}Ca_{0.7}Fe_{0.7}Cr_{0.3}O_{3-\delta}$ +GDC	Combustion	1100	Perovskite	$Ce_{0.9}Gd_{0.1}O_{3-\delta}$ (GDC)	-	0.22 (800°C)	-	65
7	$La_{0.3}Sr_{0.7}Fe0_{.7}Cr_{0.3}O_{3-\delta}$ (LSFC-3)	Glycine nitrate process	1200	Perovskite	$La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM)	16.30	0.10 (800°C)	0.63	68
8	$Pr_{0.93}BF$	Sol-gel	950	Orthorombic and tetragonal perovskite	$Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC)	15.95	0.13	0.97	69
9	$Pr_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_{3-\delta}$	Sol-gel	950	Cubic perovskite	$Ce_{0.9}\,Sm_{0.1}O_{1.95}$ (SDC)	17.30	0.04 (800°C)	0. 36	70
	$Nd_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_{3-\delta}$			Orthorombic perovskite		17.19	0.09 (800°C)	0.31	
	$Sm_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_{3-\delta}$			Orthorombic perovskite		16.72	0.10 (800°C)	0.25	
	$Gd_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_{3-\delta}$			Orthorombic perovskite		12.89	0.16 (800°C)	0.10	
10	$Sm_{0.5}Sr_{0.5}Fe_{0.8}Cr_{0.2}O_{3-\delta}$	Solid state reaction	1000	Perovskite	SDC	4.70	-	-	72
11	$BaFe_{0.95}Zr_{0.05}O_{3-\delta}$ (BFZ)	Solid-state reaction	1250	Perovskite	SDC	-	0.02	-	73
12	$BaFe_{0.9}Nb_{0.1}O_{3-\delta}$	Solid-state reaction	1100	Tetragonal	$Ce_{0.9}Gd_{0.1}O_{3-\delta}$ (GDC)	-	0.10	-	74
13	$PrBaFe_{1.9}Zn_{0.1}O_{5+\delta}$ (PBFZ)	Self-ignition combustion	1000	-	$BaZr_{0.7}Ce_{0.2}Y_{0.1}O_{3-\delta}$ (BZCY)	12.98	0.518	0.513	75
14	$PrBaFe_{2}O_{5+\delta}$ (PBF)			-		16.29	0.97	0.313	
15	$SrFe_{0.7}Cu_{0.2}\,Mo_{0.1}O_{3-\delta}$ (SFCM0.2)	-	1000	Cubic perovskite	$La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM)	21.8	0.155	0. 342	76
16	$La_{1.5}Ba_{1.5}Cu_{3}O_{7\pm\delta}$	Sol-gel	975	Cubic perovskite	$La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM)	15.5	0.041	0.458 (750°C)	77
17	$La_{0.5}Sr_{0.5}Fe_{0.9}Mo_{0.1}O_{3-\delta}$	Sol-gel	1300	Rhombohedral	$Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC)	14.9	0.211	0.269	78
	$Nd_{0.5}Sr_{0.5}Fe_{0.9}Mo_{0.1}O_{3-\delta}$					14.4	0.446	0.261	
	$Pr_{0.5}Sr_{0.5}Fe_{0.9}Mo_{0.1}O_{3-\delta}$					14.0	0.469	0.233	
18	$9SrFe_{0.9}Ti_{0.1}O_{3-\delta}-1Ce_{0.8}Sm_{0.2}O_{1.9}$ (9SFT-1SDC)	Print screen	1250	-	$Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC)	-	0.12 (800°C)	-	81
19	$BaCO_3$ modified $La_{0.8}Sr_{0.2}FeO_{3-\delta}$-$Gd_{0.2}Ce0_{.8}O_{2-\delta}$ ($BaCO_3$LSF-GDC)	Modified Pechini	1000	Orthorhombic perovskite	YSZ	-	0.21	0.858	82
20	$La_{0.8}Sr_{0.2}Fe_{0.8}Cu_{0.2}O_{3-\delta}$ ($LSFCu_2$)	Electrospinning	800	Perovskite	$Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC)	-	0.674 (650°C)	0.362	83
21	$BaCe_{0.2}Fe_{0.6}Pr_{0.2}O_{3-\delta}$ (BCFPr)	Sol-gel	1300	Orthorhombic	$BaCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-\delta}$ (BCZY)	15.6	0.057	0.562	84
22	$La0_{.5}Ba_{0.5}Cu_{0.5}Fe_{0.5}O_{3-\delta}$ (LBCF55)	Combustion	600-920	Perovskite	$BaCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-\delta}$ (BCZY)	16.12	0.068	0.820	85
23	Sc-doped $Sr_2Fe_{1.5}$-$Mo_{0\cdot5}O_{6-\delta}$ (SFMSc)	Combustion	800	-	$BaCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-\delta}$ (BCZY)	-	0.043	1.258	86
24	$Bi_{0.7}Sr_{0.3}FeO_{2.9}F_{0.10}$ (BSFF0.10)	Combustion	1000	cubic perovskite	$Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC)	13.7	0.12 (600°C)	0.837 (600°C)	87

7. Conclusion

New research efforts are in progress to reduce the use of fossil fuels in energy production. As nations and businesses around the globe look for ways to reduce their carbon footprint and transition to more sustainable energy sources, there has been a rise in interest in hydrogen technologies in recent years. Concerns about climate change, improvements in renewable energy technologies, and rising energy consumption worldwide have all contributed to this interest. Hydrogen is a highly sustainable fuel source that is gaining significant attention in the field of renewable energy. Unlike traditional fossil fuels such as oil and gas, hydrogen is a clean and abundant resource that can be produced from a variety of sources including water, biomass, and waste.

Researchers are working hard to develop new and innovative ways to produce, store, and use hydrogen, including the development of reversible SOFCs. These fuel cells have the potential to generate electricity from hydrogen and other fuels, and can also convert excess electricity into hydrogen for storage and later use. The integration of reversible operation in SOFCs has the potential to revolutionize the energy sector by providing a more sustainable and efficient source of power. Among all hydrogen technologies, RSOFCs are one of the best candidates for producing and converting back hydrogen into electricity even though it is not fully commercialized yet.

Research concerning all aspects of SOFC has constantly intensified over the years with special focus on developing cathode materials especially. As expected these developments also contributed to the RSOFC systems. The main focus of this article is to review studies on cobalt-free RSOFCs. The development of cobalt-free cathode materials still continues to be popular due to the great moral problems experienced in cobalt mines, cobalt is a rare and expensive metal that is not readily available in large quantities, which can limit the scalability and commercial viability of SOFC technology that relies on cobalt-based cathode materials. Besides, the use of cobalt in SOFCs can have negative environmental impacts, as the mining and processing of cobalt can result in significant environmental degradation, including deforestation, air pollution, and water contamination. Addition of socio-economical issues, there is also technical problems that need to be overcome due to the usage of cobalt.

Fuel cells are operated at high temperatures that affect the life and stability of the system. Therefore, studies in the field of cobalt-free cathode materials with high performance in IT-SOFC have come into prominence. In addition, the incompatibility of the thermal expansion coefficient of the cobalt based cathode materials with the electrolyte layer at intermediate temperatures also creates big problems in terms of complatibility of cathode materials. Therefore, the development of cobalt-free cathode materials has become a critical research focus in the field of reversible SOFCs. In order to eliminate these burdens, new innovations take place in the literature day by day. These studies aim to design a porous electrode structure with long-term stability, improved kinetics of oxygen reduction by changing the composition and microstructure of the cathode materials in order to eventually increase the performance of the cathode materials. Promising works on electrode materials especially cobalt-free cathode materials are observed at an accelerating pace. Furthermore, there is a great advantage that cobalt-free cathodes can also be used as anode in RSOFCs. The subject of cobalt-free RSOFCs is a promising research area open to further development and continued research and development in this area is crucial in advancing the use of SOFCs as a reliable, sustainable, and efficient source of energy.

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