UTILIZATION OF \((La_{1-x}Sr_x)CoO_{3-\delta}/(La_{1-y}Sr_y)CoO_{4+\delta}\) HETEROSTRUCTURES AS CATHODE FOR IT-SOFCs

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

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IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
METALLURGICAL AND MATERIALS ENGINEERING

JUNE 2017
Approval of the thesis:

**UTILIZATION OF**(La$_{1-x}$Sr$_x$)CoO$_{3-\delta}$/ (La$_{1-y}$Sr$_y$)$_2$CoO$_{4+\delta}$

**HETEROSTRUCTURES AS CATHODE FOR IT-SOFCs**

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ABSTRACT

UTILIZATION OF (La$_{1-x}$Sr$_x$)CoO$_{3-\delta}$/(La$_{1-y}$Sr$_y$)$_2$CoO$_{4+\delta}$ HETEROSTRUCTURES AS CATHODE FOR IT-SOFCs

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June 2017, 151 pages

Perovskite type ABO$_3$ oxides have been studied as one of the promising candidates for the cathode of intermediate temperature (500-700 °C) solid oxide fuel cells (SOFCs). The one of the best one among them is (La$_{1-x}$Sr$_x$)CoO$_{3-\delta}$ (LSC$_{113}$) in terms of SOFC cathode performance. However, LSC drastically suffers from strong chemical instability problem manifested as surface Strontium segregation, triggered by increasing operation temperature. Lowering temperature, on the other hand, blocks oxygen reduction performance of cathode, constituting a contradiction.

Recently, a thousand times greater oxygen reduction reaction coefficient, k (cm/s), around the (La$_{1-x}$Sr$_x$)CoO$_{3-\delta}$/(La$_{1-y}$Sr$_y$)$_2$CoO$_{4+\delta}$ interface than LSC$_{113}$ has been reported in recent years. This hetero-interface can decrease operation temperature of SOFC cathode to reasonable levels by facilitating oxygen reduction. The aim of this study is to utilize this hetero-interface for cathode by integrating different interface construction approaches and examine their results in terms of their compatibility at desired low temperatures. Simultaneous-sputtering of (La$_{1-x}$Sr$_x$)CoO$_{3-\delta}$ and (La$_{1-x}$Sr$_x$)CoO$_{3-\delta}$
\( \text{Sr}_2\text{CoO}_4\pm\delta \) as thin film cathode and dual phase synthesis from one solution as route-oriented conventional thick cathode has been adopted as the progressive ways to maximize interfaces, the former of which yielded positive results in terms of increasing hetero-interface and reducing cathode resistance. On the other hand, although dual phase syntheses of powders were successful, were not composed of agglomerates of two phases and did result in finely dispersed nano-particles, it yet resulted in poor performance improvement and temperature reduction in form of conventional thick film cathode application.

**Keywords:** SOFC cathode, LSC\textsubscript{113}/LSC\textsubscript{214} hetero interface, one-pot synthesis, magnetron co-sputtering, in situ EIS
ÖZ

ORTA SICAKLIK KATI OKSİT YAKIT PİLLERİ İÇİN
(La_{1-x}Sr_x)CoO_3-δ/(La_{1-y}Sr_y)_{2}CoO_{4+δ} ÇOKLU YAPILARIN KATOT OLARAK KULLANIMI

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Perovskit tipi ABO_3 oksitleri orta sıcaklık (500-700 °C) katı oksit yakıt pilleri (KOYP) katotları için gelecek vaat eden adaylardan biri olarak çalışılmaktadır. (La_{1-x}Sr_x)CoO_3-δ (LSC_{113}) bileşği, bu oksitler arasında KOYP katot performansı bakımından en iyi olanlardan biridir. Ancak LSC_{113} artan çalışma sıcaklığının etkisi nedeniyle yüzeye Sr ayrışması olarak zahmet eden yüksek kimyasal kararsızlıktan muzdarıptır. Öte yandan çalışma sıcaklığı düşürmek katodun oksijen indirgeme performansını azaltır ve bir çelişki teşkil eder.

Son yıllarda (La_{1-x}Sr_x)CoO_3-δ/(La_{1-y}Sr_y)_{2}CoO_{4+δ} çoklu arayüzü çevresinde LSC_{113}’ten bin kat yüksek bir oksijen indirgeme tepkime sabiti, k (cm/s) rapor edilmiştir. Bu çoklu arayüz oksijen indirgemeyi kinentiğini arttırarak KOYP çalışma sıcaklığını makul düzeylere düşürebilir. Bu çalışmanın amacı farklı arayüz inşa yöntemlerini benimseyip bu çoklu arayüzden istifade etmek ve istenen düşük sıcaklıkta uyumluğu incelemektir. İnce film katot olarak (La_{1-x}Sr_x)CoO_3-δ ve (La_{1-y}Sr_y)_{2}CoO_{4+δ} fazlarının eş zamanlı sicratma çekilmiş ve üretim odaklı olarak tek bir
çözeltiden iki fazlı yapının sentezi, çoklu arayüzün azamileştirilmesinin yenilikçi yöntemleri olarak benimsenmiştir. Bunlardan ilki çoklu arayüzü artırmak ve katot direncini düşürmek bakımından müspet sonuçlar vermiştir. Öte yandan çift faz sentezleri, her ne kadar başarılı olmuş, iki fazın büyük topaklarından oluşmuş ve nano parçaların ince ölçekte dağılımı sonucunu vermişsse de, bunlar beraber tozların geleneksel kalın film katot biçimindeki uygulaması zayıf bir performans artış ve sıcaklık düşüşüyle sonuçlanmıştır.

Anahtar Kelimeler: KOYP katodu, LSC_{113}/LSC_{214} çoklu arayüz, tek pota sentezi, eş zamanlı sıçratma köktörme, yerinde EIS
In Memory of Yener Kuru
PREFACE

This work has been conducted under extraordinarily unfortunate conditions leading that considerable portion of our faculty members had contributions from giving helpful discussions to supplementing lab equipment. Hence, this study owes appreciations, making this preface longer than customary ones.

Prior to my appreciations, I must highlight that I wanted this thesis to constitute a review for reader since this thesis is the first solid oxide fuel cell study in my department and I wish this study to ease things more or less for new researchers. Furthermore, this study is based on more efficient use of existing energy sources. I know that the fundamental problem making energy so crucial is organized but unplanned, irrational production favored by capitalism. I hope our days in which productive activity of mankind will be rational and planned are close.

During my studies, my advisor Assoc. Prof. Dr. Yener Kuru was deceased on 03.04.2016. I have so many things to tell about him. But I am forced to briefly say that he had always been a special and distinguished researcher having an appreciable insight. He was keen on essence rather, not in appearance in our degenerated age in which everything is judged and evaluated more or less with its appearance and/or form regardless of what fills it. He never evaluated me (and his other students) with formal so-called suitability parameters in this sense. When I was senior in undergraduate, he opened the research path for me. I can definitely state that any other faculty member in my department would never insist on me like him to direct me to research path. I will miss him.

Work reported in this thesis was carried out in conjunction with “Interface Engineering in Metal Hydride Coupled Solid Oxide Fuel Cell”, a part of an ERAfrica Project, supported by TÜBİTAK with project number 114M128. Due to their great support during this project both mentally and intellectually, I am very grateful to my supervisors Prof. Dr. Tayfur Öztürk and Assoc. Prof. Dr. Yunus Eren Kalay.
In an extremely critical time interval in which I must learn and conduct a part of my experiments, Assist. Prof. Dr. Oktay Demircan, who has significant contribution to impedance experiments, did lead me. Likewise, I am grateful to Prof. Dr. Meltem Asiltürk not only because of her academic assistance but also her sincere friendship. During my research, I earned noticeable vision thanks to Prof. Dr. Mehmet Kadri Aydınol and Prof. Dr. Tarık Ömer Oğurtanı.

Mehmet Hazar Şeren was my only laboratory colleague during this period. In the absence of our advisor, we helped and supported each other, making us more than two laboratory colleagues. I will remember that. I also owe an appreciation to my project colleague Doğancan Sarı, thanks to whom and with his supports, aim in this project has been achieved. I was also lucky in this period thanks to existence of my friends İsrafil Yıldırım, Yunus Özden, Mete Batuhan Durukan and Mustafacan Kutsal. A good start up has always been a great luck; I am grateful to my unique teachers from Açılım Dershanesi.

These unfortunate years of my research now are identified with my prospective wife Gizem Ucuz and my dearest, my mother Sabiha Torunoğlu. They are my mind, my eyes, and my feels. They are my fortune.

Goethe says in Faust that “human being knows her/himself only at human being”. All those people are more or less the ones by whom I figure out myself.
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NOMENCLATURE

APT : Atom Probe Tomography
ASR : Area Specific Resistance
BBP : Benzyl Butyl Phthalate
BSCF : (Ba$_{1-x}$Sr$_x$)(Co$_{1-y}$Fe$_y$)O$_{3-\delta}$
CTE : Coefficient of Thermal Expansion
D : Diffusivity
DWSB : (Dy$_x$W$_y$Bi$_{1-x-y}$)O$_{2-\delta}$
EDS : Energy Dispersive X-rays Spectroscopy
EIS : Electrochemical Impedance Spectroscopy
ESB : (Er$_{1-x}$Bi$_x$)O$_{3-\delta}$
FIB : Focused Ion Beam
GDC, CGO : Gadolinium Doped Ceria-(Ce$_{1-x}$Gd$_x$)O$_{2-\delta}$
k* : Tracer Oxygen-Surface Exchange Coefficient
k$^q$ : Electrical Oxygen-Surface Exchange Coefficient
$l_\delta$ : Critical Utilization Length
LSC$_{113}$ : (La$_{1-x}$Sr$_x$)CoO$_{3-\delta}$-Perovskite
LSC$_{214}$ : (La$_{1-y}$Sr$_y$)$_2$CoO$_{4+\delta}$-Ruddlesden Popper
LSCF : (La$_{1-x}$Sr$_x$)(Co$_{1-y}$Fe$_y$)O$_{3-\delta}$
LSF : (La$_{1-x}$Sr$_x$)FeO$_{3-\delta}$
LSGM : (La$_{1-x}$Sr$_x$)(Ga$_{1-y}$Mg$_y$)O$_{3-\delta}$
LSM : \((\text{La}_{1-x}\text{Sr}_x)\text{MnO}_{3+\delta}\)

MIEC : Mixed Ionic and Electronic Conductive

MHz, mHz : \(10^6 \text{ Hz}, 10^{-3} \text{ Hz}\)

ORR : Oxygen Reduction Reaction

PEG : Polyethylene Glycol

PLD : Pulse Laser Deposition

PVB : Poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate)

S/cm : Siemens Per Centimeter

ScSZ : \((\text{Zr}_{1-x}\text{Sc}_x)\text{O}_{2-\delta}\)-Scandia Stabilized Zirconia

SEM : Scanning Electron Microscopy

SOFC : Solid Oxide Fuel Cell

TEM : Transmission Electron Microscopy

TPB : Three (Triple) Phase Boundary

XRD : X-Ray Diffraction

YSZ : \((\text{Zr}_{1-x}\text{Y}_x)\text{O}_{2-\delta}\)-Yttria Stabilized Zirconia

\(\sigma_e\) : Electrical Conductivity

\(\sigma_i\) : Ionic Conductivity

\(\delta\) : Oxygen Vacancy
CHAPTER 1

INTRODUCTION

SOFCs are energy conversion devices capable of converting chemical energy of fuels directly to electricity without the limitations of Carnot cycles [1]. Hence as opposed to internal combustion engines, SOFCs yield significantly higher energy conversion efficiencies namely 40-50% [2,3] which can be improved to higher values with the assistance of cogenerations systems [4] as stationary applications.

It is, no doubt, very easy to combust a fuel, which is process of anode part in a fuel cell. But the key is the oxygen reduction process occurring on the cathode part and having high activation energy. This situation makes oxygen reduction reaction (ORR) at the cathode rate-limiting step of SOFC operation [5]. In other words, high activation energy requirement for ORR, constituting the main utilization problem of SOFCs, is the cost of high energy conversion efficiency of SOFCs.

Fortunately, this cost has been satisfied by mixed ionic and electronic conductive (MIEC) oxides at temperatures around and above 800 °C [3,6]. It is known that electrochemical redox reactions are catalyzed at triple phase boundaries (TPB) at which gas phase, electrically conductive phase and ionic conductive phase meet [7]. These doped oxides (MIEC oxides) involve both type of conductivities within their crystals, extending the TPB to complete material. That’s why introduction of these oxides have accelerated the researches on SOFCs in a consequence of catalytic effect of them on oxygen reduction process [6]. These oxides, in most of the time, are in the form of ABO$_3$ compound named as perovskite where A site is shared by both rare earth and alkaline earth elements (i.e. La and Sr) and B represents reducible transition
metal such as Fe, Co, Mn, Ni. Thanks to their mixed electronic and ionic conduction (MIEC) and resulting catalytic effect, overall ORR have been facilitated significantly. However, reduction of molecular oxygen gas is not an easy process, still demanding elevated temperatures in spite of positive effect of MIEC oxides. Thus, rendering a SOFC feasible alternative to internal combustion systems by yielding a commercial SOFC still requires further improvements of cathode materials capable of catalyzing ORR well through the cathode not only at elevated temperatures but also at lower temperatures since high operation temperatures, namely 800 °C, is responsible for short-term degradation [8,9]. Hence operation temperature should be reduced to 500 °C or even to 400 °C for micro devices [10–12].

Among all types of ABO₃ complex oxides, LSC has always been the best in terms of both ionic and electronic conductivity [13] and outstanding regarding surface oxygen exchange properties [14,15]. This superiority is valid for all Cobalt containing perovskites in fact. However, both its very high CTE with respect to state-of-the art electrolyte materials causing crack formation or delamination [16,17] and chemical instability problem [18,19] have always been the main causes limiting their utilization. Especially in order to completely get rid of chemical stability problem, namely in most cases insulating SrOₓ segregation through cathode surface, satisfactorily reduced resistances should be achieved from cell at or below 400°C, which is critical threshold for SrOₓ segregation [18]. Low temperature regime is also safe for probable crack/delamination failures regarding cobalt containing complex oxides. On the other hand, lower temperatures require higher activation energy for oxygen reduction [20] deteriorating SOFC application by enhancing cell resistance.

Nonetheless, anomalously enhanced oxygen reduction kinetic around the (La₁₋₃Srₓ)CoO₃₋₄/[(La₁₋₃Srₓ)₂CoO₄₋₅][La₁₋₃Srₓ)₂CoO₄₋₅₋δ] interface has been reported in recent years, yielding a thousand time greater surface oxygen exchange coefficient, k, with respect to the single phases [15,21]. Exploiting this interface induced ORR promotion can decrease operating temperature of SOFC cathode, extending the chemical stability of it. Extreme maximization of this hetero interface especially through a thin film cathode can drastically reduce ASR since in case of thin film where bulk ionic transport is facile, the only source of resistance becomes hetero-interfacial electrochemical kinetic
with surface adsorption [5,22], which has already been facilitated by enhancement on surface oxygen exchange coefficient [15]. Aside from sophisticated thin film applications, maximization of this hetero interface regarding conventional thick porous cathodes has a great potential to commercialize SOFC, too. This is certainly possible if ease of fabrication is satisfied.

This study, in this way, focuses on examination of these abovementioned two approaches. As conventional thick porous cathode fabrication approach, maximization of hetero interfaces by synthesizing two phases combination from one unique solution by means of Pechini method [23] as well as physically mixing of them are adopted. Success of hetero interface maximization with this improving approach may have drastically positive consequences in applicability of cathode regarding fabrication. On the other hand, magnetron co-sputtering of each phase from different single phase oxide sputtering targets is adopted as thin film application approach. Achieving necessitated area specific resistance (ASR) by hetero interface maximization at temperatures converging to 400 °C is the main objective regardless of fabrication costs and/or difficulties.
CHAPTER 2

OVERVIEW TO SOFC CATHODES

2.1. Solid Oxide Fuel Cells
The fossil fuel based systems, on which our current technological level of development is established, are falling in such a situation that their legitimacy is getting more and more questionable due to the increasing demand of energy and limited existence of fossil fuels as well as their emissions. This case has directed many researchers to find out new and novel routes for alternative energy conversion systems. While significant portion of them makes use of converting solar energy, which is considered as 'countable infinite' energy when the life time of human being is taken into account, in reasonably economic and efficient means, the rest is rather interested in converting existing fossil fuels in highly efficient ways. The researches of this latter group in this way are situated in range of short term aims. Solid oxide fuel cells (SOFCs) fall into this latter category in a consequence of their ability to convert chemical bond energy of fossil fuels directly into electrical energy in highly efficient way namely 40-50% practically [2] and 60% theoretically [24]. This can be extended to 80% by some cogeneration systems [4]. This is because SOFCs can convert chemical energy directly to electricity without limitations of Carnot cycle as opposed to internal combustion system [1].

All the possible energy conversion systems are governed by thermodynamics. Internal combustion engines and SOFCs are not free from this. The known first law of thermodynamics governs all the energy conversion processes; in a closed system, internal energy of systems increases with heat supplied to the system and decreases as this system does work on surroundings. On condition that U is internal energy, Q is
heat supplied and W represents work done by the system, the first law of thermodynamics is expressed as;

$$dU = \delta Q - \delta W$$

While in most cases work term (W) represents P-V type mechanical work, equivalently the work done by compression or expansion of a gas, W is in fact non-homogeneous and it involves many kinds of works even in heat engines such as chemical, electrical, mechanical and so on. These work types except for mechanical work are neglected since they are not exploited.

$$\delta W = \delta W_{\text{electrical}} + \delta W_{\text{mechanical}} + \delta W_{\text{chemical}} + ...$$

Internal combustion engines convert the energy released as a consequence of breaking chemical bond in fuel into mechanical work. Thus, they are restricted to Carnot efficiency ($Eff_c$) which can be 100% if and only if temperature of cold reservoir is absolute zero and cooling process takes place reversibly [25]. Even if compressing a hot pressurized gas into conditions such that its final temperature would be absolute zero is possible, reversibility of process entails extreme slowness which practically corresponds to infinite time. In this case, work efficiency is 100% but power output is zero. So, the practical maximum efficiency of internal combustion based systems governed by Carnot cycle is at most 25-35% when they yield desired power output due to inevitable process irreversibility and loses, as well [26].

$$Eff_c = 1 - \frac{T_{\text{cold reservoir}}}{T_{\text{hot reservoir}}}$$

However, SOFC does not make mechanical work, they are not governed by Carnot cycle and they yield more efficiency whereas their energy conversion process is also governed by the first law thermodynamics. In SOFC, work type is not mechanical it is electrical work.

2.1.1. SOFC Operation

Fuel (or $H_2$) is provided to anode in SOFCs and here it is oxidized via already reduced oxygen supplied from cathode part, generating water eventually. Reduced oxygen in
cathode should migrate through electrolyte of SOFC to allow the oxidation of fuel. Hence, electrolyte should be very good oxygen ionic conductor and it must be preferentially as thin as possible [27,28]. When it is thin, CTE of electrolyte restricts cathode material. When it is thick on the other hand, both its ionic conduction and chemical compatibility with other components become crucial. So electrolyte has a deterministic effect on SOFC construction [13]. The working principle is illustrated in Figure 2-1.

![Figure 2-1 SOFC Operation](image)

It is, as expected, very easy to combust a fuel on anode part. Here supplied heat (Q) is same for both internal combustion engines and solid oxide fuel cells. But the key is the oxygen reduction process occurring on the cathode part, expressing work term. This oxygen reduction occurring at the cathode has significantly high activation energy making oxygen reduction on cathode the main rate limiting step in overall SOFC operation [5,27,29]. Low temperatures make this rate limitation more crucial and so the greatest portion of cell resistance is originated from cathode in SOFC [6,30]. That’s why SOFC researches are significantly reduced to SOFC cathode researches. What’s happening at cathode is that $O_2$ undergoes direct electrochemical reduction. In other words, cathode of SOFC catalyzes electrochemical oxygen reduction, bringing about superior efficiency. This is the main capability of SOFC cathode and the SOFC itself.
It is most of the time neglected but energy has always been extremely expensive such that the ‘easily’ obtained fossil fuels are results of millions of years of accumulation. Formation of those fuels has not been favored by natural processes of earth just like direct electrochemical reduction of oxygen in the air. Everything has a cost to be paid. This cost was millions of years for the formation fossil fuels while it is catalysis of electrochemical reduction of $O_2$ for utilizing superior SOFC efficiency. So to say, what is done by SOFC cathode researchers is to reduce this cost into capability of mankind to pay, which is expressed by the terms commercialization, feasibility, cost reduction and so on.

In this way, there released some necessities for each component of SOFC. While cathode is the most crucial one among them in terms of its contribution to overall cell polarization resistance, the other component qualifications should also be comprehended, too.
2.1.1.1. Anode Requirements
The principal necessity for anode part of SOFC is high electrical conductivity. Since what happens at anode is electro-oxidation process [31], easy flow of electrons is helpful for better anode performance. Because fuels do not have oxidative characteristics, metals as good electrical conductors can be used for anode. In addition, for more efficient penetration and access of fuel into anode as well as the gas output, high and stable porosity is required [3]. Furthermore, anode is the place at which reduced oxygen meet with fuel provided and forms resultant gases. However, metals are prone to sintering even at intermediate temperatures. In order to sustain porosity, these metals are used to make composite anodes involving an additional ionic conductor [17]. This ionic conductor is commonly the electrolyte material for a successful compatibility, which is to specify CTE and chemical match with electrolyte. Addition of ionic conductor provides TPB at which electrochemical processes are favored [6]. Furthermore, not only with electrolyte but also compatibility with interconnect material should be concerned.

Whereas it is modest, there an is activation energy for fuel oxidation process, which constitutes relatively well smaller part of overall resistance of SOFC as illustrated in Figure 2-2. For further reduction of this resistance, anode should be able to catalyze fuel oxidation process, which can be handled partly by introduction of TPB [7]. If possible, flexibility for fuel type is also sought in anodes. Since in most cases cell is anode supported, anode is expected to be sufficiently strong to withstand the weight of cell.

Nonetheless, fuel oxidation process is relatively complex which makes a priori evaluation of a prospective material for anode common. In this way, Ni/YSZ composite is the most widely used one for SOFC due to its capability to more or less satisfy almost all requirements for anode application except for fuel flexibility since Ni/YSZ is susceptible to carbon deposition and sulphur poisoning [32–34]. With the all improving efforts, Ni/YSZ composite is by far the best choice for anode.
2.1.1.2. Electrolyte Requirements

SOFC electrolyte is responsible for transport of reduced oxygen ions and hence should have oxygen ionic conductivity as high as possible with the lowest possible electrical conductivity since electrical conductivity has a reverse effect on ion migration from cathode through anode part [35,36].

![Figure 2-3 Temperature-thickness-conductivity diagram for state-of-the art electrolytes](image)

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Generally, 0.01 S/cm at current operation temperature is accepted to be the sufficient ionic conductivity for SOFC electrolyte [14,37]. Since porosity is a scattering factor for ion transport, electrolyte should also be dense and as thin as possible along with stability under both reducing and oxidizing environments [38]. However, this thin electrolyte necessitates very high thermo-mechanical compatibility with other components, that is to say that CTE matching of electrolyte with both anode and cathode is crucial. Relationship among temperature, thickness and conductivity is summarized in Figure 2-3.

Electrolyte should be stable both at anode and at cathode. Since it is principal component in SOFC stack [39], it should be low cost material. Cubic structure should also be satisfied in order for isotropic diffusion properties. Since this criterion is
already achieved in many electrolyte options, it is not mentioned in literature but it is still a criterion [40]. Consequently, the most suitable material for electrolyte is YSZ [17,41].

2.1.1.3. Cathode Requirements

The first and the most important parameter is the catalytic effect of it in terms of oxygen reduction. In initial investigations on SOFC, it was (and is still) believed that this electrochemical reduction takes place at three phase boundaries (TPB) where gas phase (air), electrical conductor and ionic conductor meet [6]. So a good cathode must have extended three phase boundaries for favored electrochemical reduction of oxygen. But there is more. Cathode should also be stable under oxidizing environment, which is termed as chemical stability. This chemical stability with respect to interconnects and electrolyte must also be taken into account [5].

The other important parameter is structural stability characterized by CTE mismatch between cathodes, electrolytes and interconnects. CTE mismatch must be in tolerable limits for them in order for avoiding delamination or crack formation [16,17]. Moreover, cathode should have sufficient ionic and electronic conductivities. Sun et al. [13] states 100 S/cm as threshold for electrical conductivity. Ionic conductivity is mostly characterized by oxygen ion (D) and oxygen vacancy diffusivity (Dv) [42] and if intermediate temperature range (500-700 °C) is taken into consideration, 10^{-9} cm²/s ionic and 10^{-7} cm²/s vacancy diffusivities are considerable [42,43]. Apart from Co containing cathodes, which could have even better ionic conductivities than electrolytes than electrolytes [44], typical ionic conductivity of cathodes is on the order of 10^{-3} S/cm at intermediate temperature range [13,45]. Since the crucial role of ionic conductivity is extension of active regions for oxygen reduction from TBP to whole air exposed surface, rather than ionic conductivity solely, care must be on combined effect of vacancy and oxygen ion diffusivities which together determine rate of oxygen reduction by facilitating surface oxygen exchange [27,46,47]. So ionic conductivity is indicator of cathode activity.

For cathodes which are not in thin film form, enhanced porosity becomes another crucial parameter since it promotes oxygen gas phase diffusion through cathode and
cathode/electrolyte interface [48,49]. This provides excess oxygen penetration into cathode [4]. Finally, for successful commercialization, cathode should have low cost.

In order to achieve commercial SOFC, at least in terms of transport applications, overall cell resistance should not exceed 0.5 $\Omega \text{cm}^2$ [1,32]. If one considers the greatest portion of cell resistance is originated from cathode processes, 0.2 $\Omega \text{cm}^2$ cathode resistance could be tolerable. If equal contribution from each component is assumed, then 0.15 $\Omega \text{cm}^2$ would be the aimed ASR value for cathode. In either case, the cathode offering the desired ASR as well as aforementioned requirements depending on cell conditions becomes a candidate for a commercial SOFC.

In the initial SOFC studies, cathodes were composites of noble metals for electrical conduction and ionic conductor oxides as well as they were porous to meet maximization of triple phase boundaries [6,50,51]. However, introduction of MIEC perovskites have changed this case very drastically. Both ionic and electrical conduction as well as extension of TPB has been satisfied by one single component thanks to introduction of MIEC oxide.

2.2. MIEC Perovskites

Perovskite oxides are characterized by their $\text{ABO}_3$ anion-cation stoichiometry. A and B can be any kinds of cations and anion does not have to be oxygen only in principle. N and S are other common anions regarding perovskite ceramics. But concerning SOFC cathodes, anion is oxygen, A site cation combines rare earth (La, Pr, Ce) and alkaline earth (Ba, Sr) cations and B site is transition metals namely Co, Fe, Ni, Mn, Cr. B-site substitution is also possible.

In perovskite structure, A-site cation is greater than B-site cation in terms of ionic radius. There is 12-fold oxygen ion coordination for A-site cation and 6-fold oxygen ion coordination for B-site cation in perovskite structure. This is illustrated in Figure 2-4 given below.
The fact that A site is shared by both rare earth and alkaline earth cations is important as it brings about mixed ionic and electronic conduction (MIEC) in perovskite structure. Sharing A and/or B site by at least two cations is characteristic leading to mixed ionic and electronic conduction of perovskite oxides [53]. Perovskite oxides are, one way or another, ionic materials in which charge neutrality must be preserved. Strict stoichiometry between anions and cations is either prerequisite or consequence in ionic materials when anions and cations through crystal have certain unique valence. This is the point at which conventional ceramics and MIEC perovskite oxides differ from each other. Whenever one of the constituent cations is aliovalent, that is, sites are substituted by cations having different valences, the typical conventional oxides transform to non-stoichiometric oxides.

In MIEC perovskites, A-site in crystal is doped by a cation having different valence than host atom. Host atom is generally rare earth having +3 valence and dopant is alkaline earth having +2 valence. This process deteriorates the charge neutrality within crystal structure. Substituting cation having +2 valence in place of host atom having +3 valence makes crystal structure more negative. In this case, charge imbalance creates polarization inside the crystal structure. This charge polarization becomes cumulative through subsequent lattices. At this point one must keep in mind that electrons are not free in ionic materials and they are carried by nucleus. So, movement of an electron, i.e. charge, dictates the movement of an atom itself. If it is considered
that charge polarization is cumulative and extended through subsequent lattices, i.e. all the material, all the positively charged atoms should be strictly separated from all the negatively charged atoms. Movement of so many atoms requires immense energy. This energy is called Madelung energy in literature [54]. The crystal structure ‘prefers’ to satisfy charge balance by releasing oxygen, making crystal more positive in aforementioned case where lattice becomes more negative as a consequence of lower valence cation doping. A-site is doped with a higher order positively charged cation, this would result in accepting excess oxygen atom to make crystal more negative. So oxygen non-stoichiometry is here introduced as the way to satisfy charge neutrality in oxides. This oxygen non-stoichiometry, whether in the form of deficiency or excessiveness, facilitates oxygen migration through oxide. In most of the cases, it is the oxygen deficiency in SOFC perovskites. Empty oxygen sites promote kinetics of bulk ionic transport [6] as well as surface oxygen exchange properties by providing empty available sites for molecular oxygen [55] to get reduced. In this way, oxygen deficiency reduces energy barrier for electrochemical reduction of oxygen gas in air [56].

Nevertheless, oxygen non-stoichiometry is not the only way of charge compensation. For the cases where B-site cation is multivalent, i.e. it can have different valence states, charge compensation can be derived by changing valence of B-site ‘reducible’ transition metal. This is the basis of electrical charge compensation and electrical conductivity. In this compensation process, electrical conduction by hopping mechanism is observed in MIEC perovskite [57].

In this case, B-site transition metal partially undergoes valence change in order to establish charge balance. As a consequence, there releases hopping sites for electrons/holes transition yielding n-type or p-type conductivity. Increasing number of these available hopping sites promotes electrical conductivity. Maximum electrical conductivity, in this sense, is obtained where the ratio of host cation to dopant cation is 1 in A-site [58]. This is valid of course when the dominant charge compensation mechanism is B-site cation valence transition. A good example to this is \((\text{La}_{1-x}\text{Sr}_x)\text{MnO}_3-\delta\) (LSM) in which almost all charge balance is achieved by electronic compensation, i.e. valence transition of \(\text{Mn}^{3+}/\text{Mn}^{4+}\) [59]. Regarding cathode materials,
for all cases in which trivalent A-site cation is doped with divalent cation, electrical charge compensation mechanism becomes operative. That’s why for instance BSCF has low electrical conduction since both host and dopant atoms have the same valence states. Depending mainly on B-site cation, degree of electrical conduction varies [13].

Here, prior to going further, there is a need for further elaboration. Extent of oxygen deficiency is a strong function of temperature, i.e. oxygen deficiency is triggered at increasing temperatures. This is to say that oxygen deficiency mechanism for charge compensation becomes dominant mechanism at high temperatures [60,61] by virtue of more ability to overcome vacancy formation activation energy at increasing temperatures. This is also explained by extrinsic and intrinsic conductivities in ionic crystals.

It is apparent that cation substitution triggers anion vacancy formation even in the low temperatures due to the need to maintain charge neutrality. In the absence of impurity, vacancy formation energy could not be surmounted at such low temperatures. These are impurity induced vacancies and their number is dominant over thermally induced ones at lower temperatures. But as temperature increases, formation of thermally induced vacancies becomes more favorable than formation of impurity induced vacancies (vacancies for charge compensation), resulting dominance of thermally induced vacancies. Absolutely, if there is a transition metal, valence state change is much easier than accommodating impurity induced vacancies likewise MIEC perovskites.

Since the dominant one is expected to govern the overall ionic movement, from low to high temperatures, there releases different conduction regimes separated by certain critical temperature named as ‘knee’. Dominance of thermally induced vacancies is such that ionic conductivity of oxide is what it would be if there were no substitution. So, this high temperature conductivity is called as intrinsic while the one at low temperatures dictated by substitution is called as extrinsic. Above knee temperature, lnD vs 1/T graph is seen to be linear, implying that this is activated behavior dictated by vacancy formation energy barrier. But at lower temperature the activation energy barrier is not caused by vacancy formation and thus temperature change is less
This phenomenon is expected to reduce electrical conduction at increasing temperatures since in this case, charge neutrality is achieved mainly by vacancy mechanism instead of electrical charge compensation of B-site transition metal. But of course this is just a generalized case valid especially for ionic crystals comprising high anion vacancies like LSC\textsubscript{113}. Otherwise many cathode perovskites like LSF exhibit semiconductor behavior in which increasing temperatures (up to certain degree [62]) lead to enhancement in conductivity. But this is possible only when higher temperatures do not significantly affect oxygen non-stoichiometry and band gap properties. Cobalt containing perovskites have high oxygen vacancies and particularly exhibit metallic like conduction behavior [6]. But for instance, dominance of oxygen defects can only be possible after 800 °C [62].
When \( \text{LSC}_{113} \) is heavily doped, an ongoing decrease in electrical conductivity is observed. When \( x \leq 0.2 \), raising regime with respect to increasing temperature turns out to be stationary after intermediate temperature range is surpassed [63,64].

On the other hand, \( \text{LSM} \) shows reverse behavior; higher temperatures bring about increase in electrical conduction [65]. This is because \( \text{LSM} \) accommodates excess oxygen dictating further B-site (Mn) charge disproportionation resulting in higher electrical conduction [59].

When both of the charge compensation mechanisms are effective within perovskite structure, it becomes a satisfactorily mixed ionic and electronic conductor. It should be kept in mind that all oxides are MIEC in principle. It is important to state that whether the oxide is MIEC is dependent upon sensitivity expectation from material, i.e. application requirements. Electronic mobility is around \( 10^4 \) to \( 10^8 \) times greater than ionic mobility [66]. Thus, for competent conduction among these two requires \( 10^4 \) to \( 10^8 \) times greater number of ionic charge carrier than electronic carriers, which is in fact only possible, theoretically, with ceramics already by virtue of their ability to form excess vacancies. But this is not realistic. For instance, \( (\text{La}_{0.6}\text{Sr}_{0.4})(\text{Co}_{0.8}\text{Fe}_{0.2})\text{O}_3-\delta \) is known to be a “good” MIEC perovskite having electronic conductivity of 269 S/cm and ionic conductivity of 0.058 S/cm at 800 °C [67]. In many other perovskites, difference between ionic and electronic conduction is even more drastic [13].

So it should be remembered that electronic conduction is far more than ionic conduction in mixed conductors. Nonetheless, which mechanism will be, in this relativity, dominant over another is strong function of several variables namely dopant degree (value of \( x \)), temperature, crystal/electrical structure (band gap properties) and \( P_{O_2} \). So, it is not easy to sum up with some certain conclusions. Resulting combinational properties exhibit wide variations.

But the case is different for electrolyte materials where pure ionic conduction is observed. In these oxides, electrical conduction is not required; the only charge compensation mechanism is vacancy formation. When cations are fixed in terms of valence state, this necessity can be achieved. Nevertheless, depending upon the conditions, electrolyte may also show some slight electrical conduction.
Exceptions are for confirmation of general rules. This general rule is that, introduction of mixed ionic and electrical conduction as well as superior exchange properties bring about thermodynamic instabilities manifested as structural and chemical instabilities. So, what creates superior properties in MIEC perovskites are also the fundamental reasons for instability of them which can only be solved by significantly reducing temperature.

Importance of mixed ionic and electronic conduction is originated not only from extension of TPB through bulk but also from enhanced oxygen ionic transport through bulk and electro catalytic effect on surface oxygen exchange which is also a strong or weak function of electrical conductivity, too. It is apparent that excess existence of electrons on cathode surface will favor reduction of oxygen gas. So, electrical conduction is desired. Non-stoichiometry is also effective in this reduction by virtue of providing available sites for eventual incorporation of oxygen [27,55] and oxygen transport. Steps of electrochemical reduction on surface are as follows;

Adsorption;

\[ O_2(gas) + q_{ads}^e + V_{os}^{q_s} \rightarrow (O_2)^{q_o}_{os}. \]

Dissociation;

\[ (O_2)^{q_o}_{os} + q_{ads}^e + V_{os}^{q_s} \rightarrow 2O_{os}^{q_o}. \]

Incorporation;

\[ O_{os}^{q_o} + q_{incorp}^e + V_{ob} \rightarrow O_{ob}^x + V_{os}^{q_s}. \]

Overall;

\[ O_2 + 2V_{ob} + 4e^- \rightarrow 2O_{os}^{q_s}. \]

What are meant by \( O_2, V \) and \( O \) are diatomic oxygen, oxygen vacancy, oxygen atom respectively. \( O_b \) and \( O_s \) as subscripts correspond to location of species at bulk and surface oxygen sites. Dots and minus as superscripts refer to positive and negative charges and \( q \) is simply transferred charge. Superscript \( x \) denotes the neutral charge of species.
Oxygen reduction through cathode is non-homogeneous process; it has many steps. Even only surface processes are divided into different steps and existence of vacancy, which can also be correlated by ionic diffusivity, is crucial for more facile process. Surface/bulk diffusions, charge transfer at different interfaces are other ones as [15].

Elaboration of surface process is mainly because of the fact that introduction of MIEC brings about converting double phase boundary (DPB) surface into TPB, which is point at which ionic, electronic conductors and gas phase meet. Thus surface/air contact becomes TPB. When cathode is in thin film form, all the electrochemical reduction steps given above take place at surface and surface comprises great importance. This is illustrated in Figure 2-6.

Different conduction types (ionic or electronic) have catalytic effect on different parts of overall electrochemical reduction process. Electrical conduction catalyzes adsorption process while non-stoichiometry facilitates incorporation by giving oxygen vacancies [55]. Once it is incorporated on surface, reduced oxygen should diffuse through cathode/electrolyte interface in facile manner. Non-stoichiometry is also functional in this respect.

Aforementioned surface electrochemical steps as well as bulk are characterized by surface oxygen exchange constant (k) and oxygen ion diffusivity (D) [68]. Importance
of these parameters will be comprehensively evaluated in upcoming section under the title of EIS Analysis.

Whereas mixed ionic and electrical conduction is the principle requirement in SOFC cathodes, it is not the only one; various other parameters, as stated in previous pages, should also be involved and evaluated in eventual selection. These are chemical/structural stability and CTE compatibility with electrolyte.

2.2.1. Structural Stability

Structural stability is frequently correlated with the term Goldschmidt tolerance, denoted as $t$, defined below. When $0.77 \leq t \leq 1$, perovskite is said to be stable according to this relation;

$$t = \frac{r_A + r_O}{\sqrt{2} (r_B + r_O)}$$

$r_A$, $r_O$ and $r_B$ are radii of A, oxygen and B in ABO$_3$ structure respectively. When perovskite structure is cubic, Goldschmidt tolerance is equal to unity. Approaching unity brings about more closely packed structure whether it is slightly higher or slightly lower. On the other hand, $t=1$ corresponds to the same ionic radii for both A-site atom and oxygen [69]. However, due to A-site substitution, BO$_6$ octahedron gets distorted and cubic perovskite transforms to other crystal systems such as rhombohedral, orthorhombic and hexagonal [70]. Transformation from cubic to other systems brings about anisotropy in properties through cathode. This distortion as well as Goldschmidt tolerance change as a function of dopant degree for some state-of-the-art perovskites can be found in ref [71].

A correlation between cation valences and eventual crystal system can be established. When $A^{3+}B^{3+}O_3$, cubic symmetry is not allowed while cubic symmetry is favored in $A^{2+}B^{4+}O_3$ and $A^{1+}B^{6+}O_3$ [71].
Any probable crystal structure change during heating or cooling of SOFC must also be of concern in evaluating structural stability. Change in crystal structure during heating is rare but still it should be taken into account. For example, ScSZ has been reported to change crystal structure at around 600 °C when dopant degree, $x$, is more than 0.15 [35]. BSCF on the other hand is considered to be very good candidate for SOFC cathode with its enhanced surface exchange properties and the vacancy content but its main limitation is lattice instability [27]. Alteration of its crystal structure with increasing temperature makes BSCF prone to cracks or residual stress formation.

It must be noted that, structural stability is very important and it has a deterministic effect in overall stability of cathode. Inevitable result of cation size differential brings about less closely packed structures leading thermodynamic instability as well as anisotropic properties manifesting themselves as chemical instability eventually. So, thermodynamic (or chemical) stability becomes a function of structural stability and structural stability is expressed as Goldschmidt tolerance. Its importance is such that, for example, deviation from cubic symmetry causes a decrease in ionic conductivity [72]. Or, since electrical conduction occurs via electron-hole hopping through B-O-B chains, structural changes drastically affect electrical conduction.

High oxygen reduction activities have been reported till now between $(\text{La}_{0.8}\text{Sr}_{0.2})\text{CoO}_3-\delta/(\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoO}_4\delta$ or $(\text{La}_{0.6}\text{Sr}_{0.4})\text{CoO}_3-\delta/(\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoO}_4\delta$. In both cases crystal structures are rhombohedral and tetragonal for LSC$\text{113}$ and LSC$\text{214}$ respectively. Therefore, tuning structural stability is not possible in the present work.

2.2.2. Chemical Stability
While chemical stability is important concerning all component of SOFC [73], in this text it will be evaluated only regarding cathode part. Chemical stability of cathode in most of the cases is associated with both elemental reactivity of cathode with electrolyte and dopant cation segregation through cathode surface [74,75]. But stability under various operation environments should also be concerned as well as microstructural degradation and poisoning of components [76,77]. All these chemical stability problems constitute the main underlying reason and makes it necessary to decrease operation temperatures of SOFCs.
Elemental reactivity with cathode is very significant problem especially regarding cobaltite perovskites constituting the subgroup of perovskites having the best electrical conductivity properties. The most popular and commercially most favorable electrolyte in terms of performance and ionic conduction is YSZ. However, YSZ is reactive with cobalt containing perovskites at intermediate temperatures to form insulating $\text{La}_2\text{Sr}_2\text{O}_7$ [78] and $\text{SrZrO}_3$ [74]. On the other hand, LSM is a very good state-of-the-art cathode in this aspect. Only the temperatures above $1000 \, ^\circ\text{C}$, formation of $\text{La}_2\text{Sr}_2\text{O}_7$ was observed between LSM and YSZ [59]. Thus, utilization of LSM at around $900 \, ^\circ\text{C}$ is possible in terms of reactivity with electrolyte. The main strategy to solve this problem is to make coating on YSZ surface by GDC as a barrier layer at the cost of reducing ionic conductivity slightly since there is no reactivity between Ceria based electrolytes and cobaltite [21]. While there are various and better alternatives for electrolyte in terms of ionic conductivity such as ScSZ, LSGM, DWSB and ESB, YSZ represents the optimum choice. Here it can be stated that desired ionic conductivity for electrolyte is $10^{-2} \, \text{S/cm}$ [14], which is strongly promoted by cubic structure and so type of dopants is preferred accordingly.

Other concern regarding the chemical stability is microstructural stability namely particle coarsening [73]. But this is relevant only in case of porous cathodes, which is beyond the scope of this study. But in terms of anode, this should be regarded since when cathode and electrolyte are thin, then cell should be anode supported, dictating anode to be relatively porous and thick.

A SOFC stack inevitably involves interconnect materials which are generally metals due to their strength as well as very high electrical conductivity [79]. The most popular and successful interconnect material is the doped $\text{LaCrO}_3$ as well as electrically conductive metals, both including Cr and at high temperatures Cr poisoning is observed [80]. The most drastic effect of high temperature emerges regarding this interconnection [79]. So, the greatest portion of driving force for temperature reduction is caused by interconnect material problems [17]. Significantly reduced temperature is expected to make steels useful for application.

Aforementioned aspects must be of great concern regarding SOFCs in general. But elaborating them all is beyond the scope of this work. So, the main focus, here, is LSC,
i.e. the material under study in this thesis. In this way, aside from thermo-mechanical compatibility and reactivity with YSZ, the most critical issue regarding LSC cathodes is Sr segregation towards surface, i.e. phase instability [81].

2.2.2.1. Surface Strontium Segregation

Surface Sr segregation is quite severe problem regarding LSC [9,82,83] such that ASR of cell becomes 10 times higher within only first three days [9,18]. The same surface Sr segregation problem is valid for LSM, too [8,59,81,84]. Observation of such problem even in the most stable cathode (LSM) is remarkable. But kinetic of surface Sr segregation in LSC is extremely fast.

At this point it should be pointed out that Sr migration to surface is not a problem. Contrary, in some cases, Sr migration has been proven to be functional in stabilizing some interfaces [11,85]. However, after a threshold, migrated Sr is suspected to be beyond the solubility limit of structure and this has been demonstrated to lead to phase separation as SrOₓ on surface [84]. This is the scenario that should be avoided since this SrOₓ blocks ORR [75,86]. However, phase separation and resulting blockage of ORR seem to be inevitable for long term. This ‘long time’ is very short for LSC namely several days [9].

The driving force for Sr to segregate through cathode surface has been found to be reduction in elastic energy originated from cation size mismatch [84]. Sr has higher ionic radius and this higher radius reduces compressive strains arisen on the surface when it is excess there [87]. The other key mechanism in segregation is that excess oxygen vacancies on surface causes net positive charge there. This creates driving force for negatively charged dopant to migrate to surface [20], which constitutes the electro-static aspect of origin of Sr segregation problem.
Now it can be again observed that cation segregation, one of the most important chemical stability problems, is directly relevant to structural stability phenomena; it is directly originated from structural instability determined from cation size differential.

It has been found that temperatures at above 400 °C, surface Sr segregation is unavoidable whether fast or slow [11,18,75]. Thus, in order for successful utilization of LSC, reducing temperature to 400 °C, seems to be necessary. This requires extreme maximization of highly active interfaces on the surface. That constitutes the basis on which this thesis has been constructed. Further insight on this segregation phenomenon has been gained by simulation studies, too [68,85,88].

At this point it is meaningful to emphasize the very promising approach having potential to get rid of surface chemical instability problem regarding perovskites, which is simply doping perovskites surfaces with various cations. Tsvetkov et al. [19] dipped LSC thin films into TiCl₄ solution, which resulted in Ti deposition on the surface, and it has been found that Ti modification of the surface has significantly reduced Sr segregation phenomenon, enhancing cell stability significantly. The

**Figure 2-7** Drastic ASR change as a function of time at different temperatures. Green represents stoichiometric bulk LSC, orange denotes Sr enriched regions and red boxes symbolize segregated and separated SrO-rich phase [18]
starting point is the fact that surface Sr segregation is caused by elastic energy differential between surface-bulk and electrostatic equilibrium [84]. Accordingly, types of cations by which perovskites surfaces are modified in order to reduce driving force of Sr to segregate can and will be extended. However, this approach is highly new in literature and there is, for now, lack of comprehensive understanding [19].

To sum up, it can be seen that state-of-the-art cathode materials are prone to rapid degradation by various mechanisms. No matter from exactly what source the instability is originated, it is drastically affected by temperature. This can be elemental reactivity, poisoning of components, segregation and/or coarsening. The net result is that temperature reduction is the main objective of SOFC researchers.

2.2.3. Coefficient of Thermal Expansion

On one hand, decreasing the thickness of components of SOFC is dictated by the reduction of cell resistance, on the other, as thickness of cathode decreases, any probable CTE mismatch between cathode and electrolyte becomes more and more crucial. Such a mismatch can lead to easily cause cracks and delamination on the cathode [89,90].

Among state-of-the-art cathode materials, Co is responsible for high CTE (see Table 2-1). Ferrites follow cobalt containing perovskites and the lowest CTE is found in manganite perovskites. But the key is matching of CTE between cathode and electrolyte. Cobalt containing perovskites generally give twice as much as electrolyte materials (see Table 2-1 and Table 2-2). The best matching is observed between state-of-the-art electrolytes and manganese containing perovskites.

At this point, it is remarkable to point out that lattice expansion can be originated from two reasons; linear thermal expansion characterized by CTE and chemical expansion [45,97]. Linear CTE is determined by electrostatic forces within lattice in ionic crystals. If attraction force between atoms is reduced and/or interatomic distance is raised, then CTE gets bigger. In case of Co, this interatomic distance is more since Co has relatively lower ionic radius [45,98] (see Table 2-3) causing higher linear CTE. On the other hand, as a strong function of oxygen non-stoichiometry (δ), chemical
expansion part releases at elevated temperatures, resulting from excess reduction of B-site cation and corresponding excess anion vacancy formation [97,99].

**Table 2-1** An overview to CTE of cobaltite, ferrite and manganite cathodes of SOFC

<table>
<thead>
<tr>
<th>Cathode Formula</th>
<th>CTE (x10^{-6} K^{-1})</th>
<th>T (˚C)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>(La_{0.6}Sr_{0.4})CoO_{3}</td>
<td>20.5</td>
<td>800</td>
<td>[45]</td>
</tr>
<tr>
<td>(La_{0.8}Sr_{0.2})CoO_{3}</td>
<td>19.1</td>
<td>800</td>
<td>[91]</td>
</tr>
<tr>
<td>(La_{0.8}Sr_{0.2})(Co_{0.2}Fe_{0.8})O_{3}</td>
<td>15.4</td>
<td>600</td>
<td>[92]</td>
</tr>
<tr>
<td>(La_{0.8}Sr_{0.2})(Co_{0.8}Fe_{0.2})O_{3}</td>
<td>20.1</td>
<td>600</td>
<td>[71]</td>
</tr>
<tr>
<td>(Ba_{0.5}Sr_{0.5})(Co_{0.8}Fe_{0.2})O_{3}</td>
<td>20</td>
<td>500</td>
<td>[16]</td>
</tr>
<tr>
<td>(Sm_{0.5}Sr_{0.5})CoO_{3}</td>
<td>20.5</td>
<td>700-900</td>
<td>[93]</td>
</tr>
<tr>
<td>(La_{0.7}Sr_{0.3})(Co_{0.8}Fe_{0.2})O_{3}</td>
<td>21</td>
<td>800</td>
<td>[61]</td>
</tr>
<tr>
<td>(La_{0.8}Sr_{0.2})FeO_{3}</td>
<td>12</td>
<td>750</td>
<td>[94]</td>
</tr>
<tr>
<td>(Pr_{0.5}Sr_{0.5})FeO_{3}</td>
<td>13.2</td>
<td>550</td>
<td>[44]</td>
</tr>
<tr>
<td>(Pr_{0.8}Sr_{0.2})FeO_{3}</td>
<td>12.1</td>
<td>800</td>
<td>[44]</td>
</tr>
<tr>
<td>(La_{0.8}Sr_{0.2})MnO_{3}</td>
<td>11.8</td>
<td>900</td>
<td>[95]</td>
</tr>
<tr>
<td>(La_{0.6}Sr_{0.4})MnO_{3}</td>
<td>12.7</td>
<td>800</td>
<td>[96]</td>
</tr>
<tr>
<td>(La_{0.7}Sr_{0.3})MnO_{3}</td>
<td>11.7</td>
<td>800</td>
<td>[59]</td>
</tr>
<tr>
<td>(Pr_{0.7}Sr_{0.3})(Co_{0.2}Mn_{0.8})O_{3}</td>
<td>11.1</td>
<td>800</td>
<td>[45]</td>
</tr>
</tbody>
</table>

It should be emphasized that CTE is an indirect function of electrical conductivity. Ullmann *et al.* [45] has been manifested this. When B-site cation in perovskites is easily reducible one, which is the main reason for improved electrical conductivity, a further increase in oxygen non-stoichiometry takes place at increasing temperatures since B-site has easily been reduced to lower valence states at this condition [92].

**Table 2-2** An overview to CTE of state-of-the art electrolyte materials for SOFC

<table>
<thead>
<tr>
<th>Electrolyte Formula</th>
<th>CTE (x10^{-6} K^{-1})</th>
<th>σ_{i} (S/cm)</th>
<th>T (˚C)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Ce_{0.8}Gd_{0.2})O_{1.9}</td>
<td>13.5</td>
<td>0.053</td>
<td>800</td>
<td>[5]</td>
</tr>
<tr>
<td>(Ce_{0.8}Sm_{0.2})O_{1.9}</td>
<td>12.2</td>
<td>0.095</td>
<td>800</td>
<td>[13]</td>
</tr>
<tr>
<td>(La_{0.9}Sr_{0.1})(Ga_{0.8}Mg_{0.2})O_{3}</td>
<td>10.7</td>
<td>0.1</td>
<td>800</td>
<td>[100]</td>
</tr>
<tr>
<td>(Zr_{0.85}Y_{0.15})O_{1.9}</td>
<td>10.5</td>
<td>0.03</td>
<td>800</td>
<td>[38]</td>
</tr>
<tr>
<td>(Zr_{0.85}Sc_{0.15})O_{1.9}</td>
<td>10.7</td>
<td>0.13</td>
<td>800</td>
<td>[38]</td>
</tr>
</tbody>
</table>
Since Co is more easily reducible than for instance Fe [67,101], LSC has higher CTE and higher oxygen non-stoichiometry than LSF and/or LSCF as well as it has higher electrical conductivity. Manganites, in this way, are poor ionic conductors since stable valence state of Mn is +4 in wide intermediate range of T and $P_{O_2}$ but are very good in CTE match [102,103]. The negative CTE effect of Co, the one giving the best mixed conduction, nevertheless, has been tried to be limited by B-site substitution by Fe. But this inversely affects the electrical conduction [71]. Consequently, use of LSC and LSCF have been restricted in spite of their extraordinary electrical and ionic conductivity.

So, it is understood that if high electrical conduction from MIEC cathode is preferred, which is necessary to catalyze $O_2$ reduction, it is necessary to consent high CTE. This rule is valid also for ionic conductivity in MIEC perovskites (not purely ionic conductors). As Ullmann et al. [45] manifested, pure ionic conductors deteriorate the common correlation among CTE and ionic conductivity.

In electrolyte perovskites in which there is almost no electrical conduction, excess loss of oxygen is already a reason for higher CTE [104]. In case of MIEC perovskites, additional CTE enhancement is brought about by easy reducibility of B-site cation manifested also as electrical conductivity. This is because electrolyte materials are not perovskite in which there is a competition between charge compensation mechanism with respect to T and $P_{O_2}$ such that higher T and lower $P_{O_2}$ mean ionic charge compensation rather than electrical. In electrolyte material, this charge compensation regime differentiation is not observed in mentionable manner as a result of different T and $P_{O_2}$ regimes since they are not MIEC oxides and viable charge compensation mechanism is ionic compensation [35].

Despite of this restriction of LSC and LSCF (cobalt containing perovskites in general), they have always been the focus of researches because of their unprecedented ionic and electronic conductivities such that their ionic conductivity (LSC-0.22 Scm$^{-1}$ at 800 °C [105]) for example even more than some of electrolyte materials (YSZ-0.03 Scm$^{-1}$ at 800 °C [38]). In this way, high CTE is inevitable for LSC/LSCF but its tremendous effects can be eliminated by making it operative at low temperature applications, which has been the main focus of investigations regarding LSC/LSCF and many other
MIEC perovskites. If utilization of $\text{LSC}_{113}/\text{LSC}_{214}$ hetero-interface in this study, for instance, enables operation of SOFC at 400-500 °C interval, CTE mismatch between GDC electrolyte and LSC may not lead crack formation or delamination on cathode [90,106]. In terms of CTE, that is the main motivation.

2.3. An Overview to State-of-The Art Cathodes

There is no doubt that almost all properties of MIEC perovskites are result of B-site cation type and they can only be tailored through A-site. In this way, the most popular MIEC perovskites can be classified into three group namely manganites, cobaltites and ferrites or mixing of them in terms of their B-site cations, that determine eventual properties of cathodes. A-site is generally rather a matter of adjusting Goldschmidt tolerance along with deteriorating charge balance. Prior to going further into $\text{LSC}_{113/214}$, it would be helpful to briefly review these materials.

2.3.1. $(\text{La}_{1-x}\text{Sr}_x)\text{MnO}_3$ (LSM)

The most exceptional property of LSM is its good electrical conductivity (depending upon Sr doping degree) having 300 S/cm at 900 °C well higher than 100 S/cm threshold. Even in the case of LaMnO$_3$ where no divalent cation (Sr for example) substitution takes place, electrical conduction is observed. This is because of instability of Mn$^{3+}$ resulting in disproportionation of it into Mn$^{2+}$ and Mn$^{4+}$ [107]. This provides available sites for electron/hole hopping mechanism [108]. Not only disproportionation but also intrinsic electronic structure properties resulting from crystal structure is effective in creation of electrical conduction [109].

The key here is not this electrical conductivity, rather it is the fact that such good electrical conductivity is accompanying its very low CTE ($\sim11x10^{-6}$ K$^{-1}$ [13]) matching well with the optimum electrolyte material YSZ. LSM is also compatible with GDC and LSGM as well as YSZ electrolytes in terms of elemental reactivity and it is relatively much more stable than other cathode materials [59].

Behavior of LSM is interesting; almost all charge balance is achieved by electrical compensation in LSM. Hence, LSM is poor ionic conductor ($\sim6x10^{-7}$ S/cm even at
900 °C [110]) and as opposed to other perovskites for cathode, electrical conductivity increases at increasing temperatures with the p-type conductivity [59]. This is due to its different defect structure; LSM can accommodate both oxygen deficient and oxygen excess regimes depending on oxygen partial pressure. In normal working media of SOFCs, oxygen excess regime prevails [109,111,112]. Since excess oxygen cannot reside interstitially due to the fact that LSM has a close-packed structure, cation vacancies are formed to satisfy charge neutrality destroyed by the existence of Sr at A-site [59]. Thus, in fact, there is no any other oxygen apart from the ones residing normal oxygen sites of perovskite. What makes \( \delta>0 \) in \((\text{La}_{1-x}\text{Sr}_x)\text{MnO}_{3+\delta}\) is the deficiency in cations. Vacancies of which cations are dominant is still debatable [8].

If it is considered that electrochemical reduction of oxygen takes place at TPB, it is seen that LSM is poor in enhancing TPB as single phase material. That is, for extension of TPB and reducing cell resistance, an additional ionic conductivity is required which is not the case for LSM alone. Hence it is generally used as composite form with additional ionic conductor such as YSZ [50].

![Figure 2-8](image.png)

**Figure 2-8** Cross sectional image of Siemens/Westinghouse SOFC in which LSM is used as cathode (air electrode) [3]
Simultaneous existence of performance stability, low CTE and good electrical conductivity as well as catalytic activity have made LSM only conventional cathode material for SOFCs which has been first utilized by Siemens in 1997 [113,114]. In experience of Siemens/Westinghouse, they used YSZ as electrolyte, LSM as cathode and Ni-YSZ cermet as anode. This cell operating at 1000 °C yielded 46% conversion efficiency, 0.1% performance degradation per 1000 hours over successful operation for 16600 hours [17,114] and no delamination up to 100 times thermal cycles [3].

These statistics are excellent and represent a successful SOFC operation. But still very high cost has been problem. Lowering temperature will enhance lifetime of SOFC, commercializing SOFC by virtue of making it cheaper. However, decreasing temperature drastically restricts electrical conductivity and increases ASR of LSM cathode whereas temperature reduction is a must to overcome short term degradation problems. Thus, LSM is not a suitable candidate for intermediate temperature SOFCs dictating the use of different alternatives. For further information about LSM, reader can refer to highly comprehensive review on LSM given by Jiang [59].

2.3.2. (La1-xSr0.x)CoO3-δ (LSC)

Sr doped lanthanum cobaltite (and cobalt containing perovskites in general) is the best material in terms of electrical and ionic conductivities among all alternatives and it has the highest oxygen exchange coefficient after BSCF and Sr(Co1-xFey)O3-δ [6,42,46]; Sase et al. [15] reported 2.1x10^-8 cm/s at 500 °C at ambient P_O2 for (La0.6Sr0.4)CoO3-δ, which is very remarkable among state-of-the-art SOFC cathode materials. However, existence of Co as B-site cation yields more than 21.3x10^-6 K^-1 CTE, which is twice as much higher than common electrolyte materials (see Table 2-2). Moreover, use of LSC necessitates use of for instance GDC as electrolyte since LSC has reactivity problem with YSZ as explained previous section [78].

As explained previously, electrical properties are originated from the type of B-site cation, crystal structure of perovskite (O-B-O bond angle) and interaction of atoms and their orbitals (electronic structure) within this crystal structure, which is in turn a function of ionic radii. If it is considered that cobalt containing perovskites are
definitely the best ones amongst all in terms of both ionic and electrical conductivities and the worst one in terms of CTE compatibility [74], underlying reasons should be sought in these relations.

CTE is strong function of A-O and B-O bond strength [12,104]. Many of the studies state that high CTE of LSC is due to its high ability of it to create oxygen vacancies originated from promotion of the reduction from Co$^{4+}$ to Co$^{3+}$. Since Co$^{3+}$ has higher ionic radii, B-O bond strength is reduced, increasing eventual CTE [98,105]. However, asserting the reverse relationship may be possible also; since the most unstable abnormal valence (+4 state) is found in Co among Co, Fe and Mn, it has the highest tendency towards achieving its normal valence state which is +3 [101]. For instance, +4 valence state of Mn has been found to be stable till 850 °C [101] explaining the reason why Mn is oxygen excess rather than oxygen deficient in wide range of T and $P_{O_2}$. Teraoka et al. [101] have reported that Fe is superior in oxidizing, i.e. changing its trivalent state to tetravalent state. Eventually, since Co has the highest tendency towards reduction to trivalent state, it has the lowest activation energy for vacancy formation, resulting in CTE enhancement indirectly [12].

![Figure 2-9 Illustration of Co-O-Co bond angle change effects on electronic structure (adapted from [103])](image-url)
So, as well as high CTE, this relationship also explains the extraordinary ionic conductivity providing that crystal structure effect is not considered; higher reducibility means higher capability to create oxygen vacancies [115,116]. If structural stability (crystal structure) is considered, higher MIEC is brought about by higher symmetry and/or limited distortion on BO$_6$ octahedron due to its effect of diffusing jump [71]. One should also note that surface oxygen exchange properties are also a function of adsorption desorption properties of materials which is in turn related with the capability of creating oxygen vacancy [27]. So this also explains the high exchange constant of LSC by part.

However, extraordinary electrical conductivity still needs further explanation. What happens in LSC is simply overlapping of 3d orbitals of Co and 2p orbitals of oxygen. When it takes place, band width is reduced and electrical conductivity via “itinerant” (delocalized) electrons is promoted as illustrated in Figure 2-9. This brings about metallic conduction behavior surely depending upon Sr doping degree [6]. Metallic conduction behavior is something uncommon among perovskite oxides. This overlap is definitely very strong function of Co-O distance and hence crystal structure as Mineshige $et$ $al.$ [64] pointed out. Different structures mean different degree of overlap and Co-O-Co bending, latter of which is functional in hopping conduction while former is important for releasing of itinerant electrons and metallic conduction. For various A-site cations, crystal structure of perovskite is orthorhombic if Sr doping degree, x, is small but when it is La, structure is rhombohedral at low x and cubic at high x, making LSC superior in electrical conductivity [12,103]. Thus, the crystal symmetry as well as inter-atomic distance within crystal are the main variables determining the eventual electrical conduction.

**Table 2-3** Ionic radii of Co$^{+3}$, Mn$^{+3}$ and Fe$^{+3}$ at different spin states [98]

<table>
<thead>
<tr>
<th>Atom</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Spin</td>
<td>0.58</td>
<td>0.55</td>
<td>0.545</td>
</tr>
<tr>
<td>High Spin</td>
<td>0.645</td>
<td>0.645</td>
<td>0.61</td>
</tr>
</tbody>
</table>
But at this point, it should be highlighted that those variables are also functions of ionic radii, or equivalently atom types that determine covalency of B-O bonds considered to be crucial electronic conduction through BO₆ chains [71]. Higher covalency is expected in case of smaller cation, higher anion size and more positively charged cation. These characterize covalency by virtue of their ability to determine polarizing power of cation. In this way, Goldschmidt asserts a way to measure polarizing power by Coulomb potential denoted as Ze²/rₜ where Z is formal valence of cation, e is elementary charge and rₜ is ionic radius of B cation [70]. Higher charge on B-site cation with a small radius as well as lower Zₐ/rₐ promote polarizing power and so covalency [71]. For the same valence state, Co has lower ion size and higher covalency as can be inferred from the Table 2-3 given. Now one can infer at this point that high CTE can be tuned by altering A-site cations even in the presence of Co as B-site since Zₐ/rₐ is also a variable. In this way it is suitable to consider A-site atoms as the way of providing ionic network stabilizing BO₆ octahedron through which conduction takes place.

At low temperatures, polarizing power of Co is higher since it has +4 valence state and lower ionic radius. However, this covalency and electrical conductivity is drastically deteriorated at higher temperatures and low P₀₂ due to the increase in the number Co⁺³ ions resulting from domination of ionic compensation mechanism. Furthermore, as a new fact in LSC, an additional reduction in Coulomb potential is caused by spin state transition of Co⁺³ ions unlike to Mn⁺³ and Fe⁺³ which are keeping their high spin states [116,117]. For Co⁺³ ions, from low spin (t₂g⁶,e_g⁰) to intermediate (t₂g⁵,e_g¹) or high spin (t₂g⁴,e_g²) is seen in cobaltites [116,118]. Extreme increase in CTE of LSC can be partly attributed to this effect, too [12]. At this point, in order to inform reader, it would be good to point out that even at low temperatures, electrical charge compensation can only dominantly be operative when x < 0.4 in (La₁₋ₓSrₓ)CoO₃₋δ and more Sr doping leads to vacancy formation even at low temperatures [103]. Exceptional electrical and ionic conductivities together with catalytic activity of cobalt containing perovskites necessitated relatively long explanation for formation of them. But in evaluation of cathode materials, it is better to use ASR data in the time domain,
that is its stability. In terms of ASR values, the lowest value obtained from pure LSC reported to date is 0.023 Ωcm² at 600 °C [119–121]. Some other values have been summarized by Kilner et al. [14] as illustrated in Figure 2-10.

![Figure 2-10 ASR of LSC in different studies (retrieved from [14,122])](image)

Such extremely low polarization resistances are not surprising regarding extraordinary properties of LSC. However, all these properties and exceptional ASR are at the cost of instability of LSC. Unfortunately, LSC derivatives are highly susceptible to short term degradation especially by means of surface Strontium segregation [9]. Even after several days, SrOₓ formation on the air exposed surface blocks ORR and this is inevitable whether slow or fast so long as temperatures above 400 °C [9,11,18]. Recently, surface modification with some metals inhibiting Sr segregation has been adopted as a way to eliminate this problem and make the use of LSC at intermediate temperatures possible for long term use [87].

Whereas high CTE and chemical instability are extremely significant obstacles for use of LSC, its extraordinary electrical and ionic conductivities are such that its ionic conduction is sometimes more than the state-of-the art electrolyte materials still attracts the attention.
2.3.3. (La$_{1-x}$Sr$_x$)FeO$_{3-\delta}$ (LSF)

The driving force for transforming B-site cation from Co to Fe is the high CTE of LSC. By replacing Co with Fe significantly reduces CTE to state-of-the art electrolyte values ($12x10^{-6}$ °K$^{-1}$ [94]) due to higher stability of $+3$ state of Fe [101] but it also reduces both electrical and ionic conductivities drastically because of the absence of Co. Nevertheless, electrical conductivity of various Sr compositions in LSF is still higher than 100 S/cm at intermediate temperatures converging lower limits [58] as well as its significant vacancy amounts manifested as oxygen diffusivity [60]. Electrical conduction occurs only via hopping mechanism unlike to cobaltites. What’s more, LSF has almost same catalytic activity as LSC towards ORR depicted by surface exchange coefficient $k_i$, both has around $10^{-6}$ cm/s exchange coefficient at 750 °C depending upon Sr and $P_{O_2}$ [15,46,123] with well smaller activation energy for LSC [22].

By virtue of LSF, 0.1 Ωcm$^2$ at 800 °C is achieved when $x$ was 0.2 [124,125]. This cell was operated 500 hours without any performance degradation. At this same composition of LSF, Simner et al. [94] reported more than 0.9 W/cm$^2$ peak power densities for 300 hours stable performance at 750 °C. The lowest possible temperature, however, seems to be 676 °C yielding 0.168 Ωcm$^2$ as reported in the study by Leonide et al. [123] in which La deficiency at A-site was adopted to facilitate the overall kinetic. Beyond all of these promising performances, the most remarkable advancement that LSF has been the efficiently matched CTE with YSZ electrolyte [126].

Even though kinetic of it is significantly reduced with Fe as B-site cation, reactivity problem with YSZ is the same as LSC. But in this case, reactivity is in the form of Zr and La inter diffusion and incorporation of Zr into B-site [125,127–129] rather than lanthanum zirconate formation [124]. In this way, LSF is not free from performance degradation over time like LSC [94]. However, this problem can be significantly overcome by the help of implementing ceria based protecting barrier onto YSZ electrolyte or direct use of them [130].
Thus, LSF seems to be a suitable candidate for intermediate temperature SOFC in terms of cathode resistance and CTE match. The best composition reported is (La$_{0.8}$Sr$_{0.2}$)FeO$_{3-\delta}$ [94]. However, 700 °C seems to be the lowest possible operation temperature in its single phase utilization if it is considered that 0.15 Ωcm$^2$ is targeted ASR value and this temperature is still a source of problem regarding interconnect materials [131]. Furthermore, long term performance degradation is still a problem in LSF. There is still lack of comprehensive long term performance tests in literature.

2.3.4. (La$_{1-x}$Sr$_x$)(Co$_{1-y}$Fe$_y$)O$_{3-\delta}$ (LSCF)

Fe has been observed to be very effective in optimization CTE match with electrolytes along with preservation of conductivity thresholds. Nevertheless, operation temperature is still behind the expectations. Hence, partial substitution of B-site by Co was adopted an alternative way for further optimization. Coexistence of cobalt and iron may well converge the performance of LSF to LSC along with minimizing the drawbacks of LSC such as high CTE.

Indeed, this approach brought about superior performance with respect to LSF. LSCF shows wide variations of performances as function of both A and B-site doping degrees. Petric et al. [61] observed increasing CTE as well as MIEC with increasing Co content. Hence, only small extend of Sr and Co doping are acceptable in terms of conservation of reduced CTE of LSF in the acceptable ranges. Some compositions and corresponding properties are given in Table 2-4.

<table>
<thead>
<tr>
<th>Composition</th>
<th>CTE (10$^{-6}$ K$^{-1}$)</th>
<th>$\sigma_e$ (S/cm)</th>
<th>$\sigma_i$ (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(La$<em>{0.8}$Sr$</em>{0.2}$)(Co$<em>{0.2}$Fe$</em>{0.8}$)O$_{3-\delta}$</td>
<td>14.8 [45]</td>
<td>125 (600 °C [132])</td>
<td>0.0022 (800 °C [45])</td>
</tr>
<tr>
<td>(La$<em>{0.6}$Sr$</em>{0.4}$)(Co$<em>{0.2}$Fe$</em>{0.8}$)O$_{3-\delta}$</td>
<td>15.3 [132]</td>
<td>300-330 (500-750 °C [14])</td>
<td>0.008 (600 °C [13])</td>
</tr>
<tr>
<td>(La$<em>{0.8}$Sr$</em>{0.2}$)(Co$<em>{0.8}$Fe$</em>{0.2}$)O$_{3-\delta}$</td>
<td>20.7 [92]</td>
<td>1050 (600 °C [92])</td>
<td>0.04 (800 °C [61])</td>
</tr>
<tr>
<td>(La$<em>{0.8}$Sr$</em>{0.2}$)(Co$<em>{0.5}$Fe$</em>{0.5}$)O$_{3-\delta}$</td>
<td>17.6 [61]</td>
<td>354 (800 °C [45])</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2-4 CTE, electrical and ionic conductivities of various LSCF cathodes
Along with the properties given in Table 2-4, even in case of (La_{0.6}Sr_{0.4})(Co_{0.2}Fe_{0.8})O_{3-\delta}, in which there is high iron content, diffusivity and exchange coefficients are almost the same as LSC [71]. This overall picture suggests that LSCF can be treated like LSC but together with reduced CTE. However, the most explicit parameter for evaluation of suitability of a material is the desired ASR at given temperature and stability.

In this way, various attempts have been made for utilizing LSCF cathodes in SOFC stacks. At this point, it is remarkable that when LSCF cathodes are in thin dense film form, they show so high ASR that its use becomes impossible even at around 800 °C. Figure 2-11, belonging to the study in which cathodes are derived via PLD [133,134] and sputtering [135] is a good illustration of this. As can be seen, even at 800 °C and high Co content, targeted ASR value (0.15 Ωcm²) is not achieved, which is even worse than LSF cathodes.

![Graph showing ASR values of various LSCF dense thin films.](image)

**Figure 2-11** ASR values of various LSCF dense thin films. Figure is retrieved from ref [134]. Data in the box is from ref [134]. Data from Baumann *et al.* [133] and Xiong *et al.* [135]

Ralph *et al.* [124] utilized porous LSCF cathodes having approximately 200 μm thicknesses. They used Fe rich compositions and reported around 0.2 Ωcm² at 700 °C.
This is remarkable as compared to dense thin film results. As the latest, porous (La$_{0.58}$Sr$_{0.4}$)(Co$_{0.2}$Fe$_{0.8}$)O$_{3-\delta}$ has been found to exhibit 0.13 $\Omega$cm$^2$ ASR at 600 °C, which is the lowest reported value to date [136]. In this study, A-site La deficiency was adopted. Nevertheless, LSCF suffers from severe performance degradation over time namely 0.05% per hour [137].

Aside from existence of abovementioned parameters, mechanisms with which they occur as functions of T and $P_{O_2}$ are quite complicated since in ferrites, n and p-type conductivities are observed while cobalt as B-site cation induces metallic conduction behavior due to itinerant electrons of it. So, it is not reasonable to sum up with certain tendencies as function of T and $P_{O_2}$ especially in terms of conductivities.

2.3.5. (Ba$_{1-x}$Sr$_x$)(Co$_{1-y}$Fe$_y$)O$_{3-\delta}$ (BSCF)

BSCF is very recent and definitely the best choice in terms of both surface oxygen exchange rate [138,139] and bulk transport [140] manifested as k and D respectively. The most distinguishing character of BSCF is the fact that both of A-site host and dopant atoms are alkaline earth elements having +2 valence (Ba and Sr) as opposed to other types of perovskite alternatives in which A-site host atom is rare earth element namely La. In conventional perovskite complex oxides, A-site is doped with a cation having different valence state than host atom resulting electrical conduction as explained in previous pages. Due to the same valence state at A-site (Ba and Sr) electrical conductivity of BSCF is relatively low (30 S/cm at 500 °C [16]) as compared to other cathode materials (as stated in page-11 previously, 100 S/cm electrical conductivity is considered to be lower threshold). However, this is compensated by extraordinary k and D values of BSCF introduced by better oxygen vacancy mobility than others [27,46,140].

The first attempt to substitute BSCF as SOFC cathode was done by Shao and Haile [139]. As consequence of its extraordinary surface exchange and transport properties found in this study, 0.055-0.071 $\Omega$cm$^2$ and 0.51-0.60 $\Omega$cm$^2$ cathode resistance at 600 and 500 °C could be achieved, respectively. These excellent results attracted significant attention, making BSCF focus of many researches [138,141–143]. It can
be deduced from all these studies that magnificent properties of BSCF are directly proportional to Ba and Co content; Ba doping to A-site stabilizes the structure by virtue of making Goldschmidt tolerance to unity (cubic structure).

The latest and the most comprehensive study concerning BSCF has been conducted by Kuklja et al. [27] by help of ab initio simulations as well as experimental approaches. The A and B site composition combination giving the best results associating the best performance has been found to be with \((\text{Ba}_{0.5}\text{Sr}_{0.5})(\text{Co}_{0.8}\text{Fe}_{0.2})\text{O}_3-\delta\). This is because this \(x\) and \(y\) values combination gives the highest oxygen deficiency and resulting the highest surface exchange constants. These superiorities in terms of transport and surface exchange properties are originated from excess oxygen deficiency as well as superior vacancy mobility of BSCF over all other cathode materials. However, this high oxygen deficiency makes this best composition fall into immiscibility region of cubic and hexagonal structures, causing phase instability in case of superior BSCF [144].

In long term, phase decomposition will dictate itself and such a decomposition reduces both \(k\) and \(D\). Definitely, adjusting A/B-site compositions and so converging oxygen deficiency to unity would suppress phase instability but this time advantageous properties of BSCF can’t be utilized.

Another drawback of BSCF that must be concerned is carbonate formation below 900 °C not only with YSZ but also in case of GDC electrolyte [27,142]. Moreover, at temperatures exceeding 800 °C, reactivity with YSZ begins [14]. High CTE of BSCF like all Cobalt containing perovskites is also a problem even BSCF is capable of being operated at 600 °C.

To sum up, similar to other cathode materials whose eventual properties are originated from crystal structure-atom type combination, superior properties of BSCF are commonly referred to well-known size mismatch between A and B site atoms. What is new in BSCF is that it can withstand cubic structure for short period as opposed to state-of-the art cathode oxides, giving extraordinary performance whereas for long term applications, but it is well suspected to degrade by virtue of its decomposition into cubic and hexagonal structures [27,144].
2.3.6. Ruddlesden-Popper (A\textsubscript{2}BO\textsubscript{4}) Type LSC\textsubscript{214}

The key property of (La, Sr)\textsubscript{2}CoO\textsubscript{4±δ} or A\textsubscript{2}BO\textsubscript{4} type structures in general is the ability to form interstitial oxygen atoms at rock salt layer even without need to A-site doping. This is manifested as oxygen excess regime in wide range of T and P\textsubscript{O\textsubscript{2}} resulting in high diffusion coefficients [145].

![Figure 2-12 Ruddlesden-Popper (K\textsubscript{2}NiF\textsubscript{4} type) LSC\textsubscript{214} Structure [21]](image)

(La\textsubscript{1−y}Sr\textsubscript{y})\textsubscript{2}CoO\textsubscript{4±δ} belongs to this family. Its crystal structure is tetragonal for 0.3 < y < 1, comprising a rock salt layer sandwiched between two perovskite layers [72] as illustrated in Figure 2-12. That’s why it is also called layered perovskite [146].

Consequently, oxygen migration is significantly facilitated even without need for A-site substitution (La\textsubscript{2}CoO\textsubscript{4+δ} here), which is responsible for chemical and structural instability problems in conventional perovskites. Superior chemical stability of La\textsubscript{2}CoO\textsubscript{4+δ} hence makes stoichiometric Ruddlesden-Popper structure advantageous over conventional SOFC cathode materials by virtue of its ability to enhance long term stability by suppressing poisoning and cation segregation [27]. Munnings et al. [147] reported surface exchange coefficient around 10^{-5} – 10^{-6} cm/s at between 500-700 °C and diffusivity around 10^{-7.5} cm\textsuperscript{2}/s at 650 °C for La\textsubscript{2}CoO\textsubscript{4+δ}. These values are promising but stoichiometric LSC\textsubscript{214} (La\textsubscript{2}CoO\textsubscript{4+δ}) is highly poor in terms of electrical conductivity such that La\textsubscript{2}CoO\textsubscript{4+δ} has reported to give less than 1 Scm\textsuperscript{-1} electrical conductivity.
conductivity at 500 °C [148]. Electrical conductivity rapidly increases with increasing Sr doping, [149] but it reaches to at most 50 Scm⁻¹ when it is LaSrCoO₄⁺δ [150].

Considering Sr doped La₂CoO₄⁺δ, good diffusion property is accompanied with only moderate electrical conductivity, which is function of Sr doping [148,150]. However, higher Sr amount corresponds to reduction on surface exchange kinetic as recently demonstrated even more drastically than crystallographic orientation by virtue of their ability to enhance surface Sr segregation shadowing orientation effect [75].

It should be kept in mind that depending upon Sr doping degree, oxygen stoichiometry varies. To be valid at ambient P₀₂ and intermediate T range, for relatively low Sr, LSC₂₁₄ accommodates oxygen interstitials (oxygen excess regime) while at increasing Sr degree, it transforms to be oxygen deficient making vacancy mechanism dominant [151]. The statement “low Sr doping” covers y=0.5 in (La₁₋₅Sr₅)₂CoO₄⁺δ, yielding oxygen excess regime in (La₀.₅Sr₀.₅)₂CoO₄⁺δ [152]. This regime is mainly responsible for high diffusivity in Ruddlesden-Popper type structure in general.

In addition, serious anisotropy is observed in this structure especially in terms of both diffusivity and CTE [153–155]. Surface exchange kinetic has not been extensively studied till now. Along with this, high CTE is a problem for LSC₂₁₄ due to existence of Co ions as opposed to Ln₂NiO₄⁺δ (Ln denotes lanthanide elements namely La, Ce, Pr Sm Gd etc.) having relatively compatible CTE for example [155]. Similar to LSC₁₁₃, LSC₂₁₄ is also not free from surface Sr segregation [75]. So, LSC₂₁₄ brings about the problems related to existence of Co. LSC₂₁₄ is only differentiated in terms of its high and anisotropic D and k values and significantly reduced electrical conductivity.

In terms of ASR, as the most viable parameter in evaluating SOFC cathodes, LSC₂₁₄ as well as Ruddlesden-Popper type oxides seem to be unsuitable for intermediate temperature range as a single phase component [146,156]. The best one among Ruddlesden-Popper type oxides is Pr₂NiO₄⁺δ yielding 0.5 Ωcm² at 610 °C [157]. Nickel based Ruddlesden-Popper oxides have been widely and intensively investigated till now as opposed Cobalt based ones, especially in terms of overall SOFC cathode performance by probing ASR [36,158–160]. One of the recent study utilizing LSC₂₁₄ with different Sr dopant amount showed more than 2 Ωcm² even at
700 °C [155]. This work also exhibits ASR values obtained from sub-micron thickness LSC\textsubscript{214} cathodes. The probable reason for high ASR in spite of very good exchange kinetic and accompanying high diffusivity is low electrical conductivity of LSC\textsubscript{214}, reducing TPB.

The situation for Cobalt based Ruddlesden-Popper oxide is also in a good agreement with what Laberty et al. [156] proposed for Ruddlesden-Popper oxides in general; they are not functional materials for SOFC cathode operation at intermediate temperatures. However, not only in composite form with different ionic conductor materials such as GDC [155], but Ruddlesden-Popper type can also be extremely functional in case of oxide hetero-structures like the case of LSC\textsubscript{113}/LSC\textsubscript{214} [11,15,21]. Hence, they may not be promising candidates at intermediate temperature ranges as single phase but they might be well functionalized by use of different probable strategies. It can be stated finally that there is still lack of comprehensive investigations on K\textsubscript{2}NiF\textsubscript{4} type structures as SOFC cathode materials.

2.3.7. Final Remarks Regarding State-of-The Art Cathodes

The most popular cathode materials have been introduced briefly. Although it is excluded, composite cathodes have also been an alternative. In this approach, two components, each of which has relatively high conductivity in one type and poor in the other, are combined such as LSM-YSZ cathodes [50,51,65,161]. But in this study, such an approach is treated to be contradictory to MIEC phenomena, capable of extending electrochemical reduction, to which all the high energy conversion is owed, from TBP to whole air exposed surface.

Furthermore, there are many combinations of A and B-site cations exhibiting promising performances, too [157,162–165]. These are namely Gd, Sm, Bi, Pr, Ce, Nd as A-site and Ni, Cr, Cu, Ga, Mg as B-site. But, no matter how slightly better their performance is, they also suffer from the similar drawbacks caused by their B-site cation, which is deterministic component of ABO\textsubscript{3} oxides. The reason why this brief review of cathode materials has been restricted to these five cathodes is because such a picture is considered to be representative to take a general look at SOFC cathodes, advantages, drawbacks and underlying reasons for their properties.
Much further tailoring is possible since all the properties are determined by the atom characteristics and their ordering type (crystallography) eventually. Much rarer elements can be replaced into these oxides but this time economic feasibility problem arises. Apart from these impractical approaches, all commercially promising possibilities per certain one kind of ABO₃ oxide seems to have been tested in terms of material properties such as exchange rate, diffusivity and conductivities. Synthesizing single phase ABO₃ oxides seem to have reached its limit in this way.

Nevertheless, various improvement routes are still open with regard to hetero structuring and surface modifications. Effect of different fabrication route and parameters for cathode as well as surface modifications are still in progress. Among them, comprehensive understanding of surface cation segregation constitutes extremely crucial task in order to get rid of surface instability problem, from which almost all A-site substituted ABO₃ oxides suffer. Likewise, ORR kinetic at around hetero interfaces is also something new in this field. Revealing the outstanding roles of such heterogeneities are still under investigation. LSC₁₁₃/2₁₄ hetero interface in this way seems to be the highly salient one among those.

2.4. LSC₁₁₃/LSC₂₁₄ Hetero Interface

Extraordinary surface exchange property of LSC₁₁₃/LSC₂₁₄ hetero interface has been first discovered accidentally by Sase et al. [15]. During this research, as a result of over sintering of (La₀.₆Sr₀.₄)CoO₃₋δ at elevated temperatures, LSC₂₁₄ phase was formed accidentally. Only after the discovery of the secondary phase (LSC₂₁₄), hetero interface was investigated in this study by secondary ion mass spectroscopy (SIMS) and this revealed that k* (8x10⁻⁶ cm/s) is around three orders of magnitude higher than that (2x10⁻⁸ cm/s) of (La₀.₆Sr₀.₄)CoO₃₋δ at the same temperature. Following studies concerning the high exchange constant of hetero interface was conducted by Yashiro et al. [166] and Crumlin et al. [21].

What Yashiro et al. [166] did was the examination of symmetric cells obtained via horizontally screen printing phases subsequently onto GDC pellet. Since in this case LSC₁₁₃ and LSC₂₁₄ form parallel path for electron flow, faster one in terms of
conduction will be dominating one. This is LSC$_{113}$ phase. That’s why performance of cells having LSC$_{214}$ on LSC$_{113}$ (or equivalently interfacial enhancement) did have slightly better than LSC$_{113}$. Reported enhancements were around 0.5 orders of magnitude greater $k^3$ (correlated from electrical conductivity) than LSC$_{113}$ and 1-2 orders of magnitude greater than $k^4$ of LSC$_{214}$.

In fact, this was not the exact determination of hetero interfacial enhancement since the cell in study of Yashiro et al. [166] constituted parallel electron flow path. Moreover, in this study, cathodes were not in the form of thin film. Furthermore, enhancement of what Yashiro et al. [166] achieved was not as high as what Sase et al. [15] discovered. Hence, for further clarification, Crumlin et al. [21] obtained epitaxial thin film cathodes by PLD. They deposited LSC$_{214}$ on LSC$_{113}$ with both full coverage and partial coverage. They, accordingly, revealed active region somehow affected by TPB (LSC$_{113}$-gas-LSC$_{214}$) which was around 20 μm. When the thickness of deposited LSC$_{214}$ on LSC$_{113}$ gets increase more than only several nanometers, the ASR gets dramatically increased. In this sense, Crumlin et al. [21] detected 3-4 orders of magnitude enhancement in $k^4$ which is correcting what Sase et al. [15] found first. Problems in measurements done by Yashiro et al. [166] were originated from the fact that enhancement region is very narrow as can be understood from study of Crumlin et al. [21] and thick cathodes were used [166]. Hence, rather than recording the enhancement just at interface, they recorded the effect of hetero interface in overall resistance, which was at most one order of magnitude consistently [166].

This chronology, revealing very narrow distance range [21] (1-200 nm [167]) over which enhancement was actually originated, required atomic scale characterization and understanding which is quite difficult without ab initio calculations. In this way, further investigations have been based on such simulations. One of the initial first principle calculations was done by Han et al. [151]. In their simulation, they found 400 times enhancement in oxygen reduction kinetic at 500 °C and attributed it to anisotropy in LSC$_{214}$ leading to very fast kinetic at (100) plane and lattice strain in LSC$_{113}$ phase. Nevertheless, along with underestimation of 3-4 orders of magnitude enhancement, this DFT study considers each individual phase rather than hetero interface as a new phenomenon as they stated [151].
First principle calculations have been accompanied by experimental studies, too. By use of grazing incidence FIB milling, which has been adopted first time by Kuru et al. [168], Chen et al. [167] probed LSC\textsubscript{113}/LSC\textsubscript{214} interface and discovered electronic activation of LSC\textsubscript{214} by LSC\textsubscript{113} starting from 200-300 °C. This is illustrated in Figure 2-13.

![Figure 2-13 FIB milling at grazing incidence angle [169]](image)

Wider band gap of LSC\textsubscript{214} is interestingly reduced when it is in contact with LSC\textsubscript{113} [167]. At low temperatures, charge compensation of LSC\textsubscript{113} phase is mainly done by partial oxidation of Co. This induces electrical conductivity and these electrons from LSC\textsubscript{113} phase are injected to LSC\textsubscript{214}, which is very rich in interstitial oxygen [145] and suffering from low electrical conductivity [148,150]. Interstitial oxygen of LSC\textsubscript{214} can easily find electrons from LSC\textsubscript{113} to be more effectively reduced and adsorbed by LSC\textsubscript{113}. But this requires empty sites for reduced oxygen to jump in LSC\textsubscript{113} phase. Moreover, migration of electrons through interface is supposed to bring about driving force for migration of oxygen vacancies, too. Such a migration is not however favored at lower temperatures. Increasing temperatures provides creation and mobility of oxygen vacancies for this purpose [111,147]. That’s why electronic activation takes place after certain temperature range is attained, after which the combination of desirable properties of each phase results in fast oxygen reduction kinetic.
Nonetheless, whether it is capable of causing 1000 times enhancement on $k$ at hetero interface alone or not is still question, answer of which is sought in following sections.

![Figure 2-14 Illustration of proposed ORR mechanism for LSC$_{113}$/LSC$_{214}$ by Chen et al. [169]](image)

One might at this point claim that electronic activation is observed in epitaxial film [167], LSC$_{214}$ is known to show fast oxygen reduction kinetic on (100) surfaces [158] and so electronic activation found here is plane specific [11]. However, previous studies based on both EIS [21] and SIMS [15] that are showing similar fast oxygen reduction kinetic without any epitaxy demonstrates that this is an intrinsic phenomenon.

Moreover, it is also notable that proposed electronic activation mechanism is deteriorated with increasing temperatures since electrical conductivity of LSC$_{113}$ phase (at least with highly Sr doped ones) is reduced with increasing temperatures [64]. However, as stated previously, fast kinetic has been reported to be at 500-600 °C, too. Whether degree of observed fast kinetic at around 200-300 °C is similar to degree of it at elevated temperature is questionable. If answer is “similar”, what triggers the same enhancement degree at the cost of lowering electrical conductivity at elevated temperatures becomes a crucial question. What happened at increasing temperatures is vacancy formation and enhanced vacancy mobility, not increase in electrical conductivity. So, activation at higher temperature should be originated from something related to vacancies if the same degree of ORR enhancement is predicted.
Gadre et al. [68] in this way reported strong driving force for Sr diffusion through hetero interface and corresponding La diffusion in reverse direction between \((\text{La}_{0.75}\text{Sr}_{0.25})\text{CoO}_{3-\delta}\) and \((\text{La}_{0.5}\text{Sr}_{0.5})\text{CoO}_{4+\delta}\) by use of DFT-based simulations. These driving forces are evaluated under different T and \(P_{O_2}\) conditions. Resultant (proposed) possible inter-diffusion across interface and Sr enrichment in LSC\(_{214}\) phase are susceptible to form excess vacancy accumulation at elevated temperature near interface in the side of LSC\(_{214}\). However, such a vacancy accumulation near interface is only partially capable of reasoning the 3-4 orders of magnitude enhancement in \(k=k^*\) found by Sase et al. [15] and Crumlin et al. [21] under similar experimental conditions. Nevertheless, Gadre et al. [68] showed that further mechanisms beyond electronic activation exist.

In study conducted by Gadre et al. [68], Sr enrichment in LSC\(_{214}\) is reasonably corresponds to Sr depletion in the side of LSC\(_{113}\) phase, which is supposed to significantly decrease oxygen vacancy concentration near interface especially in the side of LSC\(_{214}\). Such a case (vacancy decrease in LSC\(_{113}\) side) would negatively compensate what is gained in LSC\(_{214}\) in terms of \(k\) enhancement. However, Gadre et al. [68] suggest that this inter-diffusion predicts slight Sr enrichment very near interface in the side of LSC\(_{113}\), too. Consequent La accumulation is expected to occur rather at bulk of LSC\(_{113}\), not interface. Definitely what is stated is a prediction. What is happening near this interface, especially at the side of LSC\(_{113}\) necessitates experimental and quantitative probing of this interface, which is very hard task.

Nonetheless, some of studies, which are not mainly concerned with identification of underlying reasons, qualitatively confirm the claim supporting activation mechanisms apart from electronic activation. Ma et al. [11] discovered that there is a significant deviation between degree of enhancement at lower temperatures; there is 3-4 orders of magnitude enhancement reported in between 500-600 °C [15,21], while this enhancement is 10 times in between 320-400 °C in their analysis [11].

This apparently means that at increasing temperatures, an additional and/or different ORR activation mechanism becomes operative, which was anticipated by Gadre et al. [68]. Ma et al. [11], however, asserts that remaining 100 times enhancement is attributed to fast oxygen incorporation kinetic along (100) plane of LSC\(_{214}\) [151],
which was parallel to cathode film surface in their experiments, consequently making utilization of its ORR superiority through [100] plane impossible. anticipate

However, it is possible to argue that even this strong explanation still underestimates the negative effect of gradually reducing electrical conductivity of LSC$_{113}$ (at higher temperatures), which is simply electron source of that composite cathode system. Attribution of this greater portion of enhancement (100 times) to anisotropy of LSC$_{214}$ phase necessitates an explanation for three orders of magnitude enhancement found in polycrystalline pellet in which no epitaxial relation probably prevails [15]. At least, the same experiment as in ref [12] based on LSC$_{113}$ pellet should be done once more prior to this assertion and nucleation-growth vs crystallography relationship of LSC$_{214}$ in LSC$_{113}$ pellet should have been clarified.

For example, owners of this assertion (Ma et al. [11]) did not add the information whether it nucleates-grows through certain direction during the high temperature formation of LSC$_{214}$ and enhancement is 10$^3$ times higher, or not. Aside from this, it is already known that such giant grains [15] do not generally grow coherently with the matrix phase (LSC$_{113}$) [170] since this would extremely increase surface potential ($\gamma$A). Probable incoherency at interface along with the results implying Sr migration (vacancy formation on LSC$_{214}$ part) near surface based on simulations [68] is strong indication of additional operative orientation-independent mechanisms near interface rather than plane-specific fast ORR.

Not only simulations, but also the experimental demonstration of robust Sr migration contiguous to interface and corresponding vacancy formation has been first reported by Feng et al. [88] on epitaxial thin film composed of LSC$_{214}$-on-LSC$_{113}$ with their coherent Bragg rod angle (COBRA) analysis by use of X-ray radiation. That has been the first implicit atomic scale and experimental characterization revealing strong Sr segregation from perovskite to Ruddlesden-Popper in this way. Not only Feng et al. [88] but also the same research group, having assertion based on orientation dependent k enhancement [11], has recently disclaimed by themselves in study of Chen et al. [75]; they ‘discovered’ orientation independent k enhancement.

To reveal underlying reasons, this interface has been aimed to be used in various studies. One of the final approach aiming interface utilization was to yield vertically
aligned epitaxial interfaces by PLD method [11]. This study yielded vertically aligned nanostructures of hetero interface in the 200-300 nm domain dimensions spatially. This corresponded to significant interface maximization. Ma et al. [11] in this study have found around 1000 Ωcm² ASR at 400 °C in this composite cathodes including vertically aligned LSC$_{113/214}$ interfaces. This ASR value is 10 times smaller than ASR of single phase cathodes between 320-400 °C interval. Moreover, they state that 400 °C is a critical threshold above which surface Sr segregation is inevitable whether fast or slow depending upon T while below this temperature surface chemical instability phenomenon is not seen. Another interesting observation that they make, hetero interface has a capability to postpone chemical degradation of surface giving a stability effect to hetero interface which was previously reported, too [85].

Crumlin et al. [21] also adopted epitaxial thin film cathodes of LSC$_{214}$-on-LSC$_{113}$ as a function of LSC$_{214}$ horizontal coverage of LSC$_{113}$ surface. Their film thickness was around 50 nm, which was extremely small. What they found consequently was around 1.5 Ωcm² at 550 °C and 1% oxygen. Depending on surface coverage, this ASR value was well larger.

Yashiro et al. [166], prior to those epitaxial thin film approaches, made use of thick cathodes where LSC$_{214}$ was screen printed onto LSC$_{113}$ phase. Due to high thicknesses resistances were well high with regard to requirement. No area specific resistance was analyzed but they did find 1-fold enhancement in resistance they obtained. The reason for this significantly reduced enhancement degree with respect to similar studies [11,15,21,68] is probably the horizontal alignment of constituent phases.

The another recent approach to utilize and maximize hetero interface has been adopted by Hayd et al. [122], giving 7 mΩcm² ASR at 600 °C and 1.9 Ωcm² at 400 °C. They constructed hetero interfaces by use of metal organic deposition (MOD) method which simply corresponds to crystallization of each phase from one solution having slight A and/or B-site deficient/excess cation stoichiometry. In other words, this was an in situ dual phase synthesis of LSC$_{113}$/LSC$_{214}$ system. In their MOD derived thin film cathodes both LSC$_{113}$ and LSC$_{214}$ as well as trace amount of Co$_3$O$_4$ precipitates were formed. But they reported 47 times higher $k^q$ for dual phase cathodes than single phase perovskite as opposed to previous studies. The reason for reduced enhancement may
be deficiency of A and/or B-site cation stoichiometry of the solution, which may have led to reduced formation of secondary \( \text{LSC}_{214} \) phases. Tuning these deficiencies may bring about further enhancement in ASR. Along with the promising ASR, MOD based derivation of thin film cathodes constitutes the lack of well-controllability of cathode production process especially in terms of microstructure. Definitely much of those studies probing hetero interface did exclude the chemical stability since their great concern was either revealing underlying reasons or achieving the lowest possible ASR.

As can be inferred from the literature information without giving reference to specific details, there are still debates in underlying reasons for anomalous activity of \( \text{LSC}_{113}/\text{LSC}_{214} \) interface \([11,15,68,75,85,88,151,168,169]\). Assertions are generally done for lower and higher temperature regimes. Mapping this activity with underlying reasons as a function of temperature has a potential to end the debatable issues surrounding the phenomenon. However, such an attempt is not aimed in this thesis. Rather, the aim is the maximization of hetero interfaces with different compositions in order to yield the lowest possible cathode resistance with the help of different approaches.

In this study, accordingly, ASR values obtained by Crumlin et al. [21], Ma et al. [11] and Hayd et al. [122], all of which are corresponding to the highest degree of \( \text{LSC}_{113}/\text{LSC}_{214} \) dissimilar interface maximization in literature, will be success criteria together with accompanying process parameters such as cost, stability etc. In order to determine ASR for not only complete cathode but also ASR for surface oxygen exchange step, electrochemical impedance analysis is a powerful technique.

2.5. Motivation of The Work

The main starting point of this study is to maximize usable \( \text{LSC}_{113}/\text{LSC}_{214} \) hetero interfaces. Two methods have been adopted for this purpose. Firstly, rendering interfaces economically more feasible way has been adopted. Dual phase synthesis of \( \text{LSC}_{113}/\text{LSC}_{214} \) system from one solution via conventional Pechini method has been utilized with varying solution cation stoichiometry. So long as nano-crystals of each phase nucleates separately through synthesis process, their sizes are below the critical
utilization length [6,171] and their penetration to each other is highly successful, dual phase synthesis is expected to result in continuous hetero interface formation and successful ASR reduction. This is because continuous hetero interfaces are expected to spread over all the microstructure in as-synthesized powders. Such a result would correspond to quite economic way to derive quite densified hetero interfaces regarding conventional and relatively cheap SOFC cathode preparation methods.

In the second approach, due to the apparent advantages of deriving vertical hetero interfaces, these hetero-interfaces will be tried to be derived with possibly higher spatial density. In this approach, magnetron co-sputtering has been used. This is expected to make contribution to oxygen reduction activity in the hetero-structured cathode as well as varying degree of hetero-interfaces through film as a result of sputtering from differently positioned targets.

As the first time, dual phase synthesis of $\text{LSC}_{113/214}$ system via low temperature solution based method has been used. Simultaneous sputtering of phases with magnetron sputtering is also the first in literature.
CHAPTER 3

IN SITU ELECTROCHEMICAL IMPEDANCE ANALYSIS

3.1. In situ Electrochemical Impedance Spectroscopy

The concept of resistance is a well-known and understood phenomenon, which simply expresses the ability of material to resist electron flow formulated via Ohm’s Law, \( R = V/I \), where \( R \) is resistance, \( V \) is voltage and \( I \) is current. For direct current flow, each term in this equation reaches an ultimate equilibrium value and this ultimate value of resistance is denoted as \( R \). However, under alternating current, concept of impedance releases where both \( V \) and \( I \) values becomes functions of time yielding equation \( Z = V(t)/I(t) \) [36]. Application of a certain voltage amplitude, \( E_0 \), with a certain frequency, \( \omega \), brings about current with varying amplitude, which is shifted in phase, with respect to applied potential, denoted as \( \phi \). Therefore, impedance is characterized by the fact that potential and current are not in phase; they are non-synchronized.

\[
Z = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \varphi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \varphi)} = Z_0 (\cos(\varphi) + j \sin(\varphi))
\]

Here \( j = \sqrt{-1} \), resulting in typical Nyquist plot displaying both real \( Z_{\text{real}} = Z' = |Z|\cos(\varphi) \) and imaginary \( Z_{\text{imaginary}} = Z'' = |Z|\sin(\varphi) \) as illustrated in Figure 3-1 given below.
Figure 3-1 $|Z|$ corresponds to certain value of impedance at unique perturbation frequency [172]

Figure 3-2 Nyquist Plot of Fe doped SrTiO$_3$ and corresponding equivalent circuit [173]

How fast the system responses to the applied voltage is determined by its kinetic, which inevitably forms a phase shift between voltage and current, making EIS a powerful technique for reaction kinetic investigations.

In Figure 3-2, there releases two separated and serially connected resistances, both of which are connected in parallel with an ideal capacitor of constant phase element (CPE). CPE differs from ideal capacitor behavior with its shape constituting extended
semicircle in diameter while in ideal capacitor, shape is an exact semicircle. Usually low frequencies yield constant phase element due to very long response recording time intervals of low frequencies. So, CPE is an experimental defect especially in case of solid state impedance characterizations with low frequencies [134,174,175]. There are also other circuit elements such as Gerischer and Warburg [172,176]. EIS is a broad area. So, this study is rather keen on experimental considerations.

3.2. Considerations Regarding Solid State Analysis
In cathode EIS analysis, system or material is perturbed by use certain voltage amplitude. Providing that the chemical processes triggered via current supplied (or equivalently electron flow), it must response to this flow. If the chemical process is slow, changing the direction of perturbation voltage amplitude with high frequencies, i.e. 1 MHz, results in making chemical species immobile since reaction is already slow. For this slow reaction to take place, more time should be supplied to system in order to record responses. Reverse is also true. Therefore, slow processes can be source of resistance if and only if they are perturbed with low frequencies. That’s why the impedance arc associated with surface oxygen exchange process is named as ‘low frequency arc’ while charge transfer processes can yield impedances only when high frequency perturbation is used [133,134,177] since charge transfer is fast process. So, fast processes can be perturbed via high frequencies and slow processes can give resistance with low frequencies.

In dense thin film cathode examinations by EIS, bulk transport does not constitute a source resistance since the length over which ion migration must take place is extremely small. The remaining two processes are ion exchange at electrode/electrolyte interface and surface oxygen exchange. Between these two, surface exchange is much slower than ion exchange at electrode/electrolyte interface. So, surface exchange process can only give resistance at low perturbation frequencies; at very high frequencies oxygen gas near the surface stays immobile. That’s why in EIS examinations, low frequency arc is associated with surface oxygen exchange process. This is possible only when the film thickness is below the critical utilization length denoted as \( l_\delta = D^q/k^q \) [6,173]. For the film thicknesses smaller than \( l_\delta \), this
low frequency arc becomes *independently* visible. Real component of this arc is
directly attributed to surface oxygen exchange process. A representative illustration in
which high and low frequency arcs are well separated is seen in Figure 3-2.

![Figure 3-3](Image)

**Figure 3-3** Dense thin film cathode where L represents critical utilization length
(adapted from [178])

Since oxygen exchange kinetic is a function of surface area, resistance obtained from
low frequency arc (oxygen exchange) is multiplied with cathode surface area. So long
as lattice oxygen content is known, surface oxygen exchange constant \( k^q \) can be
directly calculated [133,173] follows;

\[
k^q = \frac{k_B T}{4e^2 R_s C_O}
\]

\( k_B \) is Boltzmann constant, \( T \) absolute temperature, \( e \) is elementary charge, \( C_O \) is lattice
oxygen content [111] in given temperature characterized by oxygen non-stoichiometry
and finally \( R_s \) (Area * R) is area specific resistance.

At first glance, this equation gives impression of linear correlation between \( R_s \) and
temperature. However, \( C_O \) is also a function of temperature changes due to formation
of oxygen vacancies with varying T. One must at this point be informed that surface
oxygen exchange step is activation limited and expected to obey Arrhenius behavior
[179]. Combining these information foresees linear relationship between ASR and
\( \ln(1/T) \). This is in turn a crosscheck of that whether measured resistance is originated
from surface exchange or diffusion of species.
When cathode is not thin dense film, then system is said to be not well defined [133] so as to separate the responses originated from different chemical processes and/or microstructural features constituting source of resistance such as grain boundary, surface exchange, various interfaces and ion exchange. While some of these are charge transfer processes (ion-exchange at electrode/electrolyte interface), the others namely surface exchange and solid state diffusion are called non-charge transfer steps [180].

In dense thin film, one charge transfer (ion exchange) and one non-charge transfer step (surface exchange) constitute the overall cathode resistance. But thick cathodes for example involve additional grain boundaries as a new source of resistance [181]. While there are many proposed circuit models as a way for interpretation of eventual response, the most popular and accepted one is ALS (Adler-Lane-Steele) model [182,183].

This model asserts that overall oxygen reduction in cathode is mainly and simultaneously limited by surface oxygen exchange and solid state diffusion so long as mixed conducting oxide has high both ionic and electronic conductivity and without any gas phase diffusion limitation [15]. Mathematical implication of this model is as follow;

\[
R_{chem} = \left(\frac{RT}{2F^2}\right) \sqrt{\frac{\tau}{(1 - \varepsilon)D_v c_v a \tau r_0 (\alpha_f + \alpha_b)}}
\]

Here R is gas constant, T is temperature, F is Faraday’s constant, \(\varepsilon\), \(a\) and \(\tau\) are porosity, surface area and solid state tortuosity respectively, \(D_v\) is vacancy diffusivity, \(c_v\) is vacancy concentration, \(r_0\) is the exchange flux density from which surface oxygen exchange constant (k) is extracted \(\alpha_f\) and \(\alpha_b\) constants for forward and backward reactions. \(R_{chem}\) is the resistance caused by cathode having thickness \(L < 3l_\delta\) [182]. If \(L > 3l_\delta\), this model predicts additional serially connected arcs arisen from charge transfer processes, denoted as “interfaces” in Figure 3-4 given below.
If, on the other hand, \( L < 3 \delta \), these charge transfer contributions disappear and only \( Z_{\text{chem}} \) (in the form of Gerischer response [6,176]) signal is obtained [180]. Adler [182] states that this critical \( L = 3 \delta \) value below which only \( Z_{\text{chem}} \) response is visible can be up to 20 μm for MIEC perovskites depending upon T and \( P_{O_2} \). In addition, as L significantly deviates from \( 3 \delta \) to lower values, \( Z_{\text{chem}} \) response looks more like an ideal semi-circle similar to \( Z_{\text{interface}} \) [182].

Both diffusivity and surface oxygen exchange coefficients can be derived from ALS model as can be inferred from equation. However, even for this indirect method, parameters like, surface microstructural area, tortuosity, porosity should be highly clarified in order for exactness of calculated D and k. This is possible with 3D tomography by expensive and indirect SEM-FIB method [48]. Moreover, for ALS model to be suitable and exact, homogeneity through microstructure is sought, which is some sort of idealization in another aspect. Such well-defined microstructure might not be derived always. Moreover, each cathode will have its own microstructural parameters such as porosity, tortuosity and surface area.
As a result of all these abovementioned practical reasons, namely microstructural heterogeneity, in case of cathodes having thickness $L > 3l_δ$, all responses are somehow convoluted as will be manifested in this study, as well. That is to say that arcs are penetrated to each other, making identification of them more and more difficult. An example to this is given in Figure 3-5, in which different impedance responses (arcs) are convoluted with each other.

At this point, it is worthwhile to note that every EIS response recorded, even the most complicated ones, can be expressed by use of an equivalent circuit model fitting well to this recorded response. Thanks to this matched model, deconvolution of arcs is possible.

However, this corresponds to some sort of mathematical fitting rather than a reasonable physical meaning such that any other circuit model can also be matched with recorded data. Reverse may also be true; the circuit model can be reasonable more or less. The key problem is that how representative is this matched circuit model is not exactly known in highly complicated and heterogeneous microstructures. The
general case is that as cathode thickness is reduced, equivalent circuit model is more probable to give physically reasonable deconvolution.

That is why in SOFC cathode research well defined systems are used in electrochemical characterizations. The best one among them is dense thin film cathodes in this respect. In conditions where cathode is porous due to better performance caused by for example excess air inlet, microstructure is tried to be controlled well and cathode thickness is tried to be reduced for further representative evaluation.

Apart from these, EIS is very powerful way to differentiate electrolyte response from cathode response in a SOFC stack no matter how the cathode is [184]. This is because electrolyte is purely ionic conductor inside which oxygen atom has already been completely reduced and so it cannot be further perturbed via electron flow.
CHAPTER 4

SYNTHESIS AND PERFORMANCE OF THICK LSC CATHODES

4.1. Synthesis of Powders

Examination of LSC cathodes performance begins with their synthesis. For this purpose, Pechini method, which is simply low temperature solution based method, was employed [23]. A typical flowsheet of Pechini synthesis is illustrated in Figure 4-1. As precursors, nitrates of cations are used. These are namely Co(NO$_3$)$_2$.6H$_2$O (Alfa Aesar 98-102%, product no: 36418), La(NO$_3$)$_3$.6H$_2$O (Alfa Aesar, 99.99%, product no:11267), Sr(NO$_3$)$_2$ (Alfa Aesar, 99.0%, product no:12232) for the syntheses of LSC$_{113}$ and LSC$_{214}$ powders, Ce(NO$_3$)$_3$.6H$_2$O (Alfa Aesar, 99.5%, product no:11329) and Gd(NO$_3$)$_3$.6H$_2$O (Alfa Aesar, 99.9%, product no:12917) for GDC electrolyte. These nitrates were mixed in beaker with a certain stoichiometry so that the final desired cation fractions are satisfied.

Success in attaining single phase powders by Pechini method is, in principle, dependent upon amount of chelating agent which was citric acid (C$_6$H$_8$O$_7$.H$_2$O, Merck 99.0%, product no:100244) in the synthesis process. Chelating agent is responsible for the formation and homogeneously distribution of metal-organic complexes [23] during which cations are covered by chelation agent and re-oxidation of individual cations are prevented. For this process to successfully take place, mole of citric acid must be at least twice as much as the total moles of cations in solution. For further
assurance, mole of citric acid was adjusted to be 3 times as much as the total cations mole in this synthesis. DI water was excess in solution.

Figure 4-1 Typical flowsheet of Pechini synthesis process

After addition of citric acid to aqueous solution, magnetic stirrer was put in beaker and solution was stirred up at 80 °C for at least 20 min. This was followed by addition of ethylene glycol (Merck, C$_2$H$_6$O$_2$ 99.0%, product no:109621) for poly-esterification reaction. The mole of ethylene glycol was 2 times as much as the mole of citric acid. After addition of ethylene glycol, solution temperature was raised to 120 °C. Until dried gel was obtained, solution was kept at this temperature. This was followed by calcination of dried gel at 800 °C for 5 hours. Then, eventual powders were obtained.
Aforementioned procedure (Figure 4-1) is given in terms of approach that could be altered depending on powder to be synthesized. For three different powders (phases) synthesized different details could be observed.

4.1.1. Synthesis of Single Phase LSC$_{113}$ and LSC$_{214}$

Since high oxygen reduction rate reported to be up to date has been found between (La$_{0.8}$Sr$_{0.2}$)CoO$_{3-\delta}$ and (La$_{0.5}$Sr$_{0.5}$)$_2$CoO$_{4+\delta}$ [21,166], $n_{Co}$:$n_{La}$:$n_{Sr}$ ratio was adjusted as 1:0.8:0.2 for perovskite LSC$_{113}$ and 1:1:1 for Ruddlesden-Popper LSC$_{214}$, respectively. Relative amounts of nitrate precursors were added into solution accordingly. Relative amounts of citric acid and ethylene glycol were kept constant as it was stated previously; $n_{cations}$:$n_{citric-acid}$:$n_{ethylene-glycol}$ was 1:3:6. This is exemplified in Table 4-1.

<table>
<thead>
<tr>
<th>La$<em>{0.8}$Sr$</em>{0.2}$CoO$_3$-(MA=235.546 gr)</th>
<th>M$_A$ (gr)</th>
<th>Amount (gr)</th>
<th>Mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(NO$_3$)$_2$.6H$_2$O</td>
<td>291.04</td>
<td>4.000</td>
<td>0.013744</td>
</tr>
<tr>
<td>La(NO$_3$)$_3$.6H$_2$O</td>
<td>433.01</td>
<td>4.761</td>
<td>0.010995</td>
</tr>
<tr>
<td>Sr(NO$_3$)$_2$</td>
<td>211.63</td>
<td>0.582</td>
<td>0.002749</td>
</tr>
<tr>
<td>Citric Acid Monohydrate</td>
<td>210.14</td>
<td>17.329</td>
<td>0.082464</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>62.07</td>
<td>20.474</td>
<td>0.329856</td>
</tr>
</tbody>
</table>

However, there were differences in the final calcination temperature and time for each phase. Different from that illustrated in Figure 4-1, calcination temperature was found to be at least 740 °C for (La$_{0.8}$Sr$_{0.2}$)CoO$_{3-\delta}$ phase. Full crystallization of (La$_{0.8}$Sr$_{0.2}$)CoO$_{3-\delta}$ powder could be attained in calcination temperature-time combination of 750 °C and 5 hours.

On the other hand, subsequent calcinations at incrementally increased temperatures starting from 700 °C demonstrated that the minimum calcination temperature for LaSrCoO$_{4+\delta}$ was found to be at least 800 °C. Calcination at 775 °C even more than 30 hours did not yield fully crystalline structure. But 5-hour calcination at 800 °C was sufficient for obtaining fully crystalline LaSrCoO$_{4+\delta}$ powder. These observations
imply an earlier formation of \((\text{La}_{0.8}\text{Sr}_{0.2})\text{CoO}_3\) over \(\text{LaSrCoO}_{4\pm\delta}\). But this statement requires verification via in situ monitoring of nucleation growth process in the synthesized powders.

Aforementioned single phase powders were synthesized in pursuit of physically blending them and maximizing \(\text{LSC}_{113/214}\) hetero interface in that way. But prior to cell fabrication and performance characterization by EIS, powders were characterized structurally by use of XRD analysis.

In order to ensure the absence of any undesired second phase in as-synthesized powders, X-ray diffraction analyses were completed. For all of the as-synthesized powders, diffraction patterns were collected with 0.016 °/min scan rates between 20=5° and 20=120°. Such small scan rate was selected in order to perform Rietveld refinement of XRD pattern.

Copper gun with Ni filter was used for X-ray generation (Rigaku) offering CuKα radiation and creating wavelength of \(\lambda=1.54056\) Å. X-ray generator voltage and current were adjusted and kept constant as 40 kV and 40 mA, respectively. XRD results with accompanying Rietveld refinement quantitatively revealed the crystal structures, site occupancies as well as lattice parameters and phase fractions. GSAS-II/EXPGUI software was used for Rietveld analysis.

Instrumental flaws manifested through XRD patterns have been first revealed to exclude the effects of them on patterns. For this purpose, XRD pattern of a standard sample, about which whole crystallographic information was initially known, has been obtained. This standard sample was Silicon named as Nist640d. It is known to have face centered cubic structure with “F d \(\bar{3}\) m” space group and 5.43123 Å lattice parameters. Keeping these constant, instrumental parameters, namely Cagliotti terms, have been extracted as given in Table 4-2, manifesting also the degree of fitting by virtue of \(\chi^2\), \(R_p\) and \(R_{wp}\) values, which are indicating strong fit between calculated and observed patterns. Figure 4-2 illustrates how good the match is for standard sample refinement, making analysis confident on the values of Cagliotti terms.
Figure 4-2 Refined profile of standard Silicon powder sample Nist640d

Table 4-2 Rietveld refinement results for standard Silicon powder sample

<table>
<thead>
<tr>
<th>Silicon-Nist640d Rietveld Refinement-Space Group: (Fd 3 m)</th>
<th>Fitting Parameters</th>
<th>Cagliotti Terms</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\chi^2$</td>
<td>$R_p$</td>
</tr>
<tr>
<td></td>
<td>3.875</td>
<td>0.0774</td>
</tr>
</tbody>
</table>

Refinements were initially conducted on (La$_{0.8}$Sr$_{0.2}$)CoO$_{3-\delta}$ and (La$_{0.5}$Sr$_{0.5}$)$_2$CoO$_{4+\delta}$ single phase powders in the light of Cagliotti terms. Results apparently indicate that there is no any undesired phase and single phase powders have successfully been synthesized. Refined patterns are given in Figure 4-3 and Figure 4-4. Studies conducted by Sikolenko et al. [185] and Sanchez-Andujar et al. [186] have been referred in terms of crystallographic information data.

Refinement parameters for all single phase powders are given in Table 4-3 given below. All refinements manifested preferred orientation in powders. In case of (La$_{0.8}$Sr$_{0.2}$)CoO$_{3-\delta}$ powders (300), (214) are the planes through which strong preferred orientation took place. Similarly, significant preferential orientation was
observed through (114), (303) and (215) reflection planes in (La$_{0.5}$Sr$_{0.5}$)$_2$CoO$_{4+\delta}$ phase.

**Figure 4-3** Refined XRD pattern of (La$_{0.5}$Sr$_{0.2}$)CoO$_{3.5}$

**Figure 4-4** Refined XRD pattern of LaSrCoO$_{4+\delta}$
Table 4-3 XRD analysis results of single phase \((\text{La}_{0.8}\text{Sr}_{0.2})\text{CoO}_3\) and \(\text{LaSrCoO}_{4+\delta}\) powders

<table>
<thead>
<tr>
<th></th>
<th>((\text{La}<em>{0.8}\text{Sr}</em>{0.2})\text{CoO}_3)</th>
<th>(\text{LaSrCoO}_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lattice Parameters</strong> (in Å)</td>
<td>a 5.442</td>
<td>a 3.805</td>
</tr>
<tr>
<td></td>
<td>c 13.183</td>
<td>c 12.506</td>
</tr>
<tr>
<td><strong>Fitting Parameters</strong></td>
<td>(\chi^2) 3.745</td>
<td>(\chi^2) 5.112</td>
</tr>
<tr>
<td></td>
<td>(R_p) 0.117</td>
<td>(R_p) 0.128</td>
</tr>
<tr>
<td></td>
<td>(R_{wp}) 0.149</td>
<td>(R_{wp}) 0.162</td>
</tr>
<tr>
<td></td>
<td>(L_X) 13.219</td>
<td>(L_X) 11.426</td>
</tr>
<tr>
<td><strong>Scherer Crystallite Size (in nm)</strong></td>
<td>60.126</td>
<td>69.562</td>
</tr>
<tr>
<td><strong>Space Group</strong></td>
<td>(R 3 c)</td>
<td>(I 4/m mm)</td>
</tr>
</tbody>
</table>

The lattice parameters in Table 4-3 are consistent with the literature values for current Sr compositions of phases [185–187]. Fitting parameters as well as degree of fit as illustrated in Figure 4-3 and Figure 4-4 make refinements confident. Based on this confidence, Lorentzian isotropic crystallite size broadening term, \(L_X\), is extracted and by inserting it into Scherer Equation given below, average crystallite sizes have been found. \(P\) is crystallite size, \(K\) is shape factor and equal to 0.9 and \(\lambda\) is wavelength of X-rays

\[
p = \frac{18000 \times K \times \lambda}{\pi \times L_X}
\]

If it is considered that Scherer equation can estimate sizes lower than 45 nm accurately and sizes lower than 90 nm roughly [188], current \(L_X\) values are reasonable. However, SEM images of LSC113 and LSC214 in Figure 4-5 show higher particle sizes than calculated ones. In this case, what is said to be crystallite is not equivalent to particle, which means that particles are not defect or strain-free. But, powders were result of solution based synthesis, which is supposed to make them non-susceptible to strain formation. In this way, this is a noticeable result.
To sum up, XRD patterns accompanied by Rietveld refinement results clearly shows that single phase synthesis of \((\text{La}_{0.8}\text{Sr}_{0.2})\text{CoO}_3-\delta\) and \(\text{LaSrCoO}_{4+\delta}\) were very successful. Lattice parameters are in good agreement with literature. It is also seen that “structural” size determined based on Rietveld refinement refers to crystallite size and not to particle size. However, SEM images are obvious indicators of particle sizes.

4.1.2. In situ EIS Analysis of Porous Cathodes of Physical Mixture

Independently synthesized single phase powders of \((\text{La}_{0.8}\text{Sr}_{0.2})\text{CoO}_3-\delta\) and \(\text{LaSrCoO}_{4+\delta}\) were mixed with 1:1 molar ratio in order to obtain physically blended LSC\(_{113/214}\) two phase structure. By means of physical blending, hetero interface extension was aimed. Final mixed powders were examined by electrochemical impedance spectroscopy (EIS) concerning the degree of hetero interface formation-extension success.

4.1.2.1. Symmetric Cell Preparation via Powders

Prerequisite for analyzing performance of powders is, certainly, preparation of cell, which is comprehensively explained in following pages from slurry preparation to EIS experimental parameters.
4.1.2.2. Electrolyte Synthesis and Fabrication

The underlying reason for seeking the lowest possible temperature-time combination for calcination of LSC powders was to prevent grain growth while allowing porosity in the structure. This is because porosity is sought in cathodes. However, (Ce$_{0.9}$Gd$_{0.1}$)O$_{2-\delta}$ powder was synthesized for electrolyte fabrication performed via sintering and there was no particle size concern. Therefore, flowsheet in Figure 4-1 was followed for GDC powders and calcination was carried out at 800 °C, although it was experienced that lower temperatures were also sufficient for GDC calcination.

![Observed, Difference, Calculated](image)

Figure 4-6 Refined XRD pattern of (Ce$_{0.9}$Gd$_{0.1}$)O$_{1.95}$

<table>
<thead>
<tr>
<th>Space Group</th>
<th>(F m 3 m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice Parameters</td>
<td>5.418 Å</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fitting Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi^2$</td>
</tr>
<tr>
<td>$R_p$</td>
</tr>
<tr>
<td>$R_{wp}$</td>
</tr>
<tr>
<td>$L_x$</td>
</tr>
</tbody>
</table>

| Scherer Crystallite Size | 43.779 nm |

69
Following the prescribed flowsheet, single phase GDC powders were synthesized successfully as manifested by Rietveld refinement on XRD patterns in Figure 4-6. Brauer et al. [187] is referred in terms of crystallographic information data in pursuit of Rietveld refinements of GDC powders XRD pattern. Comprehensive resultant structural information is given in Table 4-4. Refined pattern of \((\text{Ce}_{0.9}\text{Gd}_{0.1})\text{O}_{2-\delta}\) powder indicated preferential orientation through (220) and (311) planes. Fitting parameters values are assuring the refinement. In case of GDC, there is more deviation between Scherer crystallite size and particle size as revealed by scanning electron microscope image of it (see Figure 4-7).

![Figure 4-7 SEM image of \((\text{Ce}_{0.9}\text{Gd}_{0.1})\text{O}_{2-\delta}\) with 40k magnification](image)

After assuring the structural characteristics of GDC powders, they were used to fabricate electrolytes of prospective symmetric cells. For this purpose, as-synthesized GDC powders were pressed into 18-mm diameter and 1 mm-thick pellets that was followed by sintering of pellets at 1350 °C for 8 hours at ambient air. Final dense GDC pellets, on which cathode slurries were applied, were used as electrolyte of the final symmetric cells.
4.1.2.3. Slurry Preparation

After testing powders structurally, slurries were prepared with the powders. These slurries were then used to fabricate porous thick cathodes of symmetric cells. Addition of each chemical was followed by 15-min ball milling (160 revolutions per minute) with 5 mm diameter ZrO\textsubscript{2} balls. Sequence of addition of chemicals is the same as the sequence of Table 4-5 given below. After addition of chemicals and ball milling for a good blending, slurries were ready to be a part of symmetric cells. Slurries, and so symmetric cells, were prepared both from single phase (La\textsubscript{0.8}Sr\textsubscript{0.2})\textsubscript{2}CoO\textsubscript{4-δ} and (La\textsubscript{0.5}Sr\textsubscript{0.5})\textsubscript{2}CoO\textsubscript{4+δ} powders and the physical mixture of them. This physical mixture is denoted as PM in EIS analyses.

Table 4-5 Chemicals used to prepare cathode slurry

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Function</th>
<th>Gram per 0.5 gr powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fish Oil</td>
<td>Dispersant</td>
<td>0.0117</td>
</tr>
<tr>
<td>Toluene</td>
<td>Solvent</td>
<td>0.2350</td>
</tr>
<tr>
<td>PEG</td>
<td>Plasticizer</td>
<td>0.0365</td>
</tr>
<tr>
<td>BBP</td>
<td>Releasing agent</td>
<td>0.0475</td>
</tr>
<tr>
<td>PVB</td>
<td>Binder</td>
<td>0.0265</td>
</tr>
</tbody>
</table>

![Figure 4-8](a) Top view and (b) cross section of half cells accommodating thick porous cathodes
4.1.2.4. Cell Fabrication

After the final ball milling, slurries were applied onto GDC pellets over the plasters having apertures with 5x5 mm² area. The thickness of plaster was 80 μm, which makes final cathode thickness expectations around 80 μm, too. Application of slurries were followed by firing cell at 400 °C for 5 hours in order to completely remove organics from cathode. This same process was applied onto each face of the pellet. One of the sides acted as counter electrode while the other acted as working electrode (see Figure 4-8).

Once the symmetric cells were made, gold wires (0.1 mm in diameter) were contacted via gold paste just onto cathode surfaces. This was followed by firing this contact point at 400 °C for 2 hours for good adhesion to cathode surface. Same procedure was applied for each face of cells. Then, these cells were placed on one edge of hollow shaped alumina pipes. The rest was indifferent from the procedure comprehensively explained in previous pages of this section.

4.1.2.5. EIS Measurements

Final symmetric cell (see illustration in Figure 4-8) fabricated via physically mixed powders was examined in terms of its cathode performance. The temperatures of EIS analysis was selected to be 400, 500, 550, 600, 650 and 700 °C. Lower temperatures highly reduce critical utilization length (namely up to 40 nm) and expecting to attain such reduced particle size is not realistic. However, at increasing temperatures critical utilization length can even reach several tens of microns [43,146]. So, alteration in temperatures is functional in terms of tuning critical utilization length. $P_{O_2}$ were selected to be 0.01, 0.1 and 0.21 atm.

Importance of $P_{O_2}$ is originated from the fact that if overall ORR is limited by surface/interface processes purely, then impedance response must exhibit inversely $P_{O_2}$ dependent behavior; higher partial pressure of oxygen facilitates ORR while in case of bulk diffusion limited behavior, lower $P_{O_2}$ means promoted oxygen vacant sites within bulk, which significantly enhances oxygen diffusion and since ORR is limited by diffusion process, lower $P_{O_2}$ lowers ASR in this case.
Perturbation amplitude was selected to be 10 mV with 5 points per decade and frequency range was 1MHz-10mHz. The reason for selection of 10 mV is not to perturb any other possible parallel reaction and attaining signals from one unique process during this multistep non-homogeneous oxygen reduction process. Higher perturbation amplitudes such as 50 mV could well perturb reactions more rapidly by providing more driving force but in this case additional chemical steps can also be agitated. In this case, final signals can’t be confidently attributed to certain reaction step. Higher frequency ranges are always preferred but this brings about so much analysis time that even during measurement, properties of system changes. When it is considered that LSC cathodes are very sensitive to surface Sr segregation above 400 °C, it was best to keep analysis time possibly the minimum period. 1MHz-10mHz range is determined in this way.

Figure 4-9 EIS responses of physically mixed powder (denoted as PM) at differential temperatures and ambient air
Since gold paste is highly porous, in calculation of ASR, cathode area was assumed to be 0.25 cm$^2$, no significant ASR reduction was expected on surface thanks to highly porous gold paste [189]. In symmetric cells, $ASR = R_{\text{cathode measured}} \times \text{Area}/2$. Nyquist plots are drawn accordingly.

Unfortunately, Figure 4-9 (in which PM denotes physical mixture) shows that there is poor hetero-interface formation in physical blending of single phase $(\text{La}_{0.8}\text{Sr}_{0.2})\text{CoO}_3$ and $\text{LaSrCoO}_{4+\delta}$ powders, manifesting itself as a poor performance enhancement. While EIS at 400 °C mimics rule of mixture behavior, just slight enhancement which could be attributed to extension of hetero interface could only be attained at 500 and 600 °C. Besides, co-existence of two phase becomes meaningless at 700 °C. This electrochemical overview qualitatively manifests how poor the ability of physical mixing is to maximize hetero interface and promote cathode performance.

![Figure 4-10 EDS mapping of physically mixed powder at 400 magnification](image_url)
On the other hand, EDS mappings carried out on powder mixture can do this same quantitatively. Experimentally, 15kV accelerating voltage was used in order for having signals from rather near surface regions. For sufficient dead time in collecting signals, 5.5 spot size was selected. In order to reduce surface roughness, powders were pressed into pellets, were not exposed to high temperature, mounted in polyester and polished gradually.

In physically mixed powder, phases are namely (La$_{0.8}$Sr$_{0.2}$)CoO$_{3-\delta}$ and (La$_{0.5}$Sr$_{0.5}$)$_2$CoO$_4$ in which atomic fractions of La, Co and Sr are exactly known. Thus, expecting a significant contrast with mapping is reasonable at least for Sr atomic percent in case of physical mixing. Sr fractions are 0.04 and 0.14 in mixed powder for LSC$_{113}$ and LSC$_{214}$ respectively and such significant differential can easily be revealed by EDS mapping if matrix effects do not manipulate EDS. Figure 4-10 apparently proves this and manifests ~100 μm$^1$ scale of structure, as well.

In terms of Sr, huge contrast is manifested. The regions which are rich in Sr are slightly poor in terms of La as can be observed from Figure 4-10. Atomic fractions of La atoms are 0.16 and 0.14 in LSC$_{113}$ and LSC$_{214}$ respectively. EDS mapping is capable of revealing even such a slight differential, which is going to make EDS mapping quite reliable. Although it has higher atomic fraction difference (0.2 and 0.14), EDS mapping of Co atoms exhibited almost no contrast. This may be because of matrix effect when lower characteristic radiation energy (La radiation for each atom) that Co atoms yield is taken into consideration.

To sum up, both EDS mapping and EIS responses of physically blended powders confirm that physical mixture of powders is not so effective in maximizing hetero interfaces.

### 4.2. One Pot Synthesis of Dual Phase of (La$_{1-x}$Sr$_x$)CoO$_3$/(La$_{1-y}$Sr$_y$)$_2$CoO$_4$

As opposed to physically blending two phases, synthesizing two phase structure from one solution which corresponds to one pot synthesis of dual phase could be a successful way of interface extension. For this purpose, everything was same as it was

---

$^1$ Roughly calculated by random line intercept technique.
comprehensively explained before (flowsheet in Figure 4-1), except for adjusting cation stoichiometry. Otherwise all the defined procedure was operated as explained previously.

In this case, nitrates of cations were separately adjusted for each phase such that as if (La_{0.8}Sr_{0.2})CoO_{3-δ} and (La_{0.5}Sr_{0.5})_{2}CoO_{4+δ} would form in final powders. Then these adjusted nitrates were added into a beaker with varying fractions assuming that formerly adjusted Sr doping levels for each phase would manifest themselves as x=0.2 and y=0.5 for LSC_{113} and LSC_{214} respectively in finally obtained powders (see Table 4-7). The highest possible interface extension is, in principle, expected in equal contribution of each phase. Therefore, three precursors of solutions were prepared in which relative amounts of phases were surrounding 1:1 ratio. Table 4-6 accordingly shows these precursors of solutions denoted as DP-1, DP-3 and DP-5. Moreover, as the way of checking the possible degree of penetration of nano-crystals to each other, physically mixed sample that previously evaluated was considered as a reference.

Table 4-6 Abbreviations of solutions and corresponding phase fraction expectations

<table>
<thead>
<tr>
<th></th>
<th>DP-1</th>
<th>DP-3</th>
<th>DP-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>(La_{0.8}Sr_{0.2})CoO_{3-δ}</td>
<td>50%</td>
<td>60%</td>
<td>40%</td>
</tr>
<tr>
<td>(La_{0.5}Sr_{0.5})<em>{2}CoO</em>{4+δ}</td>
<td>50%</td>
<td>40%</td>
<td>60%</td>
</tr>
</tbody>
</table>

Table 4-7 below manifests the stoichiometric nitrate calculation by virtue of DP-3. Same calculation is also valid for other dual-phase precursor solutions. Moreover, in order for comparison of final powders structurally, (La_{1-x}Sr_{x})CoO_{3-δ} single phase powders with varying x (from 0-0.5) were synthesized to monitor lattice parameter variation in this study as a function of Sr doping. This is because lattice parameters referred in literature are mainly based on samples (powder or pellet), thermal history of which involved very high temperature processing. This consequently leads to lower lattice parameters in literature than what has been found in this study.

What is given in Table 4-7 represents the cation stoichiometry in the initial nitrate mixture within the beaker assuming x=0.2 and y=0.5. However, since the cation types
of both phases are exactly the same, whether any other undesired third phase would form or expected phase fractions would be achieved is not clear. Furthermore, there is no assurance for achieving presumed dopant degree of Sr in each phase as well as fictive phase fraction expectations. Contrary, deviation as a result of partitioning of Sr and La cations to each phase differently is very reasonable. Therefore, Rietveld refinement analysis is more fundamental tool in case of dual phase synthesis.

<table>
<thead>
<tr>
<th>(La_{0.5}Sr_{0.5})_2CoO_4 (2n moles)</th>
<th>M_A (gr)</th>
<th>Amount (gr)</th>
<th>Mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(NO_3)_2.6H_2O</td>
<td>291.04</td>
<td>0.25000</td>
<td>0.00086</td>
</tr>
<tr>
<td>La(NO_3)_3.6H_2O</td>
<td>433.01</td>
<td>0.37196</td>
<td>0.00086</td>
</tr>
<tr>
<td>Sr(NO_3)_2</td>
<td>211.63</td>
<td>0.18179</td>
<td>0.00086</td>
</tr>
<tr>
<td>Citric Acid Monohydrate</td>
<td>210.14</td>
<td>1.08306</td>
<td>0.00515</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>62.07</td>
<td>1.27964</td>
<td>0.02062</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>La_{0.8}Sr_{0.2}CoO_3 (3n moles)</th>
<th>M_A (gr)</th>
<th>Amount (gr)</th>
<th>Mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(NO_3)_2.6H_2O</td>
<td>291.04</td>
<td>0.37501</td>
<td>0.00129</td>
</tr>
<tr>
<td>La(NO_3)_3.6H_2O</td>
<td>433.01</td>
<td>0.44635</td>
<td>0.00103</td>
</tr>
<tr>
<td>Sr(NO_3)_2</td>
<td>211.63</td>
<td>0.05454</td>
<td>0.00026</td>
</tr>
<tr>
<td>Citric Acid Monohydrate</td>
<td>210.14</td>
<td>1.08306</td>
<td>0.00515</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>62.07</td>
<td>1.27964</td>
<td>0.02062</td>
</tr>
<tr>
<td>TOTAL</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>DP-3 (5n moles)</th>
<th>M_A (gr)</th>
<th>Amount (gr)</th>
<th>Mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(NO_3)_2.6H_2O</td>
<td>291.04</td>
<td>0.62501</td>
<td>0.00215</td>
</tr>
<tr>
<td>La(NO_3)_3.6H_2O</td>
<td>433.01</td>
<td>0.81830</td>
<td>0.00189</td>
</tr>
<tr>
<td>Sr(NO_3)_2</td>
<td>211.63</td>
<td>0.23633</td>
<td>0.00112</td>
</tr>
<tr>
<td>Citric Acid Monohydrate</td>
<td>210.14</td>
<td>2.16612</td>
<td>0.01031</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>62.07</td>
<td>2.55927</td>
<td>0.04123</td>
</tr>
</tbody>
</table>

4.2.1. Rietveld Refinement Evaluation of Dual Phase Powders
Sr site occupancies were not debatable for single phase powders since Sr fraction was already adjusted in initial solution prior to synthesis. However, this is not the case for
dual phase synthesis. In case of dual phase synthesis series, it is expectable for Sr compositions to well deviate from single phase powder by partitioning of it to phases differently. Furthermore, such uncontrolled Sr partitioning has a potential to give rise to formation of new and undesired phases and crystal structures. Thus, Rietveld refinement of XRD patterns belonging to dual phase syntheses is of significant importance.

![Figure 4-11 Refined pattern of DP-5](image)

First, apart from partitioning problem, XRD patterns of dual phase series prove that synthesizing two phase system from one unique solution in the beaker is very successful; patterns clearly look like summation of all reflection peaks of single phase powders of LSC$_{113}$ with the space group of $R\bar{3}c$ and LSC$_{214}$ with the space group of I4/mmm, sure with accompanying slight peak position changes with respect to aforementioned single phase patterns. There is not any undesired third phase$^2$. Figure 4-11, Figure 4-12 and Figure 4-13 manifest this. Crystal structures are rhombohedral

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$^2$ It should be kept in mind that XRD analysis with CuKa radiation is unable to differentiate existence of a possible additional phase less than certain limit. Therefore, the statement above should be treated with caution, since a third phase below the detectability limit might exist in the powders.
and tetragonal just like single phases, which means that $x$ in $(\text{La}_{1-x}\text{Sr}_x)\text{CoO}_3-\delta$ must be in range of $0<x<0.5$ [190] and $y$ in $(\text{La}_{1-y}\text{Sr}_y)\text{CoO}_{4.5}$ must be in the range of $0.3<y<1$ [72]. Otherwise space groups as well as crystal structures are going to change.

Small changes in both peak positions and intensities, on the other hand, are implications of lattice parameter changes and phase fraction deviations, respectively. That is why rather than certain site occupancies, phases involved are represented as $(\text{La}_{1-x}\text{Sr}_x)\text{CoO}_3$ and $(\text{La}_{1-y}\text{Sr}_y)\text{CoO}_{4.5}$ for dual phase synthesis powders in Table 4-8.

![Figure 4-12 Refined pattern of DP-1](image)

Since lattice parameter change is mainly because of A-site Sr occupation difference, site occupations were also aimed to be refined to reasonable values. The first drastic observation in pursuit of this aim was the detection of insensitivity of Rietveld refinement analysis to alteration of La:Sr site occupations at least with CuKα based XRD diffraction data of dual phase powders (for pellets sintered at very high temperatures, peaks will be very steep, making refinement easier). A variety of dummy histograms were made on the basis of profile parameters and preferred orientation information found by assuming $x=0.2$ and $y=0.5$ in phases. By keeping these parameters constant, lattice parameters as well as atomic coordinates of La and
Sr were simultaneously refined for setting certain Sr site occupations to variety of values (from 0 to 1) and unfortunately, no change in lattice parameters even for unreasonable site occupancies was found. This simply refers to that Rietveld refinement was insensitive to Sr site occupation for, at least, current conditions of X-ray radiation characteristic and/or highly porous low particle size powders. That’s why, sequential refinement to dual phase powder patterns were not adopted as the way of exact determination of site occupancies and obvious conclusion on La:Sr partitioning behavior.

Nevertheless, reasonable estimations of La:Sr site occupancies based on lattice parameter variations of phases in different powders and comparison of them with respect to literature were possible and made. Lattice parameters of the constituent phases in different dual phase powders are tabulated in Table 4-8. Fitting parameters as well as refined profiles assure lattice parameters.

**Figure 4-13** Refined pattern of DP-3
<table>
<thead>
<tr>
<th>Fitting Parameters</th>
<th>((\text{La}_{1-x}\text{Sr}_x\text{CoO}_3)) Lattice Parameters (Å)</th>
<th>((\text{La}_{1-x}\text{Sr}_y\text{CoO}_4)) Lattice Parameters (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\chi^2)</td>
<td>2.096</td>
<td>2.096</td>
</tr>
<tr>
<td>(R_p)</td>
<td>0.0881</td>
<td>0.0881</td>
</tr>
<tr>
<td>(R_{wp})</td>
<td>0.1117</td>
<td>0.1117</td>
</tr>
<tr>
<td>DP-5</td>
<td>a 5.438</td>
<td>a 3.803</td>
</tr>
<tr>
<td>(\chi^2)</td>
<td>2.656</td>
<td>2.656</td>
</tr>
<tr>
<td>(R_p)</td>
<td>0.0997</td>
<td>0.0997</td>
</tr>
<tr>
<td>(R_{wp})</td>
<td>0.1259</td>
<td>0.1259</td>
</tr>
<tr>
<td>DP-1</td>
<td>b 5.440</td>
<td>b 3.805</td>
</tr>
<tr>
<td>(\chi^2)</td>
<td>2.707</td>
<td>2.707</td>
</tr>
<tr>
<td>(R_p)</td>
<td>0.1034</td>
<td>0.1034</td>
</tr>
<tr>
<td>(R_{wp})</td>
<td>0.1288</td>
<td>0.1288</td>
</tr>
<tr>
<td>DP-3</td>
<td>c 13.142</td>
<td>c 12.509</td>
</tr>
</tbody>
</table>

At first glance, assumption of a one-to-one correlation between lattice parameter and site occupation seems to reasonable. However, this is not the case for \(\text{LSC}_{113}\). In this study, differently doped \((0.1<x<0.5)\) \(\text{LSC}_{113}\) powders were synthesized and lattice parameters detected are illustrated in Figure 4-16 and Figure 4-17. One can see here that while lattice expands in c-direction with increasing Sr, there is a fluctuating behavior in lattice within a-direction. For low \((x=0.1)\) and high Sr content \((x=0.5)\), lattice parameter ‘a’ is below 5.440 Å based on the result of this study. This is not only a finding pertaining to this study but this is also observed in literature [185,191–193]. Literature findings show that from \(x=0\) to \(x=0.15\), lattice parameter in a-direction first increases while after that point it falls whereas the case is reverse within c-direction. Till \(x=0.15\), c decreases and afterwards it restores its higher values as illustrated in Figure 4-16 and Figure 4-17 below. Peak points should not be necessarily \(x=0.15\) but it is seen that there is fluctuation. So, increasing Sr site occupation does not necessarily imply increasing lattice parameter in \(\text{LSC}_{113}\) as opposed to \(\text{LSC}_{214}\).

On the other hand, as Sr content increases in tetragonal \(\text{LSC}_{214}\), lattice enlarges through c-direction and lattice parameter ‘a’ is going to be reduced as an undeniable phenomenon. See Figure 4-14 and Figure 4-15. In Figure 4-14, Figure 4-15, Figure 4-16 and Figure 4-17, black dots represent literature values of single phase powders.
In the light of these information, Table 4-8 can be analyzed. The first notable observation was almost unchanged lattice parameters of LSC$_{214}$ as opposed to LSC$_{113}$, lattice parameters of which showed relatively wide variation. This observation implies stationary site occupation for LSC$_{214}$ along with variation of it in case of LSC$_{113}$, that is to say that from synthesis to synthesis and phase fraction to phase fraction, a site occupation was preserved in LSC$_{214}$. Furthermore, high number of Rietveld refinement iterations on the basis of tailoring various parameters yielded drastic changes on lattice parameters of LSC$_{113}$ and no change in lattice parameters of LSC$_{214}$, making this study confident on lattice constant of LSC$_{214}$. 

Figure 4-14 Change in lattice parameter a with respect to Sr doping in LSC$_{214}$

[149,186]
Figure 4-15 Change in lattice parameter c with respect to Sr doping in LSC$_{214}$ [149,186]

Figure 4-16 Change in lattice parameter a with respect to Sr doping in LSC$_{113}$ [191,192]
Thanks to undebatable lattice parameters alteration regime in LSC$_{214}$, we can *roughly* set Sr site occupation to the lattice parameters. When the lattice constants obtained from single phase LaSrCoO$_4$ powder (a=3.805 Å, c=12.506 Å) and sluggish change in lattice parameter ‘a’ are considered, it can be asserted that LSC$_{214}$ in DP-1 and DP-3 powders has almost y=0.5 corresponding to LaSrCoO$_4$ stoichiometry. DP-5 powder, on the other hand, has lower value of ‘a’ which is apparently corresponding to *slightly* higher Sr content than y=0.5 (see Figure 4-14 and Figure 4-15). Obviously, any selected Sr site occupancy for one phase will automatically dictate a certain Sr site occupancy for the other phase due to initially added constant cation amount in the beaker (see Table 4-11). Therefore, setting a certain y value in LSC$_{214}$ *must* correspond to a reasonable x in LSC$_{113}$. Figures above were generated with this restriction.
Table 4-9 Weight and phase fractions of phases in each dual phase synthesis

<table>
<thead>
<tr>
<th></th>
<th>DP-5</th>
<th>DP-1</th>
<th>DP-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSC113</td>
<td>0.328</td>
<td>0.432</td>
<td>0.532</td>
</tr>
<tr>
<td>X113</td>
<td>0.412</td>
<td>0.533</td>
<td>0.627</td>
</tr>
<tr>
<td>Expected X113</td>
<td>0.400</td>
<td>0.500</td>
<td>0.600</td>
</tr>
<tr>
<td>LSC214</td>
<td>0.675</td>
<td>0.568</td>
<td>0.468</td>
</tr>
<tr>
<td>X214</td>
<td>0.588</td>
<td>0.467</td>
<td>0.373</td>
</tr>
<tr>
<td>Expected X214</td>
<td>0.600</td>
<td>0.500</td>
<td>0.400</td>
</tr>
</tbody>
</table>

Based on these reasonable site occupation estimations which have also been correlated with lattice parameters either found in literature or detected in this study, weight fractions were extracted from refinement (Table 4-9). Weight fractions are not altered significantly with changing Sr site occupations, which makes weight fraction output of Rietveld analysis a confident reference. Still, cross-correlation between weight fraction (its resultant mole fraction output that must also be compatible with beaker based nLa/nSr ratio) and Sr site occupation was concerned and eventual site occupations were estimated accordingly. In pursuit of this task, nLa/nSr mole fraction in initial solution was determined to be an ultimate reference. Final site occupancy estimations, which was set arbitrarily and by which Table 4-9 was formed, are manifested in Table 4-10.

Table 4-10 Refined cation stoichiometry of phases

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>LSC113</th>
<th>LSC214</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP-5</td>
<td>0.14</td>
<td>0.53</td>
<td>(La$<em>{0.86}$Sr$</em>{0.14}$)CoO$_3$</td>
<td>La$<em>{0.94}$Sr$</em>{1.06}$CoO$_4$</td>
</tr>
<tr>
<td>DP-1</td>
<td>0.24</td>
<td>0.49</td>
<td>(La$<em>{0.76}$Sr$</em>{0.24}$)CoO$_3$</td>
<td>La$<em>{1.02}$Sr$</em>{0.98}$CoO$_4$</td>
</tr>
<tr>
<td>DP-3</td>
<td>0.20</td>
<td>0.51</td>
<td>(La$<em>{0.80}$Sr$</em>{0.20}$)CoO$_3$</td>
<td>La$<em>{0.98}$Sr$</em>{1.02}$CoO$_4$</td>
</tr>
</tbody>
</table>

It is notable to indicate that strength of fit between calculated and observed patterns manifested in Figure 4-11, Figure 4-12 and Figure 4-13, makes lattice parameter values highly confident but degree of current fitting strength is not strong enough to exactly converge Sr site occupancies to actual undeniable values. Hence, although site occupancies have been set to reasonable values as given in Table 4-10, their
values are approximate and phase fractions have been calculated accordingly. This must be kept in mind.

**Table 4-11** $n_{La}/n_{Sr}$ ratio in beaker used as reference for checksum of site occupancies

<table>
<thead>
<tr>
<th></th>
<th>$n_{La}/n_{Sr}$ ratio in beaker</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP-5</td>
<td>1.35</td>
</tr>
<tr>
<td>DP-1</td>
<td>1.50</td>
</tr>
<tr>
<td>DP-3</td>
<td>1.69</td>
</tr>
</tbody>
</table>

Refinements seem to be well assured in all aspects, including phase fractions, lattice parameters and their relevance to corresponding Sr site occupancies in both phases. After assurance of refinements, its results and implications can be evaluated and discussed.

First of all, formation of LSC$_{113}$ phase has apparently dominated the formation of Ruddlesden-Popper structure in all cases. Extend of this domination is least in DP-5 while it is well evident in other powders. Herein, one can infer that formation of LSC$_{113}$ is more facilitated and easier with respect to LSC$_{214}$. Anyway, during single phase synthesis-calcination process, it was observed that minimum possible calcination temperature of single phase LSC$_{214}$ was 800 °C whereas single phase LSC$_{113}$ yielded well crystalline XRD pattern even calcination temperature of 740 °C. Thus, it can be concluded that LSC$_{113}$ formation starts earlier than LSC$_{214}$ which brings about domination of LSC$_{113}$ formation within synthesis of two phase system. This confirms phase fraction calculations via Rietveld refinements.

Second, in structural analyses, certain La:Sr site occupancies were attempted to be revealed. However, though reverse was assumed, it should be kept in mind that there might not be a unique Sr site occupancy for each phase in all dual phase powders. In fact, such *Sr site occupancy differential* possibly caused by secondarily formed phases is thought to induce inevitable partial inconsistencies of lattice parameters and their relevance to site occupations as manifested in Figure 4-15. Whatsoever was attempted,
at least in one option among a and c-directions in one of the both lattices exhibited incompatibility in lattice parameter versus site occupancy diagrams. When the degree of fit among refinement and low fitting parameter values are considered, wrong calculation of lattice parameters as result of refinements is unlikely to be the reason for such incompatibilities. Probable reason is Sr site occupation differential. Detecting Sr differential quantitatively could be done by TEM analysis but in this case it is important to state and be sure about how representative of current TEM image obtained is for complete powder.

All the powders and phases involved are obtained via solution based method which simply implies nucleation-growth process in which one phase (primarily formed) constitutes nucleation site for other. Nucleation necessity of one from other may well cause some sort of divergence in lattice parameters, which is good news for interface maximization since this refers to preferred formation of phases from others surface sites. In this way, all the events are matter of La:Sr partitioning behavior during nucleation-growth from dried amorphous gel to final crystallinity, referring to atomic motilities of La and Sr in their media. Thus, Synchrotron radiation as function of increasing temperature and high number of sequential refinement is prospective solution of final site occupation determination but this would constitute a source of another complete study.

### 4.2.2. In Situ EIS Cell Responses

Hetero interface of LSC\textsubscript{113/214} can be and has been generated till now by varied sophisticated methods [11,21,88,122]. Tough success of these ways are undebatable, they are success-oriented expensive routes, making them unsuitable for massive applications. In this sense, dual phase synthesis of powders \textit{from one unique solution} in a beaker was expected to enhance hetero interfaces through complete bulk with well cheaper and easy route. Obviously, this is possible if nanocrystals of phases penetrate to each other very well. Particle penetration criterion is not sufficient. Beyond that, these particles should be below temperature-specific critical utilization lengths, below which overall ORR is limited only by surface reduction of oxygen molecules.
Figure 4-18 Particle penetration scenarios schematic illustrations (a) Extreme maximization, (b) intermediate penetration and (c) as if physical mixture.

In this picture, there would be final extreme hetero interface between nanocrystals of phases and since particles are also below critical utilization length, $l_\delta$, oxygen diffusion would not be a source of resistance, all the reaction limitation would be caused by surface/interface reduction of oxygen, which has already been facilitated by extreme generation of LSC$_{113:214}$ hetero interface and accelerated ORR there. Figure 4-18 exhibits good illustrations for possible scenarios regarding hetero interface formations.
Obviously, one pot synthesis was successful. But what about particles size, distribution and penetration? If the final case of powders is (c) in Figure 4-18, then dual phase synthesis is said to be unsuccessful and DP synthesis corresponds to physical mixing of individually synthesized powders, invalidating dual phase synthesis. If, however, the case corresponds to (a) in Figure 4-18 accompanying with sizes below \( l_\delta \), then surface limited behavior could be attained from very thick cathodes (namely more than 20-30 \( \mu \)m thicknesses). Attaining such surface limited behavior with conventional thick porous cathodes without use of sophisticated thin film deposition techniques would be first in literature and capable of significantly reduce both cost and operation temperature of SOFC. Although homogeneous mixing manifested in Figure 4-18(a) is an idealized scenario, it is still worthwhile to attempt when its possible consequences are taken into considerations.

Clarification of aforementioned motives in pursuit of dual phase synthesis is possible -at least qualitatively- by in situ EIS analysis. Symmetric cells of dual phase synthesis powders were derived following the procedures explained in 4.2.1 and EIS analyses were done in the light of experimental parameters explained in 4.1.2.5.

For \( (La_{0.8}Sr_{0.2})CoO_{3-\delta} \), critical utilization length is calculated to be around 500 nm at 400 °C [43]. If particle penetration is extremely high as illustrated in Figure 4-18(a), EIS signals must demonstrate interface ORR limited behavior even at this temperature and even for 70 \( \mu \)m cathode thickness. Such a result would be outstanding but this is not the case. It is apparent from the Figure 4-19 that, at 400 °C, \( P_{O_2} \) differential has no effect on EIS spectra. It is understood that particle penetration is not high enough for 400 °C since if interface maximization were sufficiently advanced, there would be \( P_{O_2} \) dependency in EIS spectra.
Both dual phase series and physical powder mixtures exhibited resistance caused by oxygen ion transfer at cathode-electrolyte interface with a combined Warburg like behavior (see Figure 4-19). This is reasonable since oxygen diffusion is expected to be sluggish at 400 °C \( (D_{La_{0.8}Sr_{0.2})CoO_3}^* = 10^{-15} \text{cm}^2/\text{s} \) at 400 °C [43] and \( D_{La_2CoO_4}^* = 2.5 \times 10^{-8} \text{cm}^2/\text{s} \) at 500 °C [146]) and cathode thickness already implies diffusion limited behavior. Combined effect of them seems to manifest itself as a huge cell resistance independent from \( P_{O_2} \) and far away from requirements for utilization, along with diffusion limited behavior. These are not surprising for 400 °C. Further temperatures are prone to make difference since \( l_\delta \) is getting higher with increasing temperatures. But before going further, details are worthwhile to be criticized in Figure 4-19.
Change in the position of high frequency arc associated with oxygen ion transfer at electrode-electrolyte interface is definitely because of slight changes in the thickness of GDC electrolyte. Another reason may be change in ionic/electronic conductivity properties of GDC pellet with varying $P_{O_2}$. Change in size of it on the other hand is dependent upon many parameters, most principle of which is the degree of adhesion between cathode and electrolyte. Nonetheless, these deviations are not of great importance for all specimens and they will not be evaluated once again.

A closer look at the Figure 4-19 also attracts attention to EIS spectra of DP-5, which is drawn within higher values of x and y axes. This, at first glance, gives rise to “higher” resistance and capacitance in DP-5. But whereas in case of DP-1, DP-3 and PM, lower frequency responses converge to Warburg like behavior (an endless linear line), in DP-5 spectra, EIS response is converging to finalize a complete arc. This is an implication of more facilitated process on contrary to appearance. This makes sense since particle penetration is poor for 400 °C, cathodes are thick and LSC$_{113}$ phase is poor in terms of oxygen vacancy concentration at 400 °C [195], equivalent to low ionic conductivity. Under the conditions in which pure diffusion limited behavior prevails, higher LSC$_{113}$ content corresponds to higher resistances. However, LSC$_{214}$ has interstitial and faster diffusion [151], since DP-5 powder involves more LSC$_{214}$, it more easily converged to finalize a complete arc and the other cells were incapable of this, expressed as Warburg. Comparison of single phase LSC$_{113}$ and LSC$_{214}$ supports this assertion. LSC$_{113}$ especially exhibited a proper Warburg in Figure 4-20. DP-5 signals seem to be between single phase LSC$_{113}$ and LSC$_{214}$ but rather seem to be converging to LSC$_{214}$ response as can be seen from Figure 4-20. The remaining cell responses seem to obey lever rule.

Finally, slightly higher capacitances with increasing $P_{O_2}$ at 400 °C EIS spectra is probably because higher $P_{O_2}$ means lower oxygen vacancy concentration in LSC$_{113}$ and more accumulation of raised interstitial oxygen within LSC$_{214}$ at this low temperature [152]. This cumulative effect will change in following temperatures for sure with the dominant effect of diffusion. It is apparent that by means of dual phase synthesis, it is not possible to reduce operation temperature to 400 °C, which is critical threshold for long term stability [18]. Such an astonishing result would be
revolutionary anyway. But increasing temperatures can make difference. 500 °C is the temperature at which hetero interface formation corresponds to an enhancement in overall ORR.

![Graphs showing EIS spectra](image)

**Figure 4-20** Comparison of all EIS spectra (left) and that of single phase cathodes at 400 °C and 0.21 atm $P_{O_2}$

As can be seen from Figure 4-21, all DP series cells as well as physical mixture exhibit depressed capacitances corresponding to probable arcs to be finalized at lower resistance than LSC$_{113}$ or LSC$_{214}$. Their spectra are not between two single phase responses contrary to 400 °C spectra and they hence do not imply lever rule. This can be explained by hetero interfacial enhancement. Similar to previous spectra, LSC$_{113}$ still obeys Warburg element properly. DP-5 once more is more likely to finish the arc.

Oxygen partial pressure has no significant effect on EIS responses, too, except for lowering capacitive effect, logic behind of which has already been explained in 400 °C spectra evaluations (see Figure 4-22). DP-1 and PM show the lowest capacitances and the arcs which are more likely to be finalized early, meaning lower cathode resistance at 500 °C. But it is hard to state that this case is originated from more successful interface maximization that these syntheses can do in sub-micron scale. But somehow, whether in the form of contact between single phase agglomerates in tens of microns’ scales with each other or in the form of hetero-interface creation during
nucleation growth process of solution based synthesis, there releases a catalytic effect caused by two-phase existence at 500 °C.

**Figure 4-21** Comparison of all cells at 500 °C with varying oxygen

**Figure 4-22** 500 °C EIS responses of symmetric cells of DP-5, DP-1, DP-3 and PM with respect to differential $P_{O_2}$
In previous comments, made in evaluation of EIS responses in 400 °C, slight increase in capacitance with increasing $P_{O_2}$ was attributed to cumulative effect of both phases and it was stated that this regime would change in following temperatures. 550 °C was such a temperature; spectra did not necessarily show higher capacitances with increasing $P_{O_2}$. Contrary, in DP-5, capacitance was higher in 0.01 atm than it was in 0.21 atm as illustrated in Figure 4-23. While lowering $P_{O_2}$ induces vacancy formation at this temperature within LSC$_{113}$ phase and facilitates oxygen transport, its effect on reducing the diffusion of interstitial species is more dominant in DP-5. Since other cells include more LSC$_{113}$, effect of increasing $P_{O_2}$ is more drastic with respect to 400 °C spectra; 0.21 atm capacitances deviate more than previous temperatures. This is because higher temperatures mean a transformation of charge compensation mechanism from electrical to ionic.
Another characteristic of 550 °C is disappearing of ion exchange resistance at cathode-electrolyte interface. Hetero interface enhancement is once more valid for 550 °C, too. Nonetheless, it is still debatable to point out which multi-phase cells show better performance. Cells involving more LSC\textsubscript{113} phase are situated in more advantageous position in 0.01 atm $P_{O_2}$ since with increasing temperature, oxygen vacancies formed meet more easily with interstitials oxygen of LSC\textsubscript{214} causing more depressed and reduced arcs. This is manifested in Figure 4-24, in which 0.01 and 0.21 atm responses of all cells are compared. It is seen that DP-3, DP-1 and PM, involving more LSC\textsubscript{113}, cell responses are slightly reduced while 214 and DP-5 cells exhibited slightly enhanced arcs. Similar situation will also be seen in 600 °C.

![Figure 4-24](image)

**Figure 4-24** Comparison of all cells at 550 °C with varying oxygen

The only principle alteration in 600 °C spectra is the reduced ASR values with respect to spectra of 550 °C, which is not surprising. $P_{O_2}$ dependencies of different cells are almost same for each cell (compare Figure 4-23 and Figure 4-25). There is still an enhancement in overall ORR caused by hetero interface contacts except for DP-3 as given in Figure 4-26. EIS response of DP-3 is between LSC\textsubscript{113} and LSC\textsubscript{214} at 600 °C with higher arc than LSC\textsubscript{214}. Surface Sr segregation is expected to have an effect to see such response with increasing temperatures since LSC\textsubscript{113} is highly prone to segregation and DP-3 involves significant LSC\textsubscript{113}. But this is, on the other hand, an
indication for losing enhancing effect of hetero interface with increasing temperatures after intermediate range is exceeded.

Figure 4-25 600 °C EIS responses of symmetric cells of DP-5, DP-1, DP-3 and PM with respect to differential $P_{O_2}$

The lowest recorded ASR at 600 °C is observed in DP-5, as a rich cathode in terms of LSC$_{214}$ constituent. It is 60 Ωcm$^2$. Nevertheless, use of LSC$_{214}$ at this temperature is more advantageous than use of DP-3 cathode. But the other cell responses are still in advantageous position with respect to single phase powders.
Figure 4-26 Comparison of all cells at 600 °C with varying oxygen.

Figure 4-27 650 °C EIS responses of symmetric cells of DP-5, DP-1, DP-3 and PM with respect to differential $P_{O_2}$.
At 650 °C, significant reduction in LSC$_{214}$ arc is accompanied with quite high increase in DP-3 resistance. DP-3 response converges to LSC$_{113}$. $P_{O_2}$ dependency is almost same as it was for previous cathodes; higher oxygen content of ambient meant slightly higher capacitances as illustrated in Figure 4-27 above.

As it was stated, surface Sr segregation is important reason for this ASR increase but it should also be emphasized that with increasing temperatures, electrical conductivity of LSC$_{113}$ must decrease since vacancy formation mechanism for charge balance is now more operative at such temperatures. Low electrical conductivity can’t catalyze well ORR and this caused increasing ASR in cathodes including more LSC$_{113}$. That’s why hetero interfacial ORR enhancement is operative only at intermediate temperature ranges. Examinations at 650 and 700 °C played role of demonstrating that.

The lowest ASR at 650 °C belongs to DP-5. In fact, at this temperature, coexistence of each phase is advantageous only in DP-5 cathode. Otherwise, the all other cathodes become useless with respect to utilization of LSC$_{214}$ single phase cathode. It should be at this point underlined that if the cathode thickness would be lower than that of these cathodes, other cathodes having different phase fractions than DP-5 could also be
advantageous. Nonetheless, many probable unknown parameters may also alter the situation drastically. Therefore, focusing on one of them is pointless.

Unexpectedly, inverse relationship with $P_{O_2}$ as an implication of surface signals was detected in LSC$_{214}$ at 650 ºC. Figure 4-29 illustrates a interfered surface ORR related arc changing inversely with $P_{O_2}$. This is reasonable since critical utilization length of LSC$_{214}$ is well high. As an exceptional case, surface signals were detectable at this conditions. But this is rare situation. In general, surface signals are non-detectable with these thick cathodes.

![Figure 4-29](image_url) LSC$_{214}$ response at 650 ºC with varying $P_{O_2}$

The ultimate examination temperature was 700 ºC. The most drastic conclusion that 700 ºC examinations exhibited is pointlessness of dual phase synthesis utilization at this stage. After that point, ASR of LSC$_{214}$ is the lowest anymore. Moreover, even at such a high temperature, any of the ASR observed is not sufficient to satisfy requirement of $0.15 \, \Omega cm^2$[1]. The lowest one belonging to LSC$_{214}$ is $9.55 \, \Omega cm^2$. This is remarkable consequence.
Figure 4-30 Comparison of all cells at 700 °C with varying oxygen

Figure 4-31 700 °C EIS responses of symmetric cells of DP-5, DP-1, DP-3 and PM with respect to differential $P_{O_2}$
As can be seen from the all spectra, starting point of arcs in $Z_{\text{real}}$ was non-zero. This resistance without any imaginary contribution is ionic resistance caused by GDC electrolyte (ionic conductor). As the first time at 700 °C, resistance caused by electrolyte is changing with respect to $P_{O_2}$. Higher $P_{O_2}$ corresponded to slightly higher ASR as illustrated in Figure 4-31. When it is considered that GDC could unfortunately be electrically conductive depending upon conditions [10] and total conductivity of it decreases with increasing $P_{O_2}$, which is manifested as higher ASR with higher $P_{O_2}$, EIS responses make sense [196]. Especially in DP-1, increasing ASR of GDC with is apparently observed.

700 °C was the last probable temperature at which surface limited behavior would be observed since critical utilization length at this temperatures is significantly bigger than low temperature regimes; combination of $D_{(La_{a},Sr_{b},Co_{c})O_3}^{+} = 10^{-9.75} \text{cm}^2/\text{s}$ and $k_{(La_{a},Sr_{b},Co_{c})O_3}^{+} = 10^{-6.8} \text{cm/s}$ at 700 °C [43] yields 11.2 μm critical utilization length. This is quite more in case of LSC214 oxides [146]. This means that even if agglomerates are around 10 μm, surface limited behavior is expected to be observed but this did not happen.

To sum up, the EIS responses of dual phase synthesis powders, electrochemical behaviors of symmetric cells could be classified into four different regimes as a function of temperature. In the first regime prevailing at 400-500 °C interval, EIS responses mimic rule of mixture. In the second regime (500-550 °C), dual phase powders have performance better than single phases but equivalent to physically blended powder. Third regime, prevailing at 550-650 °C, is the only one at which even better performances of dual phase powders than physically mixed one was observed. In the last regime (650-700 °C), whether in the form of physical blending or dual phase synthesis, co-existence of two phase structure becomes pointless such that single phase LSC214 has the best cathode performance. The regimes of these different performances are illustrated in Figure 4-32.

The observations reported above will be discussed with respect to three aspects. These are i) scale of structure in dual phase synthesis, ii) site occupancy in one pot synthesis and iii) the relevance of EIS responses to cathode thicknesses.
The first issue is the scale of final structure in dual phase powders and its relevance to cathode performances. Figure 4-32 manifests that beneficial effect of dual phase synthesis over physical mixture was observed only in the temperature range of 550-650 ºC and the degree of the enhancement is modest. It is, therefore, qualitatively...
inferred that degree of the hetero interface formation is modest even in case of dual phase synthesis. This aspect was checked by EDS mapping.

Figure 4-33 EDS mapping of physically mixed powder at 45000 magnification

It was expected that dual phase powders were mixed in the fine scale, interpenetrated to each other as opposed to the case of physically mixed powder. To check the scale of structure in the dual phase powder quantitatively, a special experiment was conducted. A dual phase sample was examined and EDS mapped at different magnifications, namely 400, 1000, 2000, 4000, 8000, 16000, 30000 and 45000. Unlike the physical mixture where clear elemental contrast was obtained at x400 (see Figure 4-10), there was no such contrast in dual phase powder. The contrast observed in physical mixture can be followed at magnifications as high as x45000. This was

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Aforementioned mappings results are not included not to unnecessarily increase the volume of the thesis.
considered to be the limit of elemental resolution in the current study. Dual phase powder when examined at x45000, there was no elemental contrast in terms any atom type. This implies that the scale of structure in dual phase powder is less than that observable under x45000. This roughly corresponds to a structural size of less than ~6 μm. So, EDS mappings of dual phase powder imply a successful interpenetration between phases because there is no contrast in terms of any element in broad range of magnifications. Consequently, it is understood that interpenetrated nano-porous agglomerates of constituent phases that are lower than ~6 μm in size but higher than particle size shown in SEM images namely at most 200-300 nm (refer to Table 4-3 and Figure 4-5) were attained.

Fine scale of structure implies us successful hetero interface formation in principle. Nevertheless, if such a reduced scale of structure is the case as well as significantly successful continuous contacts between phases is the case, then cathodes made up of with these dual phase synthesis powders are supposed manifest this. In other words, these cells are supposed to yield significant enhancement in overall oxygen reduction rate manifested as reduced cell polarization resistance induced by LSC$_{113/214}$ not only with respect to single phases powders but also with respect to physically mixed powder. However, aforementioned EIS responses show that beneficial effect of fine scale of structure did not reflect to cathode performance caused by LSC$_{113/214}$ hetero structures.

When disproof of the controversies surrounding the scale of structure findings in following pages in the light of site occupation are considered, excess porosity within powders which probably has led to poorly meeting constituent phases to air in fine scale is possible reason for modest electrochemical effect. Lack of triple phase boundaries is implied here. Moreover, there are thick and microstructurally heterogeneous cathodes through which many parameters can affect many things and it is hard to exactly identify what the case is as Baumann et al. [22] thoroughly states. Very high thickness (up to 100 μm) as well as porosity structure effects may have led to deficient EIS responses recorded. That is why, although dual phase synthesis did not yield huge agglomerates of two phases as opposed to physically mixing separately
synthesized powders and it gave fine scale of structure, affirmative reflection of it in overall performance was not monitored.

The second aspect is site occupations or La/Sr partitioning behavior constituting not only an interesting problem concerning one pot synthesis but also it is leading to controversies surrounding evaluation of EDS mapping results. For instance, one may assert as counter argument to “fine scale of structure” that there is still coarse scale of structure but almost same atomic fraction of all atoms in both phase inhibits any contrast. At this point it is very important to remind that even La difference between 0.14 and 0.16 could be recognized by mapping in physically mixed powder (see Figure 4-10). In order for mapping not to recognize any contrast, even such a very small difference should not be present within powder. But this is not realistic. In both phases, almost same atomic fractions possibility of all elements in phases is restricted not only by prospective lattice parameter mismatch but also this is forbidden by weight fraction calculations that Rietveld analyses revealed. One can also recommend tailoring experimental details namely accelerating voltage spot size etc. However, detecting difference even between 0.14 and 0.16 was possible in aforementioned conditions, making such tailoring senseless.

On the other hand, Sr (and/or La) site occupation differential could be considered as another source of incapability to detect contrast. However, this necessitates extremely heterogeneous distribution of La and Sr cations through complete matrix, which in turn necessitates very serious broadening of XRD patterns. Extent of broadening in this case would be so much that rather than broadening, release of new peaks pertaining to different angles would be the case. However, XRD patterns are not compatible with such high site occupation differential. Hence, although there is some sort of site occupation differential that is expected as stated before, its extent is not so much as to allow no contrast even at 45000 magnifications. Consequently, fine scale of structure cannot be opposed in the light of speculations based on site occupation uncertainties. It is also meaningful to note that EDS is not a suitable tool to detect atomic contrast at very low scale of structures. So, inability to clearly detect contrast can also be considered as an indicator of fine scale of structure.
Finally, cathode thickness effects to EIS responses should be taken into consideration. Many comments and evaluations have been done regarding all symmetric cells but credibility of these can be attained only if they are correlated with cathode thicknesses since any deviation in thickness can manifest itself as a deviation in overall cell resistance. Low thickness means low resistance in principle. Thicknesses of all cathodes have been observed in almost same thicknesses, clearing away any uncertainty of evaluations on ASR. Figure 4-34 gives cross sectional SEM images of symmetric cells showing cathode thicknesses (a) DP-1, (b) DP-3 (c) LSC$_{214}$ (d) LSC$_{113}$ (e) PM and (f) DP-5.
all cathodes. Only significant differential is observed in DP-3 and DP-5 cathodes with around 50 and 100 μm thicknesses respectively. Both deviate from the average expected values of 80 μm and DP-5 with higher thickness is expected to yield lower ASR. But in spite of higher thickness, it yielded the lowest ASR among all fortunately. Likewise, DP-3 with the lowest average cathode thickness exhibited high ASR. If for example DP-5 were to have the lower thickness, it would yield more reduced ASR. Consequently, one can not attribute performance differentials among signals pertaining to different dual phase powders to different cathode thicknesses; effect of thickness is eliminated in the light of Figure 4-34.

Fitting EIS responses to a reasonable equivalent circuit models is a fundamental task in researches based on impedance analysis. However, this is viable and significant only for the well-defined systems, which is not the case in this part of study. 70 μm thickness along with huge surface roughness and heterogeneously distributed porosities with varied sizes would makes such an attempt pointless, as comprehensively explained in previous sections.

Additionally, all of the cathodes have apparently have huge surface roughness. This situation in fact makes calculated area of air exposed surface indefinite for properly characterizing ASR. But this is valid for all cells and it should be kept in mind that the main concern is comparison of EIS responses of cells rather than determination of definite ASR for a certain cathode. Determination of suitable ASR for SOFC cathode is the task assigned to thin film cathode part in next chapter.

On the other hand, while any study that is keen on LSC cathodes must conduct a supplementary stability examination since chemical instability is of great concern for LSC cathodes, in thick film part of this study, such an attempt is pointless since current cathodes already seriously suffer from very high resistance due to thicknesses without any worthwhile hetero interfacial enhancement and poor interface maximization. Rather, chemical stability examination is also assigned to thin film cathode part in this study.
4.3. Conclusions

As the first time, synthesizing LSC$_{113/214}$ dual phase system from one unique solution via Pechini method has been successfully achieved without any undesired third phase. It has been deduced from refinements and syntheses that formation of LSC$_{113}$ has dominated the formation of LSC$_{214}$ phase. EDS mappings demonstrated that dual phase synthesis did not produce huge agglomerates of phases. The scale of structure that is attained by one pot synthesis of LSC$_{113/214}$ dual phase structure was between ~6 μm to ~200-300 nm. However, although finely dispersion of phases has been achieved, the positive effect of this in terms of hetero interface maximization has not been reflected to in situ electrochemical performances; the degree of cathode performance enhancement was modest. This might be attributed to the excess porosity resulting in low density of triple phase boundaries of LSC$_{113}$-air-LSC$_{214}$. Furthermore, beneficial effect of dual phase powders over physical blending was limited to the temperature interval of 550-650 °C. This does not mean that the use of dual phase synthesis is limited to this temperature interval, since this might change depending upon the cathode thickness and the porosity structure. Alteration of cathode thickness as well as microstructural features are susceptible to revise aforementioned useable limit. Although dual phase synthesis is incapable of making conventional thick cathode surface ORR limited, it can obviously be concluded to be a stimulating approach.
CHAPTER 5

FABRICATION AND PERFORMANCE OF THIN FILM
LSC CATHODES

5.1. Introduction
The main concern of this chapter is the success in reduction of operating temperature regardless from the cost and/or fabrication difficulties of SOFCs. Maximized LSC\textsubscript{113/214} hetero interfaces along with utilization of them through thin film cathode surface and significant temperature reduction were aimed since thin film cathodes are well-defined as opposed to thick porous cathodes and low-resistance alternatives along with cost and/or fabrication difficulties. For this purpose, as the way of LSC\textsubscript{113/214} maximization, co-sputtering (simultaneous) of (La\textsubscript{0.8}Sr\textsubscript{0.2})CoO\textsubscript{3-δ} and LaSrCoO\textsubscript{4±δ} onto (Ce\textsubscript{0.9}Gd\textsubscript{0.1})O\textsubscript{2-x} electrolyte was adopted and thin film composite cathodes were produced.

5.2. Preparation of Oxide Sputtering Targets
(La\textsubscript{0.8}Sr\textsubscript{0.2})CoO\textsubscript{3-δ} and (La\textsubscript{0.5}Sr\textsubscript{0.5})\textsubscript{2}CoO\textsubscript{4±δ} powders were synthesized via Pechini route, as details of which comprehensively explained in previous chapter, and as-synthesized single phase powders were separately pressed into 2-inches diameter oxide sputtering targets using deformable die [197]. (La\textsubscript{0.8}Sr\textsubscript{0.2})CoO\textsubscript{3-δ} and (La\textsubscript{0.5}Sr\textsubscript{0.5})\textsubscript{2}CoO\textsubscript{4±δ} targets were sintered at 1100 °C for 10 hours and air exposed surfaces of final targets were used in order for sputtering. This is because the bottom surface is in contact with crucible and loses cations to crucible. Concurrently, GDC powders were pressed into 19-mm pellets, which would act as electrolyte finally. These GDC pellets were sintered at 1350 °C for 10 hours to obtain a dense oxygen ion conducting membrane.
5.3. Fabrication of LSC Cathodes via Magnetron Co-Sputtering

Two GDC pellets were positioned in selected positions in the vacuum chamber. Then, magnetron sputtering of composite cathode was carried out on surfaces of two GDC pellets under 10^{-7} torr base pressure. Ar was maintained at a flow rate of 10 cm^3/min. Sputtering time was 10 hours for simultaneous sputtering of LSC. The substrate temperature was kept to 400 °C.

Power loading on (La_{0.8}Sr_{0.2})CoO_3 and LaSrCoO_{4±δ} were 30 Watt for each. These values were selected based on previous experiments [198] which yielded LSC_{214-10%} LSC_{113} and LSC_{214-25%} LSC_{113}. These will be named as cell-10% LSC_{113} and cell-25% LSC_{113}, respectively.

5.3.1. Fabrication of Symmetric Cell with Thin Film Cathode

![Figure 5-1](image)

**Figure 5-1** Schematic illustration of symmetric cells. (a) Cross section of cell and (b) Top/bottom view. Lateral size of air exposed surface (depicted by black) is seen in (b).

Details of final symmetric cells are illustrated schematically in Figure 5-1. Following cathode depositions to each side of GDC pellets over the circular mask having aperture size (diameter) of 12 mm, as current collector, gold was sputtered on surface cathode over a mask having 10 mm circular aperture size/diameter, which resulted in 1 mm lateral size of air exposed surface of cathode from which EIS responses were going to
be recorded. This 1 mm lateral aperture was used to calculate area of air exposed surface of cathode. Deposition time of Gold was 1 hour since Gold layer acted only as current collector and its deposition kinetic is higher because it is a metal. The same procedures were applied onto each side of GDC pellet and thereby two symmetric cells were attained for electrochemical analyses. The overall cell geometry is illustrated in Figure 5-1.

5.4. In situ Electrochemical Impedance Analysis

Final symmetric cells were analyzed by in situ electrochemical impedance spectroscopy (EIS) in the temperature range of 300-700 °C. Frequency range was 1 MHz-0.01 Hz with 10 mV perturbation amplitude. $P_{O_2}$ was kept constant to ambient air. At 300-400 °C range, temperature increment was 20 °C, which turned out to be 50 °C between 400 °C and 700 °C. At each temperature, area specific resistances of composite cathodes were extracted on the basis of equation given below.

$$ASR = \frac{R_{measured} \times Area}{2}$$

Thin film systems are well-defined systems, which reasonably enables attributing penetrated and/or separated impedance arcs to certain reaction steps, microstructural and/or chemical characteristics of cathode. This is done by fitting EIS data to certain equivalent circuit models. Hence, all spectra were fitted to equivalent circuit models, so long as this is literally recognized, possible, and physically reasonable.

In both cells, at the point at which 0.20 $\Omega cm^2$ was attained, stability study was conducted since cell instability at increasing temperatures is the main concern regarding SOFCs [9,18]. ASR values were subsequently recorded per 2 hours and degradation regime of combinatorial symmetric cells were revealed and compared with literature. Finally post mortem SEM analysis were done on symmetric cells.
5.4.1. EIS Responses of Cell-10% LSC$_{113}$

Cell-10% LSC$_{113}$ is the one having excess LSC$_{214}$ with relatively modest content of LSC$_{113}$ due to its position near to LaSrCoO$_{4+\delta}$ target. Although EIS measurements were carried out subsequently at starting from 300 °C, evaluation of EIS responses begins with 700 °C since higher temperature responses are more evident in terms of equivalent circuit models and resultant ASR values.

![Figure 5-2 EIS Spectra of cell-10% LSC$_{113}$ at 650 and 700 °C](image)

EIS spectra of cell-10% LSC$_{113}$ obtained at 700 and 650 °C are fitted to same equivalent circuit model depicted in Figure 5-2. In each case, there is one arc which is belonging to surface oxygen exchange step, which means that surface oxygen exchange step is the only rate limiting step at these temperatures. This is reasonable because at these temperatures, oxygen ionic diffusion is very fast and the length over which diffusion must take place is highly reduced, which excludes ionic transport process from being a source of resistance [173]. In the light of fitting EIS data to circuit models, ASR of cathodes have been found to be 0.439 and 0.265 Ωcm$^2$ at 650 and 700 °C, respectively. However, situation changes at 600 °C, in which an additional high frequency arc releases.
At decreasing temperatures, an additional arc pertaining to oxygen ion exchange at electrode/electrolyte interface releases. In other words, oxygen ion exchange at this interface starts to be a source resistance anymore. Consequently, two arcs partially interpenetrating to each other in one spectrum is manifested. This behavior starts at 600 °C and was observed in 550 and 500 °C, too. This is illustrated in Figure 5-4 and Figure 5-6.

The well-known equivalent circuit model to MIEC cathodes at intermediate temperature range, manifested as interpenetrated two arcs, has been manifested by Baumann et al. [133]. This equivalent circuit model prevailing in a broad temperature range and fitting very well to 600, 550, 500, 450 and 400 °C EIS responses of cell-10% LSC\textsubscript{113} is illustrated in Figure 5-5. R\textsubscript{CT} means charge transfer resistance
corresponding to the ion exchange resistance at electrode/electrolyte interface in case of SOFC. \( R_{lf} \) means low frequency resistance attributed to surface oxygen exchange step. \( \Phi \) denotes constant phase element, mainly originated from non-ideality of the system as compared to ideal capacitive behavior.

**Figure 5-5** Equivalent circuit model #2 pertaining to 600, 550, 500 and 450 °C

[133,138]

In general, underlying reason for fitting data to an equivalent model is to extraction of resistances pertaining to specified processes within electrode thanks to alternating current. However, in this study, overall ASR of cathodes are sought, which is possible only when incomplete arcs are finalized and the points at which data intersects with x-axis are revealed and/or partial interpenetration of arcs are solved by deconvolution.

**Figure 5-6** EIS Spectra of cell-10% LSC\(_{113}\) at 500 and 450 °C

\[
\text{ASR}=5.894 \ \Omega \text{cm}^2
\]

\[
\text{ASR}=22.414 \ \Omega \text{cm}^2
\]
of these interpenetrated arcs. Therefore, the reason for fitting EIS data to model is mainly to finalize these arcs, one example of which is seen in cell response at 450 °C. By fitting this data, overall cathode ASR at 450 °C has been found to be 22.414 Ωcm².

When temperature range below 400 °C is considered, Gerischer like behavior is more probable/expectable to prevail due to expected contribution of bulk ionic transport at decreasing temperatures [6]. Especially 400, 380 and 360 °C responses mimic Gerischer impedance. Nevertheless, circuit models involving Gerischer element exhibited weak goodness of fit during analyses. From 400 to 360 °C, equivalent circuit model #2 is thought to be the relevant model either because EIS responses are likely to finalize and intersect x-axis or it yielded relatively reasonable goodness of fit when used. Figure 5-8 shows EIS responses at 360 and 340 °C. ASR values, manifested in Table 5-1, have been calculated in the light of fit to model #2 in Figure 5-5.

**Figure 5-7** EIS Spectra of cell-10% LSC₁₁₃ at 400 and 380 °C
However, it is very hard to conclude with a confident circuit model for temperatures lower than 360 °C. From medium to low frequency range in 340, 320 and 300 °C spectra, EIS responses converge to linear like behavior. This is illustrated in Figure 5-8 and Figure 5-9. This linearization with decreasing frequency could be either due to Warburg element or it can typically be attributed to starting point of a semicircle. Which one is the valid is debatable. This debate enforces us to extrapolate ASR line in the ASR vs log(1/T) for the temperature in case of which fitting to equivalent circuit
model is unsatisfactory since practice of fitting and revealing the ASR is not realistic. This extrapolation was started from 400 °C. This is because even though the spectra at 380 and 400 °C was said to show nice goodness of fit, the ASR values that these fittings yield were not exactly assured and change in ASR would be able to deteriorate Arrhenius plot drastically.

Table 5-1 Calculated area specific resistances of cell-10% LSC113 and its electrolyte in the light of equivalent circuit models

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>$R_{\text{cathode}}$ (Ωcm$^2$)</th>
<th>$R_{\text{electrolyte}}$ (Ωcm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>0.265</td>
<td>2.246</td>
</tr>
<tr>
<td>650</td>
<td>0.439</td>
<td>2.7646</td>
</tr>
<tr>
<td>600</td>
<td>1.02</td>
<td>3.629</td>
</tr>
<tr>
<td>550</td>
<td>2.283</td>
<td>5.011</td>
</tr>
<tr>
<td>500</td>
<td>5.894</td>
<td>7.629</td>
</tr>
<tr>
<td>450</td>
<td>22.414</td>
<td>13.13</td>
</tr>
<tr>
<td>400</td>
<td>-</td>
<td>26.35</td>
</tr>
<tr>
<td>380</td>
<td>-</td>
<td>35.34</td>
</tr>
<tr>
<td>360</td>
<td>-</td>
<td>46.76</td>
</tr>
<tr>
<td>340</td>
<td>-</td>
<td>65.63</td>
</tr>
<tr>
<td>320</td>
<td>-</td>
<td>91.35</td>
</tr>
<tr>
<td>300</td>
<td>-</td>
<td>122.28</td>
</tr>
</tbody>
</table>

Lack of almost error-free model fitting in this study indicates that symmetric cells obtained in this study are not perfectly well-defined as opposed to many thin film systems widely studied in literature \[11,21,22,122,134,199\]. Imperfections in fitting data to models in spite of dense thin micro electrode geometry in this study is thought to be mainly originated from surface roughness dictated by GDC electrolyte/substrate obtained via pressing its powders and sintering. Moreover, as opposed to widely investigated systems, lateral thickness of air exposed surface is 1 mm (see Figure 5-1 and Figure 5-10). Such a high lateral length, over which surface diffusion of oxygen atoms also takes place, more or less prevent achieving a homogeneous signal from the system.
Figure 5-10 SEM image of cathode of cell-10% LSC$_{113}$. (a) dense microstructure of cathode free surface, (b) surface of Gold current collector and (c) lateral thickness of cathode free surface

5.4.2. EIS Responses of Cell-25% LSC$_{113}$

Cell-25% LSC$_{113}$ involves relatively more LSC$_{113}$ content than cell-10% LSC$_{113}$, which corresponds to formation of more catalytic hetero interfaces and leads to expectation of observing lower polarization resistance than cell-10% LSC$_{113}$. Truly, lower ASR values were detected in the case of cell-25% LSC$_{113}$ but only above 550 °C. Below this temperature, cathode of cell-10% LSC$_{113}$ yields lower polarization resistance. While the lowest ASR in cathode of cell-10% LSC$_{113}$ was 0.265 Ωcm$^2$, it was 0.14 Ωcm$^2$ in cathode of cell-25% LSC$_{113}$. Fortunately, the ASR pertaining to cathode of cell-25% LSC$_{113}$ is ideally lower than what is necessitated for fuel cell application [1]. However, the temperature at which these lowest ASR values have been observed, namely 700 °C, is very high in cell stability aspect. Because of 700 °C, cells are prone to be rapidly degraded.

700, 650, 600, 550, 500 and 450 °C cell responses match with equivalent circuit model illustrated in Figure 5-3. The only rate limiting step is surface oxygen exchange through these temperatures. High frequency arc which is associated with oxygen
exchange at electrolyte/electrode interface emerged at 400 °C in cathode of cell-25% LSC\textsubscript{113}. This emerging temperature was 650 °C in cathode of cell-10% LSC\textsubscript{113} involving higher LSC\textsubscript{214} content. What can be the reason?

![Figure 5-11 EIS Spectra of cell-25% LSC\textsubscript{113} at 700 and 650 °C](image)

Transport of oxygen was mainly driven by interstitial diffusion of oxygen in LSC\textsubscript{214} as opposed to LSC\textsubscript{113} through which oxygen transport occurs via oxygen vacancies. On one hand, higher temperatures promote formation of oxygen vacancies but on the other hand, this promotion is relatively more in interstitial oxygen movement of LSC\textsubscript{214}. Aside from more promotion of interstitials at higher temperatures, jumping of interstitial oxygen to electrolyte is supposed also be easier at also lower temperatures than substitutional moving of oxygen via vacancies of LSC\textsubscript{113}. Furthermore, vacancy driven diffusion is anisotropic and direction dependent, making diffusivities generally larger [170]. When the huge volume of LSC\textsubscript{113} is considered, postponed release of high frequency arc is expected to be seen in cell-10% LSC\textsubscript{113}, the one that is supposed to have higher LSC\textsubscript{214} content. However, reverse is valid. Oxygen jump to electrolyte is easier in cell-25% LSC\textsubscript{113} as manifested in EIS spectra in following pages. In such case, an insufficient interpenetration of cathode to electrolyte surface seems to be the most reasonable answer.
Another observation was based on goodness of fits of spectra to equivalent circuit models which are referred in literature. Until 450 °C, goodness of fits was highly satisfactory. The main reason for it was the availability of x-intercepts of arc. But it turned out to be insufficient after 400 °C, which makes resultant ASR uncertain and involving relatively high error. That’s why resultant ASR values are not used below 400 °C in spite of the confidence on validity of equivalent circuit models. Table 5-2 gives the resistances of cell-25% LSC$_{113}$ that fitting yields well. Empty sites are the ones extrapolated.

Figure 5-12 EIS Spectra of cell-25% LSC$_{113}$ at 600 and 550 °C

Figure 5-13 EIS Spectra of cell-25% LSC$_{113}$ at 500 and 450 °C
Figure 5-14 EIS Spectra of cell-25% LSC$_{113}$ at 400 and 380 °C

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>$R_{\text{cathode}}$ (Ωcm$^2$)</th>
<th>$R_{\text{electrolyte}}$ (Ωcm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>0.140</td>
<td>2.85</td>
</tr>
<tr>
<td>650</td>
<td>0.315</td>
<td>3.52</td>
</tr>
<tr>
<td>600</td>
<td>0.797</td>
<td>4.69</td>
</tr>
<tr>
<td>550</td>
<td>2.284</td>
<td>6.73</td>
</tr>
<tr>
<td>500</td>
<td>9.365</td>
<td>11.59</td>
</tr>
<tr>
<td>450</td>
<td>44.061</td>
<td>20.06</td>
</tr>
<tr>
<td>400</td>
<td>-</td>
<td>39.12</td>
</tr>
<tr>
<td>380</td>
<td>-</td>
<td>53.01</td>
</tr>
<tr>
<td>360</td>
<td>-</td>
<td>74.16</td>
</tr>
<tr>
<td>340</td>
<td>-</td>
<td>107.84</td>
</tr>
<tr>
<td>320</td>
<td>-</td>
<td>141.51</td>
</tr>
<tr>
<td>300</td>
<td>-</td>
<td>203.89</td>
</tr>
</tbody>
</table>

Despite of the problems regarding fitting data to circuit model and evaluation of EIS spectra at low temperature regime (namely converging to 300 °C), there is an implicit strategy in struggling with this problem; concept of critical utilization length. By determining critical utilization length at specific temperature, what kind of process is
rate determining can be estimated, which allows correlation of EIS spectra with rate determining step. If cathode thickness is below critical utilization length ($l_\delta$), then it can be stated that overall cathode resistance is limited by surface oxygen exchange step. If the reverse is valid, then bulk ionic transport is said to be rate limiting. $l_\delta$ of (La$_{0.8}$Sr$_{0.2}$)CoO$_3$ at different temperatures are listed in Table 5-3.

Figure 5-15 EIS spectra of cell-25% LSC$_{113}$ from 360 to 300 °C
Table 5-3 Critical utilization length ($l_\delta$) of ($La_{0.8}Sr_{0.2}$)CoO$_3$ at different temperatures [43]

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>$l_\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>13±1.30 μm</td>
</tr>
<tr>
<td>600</td>
<td>3.47±0.35 μm</td>
</tr>
<tr>
<td>500</td>
<td>1.43±0.14 μm</td>
</tr>
<tr>
<td>450</td>
<td>630±63 nm</td>
</tr>
<tr>
<td>400</td>
<td>400±40 nm</td>
</tr>
</tbody>
</table>

Figure 5-16 Cross section of cell-10% LSC$_{113}$ manifesting the μm level thickness

If it is considered that aforementioned cathodes are around in 1 μm thickness, it is inferred that starting from 400 °C, current thicknesses of cathodes lead the cathodes to be limited by bulk ionic transport rather not by surface oxygen exchange step after that point since cathode thickness is well higher than $l_\delta$ anymore. In addition to geometric considerations of cells explained before, critical utilization length concept explains why impedance responses exhibited unstableness after 400-450 °C. In the light of $l_\delta$ values, it is not surprising to see Warburg behavior at 300 °C and Gerischer like behavior at 450 °C. These values also explain unfinished EIS arcs in Chapter 4.
5.4.3. Stability of Cathodes

Cathode stability is one of the biggest concern mainly because of surface Sr segregation in cobalt containing perovskite [19,87]. Therefore, how stable the co-sputtered cathodes are sought. Accordingly, the temperature at which aforementioned targeted ASR value (0.2 Ωcm$^2$) was attained was determined.

![Graph](image-url)

*Figure 5-17* Cell resistances at 700 °C as function of time

Unfortunately, even at 700 °C, cell-10% LSC$_{113}$ yielded 0.265 Ωcm$^2$ and 700 °C is supposed to result in very robust performance degradation in the light of literature findings. Cai *et al.* [18] found that polarization resistance of cathode made up of with LSC$_{113}$ promotes to around 20 Ωcm$^2$ from 0.7 Ωcm$^2$ at 650 °C and within 72 hours. Similarly, Kubicek *et al.* [9] revealed an increase in cathode polarization resistance from 0.8 Ωcm$^2$ to 75 Ωcm$^2$ at again 650 °C and within 72 hours.

Cathodes of cell-10% LSC$_{113}$ and cell-25% LSC$_{113}$ were tested at 700 °C for 144 hours in the current system and these aforementioned rates are expected to be well higher in
case of them. In spite of higher temperature and testing time, however, cathodes of cell-25\% LSC\textsubscript{113} and cell-10\% LSC\textsubscript{113} exhibited resistance increase rates much lower than the literature findings stated above. Cell-10\% LSC\textsubscript{113} started from 0.265 $\Omega \text{cm}^2$ cathode polarization resistance and at the end of 144 hours, ASR was just 0.74 $\Omega \text{cm}^2$, corresponding to 20 times lower degradation rate than what Cai et al. [18] discovered. In case of cathode of cell-25\% LSC\textsubscript{113}, aside from lower ASR than cathode of cell-10\% LSC\textsubscript{113} at the same temperature, degradation rate of it is even lower as compared to cathode of cell-10\% LSC\textsubscript{113}. Its ASR raised to 0.30 $\Omega \text{cm}^2$ from 0.14 $\Omega \text{cm}^2$ in 144 hours, corresponding to 28 times lower rate than ref [18]. Therefore, co-sputtered cathodes in this study yielded outstanding stability in literature. This is a remarkable result. Nonetheless, both of the cathodes of cell-10\% LSC\textsubscript{113} and cell-25\% LSC\textsubscript{113} are still beyond the requirements for a successful commercialization not only because of limited lifetime but also their high operation temperature restricting interconnect material.

5.5. Comparative Evaluation of EIS responses

If the chemical processes occurring at SOFC cathode are namely oxygen reduction and cathode is activation limited rather than diffusion limited (non-thick film case), then overall cathode reaction should be triggered by temperature. This dictates Arrhenius behavior for aforementioned cathode when the thin dense film case is considered. Arrhenius equation, which is supposed to govern aforementioned cathodes, is given below.

$$k = A \cdot \exp \left( -\frac{E_a}{k_B T} \right)$$

Where A is pre-exponential constant, k is reaction rate, $E_a$ is activation energy, $k_B$ is Boltzmann constant and T is temperature in Kelvin. It can be transformed to another form more apparently manifesting temperature dependence characteristics.

$$\ln k = \ln A - \frac{E_a}{k_B} \frac{1}{T}$$
Equation above means that reaction rate, which is in correlation with cell resistance, is a linear function of 1/T and $E_a/k_B$ is slope of such a linear equation. Accordingly, logarithm of ASR values extracted from the EIS were drawn as function of 1/T and linearity was achieved as it is manifested in Figure 5-18, from which slopes are extracted.

![Graph of ASR vs 1/T](image)

**Figure 5-18** Temperature dependence of area specific resistance (ASR) pertaining to electrolytes and differential cathodes

Variation of ASR values pertaining to both cathodes and electrolytes with respect to inverse temperature yielded perfect linear behavior. However, below 400 °C, lines are extrapolated due to aforementioned imperfections and/or uncertainties in EIS data fitting to circuit models at lower temperatures. Extrapolation was done only for cathodes because electrolytes had no problem of goodness of fit. These extrapolated parts are identified by dashed lines in Figure 5-18. In terms of representativeness,
extrapolation was done in such a way that slope at 700-400 °C range was preserved in scale of $10^{-4}$. Thanks to extremely slight contribution of high frequency arc, associated with the resistance caused by oxygen jump from cathode to electrolyte, the slope pertaining to overall ASR is also the slope of the real contribution of low frequency arc, which is attributed to surface oxygen exchange process at the air exposed surface. Thus, ASR records which are monitored in Figure 5-18 can also be read as ‘resistance of surface oxygen exchange process’. Numeric values of these slopes and corresponding activation energies were represented in Table 5-4.

Ma et al. [11] first time adopted combinatorial sputtering by pulse laser deposition (PLD) and attained vertically aligned nano-structures (VAN), yielding $10^3 \ \Omega \text{cm}^2$ at 400 °C and ambient oxygen. Differently from this unique study in literature, magnetron sputtering was used first time as the way of combinatorial sputtering in this study. Hence, even though there are many studies utilizing LSC cathodes as well as LSC$_{113}$/214, VAN structure is the major comparison reference due to simultaneous sputtering.

### Table 5-4 Modified Arrhenius equations derived from data, corresponding slopes, activation energies and goodness of fit depicted as $R^2$

<table>
<thead>
<tr>
<th>Component</th>
<th>Equation ($y=ax+b$)</th>
<th>Slope</th>
<th>$R^2$</th>
<th>$E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode of Cell-25% LSC$_{113}$</td>
<td>$y=7.036X-8.129$</td>
<td>7.036</td>
<td>0.9997</td>
<td>1.22±0.02</td>
</tr>
<tr>
<td>Cathode of Cell-10% LSC$_{113}$</td>
<td>$y=5.42X-6.199$</td>
<td>5.420</td>
<td>0.9995</td>
<td>0.94±0.02</td>
</tr>
<tr>
<td>Electrolyte of cell-25% LSC$_{113}$</td>
<td>$y=2.515X-2.309$</td>
<td>2.515</td>
<td>0.9960</td>
<td>0.44±0.01</td>
</tr>
<tr>
<td>Electrolyte of cell-10% LSC$_{113}$</td>
<td>$y=2.678X-2.372$</td>
<td>2.678</td>
<td>0.9980</td>
<td>0.46±0.01</td>
</tr>
</tbody>
</table>

Accordingly, it can be stated that activation energies given in Table 5-4 are ultimate comparison parameter. Cathodes derived in this study exhibited relatively lower activation energies with respect to VAN structure for surface oxygen exchange process. VAN structure yields 1.35 eV activation energy while cathodes of cell-25% LSC$_{113}$ and cell-10% LSC$_{113}$ above produced 1.22 and 0.94 eV, respectively. This means that cathodes derived in this study are less sensitive to temperature increments than what literature concluded. In the light of this finding, at 400 °C, cathodes of cell-
25% LSC$_{113}$ and cell-10% LSC$_{113}$ seem to show lower ASR than VAN at first glance. But due to higher sensitivity to T changes, VAN is candidate to turn out to be a lower resistance alternative at increasing temperatures. 400 °C responses of cell-25% LSC$_{113}$ and cell-10% LSC$_{113}$ are respectively 211.4 and 71.6 Ωcm$^2$, which are well lower than 10$^3$ Ωcm$^2$ of VAN.

Furthermore, Ma et al. [11] detected one-fold enhancement caused by hetero interfaces as depicted by the blue line in Figure 5-18. As can be seen from figure, cathodes derived by magnetron sputtering in this study showed one more fold advancement in surface oxygen exchange ASR than VAN structure. Accordingly, it can also be stated that magnetron co-sputtering provided better catalytic effect at lower temperature regime than VAN structure obtained by PLD. But 3-4 orders of magnitude enhancement [15,21] have not been achieved in this study. At most 1.5 or 2-fold enhancement has been attained in surface oxygen exchange. It can be definitely stated that this is not an astonishing results and not caused by any direction dependent property of cathodes due to absence of any epitaxy within the cathodes herein. In order to explain the possible reasons, mechanism behind this enhancement as well as microstructural features of cathodes, i.e. geometry of cell, must be revealed.

One may claim at this point that VAN structure is ideal and almost defect free in terms of cathode geometry, namely surface roughness and/or lateral length of cathode free surface as well as epitaxy. This makes VAN suitable for low temperature regime evaluation as opposed to cathodes of cell-10% LSC$_{113}$ and cell-25% LSC$_{113}$ where for example significant surface roughness prevails. This is true but, effect of this surface roughness differential is too modest to explain more than 1-fold additional reduction in ASR. Thus, it can be apparently stated that magnetron co-sputtering has led to significant reduction in ASR more than PLD. Nevertheless, what kind of microscopic history has led to this is debatable. For instance, whether targeted hetero interfaces were formed or not is not known. If they are formed, how densified they are or if they are vertically aligned are debatable. Maybe both of the targeted phases were not formed but the reason for enhancement was non-crystalline structure of films at least by part. SEM images given in Figure 5-10 and Figure 5-16 manifest imperfections in cathode geometry implying that SEM analysis is inadequate for clarification of these.
Without FIB-TEM study, it is impossible to make statement on interface direction, alignment and/or geometry. Nonetheless, it is anticipated that there is no uniform hetero-interface distribution, alignment through cathode surface and/or bulk. Polycrystalline substrate and high surface roughness’s strengthen such anticipation. But still what can be the reason for unexpected reduction in ASR can be discussed.

First, when discussions on mechanisms behind LSC$_{113/214}$ induced ORR are considered, oxygen deficiencies and excessiveness in LSC$_{113}$ and LSC$_{214}$ must be respectively referred. One possibility is the formation of Sr site occupations in either LSC$_{113}$ and LSC$_{214}$ different from well-studied compositions and resulting degree of ORR enhancement that has created higher enhancement in ORR reflected by lower ASR in this study. However, its capability to yield 1-1.5 orders of magnitude additional ASR reduction is still debatable. Second, extreme dissimilar interface densification may have been employed here. But this is also not a probable reason on the basis of SEM images of cathode. Even if this is so, it is important to note the degree of interface densification in VAN structure that Ma et al. derived [11], which is the form of 200-300 nm phase domains through 200-nm thick epitaxial films. The aforementioned cathodes of this study are unlikely to surpass such a high densification degree if complexity and non-ideality of the current cathodes are taken into consideration. Consequently, at least partial non-crystallinity through the cathodes of this study is considered to be the most probable reason for surpassing ASR reduction than the unique combinatorial sputtering study of literature [11]. High stability of the current cathodes as reflected previously also supports this assertion.

Aside from comparisons/debates based on co-sputtering, abovementioned cathodes have not opened a new scope regarding not only hetero interface but also temperature regardless cathode performance. The lowest ASR reported to date, which is 0.023 $\Omega\text{cm}^2$ at 600 °C, has been obtained from thin film electrode utilizing LSC$_{113/214}$ [119]. What has been found in this study was at most 0.797 $\Omega\text{cm}^2$, which is behind such results.
5.6. Conclusions

LSC$_{113}$/LSC$_{214}$ composite cathodes were obtained for first time via magnetron co-sputtering of LaSrCoO$_4$ and (La$_{0.8}$Sr$_{0.2}$)CoO$_3$ phases. Performances of eventual dense thin film cathodes were evaluated on the basis of cell polarization resistances with the aid of EIS. First of all, target of 400 °C SOFC operation temperature could not be achieved; polarization resistances dictated by energy conversion efficiency could be acquired hardly at 700 °C. Nonetheless, studied phase fractions within cathodes yielded around 1.5-fold enhancement as well as lower activation energy of surface oxygen exchange induced by hetero-structure. This constitutes the best degree of enhancement in literature achieved from co-sputtered LSC$_{113}$/LSC$_{214}$ systems, the only study of which was based on PLD and yielded 1-fold enhancement [11]. As second, accordingly, such enhancement makes this study the best in reducing ASR of co-sputtered cells. Possible reason for such consequence in spite of relatively not as well-defined current structure than Ma et al. [11] can be the possible non-crystallinity within cathodes in this study. Finally, magnetron co-sputtering of LSC$_{113}$/LSC$_{214}$ yielded the best cell stability as compared to those reported in the literature [9,18].
CHAPTER 6

CONCLUSIONS

In this study, two approaches were adopted to utilize LSC\textsubscript{113/214} hetero structures for enhancing SOFC cathode performance. In first approach, maximization of LSC\textsubscript{113/214} hetero interface was aimed by thick porous conventional cathode, which is rather unusual in the literature. One pot synthesis of LSC\textsubscript{113/214} dual phase structure was implemented in pursuit of this target. In second approach, LSC\textsubscript{113/214} hetero structures were constructed by magnetron co-sputtering through which two phases were simultaneously sputtered in order to maximize hetero interface in dense thin film cathode.

In first approach, LSC\textsubscript{113} and LSC\textsubscript{214} powders were separately synthesized successfully. This was followed by physically blending them in order to maximize the hetero interfaces. However, the scale of structure in this method was found to be \(~100\) μm by SEM-EDS analysis, which resulted in poor cathode performance as measured by in situ EIS. One pot synthesis of LSC\textsubscript{113/214} dual phase composite was carried out by Pechini method. Synthesis of LSC\textsubscript{113/214} dual phase cathode from one unique solution via Pechini route has been successfully achieved for the first time in literature without any undesired third phase. It has been inferred from XRD refinements that the formation of LSC\textsubscript{113} is favored more than the formation of LSC\textsubscript{214} phase. EDS mappings of resultant powders showed that dual phase synthesis leads to a more refined microstructure. The scale of structure that is attained by one pot synthesis of LSC\textsubscript{113/214} dual phase structure was found to be between \(~6\) μm to \(~200-300\) nm. However, although finely dispersion of phases has been achieved, the positive effect of it in terms of hetero interface maximization has not been reflected to EIS measurements; degree of cathode performance enhancement was relatively modest.
This might be attributed to the excess porosity resulting in low density of triple phase boundaries of LSC$_{113}$-air-LSC$_{214}$. Furthermore, beneficial effect of dual phase powders over physical blending was limited to the temperature interval of 550-650 °C. This does not mean that the use of dual phase synthesis is limited to this temperature interval, since this might change depending upon the cathode thickness and the porosity structure. Alteration of cathode thickness as well as microstructural features are susceptible to revise aforementioned useable limit. Although dual phase synthesis is incapable of making conventional thick cathode surface ORR limited, it can obviously be concluded to be a stimulating approach.

The main problem in analysis of dual phase composite structure was the highly debatable partitioning of cations La and Sr between the constituent phases. Rietveld analysis based on CuKα radiation on XRD was insensitive to site occupation refinement. Exact and sensitive determination of final site occupations could be solved by neutron diffraction and corresponding Rietveld refinement.

Moreover, EIS responses are strong functions of cathode thickness in especially porous conventional cathodes. Hence, any thinner cathodes derived by screen printing or tape casting namely with the same dual phase powders are expected to yield different comparative EIS responses than what was attained in this study. When goodness in scale of structure in dual phase syntheses is considered, thinner cathodes are expected to yield more favorable results. Finally, new solution based synthesis routes could be sought by sol-gel chemists for the commercial success of dual phase synthesis.

In the second approach, LSC$_{113}$/LSC$_{214}$ composite cathodes were obtained for first time via magnetron co-sputtering of LaSrCoO$_4$ and (La$_{0.8}$Sr$_{0.2}$)CoO$_3$ phases. Performances of eventual dense thin film cathodes were evaluated on the basis of cell polarization resistances with the aid of EIS. First, target of 400 °C SOFC operation temperature could not be achieved; polarization resistances dictated by energy conversion efficiency could be acquired hardly at 700 °C. Nonetheless, studied phase fractions within cathodes yielded around 1.5-fold enhancement as well as lower activation energy of surface oxygen exchange induced by hetero-structure. This constitutes the best degree of enhancement in literature achieved from co-sputtered
LSC\textsubscript{113}/LSC\textsubscript{214} systems, the only study of which was based on PLD and yielded 1-fold enhancement [11]. As second, accordingly, such enhancement makes this study the best in reducing ASR of co-sputtered cells. Possible reason for such consequence in spite of relatively not as well-defined current structure than Ma et al. [11] can be the possible non-crystallinity within cathodes in this study. Finally, magnetron co-sputtering of LSC\textsubscript{113}/LSC\textsubscript{214} yielded the best cell stability as compared to those reported in the literature [9,18].

Non-crystallinity is proposed as the reason for ASR reduction and this can be understood by FIB-TEM analysis, a representative one of which is also essential in revealing hetero interface characteristics in the thin film. Thus, a comprehensive FIB-TEM investigation is advised regarding co-sputtering study. In addition, target of achieving 400 °C has not been achieved but only two compositions were analyzed in this study. Further variation in LSC\textsubscript{113}/214 systems obtained via magnetron co-sputtering are expected to yield lowering operation temperature than what is achieved in this study.
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