

Review

# B-Site Metal (Pd, Pt, Ag, Cu, Zn, Ni) Promoted $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ Perovskite Oxides as Cathodes for IT-SOFCs

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Abstract: Perovskite oxides  $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$  (LSCF) have been extensively investigated and developed as cathode materials for intermediate temperature solid oxide fuel cells (IT-SOFCs) due to mixed ionic-electronic conductivity and high electrooxygen reduction activity for oxygen reduction. Recent literature investigations show that cathode performances can be improved by metal surface modification or B-site substitution on LSCF. Although the specific reaction mechanism needs to be further investigated, the promoting effect of metal species in enhancing oxygen surface exchange and oxygen bulk diffusion is well recognized. To our knowledge, no previous reviews dealing with the effect of metal promotion on the cathodic performances of LSCF materials have been reported. In the present review, recent progresses on metal (Pd, Pt, Ag, Cu, Zn, Ni) promotion of LSCF are discussed focusing on two main aspects, the different synthesis approaches used (infiltration, deposition, solid state reaction, one pot citrate method) and the effects of metal promotion on structural properties, oxygen vacancies content and cathodic performances. The novelty of the work lies in the fact that the metal promotion at the B-site is discussed in detail, pointing at the effects produced by two different approaches, the LSCF surface modification by the metal or the metal ion substitution at the B-site of the perovskite. Moreover, for the first time in a review article, the importance of the combined effects of oxygen dissociation rate and interfacial oxygen transfer rate between the metal phase and the cathode phase is addressed for metal-promoted LSCF and compared with the un-promoted oxides. Perspectives on new research directions are shortly given in the conclusion.

Keywords: IT-SOFCs; cathode; LSCF; metal promotion

# 1. Introduction

In the last 20 years, solid oxide fuel cells (SOFCs), whose typical schematic diagram is shown in Figure 1, have been world-wide investigated since they can utilize various fuels to generate energy effectively in an environmental friendly way. For the moment, the commercialization of conventional SOFCs using the state-of-art strontium-doped lanthanum manganite La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3-δ</sub> (LSM) perovskite cathodes is restricted by the high operating temperature, around 1000 °C [1–3]. Lowering the operating temperature to about 600 °C–800 °C, the use of a wide range of materials for cell components would be allowed favoring an extensive commercialization of SOFC.



**Figure 1.** Schematic diagram of a solid oxide fuel cell (SOFC). (Reprinted with permission from [3], 2008, Springer Science+Business Media, LLC).

However, poor cell performance resulting mainly from the decrease in cathode kinetics becomes the biggest problem for further applications of the so-called intermediate temperature solid oxide fuel cells (IT-SOFCs). Thus, development of novel cathode materials with high electrooxygen reduction activity and stability becomes one of the major challenges in IT-SOFCs technology [4–6].

Mixed ionic and electronic conductive (MIEC) perovskite oxides,  $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$  (LSCF) [6], have attracted considerable attentions for several applications including oxygen sensors, oxygen separation membranes, cathode current-collecting materials and so on [7–10]. LSCF oxides are also promising candidates as IT-SOFCs cathodes due to excellent activity in the oxygen reduction at relative low temperature and due to the excellent ion/electron transportation properties.

The La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub> is the most widely studied composition for its proper chemical stability, electrical conductivity, oxygen reduction activity and thermal expansion coefficient (TEC) [11–18]. Oxygen reduction performances higher more than five orders of magnitude than that of LSM materials

at 900 °C are reported [19]. A comparison among La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3- $\delta$ </sub> (LSM), Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3- $\delta$ </sub> (BSCF), Sm<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3- $\delta$ </sub> (SmSC) and La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3- $\delta$ </sub> (LSCF) regarding their chemical stability, electrical conductivity, oxygen reduction activity and polarization resistance showed that LSCF was the most promising cathode material and the maximum power density (MPD) of the cell using LSCF as cathode was twice than that using LSM [20].

The applicability of LSCF as IT-SOFC cathodes is strongly dependent on the chemical composition. Usually, the oxide ion conductivity can be increased by increasing the oxygen vacancies content. The highest theoretical conductivity expected by substituting La by Sr would be at x = 0.5. For this composition the maximum oxygen vacancy content takes place to charge compensate the material. Moreover, at the B-site the oxidation to some  $\text{Co}^{3+}(\text{Fe}^{3+})$  species to  $\text{Co}^{4+}(\text{Fe}^{4+})$  may also occur [6]. However, typically, the vacancy formation is the lowest energy process and, therefore, the favorite.

While the increase of ionic conductivities is more influenced by Sr concentration at the A-site of LSCF, the increase of the electronic conductivities is affected by Fe and Co concentration at the B-site.

Moreover it has been reported that a small A-site deficiency, such as for La<sub>0.58</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3- $\delta$ </sub> (L58SCF) had a particularly positive effect on the cell performance [16]. The measured current densities of cells with this A-site deficient cathode L58SCF, were as high as 1.76 A cm<sup>-2</sup> at 800 °C and 0.7 V, which is about twice the current density of cells with (La,Sr)MnO<sub>3</sub>/yttrium-stabilized zirconia (LSM/YSZ) composite cathodes [16].

Some efforts have been focused on the application of porous LSCF in order to supply high active surface area which is favorable for charge-transfer in oxygen reduction process [21–24]. However, the control of microstructure is supposed to be limited by the high temperature sintering step applied in the conventional fabrication of SOFCs. One possible strategy is to mix LSCF with the electrolyte gadolinia-doped ceria (GDC). It is reported that after infiltration with ionic conductive GDC, the microstructure stability, the ionic conductivity, the oxygen reduction activity as well as the adhesion to electrolyte of LSCF cathode could be improved [25–31]. For instance, the polarization resistance of La<sub>0.8</sub>Sr<sub>0.2</sub>Co<sub>0.5</sub>Fe<sub>0.5</sub>O<sub>3- $\delta$ </sub>-GDC composite decreased to 1.6  $\Omega$  cm<sup>2</sup> at 650 °C [31], and that of La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3- $\delta$ </sub>-GDC, fabricated by impregnation, reached values as low as 0.24  $\Omega$  cm<sup>2</sup> at 600 °C. Such improvement was mostly due to the formation of nano-scale (~50 nm) LSCF networks [25].

In the last few years, there have been huge interests in the cathode performance of LSCF modified at the B-site with additional metal species. Experiments have been carried out on noble metals, such as Pd [31–33], Ag [34–39], Pt [38–41] and as well on low-cost transition metals, Cu [38,39,42] Zn and Ni [43]. Although the specific mechanism of metal promotion is still under investigation, previous studies have shown that metal promotion promotes the oxygen electro-catalytic reduction and influences the TEC value, implying great prospective for such materials as IT-SOFC cathodes. To our knowledge, no previous review focused on the B-site metal promotion effect of LSCF cathodes.

The aim of this work is to provide an overview of present research progress in this field focusing on the synthesis approaches and the promotion effects on the oxygen reduction activity of the metal (Pd, Pt, Ag, Cu, Zn, Ni) promoted LSCF cathodes for oxygen reduction. The results are compared with noble metals promoted LSM cathodes. Some perspectives on new research trends are given in the conclusion.

#### 2. Metal Promotion: Approaches and Effects

### 2.1. Cathodic Reactions over LSCF Material

In order to understand the mechanism of metal promotion, it is necessary to introduce the elementary cathodic reactions over LSCF material. The mainly electrochemical reaction on IT-SOFC cathodes is the oxygen reduction reaction (ORR), as described below:

$$\frac{1}{2}$$
 O<sub>2</sub> (gas) + 2 e<sup>-</sup> (cathode) = O<sup>2-</sup> (electrolyte)

Several steps are involved, such as oxygen adsorption-dissociation, oxygen surface diffusion and oxygen bulk diffusion, as it is shown in Figure 2. The former two stages are referred to as oxygen surface exchange process. It is now well established that at low operating temperature, the polarization resistance is the main reason that contributes to the power loss in IT-SOFCs. For LSCF cathodes, both surface and bulk diffusion processes play important roles, as it has been demonstrated experimentally by Jiang who investigated O<sub>2</sub> reduction reaction over LSCF cathode at temperatures from 700 to 900 °C in air with and without the presence of gaseous Cr species [19]. However, by using dense thin films of La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3-6</sub> prepared by pulsed laser deposition and standard photolithographic techniques, it has been revealed that the electrochemical resistance, measured at low-temperature (425–550 °C) and/or at zero or small dc (direct current) bias, is dominated by the oxygen exchange reaction at the surface of the electrode, with minor contributions from the electrode/electrolyte interface and the ohmic resistance of the electrolyte [44,45].

Three phase boundary (TPB), that is the region of contact between gaseous oxygen, cathode and electrolyte, plays a significant role in determining cathode performances by affecting possible ORR pathways. More than 20 years ago the importance of oxygen exchange kinetics in determining the magnitude of cathode resistivity values has been emphasized. More recently, a detailed quantitative interpretation of the behavior of porous mixed electrodes has been provided with integrates information about the various macroscopic pathways for the cathodic reduction of oxygen, such as surface exchange and bulk diffusion [46].



**Figure 2.** Schematic illustration of the two possible oxygen incorporation paths in  $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$  (LSCF) cathode.

Two possible pathways for ORR over LSCF cathodes are illustrated in Figure 2, surface pathway and bulk pathway. In the surface path, oxygen molecules dissociatively adsorb on the surface, get partially reduced, diffuse to the TPB, become fully reduced and get incorporated into the electrolyte. In the bulk pathway, oxygen molecules dissociatively adsorb on the surface, are fully reduced and incorporated as  $O^{2-}$  into the LSCF, diffuse through the bulk and get transferred into the electrolyte.

## 2.2. Metal Promotion

## 2.2.1. LSCF Surface Modification

Noble metal nanoparticles are well known to activate oxygen and to promote oxidation reactions. The dispersion of metal particles on the surface of LSCF enhances the cathode properties, combining the advantages of both noble metals and perovskite materials. In fact, most research for metal promotion is focused on this direction, herein called surface modification. It should be pointed out that since LSCF-GDC composites are one of the main subjects in IT-SOFC cathode field, surface modification is often carried out on LSCF-GDC. The influence on cathode properties coming from GDC and metal species interactions is rarely mentioned in the literature. Only few examples are reported. Wang *et al.* [35] studied the properties of a La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3</sub>-Ce<sub>0.8</sub>Gd<sub>0.2</sub>O<sub>1.9</sub>-Ag cathode on a Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>1.9</sub> electrolyte. The electrode consisted of a porous layer of La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3</sub>-Ce<sub>0.8</sub>Gd<sub>0.2</sub>O<sub>1.9</sub>-GO<sub>2</sub>O<sub>1.9</sub> (30 wt.%) and a layer of Ag particles coated on the surface. The Ag coating was used to improve the oxygen exchange reaction activity.

The synthesis approach has great effect on the catalytic performance of metal particles by dominating the microstructure and crystallinity effects. Hence, it becomes one of the main factors that must be considered in discussions of surface modification. LSM modification by noble metals is also reported in the literature and hereinafter an example is reported for comparison with LSCF systems.

The addition of Pd, Ag, or Pt to a LSM cathode was described by using four different routes [47]. Infiltration of cathodes with a Pd solution, deposition of Pt on the electrolyte surface, mixing of La<sub>0.65</sub>Sr<sub>0.30</sub>MnO<sub>3</sub> (LSM) and YSZ cathode powders with different metal precursors (Pt and Pd black, Pd on activated carbon, Ag powder, Ag<sub>2</sub>O, Ag acetate, Ag citrate, Ag<sub>2</sub>CO<sub>3</sub>, colloidal Ag, AgNO<sub>3</sub>), and synthesis of LSM powder with the addition of AgNO<sub>3</sub>.

Similarly to LSM, a widely used approach in LSCF surface modification is the impregnation or infiltration method, as recently reviewed [2]. Typically, metal precursors, usually metal nitrates aqueous solutions, are infiltrated into LSCF or LSCF/GDC backbones and decomposed into metal or metal oxide dispersed on the surface of LSCF after calcination treatment at around 800 °C. Figure 3 shows the SEM images after fuel cell testing of LSCF before and after Pd impregnation. It can be clearly seen that after impregnation, very fine metal particles can be formed and homogeneously dispersed on the surface of LSCF and even after fuel test no remarkable damage was found in the microporous structure. Experiments on perovskites modified by Ag, Pt and Cu confirmed that the impregnation method is effective for surface modification. Nevertheless, the dispersion of metal is hard to control. Usually, ethylene glycol and citric acid are used, the so called complex-polymerization method [34] and a multitude of repeated infiltration step is required in order to fill enough metal into LSCF backbone. However, due to the low specific surface area typical of perovskites and due to the sintering effects

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during the calcination process, metal particles tend to agglomerate, affecting the catalytic property and also leading to LSCF pore clogging [7,34].

The infiltration of porous La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3</sub> (LSCF) electrodes with AgNO<sub>3</sub> solutions in citric acid and ethylene glycol in order to deposit about 18 wt.% Ag fine particles into LSCF resulted in the enhancement of the power density of about 50% [36].

Most recently, Jun *et al.* [37] reported the application of plasma method technique to deposit nano-sized Ag on La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.3</sub>Fe<sub>0.7</sub>O<sub>3-δ</sub>. Experimental results showed that Ag nanoparticles were well attached onto LSCF and strong physical linkage between Ag and LSCF was observed by FT-IR spectroscopy which can prevent agglomeration of Ag nanoparticles during heat treatment.

Huang and Chou [39] added by impregnation Pt, Ag or Cu (2 wt.% with respect to LSCF) to La<sub>0.58</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub> (LSCF)-GDC used as cathode and investigated the effect of metal on O<sub>2</sub> dissociation and interfacial O transfer rates. LSCF and GDC powders were mixed at a ratio of LSCF/GDC of 100:50 in weight and designated as LSCF-50GDC. H<sub>2</sub>Pt(OH)<sub>6</sub>, AgNO<sub>3</sub> and Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O solution, were used as precursors, respectively. The metal-added LSCF-GDC composite was designated as LSCF-50GDC-2Cu and so on. After calcinations at 800 °C, Pt and Ag were in metallic state, while Cu was as oxide. It was found that Cu addition led to the best SOFC performance [39].

In order to develop a cathode for reduced-temperature solid oxide fuel cells, cermetting effect of LSCF with Pt was investigated [41]. However, the obtained cathode activity was only an order of 0.5 S/cm<sup>2</sup> at 973 K. Electrochemical results suggested that Pt has both enhancing and obstructing effects. Based on SEM observation, the main reason of these controversial results was due to poor porosity and narrow surface area determined by the high sintering temperature.

Recently, Shin *et al.* [48] found that after current conditioning, the cathode performance of LSM could be enhanced. As confirmed by SEM and TEM images, the deposition of vaporized Pt species from a current collector at the TPB resulting from the oxygen partial pressure difference was responsible for the enhancement. Similar effect was reported on LSCF, suggesting a possible approach for metal surface modification.



**Figure 3.** SEM pictures of fractured cross sections of (**a**) pure LSCF; (**b**) PdO-impregnated LSCF electrodes after fuel cell testing. (Reprinted with permission from [31], 2009, Elsevier).

#### 2.2.2. Metal Ion Substitution at the B-Site of the Perovskite

It is well known for LSCF oxides that the increase of the electronic conductivities is strongly influenced by Fe and Co concentration at the B-site [6]. Moreover, LSCF are reported to be more reactive for oxygen reduction than  $La_{1-x}Sr_xCoO_{3-\delta}$  (LSC) or  $La_{1-x}Sr_xFeO_{3-\delta}$  (LSF) [49–52].

Crystal structure, thermal expansion, and electrical conductivity were studied for the system La<sub>0.8</sub>Sr<sub>0.2</sub>Co<sub>1-y</sub>Fe<sub>y</sub>O<sub>3</sub> with  $0 \le y \le 1$  as function of Co/Fe ratio and temperature, in air [51]. The electrical conduction mechanism was attributed to the adiabatic-hopping of p-type small polarons. At high temperatures, oxygen deficiency caused lattice expansion and diminished the electrical conductivity. The observed temperature dependence of the Seebeck coefficient was attributed to changes in carrier concentration caused by a thermally excited charge disproportionation of Co<sup>3+</sup> ions and by the ionic compensation of the Co/Fe ratio was interpreted using a two-site hopping and the site-percolation model. It was suggested that a preferential electronic compensation of Fe ions over Co ions may occur in this system [51].

On this basis partial substitution of Co or Fe component at LSCF B-site with a third metal, with redox properties, is supposed to be effective for further cathode promotion.

The solid state reaction method has been used in the synthesis of perovskites substituted at the B-site by Cu, Zn and Ni [42,43]. In such method, high purity metal oxide powders in stoichiometric amounts are used as the starting materials and solid state reaction takes place after long term ball milling and treatment at high temperature. Solid state reaction process is simple and low cost. It provides great homogeneity and leads to direct interaction between the metal and the lattice of LSCF crystalline phase, since the metal species participate in LSCF formation process. However this approach has been found to be time and energy consuming. Furthermore, the crystalline phase and physical properties of the resulting LSCF perovskites depend critically on the experimental parameters used, thus reproducibility problems may occur and it results difficult to compare materials prepared in different laboratories.



Figure 4. XRD patterns of  $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ ,  $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.7}Cu_{0.1}O_{3-\delta}$  and  $La_{0.6}Sr_{0.4}Co_{0.1}Fe_{0.8}Cu_{0.1}O_{3-\delta}$  powders calcined at 1000 °C for 4 h. (Reprinted with permission from [42], 2011, Elsevier.).

Wang *et al.* [42] found that during the synthesis of LSCF-Cu by solid state reaction, Cu content exceeding 30% of B-site ions will trigger the formation of the second phase of CuO, while with lower content, no second phase can be found by X-Ray Diffraction (XRD) analysis. In Figure 4 is shown the XRD pattern of (LaSr)(CoFeCu)O<sub>3-δ</sub> synthesized by solid state reaction after calcination at 1000 °C for 4 h. A rhombohedrally distorted structure was formed without second phase, except for slightly increase of c/a ratio, implying Cu atoms substitute into LSCF B-site without impacting its structure [42]. The successful synthesis of La<sub>0.6</sub>Sr<sub>0.4</sub>(Co<sub>0.18</sub>Fe<sub>0.72</sub>X<sub>0.1</sub>)O<sub>3-δ</sub> (x = Cu, Zn and Ni) by solid oxide reaction was also reported elsewhere [43].



**Figure 5.** The fitting extended X-ray absorption fine structure (EXAFS) data of the samples LSCF0.2-Pd (B), LSCF0.8-Pd (D) and Pd oxide. (Reprinted with permission from [53], 2014, Royal Society of Chemistry).

Some of us have recently reported the first example of synthesis by one pot citrate method of La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.8</sub>Fe<sub>0.17</sub>Pd<sub>0.03</sub>O<sub>3- $\delta$ </sub> (LSCF02-Pd) and La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.77</sub>Pd<sub>0.03</sub>O<sub>3- $\delta$ </sub> (LSCF08-Pd) perovskites as possible cathode materials [53]. The local environment of Pd was investigated in details. Extended X-ray absorption fine structure (EXAFS) spectroscopy showed a very short B-site Pd-O distance of about 1.9 Å which is definitely different from the shortest Pd-O distance in palladium oxide (2.02 Å), pointing to a high Pd oxidation state in LSCF-Pd (Figure 5). Further studies showed that a Pd atomic fraction of 45% in LSCF02-Pd and of 62% in LSCF08-Pd, respectively, is arranged at the B- site of the perovskite as Pd<sup>4+</sup> and the rest Pd metal clusters of about 2 nm were embedded into the matrix and strongly interact with the bulk [53]. The results indicated that even with low metal content (such as 0.03 molar fraction) only partially insertion into the lattice can be achieved and the extent of the substitution may have great relationship with the composition of B-site or the dopant metal radius [38,39,43]. The main effect of Pd insertion into the lattice of the perovskite was the formation of bulk oxygen vacancies that increased oxygen chemisorption properties of such materials.

## 2.3. Cathode Performances

Hwang *et al.* investigated symmetrical electrochemical cells with various electrodes, La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub>, (LSCF), LSCF-(Gd<sub>0.2</sub>Ce<sub>0.8</sub>O<sub>2</sub>) GDC, LSCF-platinum (Pt) and LSCF-GDC-Pt [40]. Both the LSCF-GDC and LSCF-Pt composite electrodes performed better than the LSCF electrode for oxygen reduction. The polarization resistance was significantly reduced in the case of the composite electrodes. The incorporation of Pt particles in the LSCF electrode was found to be effective over the entire temperature range for which measurements were taken. It seems that fine platinum particles, incorporated into LSCF via chemical precipitation technique, might accelerate the oxygen adsorption at high temperature. In Figure 6, the impedance spectra, measured at 700 and 500 °C, in 20% oxygen atmosphere, taken for the LSCF and LSCF-Pt composite electrodes are shown. The addition of Pt was found to be very effective at 500 °C, as well as at 700 °C. An interesting feature is that the polarization resistance decreased with decreasing Pt content in the case of the LSCF-Pt composite electrode. At 500 °C, the polarization resistance of the LSCF-0.5 vol% Pt composite electrode was nearly one fifth of that of the LSCF electrode. In conclusion, a small amount (0.5 vol%) of Pt was found to be sufficient to reduce the polarization resistance of the LSCF.



**Figure 6.** Impedance spectra of LSCF and LSCF-Pt (0.5 and 1 vol %) composite electrodes at 700 °C (**left**) and 500 °C (**right**). (Reprinted with permission from [40], 2005, Elsevier).

 $Cu^{2+}$  ions doped La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3</sub>- $\delta$  cathodes were prepared by Wang and coworkers using solid state reaction method [42]. The electrochemical performances of the cells fabricated with such cathodes are shown in Figure 7. The maximum electrical conductivities of Cu-doped LSCF discs are higher than that of LSCF. It is evident that the doping of Cu<sup>2+</sup> ions in LSCF is beneficial to the electrochemical performance of the cells.

Some representative electrochemical results in terms of MPD and AC impedance values evaluated from the area specific resistance (ASR) are summarized in Tables 1 and 2 for metal substituted LSCF perovskites, focusing on the synthesis method, metal type and content.

In general, it can be concluded that both surface modification and B-site substitution can improve cell performances by decreasing cathode resistance, especially the polarization resistance at low temperature. As above mentioned, B-site substitution leads to higher interaction between metal and LSCF lattice, hence may induce better promotion effect than surface modification.

Although Cu, Zn, Ni and Pd substituted LSCF have been successfully synthesized, only few reports investigating cell performances of substituted LSCF have been reported. Most researches dealing with

Cu surface modification focus the attention on the elementary properties of the modified cathodes and, as far as we know, no systematic comparison on different synthesis approaches has been reported. Interestingly, Huang *et al.* [38,39] investigated the cathodic property of 2 wt.% Cu, Pt and Ag impregnated LSCF and LSCF-GDC composites respectively, despite of better catalysis activity of Pt and Ag, Cu infiltrated samples showed the best property as a function of Cu content, negative effect is also reported. In order to clarify the effect of synthesis approaches, the metal species as well as the different metal content we focus on the conclusion of promotion mechanism in this work.



**Figure 7.** Nyquist plots of electrochemical impedance spectra of the single cells containing La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3- $\delta$ </sub>, La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.7</sub>Cu<sub>0.1</sub>O<sub>3- $\delta$ </sub> and La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.1</sub>Fe<sub>0.8</sub>Cu<sub>0.1</sub>O<sub>3- $\delta$ </sub> cathodes measured at (**a**) 650 °C and (**c**) 550 °C and I–V curves and the corresponding power densities of the anode supported single cells with various cathodes measured at (**b**) 650 °C and (**d**) 550 °C. (Reprinted with permission from [42], 2011, Elsevier).

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Table 1. Summary of rec	cent results on meta	- substituted LSCF	perovskites:	synthesis ap	pproach, 1	metal c	content an	d AC	impedance	values
measured at different temp	peratures.									

Entry	Composites	Synthesis approach	Metal content	EIS Measurement T (°C)	AC Impedance ( $\Omega$ cm <sup>2</sup> )	Reference	
1	$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$	-	-	530	0.63	[36]	
2	$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$	-	-	700	< 0.15	[33]	
3	$La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$	-	-	800	3.86	[38]	
4	$La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ -50GDC	-	-	800	5.54	[39]	
5	$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}-Ag$	IMP <sup>a</sup>	18 wt.%	530	0.46	[36]	
6	$La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}-Ag$	IMP	2 wt.%	800	1.9	[38]	
7	$La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}GDC\text{-}Ag$	IMP	$10-15 \text{ mg cm}^{-2}$	600 700	0.9 0.23	[35]	
8	$La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ -50GDC-2Ag	IMP	2 wt.%	800	6.66	[39]	
9	$La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}-Cu$	IMP	2 wt.%	800	1.22	[38]	
10	$La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ -50GDC-2Cu	IMP	2 wt.%	800	5.85	[39]	
11	$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.7}Cu_{0.1}O_{3-\delta}$	ST <sup>b</sup>	2.86 wt.% <sup>c</sup>	700	<0.1	[42]	
12	$La_{0.6}Sr_{0.4}Co_{0.1}Fe_{0.8}Cu_{0.1}O_{3-\delta}$	ST	2.87 wt.% <sup>c</sup>	550	~0.2	[42]	
13	$La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}-Pt$	IMP	2 wt.%	800	3.41	[38]	
1.4	La Sr Ca Ea O Dt	IMP	0.5 vol%	700	~0.025	[40]	
14 $La_{0.6}$	La0.6510.4C00.2Fe0.8O3-8-Ft			500	~3	[40]	
15	$La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ -50GDC-2Pt	IMP	2 wt.%	800	12.1	[39]	
16	$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}$ -Pd	IMP	$7.5 \text{ mg cm}^{-2}$	700	<0.05	[33]	
	La Sr Ca Fa O d	IMP	1 wt.%	800	0.155 <sup>d</sup>	[32]	
17 La				750	0.193 <sup>d</sup>		
	La0.58510.4C00.2 Fe0.8O3-8-PU			700	0.247 <sup>d</sup>		
				650	0.468 <sup>d</sup>		
18	$La_{0.8}Sr_{0.2}Co_{0.5}Fe_{0.5}O_{3-\delta}-Pd$	IMP	$1.2 \text{ mg cm}^{-2}$	750	0.22	[31]	
19		IMP	1 wt.%	800	0.169 <sup>d</sup>	_	
	Las coSta (Cos oFee oOs o Ph			750	0.204 <sup>d</sup>	[32]	
	La <sub>0.58</sub> SI <sub>0.4</sub> C0 <sub>0.2</sub> Fe <sub>0.8</sub> O <sub>3-8</sub> -Kn			700	0.261 <sup>d</sup>	-	
				650	0.468 <sup>d</sup>		

<sup>a</sup> Samples prepared by the impregnation (IMP) method; <sup>b</sup> Samples prepared by the solid state (ST) reaction. Metal content is with respect to LSCF; <sup>c</sup> Metal content calculated from the given composition; <sup>d</sup> AC impedance evaluated from ASR.

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Entry	Cell anode/Electrolyte(/interlayer)/cathode	<i>T</i> (°C)	MPD (Wcm <sup>-2</sup> )	Reference	
1	Ni-YSZ <sup>a</sup> /YSZ/GDC/La <sub>0.6</sub> Sr <sub>0.4</sub> Co <sub>0.2</sub> Fe <sub>0.8</sub> O <sub>3-δ</sub>	630	0.16	[36]	
2	N: CDC/CDC/La Sr Ca Fa O	530	0.32	[36]	
Z	NI-GDC/GDC/La <sub>0.6</sub> S1 <sub>0.4</sub> C0 <sub>0.2</sub> Fe <sub>0.8</sub> O <sub>3-δ</sub>	580	0.51	[30]	
3	Ni-GDC/YSZ/La <sub>0.58</sub> Sr <sub>0.4</sub> Co <sub>0.2</sub> Fe <sub>0.8</sub> O <sub>3-6</sub> -50GDC	800	0.053	[39]	
4	Ni-GDC/GDC/La <sub>0.58</sub> Sr <sub>0.4</sub> Co <sub>0.2</sub> Fe <sub>0.8</sub> -GDC/La <sub>0.58</sub> Sr <sub>0.4</sub> Co <sub>0.2</sub> Fe <sub>0.8</sub> O <sub>3-δ</sub>	800	0.021	[39]	
5	Ni SDC/SDC <sup>b</sup> /LauSruCourFerrOrd	650	(1.03)	[42]	
	N-5DC/5DC / La0.6510.4C00.21 C0.803-6	550	(0.46)	[42]	
		630	0.25		
6	Ni-YSZ/YSZ/GDC/La <sub>0.6</sub> Sr <sub>0.4</sub> Co <sub>0.2</sub> Fe <sub>0.8</sub> O <sub>3-δ</sub> -Ag	530	0.05	[36]	
		730	0.74		
		530	0.42	[36]	
7	Ni-GDC/GDC/La <sub>0.6</sub> Sr <sub>0.4</sub> Co <sub>0.2</sub> Fe <sub>0.8</sub> O <sub>3-δ</sub> -Ag	570	0.73		
		680	~1.2		
8	Ni-GDC/GDC/La <sub>0.6</sub> Sr <sub>0.4</sub> Co <sub>0.2</sub> Fe <sub>0.8</sub> O <sub>3-δ</sub> -GDC/La <sub>0.58</sub> Sr <sub>0.4</sub> Co <sub>0.2</sub> Fe <sub>0.8</sub> O <sub>3-δ</sub> -Ag	800	0.045	[38]	
9	Ni-GDC/YSZ/La <sub>0.58</sub> Sr <sub>0.4</sub> Co <sub>0.2</sub> Fe <sub>0.8</sub> O <sub>3-8</sub> -50GDC-2Ag	800	0.050	[39]	
10	Ni-GDC/GDC/La <sub>0.6</sub> Sr <sub>0.4</sub> Co <sub>0.2</sub> Fe <sub>0.8</sub> O <sub>3-δ</sub> -GDC/La <sub>0.58</sub> Sr <sub>0.4</sub> Co <sub>0.2</sub> Fe <sub>0.8</sub> O <sub>3-δ</sub> -Cu	800	0.052	[38]	
11	Ni-SDC/SDC/La <sub>0.6</sub> Sr <sub>0.4</sub> Co <sub>0.2</sub> Fe <sub>0.8</sub> O <sub>3-<math>\delta</math></sub>	700	1.07	[42]	
12	Ni-SDC/SDC/La <sub>0.6</sub> Sr <sub>0.4</sub> Co <sub>0.2</sub> Fe <sub>0.7</sub> Cu <sub>0.1</sub> O <sub>3-8</sub>	700	1.15	[42]	
13	Ni-SDC/SDC/La <sub>0.6</sub> Sr <sub>0.4</sub> Co <sub>0.1</sub> Fe <sub>0.8</sub> Cu <sub>0.1</sub> O <sub>3-<math>\delta</math></sub>	700	1.24	[42]	
14	$Ni-GDC/YSZ/La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}-50GDC-2Cu/La_{0.58}Sr_{0.4}CO_{0.2}Fe_{0.8}O_{3-\delta}-50GDC-2Cu/La_{0.58}Sr_{0.4}CO_{0.2}Fe_{0.8}O_{3-\delta}-50GDC-2Cu/La_{0.58}Sr_{0.4}CO_{0.2}Fe_{0.8}O_{3-\delta}-50GDC-2Cu/La_{0.58}Sr_{0.4}CO_{0.2}Fe_{0.8}O_{3-\delta}-50GDC-2Cu/La_{0.58}Sr_{0.4}CO_{0.2}Fe_{0.8}O_{3-\delta}-50GDC-2Cu/La_{0.58}Sr_{0.4}CO_{0.2}Fe_{0.8}O_{3-\delta}-50GDC-2Cu/La_{0.58}Sr_{0.4}CO_{0.2}Fe_{0.8}O_{3-\delta}-50GDC-2Cu/La_{0.58}Sr_{0.4}CO_{0.2}Fe_{0.8}O_{3-\delta}-50GDC-2Cu/La_{0.58}Sr_{0.4}CO_{0.2}Fe_{0.8}O_{3-\delta}-50GDC-2Cu/La_{0.58}Sr_{0.4}CO_{0.2}Fe_{0.8}O_{0.4}CO_{0.4}Fe_{0.8}O_{0.4}CO_{0.4}Fe_{0.4}O_{0.4}Fe_{0.4}O_{0.$	800	0.066	[39]	
15	$Ni-GDC/YSZ/La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}-50GDC/La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}-50GDC-2Cu$	800	0.055	[39]	
16	Ni-GDC/YSZ/GDC/La <sub>0.58</sub> Sr <sub>0.4</sub> Co <sub>0.2</sub> Fe <sub>0.8</sub> O <sub>3-6</sub> -50GDC-2Cu	800	0.016	[39]	
17	Ni-GDC/YSZ/La <sub>0.58</sub> Sr <sub>0.4</sub> Co <sub>0.2</sub> Fe <sub>0.8</sub> O <sub>3-8</sub> -50GDC-2Cu	800	0.055	[39]	
18	$Ni-GDC/GDC/La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}-GDC/La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}-Pt$	800	0.023	[38]	
19	Ni-GDC/YSZ/La <sub>0.58</sub> Sr <sub>0.4</sub> Co <sub>0.2</sub> Fe <sub>0.8</sub> O <sub>3-δ</sub> -50GDC-2Pt	800	0.026	[39]	
		800	1.99		
20	N; VSZ/VSZ/CDC/La Sr Ca Ea O Dd	750	1.47	[33]	
	NI-15Z/15Z/0DC/La0.6510.4C00.2FC0.8O3-8-FU	700	1.05		
		650	0.59		
21	$Ni-YSZ/GDC/La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}-Pd$	650c	~0.15	[22]	
		550	~0.04	[33]	
22	$Ni-YSZ/YSZ/GDC/La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}-Rh$	800	1.83		
		750	1.46	[22]	
		700	1.03	[32]	
		650	0.6		

**Table 2.** Summary of fuel cell performance, cell components and maximum power density (MPD) values at different temperatures.

<sup>a</sup> Yttrium-stabilized zircon; <sup>b</sup> Sm<sub>0.2</sub>Ce<sub>0.8</sub>O<sub>2-δ</sub>.

## 3. Metal Promotion Effects

The effect of metal promotion on oxygen transport over LSM and LSCF cathodes is still not clear, sometime controversial and detailed knowledge of the oxygen reduction mechanism is still lacking. Watanabe and coworkers [54] employed samaria-doped ceria (SDC) promoted by highly dispersed noble metals as anode material and LSM particles catalyzed with microcrystalline Pt as cathode. It was found that the anodic polarization resistance and its activation energy were greatly decreased by loading only a small amount of the catalysts (such as Ru, Rh, and Pt) onto the SDC particles. Moreover, an effective promotion of Pt species on the dissociation of O<sub>2</sub> molecules and/or the exchange reaction between oxygen atoms and oxygen vacancies in LSM was reported.

Contradictory effects were described for Pd, Ag and Pt promoted LSM cathodes [47]. Between 750 and 900 °C no electrocatalytic effect occurred with respect to the presence of Pt, independently on the preparation method, deposition on the electrolyte or mixing with cathode powders. Infiltration of the cathode with a Pd solution or mixing with Pd black did not result in a positive effect either. A catalytic effect was only found with Pd on activated carbon and in particular at lower temperatures. Cells prepared with Ag powder and Ag<sub>2</sub>O showed an improved electrochemical performance compared to Ag-free cells sintered at the same temperature (920 °C). However, in comparison to Ag-free cells sintered at the standard temperature (1100 °C) lower current densities were measured [47].

Similar effects are proposed in the case of LSCF cathodes, as below discussed. Nevertheless, further fundamental studies on mechanism of ORR are highly desirable.

## 3.1. Effects on LSCF Surface Promoted

It is generally accepted that for LSCF surface promoted by metal particles, reactions take place between metal particles and the most external planes of LSCF crystallite. Serra [32] confirmed by XPS that in the case of Pd impregnation, around 20% of the Pd is present as metal and the rest exists in an oxidation state, which is presumably incorporated into LSCF B-site. The coexistence of surface and metal substituted into the lattice was also reported by other groups and reversible behavior under different conditions (oxygen pressure, temperature) was pointed out [32,33]. However, only few detailed investigations were done.

The presence of metal clusters at the LSCF surface will enlarge TPB by enlarging the electrode surface area directly [34,37,55]. However, the main contribution to ORR is the catalytic effect on oxygen adsorption-dissociation. Huang *et al.* [38,39] proposed that the promotion trend of Cu > Ag > Pt has great relationship with the oxygen affinities of the metals. Hence, it can be speculated that the higher the oxygen chemisorption over the metal with respect to the LSCF, the higher is the oxygen concentration difference leading to oxygen migration towards LSCF [35,38,39]. This mechanism suggests that a balance between oxygen adsorption-dissociation, oxygen surface and bulk diffusion is crucial for ensuring an improvement in ORR process, and can explain the influence of synthesis approach and the effect of metal content.

## 3.2. Effects on LSCF Promoted by Metal-in-the B-Site of the Perovskite

In order to develop new promising LSCF substituted materials it is helpful to classify the already known perovskites according to their properties. The stability of perovskites relative to their crystalline structures is frequently defined in terms of the Goldschmidt tolerance factor t [56]. Stable perovskite structures are predicted for  $0.77 \le t \le 1.00$  [29]. The perfect cubic structure (t = 1) is achieved when the A-site cation has the same size as the oxygen ion (1.40 Å). The evolution of tolerance factor t as a function of A-site substitution with strontium has been calculated using the Shannon's ionic radii.

By increasing *x* the symmetry of the structure of  $La_{1-x}Sr_xFeO_{3-\delta}$  changes from orthorhombic  $(0 \le x \le 0.2)$  via rhombohedral  $(0.4 \le x \le 0.7)$  to cubic  $(0.8 \le x \le 1.0)$ . The trend of the tolerance factors of  $La_{1-x}Sr_xCoO_{3-\delta}$  and  $La_{1-x}Sr_xCoO_{3-\delta}$  is similar to that of LSF but the values are larger and exceed unity, because of the smaller radii of  $Co^{3+}/Co^{4+}$  compared with  $Fe^{3+}/Fe^{4+}$ . A change of the symmetry from the rhombohedrally distorted  $(0 \le x \le 0.5)$  to the cubic  $(0.55 \le x \le 0.7)$  perovskite phase has been observed. Therefore with a detailed knowledge of the radii it is possible to design different materials with very similar tolerance factors, *i.e.*, crystal structures. It is well known that a larger ionic radius at the A site (e.g., substituting  $La^{3+}$  by  $Sr^{2+}$ ) reduces the critical radius. The critical radius should be as large as possible in order to enhance oxygen ionic conductivity. On the one hand, substitution of  $La^{3+}$  by  $Sr^{2+}$  introduces oxygen vacancies which enhance the ionic conductivity. Indeed, as described for  $La_{1-x}Sr_xCo_{0.8}Fe_{0.2}O_{3-\delta}$  the ionic conductivity increased monotonically with increasing *x* [56]. This indicates vacancy formation to be more important than the critical radius.

The bulk structure was investigated by Kuhn and Ozkan for Fe-based perovskite-type oxides with the formula La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>y</sub>Fe<sub>1-y</sub>O<sub>3- $\delta$ </sub> (*y* = 0.1, 0.2, and 0.3) [57]. They found that transition from rhombohedral to cubic structure occurred at lower temperatures for higher Co content in the perovskites. Some years later, the same group reported that for La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3- $\delta$ </sub> (LSCF-6428) after substitution with Zn (10 mol% at the B-site) (LSCF-Zn), the transition temperature from rhombohedral to cubic decreased from 550 °C for LSCF-6428) to around 400–500 °C for LSCF-Zn [43]. The transition was reversible and the sample reverts back to a rhombohedral phase upon cooling. Moreover, it was reported that by doping the La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3- $\delta$ </sub> at the B-site with Zn, Ni and Cu oxygen activation and vacancy generation properties increased, being the Zn-doped catalyst the best performing [43].

The electrical conductivity is also affected by metal-in-the B-site of perovskite. The maximum electrical conductivities of the La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.7</sub>Cu<sub>0.1</sub>O<sub>3- $\delta}$ </sub> and La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.1</sub>Fe<sub>0.8</sub>Cu<sub>0.1</sub>O<sub>3- $\delta$ </sub> sintered at 1100 °C is 438 S cm<sup>-1</sup> and 340 S cm<sup>-1</sup>, which is much higher than that of La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3- $\delta$ </sub> sintered at the same temperature, 81 S cm<sup>-1</sup> [42]. Besides the change in material density and the formation of conductive network induced by metal species insertion into the lattice [58], the improved electronic conductivity behavior can be greatly attributed to the change in the structure after substitution, such as the Jahn-Teller distortion of the MO<sub>6</sub> octahedron [38,39,42].

Ozkan and co-workers confirmed the improvement in oxygen vacancies generation after B-site substitution by using thermogravimetric analyses (TGA) coupled with temperature programmed reduction (TPR) experiments [43,57]. As is shown in Figure 8, the oxygen vacancy evolution in LSCF-Zn by solid oxide reaction is better than LSCF. The evolution of oxygen vacancies can be well explained by the charge imbalance caused by low valence substitution. In fact, substitution with the same valence metal can also influence the generation of vacancies, which can be attributed to different binding

capabilities of metal species with extra oxide ions [49,52,59,60]. For the same reason the diffusion coefficient of oxide ions in LaFeO<sub>3</sub> is much lower than that of LaCoO<sub>3</sub> [61,62].



**Figure 8.** Oxygen vacancy generation of La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.18</sub>Fe<sub>0.72</sub>X<sub>0.1</sub>)O<sub>3- $\delta$ </sub> (where *X* = Zn, Ni or Cu) synthesized by solid state reaction in air as a function of temperature measured by TGA. La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3- $\delta$ </sub> catalyst served as the baseline for comparison. (Reprinted with permission from [43], 2011, Elsevier).

Similarly, some of us found an increase of oxygen vacancy content in presence of Pd as suggested by carrying out TGA and Oxygen storage capacity (OSC) experiments [53]. Among the LSCF and LSCF-Pd samples prepared with two different Fe content, La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.8</sub>Fe<sub>0.17</sub>Pd<sub>0.03</sub>O<sub>3- $\delta}$ </sub> (LSCF0.2-Pd) and La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.77</sub>Pd<sub>0.03</sub>O<sub>3- $\delta}$ </sub> (LSCF0.8-Pd) showed higher oxygen chemisorption capacity than the corresponding undoped LSCF perovskites, La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.8</sub>Fe<sub>0.17</sub>O<sub>3- $\delta}$ </sub> (LSCF0.2) and La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.77</sub>O<sub>3- $\delta$ </sub> (LSCF0.8), giving the higher weight loss (see Table 3). The increase of oxygen vacancy content in presence of Pd was also suggested by carrying out TGA experiments. It was confirmed that LSCF0.2 and LSCF0.2-Pd showed the highest oxygen chemisorption capacity giving the highest weight loss (%). Once again, metal doping had a beneficial effect. Moreover, such Pd doped perovskites have very similar lattice parameters than the LSCF0.2 and LSCF0.8 samples and the XRD patterns have been refined in the rhombohedral R3*CH* space group [53]. Then, the insertion of Pd<sup>4+</sup> cations into the perovskite lattice did not produce any appreciable modification of the structure. This is not surprising because the ionic radius of Pd<sup>4+</sup> matches that of the Fe<sup>2+</sup> cation.

Sample	O <sub>2</sub> Chemisorbed values (mL g <sup>-1</sup> ) at 600 °C	Weight loss (%) due to O <sub>2</sub> release
LSCF0.2	2.2	1.90
LSCF0.2-Pd	2.5	2.05
LSCF0.8	1.1	1.21
LSCF0.8-Pd	1.3	1.35

**Table 3.** Results of oxygen storage capacity (OSC) and thermogravimetric analysis (TGA) analyses on LSCF and LSCF-Pd perovskites [53].

In general, the improvement in MIEC can supply more TPBs for ORR and at the same time promotes the electrochemical process by accelerating the electronic transportation [32].

In the 1982, Kilner and Brook determined by experimental methods and theoretical calculations the effects of structure and host cation type on the migration enthalpies and the effect of dopant cation size on the association enthalpies, for doped non-stoichiometric oxides with oxygen ion conductivity [63]. It was concluded that dopant cation size in the association enthalpies is the most important factor in the determination of the magnitude of oxygen ion conduction. Some years later, in the 1993, oxygen permeability measurements were carried out on  $La_{0.6}Sr_{0.4}CoO_{3-\delta}$  [64]. The occurrence of order-disorder transitions in the range of temperatures 790–940 °C has been confirmed by combined thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements of the sample slowly cooled or quenched from high temperature after annealing in different atmosphere. The oxygen permeability found upon exposing the material to a stream of air and of He increased sharply at the onset of the transition from the low-temperature vacancy-ordered state to the defective perovskite structure.

Definitely in a defective perovskite higher vacancy content can be related to higher ionic conductivity as demonstrated from theoretical calculations and experimental studies as well.

However, the specific effect of metal at the B-site on the SOFC performances of promoted perovskites is difficult to explain. It has been suggested by Serra *et al.* [32] that Pd substitution may accelerate the redox cycles of the charge carriers,  $Co^{3+}/Co^{4+}$  and  $Fe^{3+}/Fe^{4+}$  at B-site, hence may improve the reduction of oxygen atoms. Other metals which have been studied include Pt [40,41,47], Ag [35,47] and Cu [38,42,43]. The reactivity for O<sub>2</sub> dissociation over Pt is well known to be much better than Cu while that over Ag is worse than Cu. However, the SOFC performance with Pt-added LSCF as the SOFC cathode has been shown to be much worse than that with Cu or Ag-added LSCF [38].

Notably, the oxygen-ion migration in the LSCF lattice can become the rate-limiting step in the overall process of oxygen transport from the cathode to the anode via the oxygen-ion conducting materials. When the ionic conductivity increases, the oxygen ion migration becomes faster and thus the interfacial O transfer can become the rate limiting step. When metal is added to the perovskite and it is not well interacting with the perovskite lattice, an interfacial resistance for O transfer occurs.

Thus, the variation of the SOFC performance after metal addition can be due to either the effect of the oxygen dissociation reactivity of the metal or that of the interfacial oxygen transfer rate between the metal phase and the oxygen-ion conducting cathode phase. The combined effect of oxygen dissociation and interfacial oxygen transfer rates seems the balance factor (see paragraph 3.3).

Finally, we want to mention the effect of metal substitution on TEC values of LSCF. It has been reported that TEC values can be adjusted by B-site substitution on LaCoO<sub>3</sub> [65], LaFeO<sub>3</sub> [66], La<sub>1-x</sub>Sr<sub>x</sub>FeO<sub>3-δ</sub> [58] and La<sub>1-x</sub>Sr<sub>x</sub>CoO<sub>3-δ</sub> [67]. Previous studies suggested that B-site substitution also affects the TEC of LSCF, which may have relationship with the formation of oxygen vacancies [7]. Taken Cu substitution for example, the calculated TEC of La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.7</sub>Cu<sub>0.1</sub>O<sub>3-δ</sub> and La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.1</sub>Fe<sub>0.8</sub>Cu<sub>0.1</sub>O<sub>3-δ</sub> is 17.6 × 10<sup>-6</sup> K<sup>-1</sup> and 12.2 × 10<sup>-6</sup> K<sup>-1</sup>, respectively, which is different from that of undoped La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub>, 15.9 × 10<sup>-6</sup> K<sup>-1</sup>. The decreased TEC for La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.1</sub>Fe<sub>0.8</sub>Cu<sub>0.1</sub>O<sub>3-δ</sub> is considerably beneficial to cathodic use in IT-SOFC [42].

## 3.3. A Balance between Two Effects

The influence of metal species and metal content can be well explained by the matching between oxygen adsorption-dissociation and oxygen interfacial diffusion, *i.e.*, the balance between metal clusters and metal in the perovskite lattice. In order to transfer the as dissociated O into LSCF bulk, surface oxygen vacancy as well as high fractional lattice-site interaction between metal and LSCF is needed.

In Figure 9(a-c) the schematic diagram of the Cu content effect on the electrochemical reaction of oxygen over a composite cathode La<sub>0.58</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-6</sub> (LSCF)-50GDC is shown [39]. The a, b and c diagrams simulate the behavior of LSCF-GDC doped with Cu, 1 wt.%, 2wt.% and 5wt.%, respectively. The electrochemical reaction rate is related to the amount of TPB. Without any metal enhancement, the electrochemical reaction takes place at the TPB by adsorbing and dissociating O<sub>2</sub> (Figure 9a). The adsorbed O species ( $O_{ads}$ ) is transformed to an oxygen ion ( $O^{2-}$ ) via the charge transfer reaction, the formed  $O^{2-}$  then migrates via the oxygen-ion conducting material. The presence of the Cu species, Cu 1wt % as an example, can enhance the dissociation of O2 and thus accelerates the electrochemical reaction (Figure 9a). On the other hand, although Cu may enhance O<sub>2</sub> dissociation, it also forms a separate phase from that of the oxygen-ion conducting materials. The interfacial transfer of the formed O species from the metal to the oxygen vacancy can be retarded due to a poor interaction of the metal with the lattice of the oxygen-ion conducting materials; as a consequence, the electrochemical reaction rate decreases. Therefore, the addition of metal can be detrimental to the electrochemical reaction rate if the interaction of the metal with the oxygen vacancy is not good enough. In Figures 9b and c the blockage of the TPB by the Cu particles is displayed. Such Cu particles should obstruct the path for interfacial O transfer and decrease its rate. If the overall rate of electrochemical reaction cannot be compensated by the higher rate of O<sub>2</sub> dissociation, the SOFC performance should become worse [39].

In conclusion, the authors pointed out that an optimum Cu content exists. When the Cu content increases from 1 to 2 wt.%, the O<sub>2</sub> dissociation reactivity increases and thus the SOFC performance can become better. However, as the Cu content increases further to 5wt %, the SOFC performance drops dramatically.

It is worth noting that the extent of interaction of the metal with the lattice of the oxygen-ion conducting LSCF perovskite strongly depends on the synthesis approach, calcination temperature and may be associated with the size of the metal cation in comparison with that of the A-site or B-site cation in the ABO<sub>3</sub> perovskite. As reported by Huang and Chou [39], the cation radius of  $Cu^{2+}$  (0.73 Å) is close to that of LSCF B-site  $Co^{2+}$  (0.75 Å); this results in a good interaction of Cu with LSCF B-site cations due to the insertion of  $Cu^{2+}$  cation in the LSCF B-site lattice. On the other hand, the cation radius of Ag<sup>+</sup> (1.26 Å) is close to that of the LSCF A-site La<sup>3+</sup> (1.16 Å), resulting in a good interaction of Ag with LSCF A-site cations due to the insertion of Ag<sup>+</sup> (0.63 Å), is much smaller than that of LSCF B-site cations. This would result in a poor interaction of Pt with LSCF B-site cations and in the stabilization of metallic Pt. Consequently, although Pt has excellent reactivity for O<sub>2</sub> dissociation, the interfacial O transfer should be slow and thus the electrochemical reaction rate can become low. In conclusion, the rate of interfacial O transfer can be associated with the extent of interaction of the metal with the lattice of the oxygen-ion conducting materials. A balance between the reactivity of oxygen dissociation and the rate of interfacial O transfer is needed for the best SOFC performance.



**Figure 9.** Schematic diagram of the Cu content on the electrochemical reaction of oxygen over the cathode TPB. The diagrams of a, b and c simulate LSCF-GDC doped with Cu, 1 wt.%, 2wt.% and 5wt.%, respectively. (Reprinted with permission from [39], 2010, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim).

*Ab initio* modeling of multicomponent BSCF/LSCF perovskite solid solutions has proven to be extremely helpful in understanding oxygen ion conduction mechanism. Quite a complex system of  $(La,Sr)CoO_{3-\delta}$  has recently been investigated by *ab initio* calculations. One study interprets the experimentally observed increased oxygen exchange rate at such interfaces [68] as caused mainly by a redistribution of Sr from the perovskite to the interface region coupled with a respective strong local increase of the oxygen vacancy concentration. Another investigation focuses more on the strain caused at the hetero interface leading to increased oxygen vacancy mobility [69]. There is also an idea that the transition state structure of the perovskite may play an important role in the course of the vacancy diffusion [70–73]. Variations in structural disorder also were pointed out as a factor.

## 4. Conclusions and Perspectives

Recent results for metal (Pd, Pt, Ag, Cu, Zn, Ni) promoted LSCF cathodes for IT-SOFCs have been reviewed in this paper, focusing on the different synthesis approaches used (infiltration, deposition, solid state reaction, one pot citrate method) and as well on the effects of metal promotion on structural properties, oxygen vacancies content and cathodic performances.

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It has been discussed that both noble and transition metals can improve LSCF cathodic properties by affecting electrochemical reactions, oxygen bulk transportation and TEC. A good match between oxygen adsorption-dissociation, oxygen surface and bulk diffusion is necessary to achieve optimum ORR performances. Besides metal species and content, the synthesis approach is also a key factor for the final performance. As reported by Huang and Chou [39], the addition of proper metal (Pt, Ag, Cu) loading (2 wt.%) can promote the electrochemical reaction rate of LSCF-GDC composite cathode, but can be detrimental when the amount of TPB dramatically decreases. Indeed, metal addition increases the O<sub>2</sub> dissociation and interfacial O transfer is needed for the best SOFC performance.

However, investigations on metal-promoted LSCF cathodes are still challenging. When noble metals are used in order to promote LSCF, the melting point of such metals must be considered and related to the operating temperature. For instance, the melting point of silver is 961 °C; therefore, metallic silver is a potential component for the cathode in SOFCs operated at less than 800 °C because of its good oxygen reduction activity, high electrical conductivity, and its relatively low cost [6].

Moreover, it should be pointed out here that the addition of noble metals, in particular Pd and Pt, by impregnation method on the surface of the perovskite does not seem a good solution to improve the performances of cathodes due to agglomeration tendency of metal particles occurring after high-temperature operation. Moreover, high loading of noble metals should be avoided since one target to commercialization of SOFC is to decrease the price. To this respect, the addition of very small amount of noble metals and the use of new synthesis approaches, such as the one pot citrate method is highly recommended since it allows the stabilization of the doping metal (Pd) in two forms in dynamic equilibrium, partially as nanoparticles and partially as cations into the lattice. Such a method may open new perspectives for the design of new high-performing B-site doped perovskite.

Among other methods used for the synthesis of perovskites metal substituted at the B-site, the solid state reaction must be mentioned. Such a process is simple and low cost. It provides greater homogeneity and leads to deep interaction between the metal and the LSCF crystalline phase, since the metal species participate in LSCF formation process. However, the physical properties of the resulting LSCF perovskites depend critically on the experimental parameters used; thus, reproducibility problems may occur.

Deeper investigations need to be carried out in order to get fundamental understanding in the kinetics of ORR over metal-promoted LSCF cathodes. Theoretical investigation, such as density functional theory (DFT) calculations will be a powerful tool in this field, since detailed information is not obtained by experimental studies. The main use of DFT studies is to provide specific micro-scale mechanisms of chemical processes that are not attainable from experiment alone and that help to interpret experimental measurements.

As previously mentioned, DFT investigations have been successfully applied to investigate processes determining cathode performance and oxygen vacancy formation and migration in LSM, BSCF and LSCF [70–73]. Since such investigation has been not yet reported on metal (Pd, Pt, Ag, Cu, Zn, Ni) substituted LSCF, it will be meaningful to carry out such studies on perovskite metal substituted at the B-site. Meanwhile, in order to get more insights into the structural modifications occurring under operating conditions typical of IT-SOFCs in metal promoted LSCF cathodes, such as the reversible behavior between metal nanoclusters and metal ions into the lattice of the perovskite, "in situ" EXAFS and XRD experiments are highly recommended.

The controlling of metal dispersion, particle microstructure and the level of substitution remains an outstanding challenge. The application of new synthesis approaches and new metal species is still the main direction. Most recently the application of plasma and electrical depositions in surface modification and sol-gel in B-site substitution has been tried and instead of noble metal, more transition metals are used, especially on B-site substitution.



**Figure 10.** Impedance spectra of Ni–YSZ/YSZ/GDC/LSCF–Ag before operation and after 150 h operation at 730 °C. (Reprinted with permission from [36], 2008, Elsevier).



**Figure 11.** Time dependence of the power density at 700 °C and 0.7 V. (Reprinted with permission from [36], 2008, Elsevier).

Moreover, even in the case of excellent properties of fresh LSCF cathodes, the chemical and thermal stability under operating condition is an important issue to be addressed for practical applications [51,74,75]. A study of Ni-YSZ/YSZ/GDC/LSCF-Ag cell showed that the good initial performances of Ag infiltrated cathodes are maintained after 150 h operation at 730 °C (Figure 10 [36]). Moreover, no significant degradation of out-put power was observed for 150 h at 0.7 V and 700 °C (Figure 11).

Future improvements of LSCF cathodes should claim Sr-low content perovskites obtained by insertion into the LSCF A-site lattice of metal cation with radius similar to that of  $Sr^{2+}$ . Such materials can be advantageous, helping to decrease long-time degradation processes caused by cation segregation and poisoning by gaseous chromium oxide or SO<sub>x</sub> species, forming SrCrO<sub>4</sub> or SrSO<sub>4</sub> precipitates that may block the active surface [70].

However, it is worth noting that about Sr segregation there are some contradictory results. Indeed, it has been recently reported [76] that surface-decoration of perovskites can strongly affect the oxygen reduction activity, and therefore is a new and promising approach to improve SOFC cathode materials. In this study, it has been demonstrated that a small amount of secondary phase (La-, Co-, and Sr-(hydr)oxides/carbonates) on a (001) La<sub>0.8</sub>Sr<sub>0.2</sub>CoO<sub>3-δ</sub> surface can either significantly activate or passivate the electrode. Although the physical origin for the enhancement is not fully understood, results from atomic force microscopy, X-ray diffraction, and X-ray photoelectron spectroscopy suggest that the observed enhancement for "Sr"-decorated surfaces can be attributed largely to catalytically active interface regions between surface Sr-enriched particles and the LSC surface.

Finally, IT-SOFC properties are also limited to a large extent by solid state reactions at the interface with the electrolyte. Despite of excellent initial cathode performances, the solid-state reactions occurring at high temperature between LSCF and the electrolyte, YSZ or YSZ-GDC, are still big problem to be addressed [77]. For commercialization, the chemical and physical match between LSCF cathode and GDC electrolyte is still challenging.

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# **Author Contributions**

Guo Shaoli wrote the first draft of the article which was then extensively improved by the comments and suggestions of Hongjing Wu and Fabrizio Puleo; Leonarda Francesca Liotta coordinated the entire work and performed the revision.

## **Conflicts of Interest**

The authors declare no conflict of interest.

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