

T.R.
GEBZE TECHNICAL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

**STABILITY AND PERFORMANCE OF PEROVSKITE-BASED
THIN FILM CATHODES FOR SOLID OXIDE FUEL CELLS**

MEHMET SEZER
**A THESIS SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY**
DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING

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T.C.
GEBZE TEKNİK ÜNİVERSİTESİ
FEN BİLİMLERİ ENSTİTÜSÜ

KATI OKSİT YAKIT HÜCRELERİNDE
KULLANILAN PEROVSKİT ESASLI İNCE
FİLM KATOTLARIN KARARLILIĞI VE
PERFORMANSI

MEHMET SEZER
DOKTORA TEZİ
MALZEME BİLİMİ VE MÜHENDİSLİĞİ ANABİLİM DALI

DANIŞMANI
PROF. DR. AHMET YAVUZ ORAL

GEBZE
2022

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SUMMARY

The prolonged electrochemical performance of polymeric precursor-derived (La,Ca)CoO₃ (LCC) and (La,Sr)CoO₃ (LSC) perovskite membranes were examined in the current study with a sudden change in oxygen partial pressure utilizing electrical conductivity relaxation to obtain surface oxygen exchange coefficient and diffusion coefficient. It was revealed that the k_{chem} and D_{chem} values of Ca-doped LaCoO₃ samples were generally greater than those of Sr-doped ones. The 20% doped LaCoO₃ samples were more stable than the 40% series, despite the fact that the 40% doped LaCoO₃ samples produced higher k_{chem} and D_{chem} values.

Also, we focused on the prolonged electrochemical efficiency of thin films that obtained from polymeric precursor of LaCoO₃ substituted with Ca²⁺ (LCC). According to the findings, pre-calcination at 800 °C (20 % Ca-doped LCC-800) led to greater electrochemical performance but weaker prolonged stability than pre-calcination at 700 °C (20 % Ca-doped LCC -700) or 900 °C (20 % Ca-doped LCC -900). Increased Ca²⁺ concentration (40 % Ca-doped LCC -800) resulted in a small increase in initial electrochemical performance, but at the expense of significantly reduced long-term stability.

In addition, the prolonged electrochemical performance of polymeric precursor-derived films of Ca²⁺-substituted LaCoO₃ (LCC) was examined by varying deposition parameters. It was revealed that to increase the spinning rate results in a lower polarization resistance and a better long-term stability.

Key Words: Solid Oxide Fuel Cell (SOFC), Cathode, Oxygen Separation Membrane, Electrochemical Impedance Spectroscopy (EIS), Electrical Conductivity Relaxation (ECR), Ca doped LaCoO₃ (LCC).

ÖZET

Bu çalışmada polimerik öncüllerle hazırlanan (La,Ca)CoO₃ (LCC) ve (La,Sr)CoO₃ (LSC) perovskite membranların uzun süreli elektrokimyasal performansı, elektriksel iletkenlik gevşemesi (ECR) kullanılarak oksijen kısmi basıncı ani değiştirilerek ölçülmüştür. Yüzey oksijen değişim katsayısı (k_{chem}) ve difüzyon katsayısı (D_{chem}) ECR dataları fit edilerek elde edilmiştir. Ca katkılı LaCoO₃ örneklerinin k_{chem} ve D_{chem} değerlerinin genel olarak Sr katkılı olanlardan daha yüksek olduğu gözlenmiştir. %20 katkılı LaCoO₃ örnekleri, %40 katkılı LaCoO₃ örneklerden daha düşük k_{chem} ve D_{chem} değerlerine sahip olmasına rağmen, bu değerler %40 serisinin değerlerinden daha stabildir. Uzun süreli ısıtma işlemi boyunca, hemen hemen bütün numunelerde D_{chem} , k_{chem} 'e göre daha sabittir.

Ayrıca, Ca²⁺ (LCC) ile katkılanmış LaCoO₃'ün polimerik öncüsünden elde edilen ince filmlerin uzun süreli elektrokimyasal verimliliğine incelendi. Bulgulara göre, 800 °C' de ön kalsinasyona maruz bırakılan numuneden (%20 Ca katkılı LCC-800) daha yüksek elektrokimyasal performans elde edildi, ancak diğer sıcaklıklarda ön kalsinasyon gören numunelere göre daha fazla degradasyon tespit edildi. Artan Ca²⁺ konsantrasyonu (%40 Ca katkılı LCC -800), başlangıçtaki elektrokimyasal performansta küçük bir artışa neden oldu, ancak uzun vadeli stabilitenin önemli ölçüde azalmasına sebep oldu.

Ek olarak, Ca²⁺ katkılı LaCoO₃'ün (LCC) polimerik öncül türevli filmlerinin uzun süreli elektrokimyasal performansı, değişen biriktirme parametreleriyle incelendi. Kaplama dönme hızının artırılması, daha düşük bir polarizasyon direncine ve daha uzun ömürlü stabiliteye sebep oldu.

Anahtar Kelimeler: Katı Oksit Yakıt Hücresi (KOYH), Katot, Oksijen Ayırma Membranı, Elektrokimyasal Empedans Spektroskopisi (EES), Elektrik Gevşemesi İletkenliği (EGR), Ca Katkılı LaCoO₃ (LCC).

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LIST OF ABBREVIATIONS AND ACRONYMS

<u>Abbreviations</u>	<u>Explanations</u>
<u>and Acronyms</u>	
pO_2	: Oxygen Partial Pressure
pH_2O	: Water Partial Pressure
ΔW	: Electrical Work
ΔG	: Gibbs Free Energy
ΔG°	: Standard Gibbs Free Energy
η	: Amount of Moles of Electrons
S	: Siemens
Cm	: Centimeter
mV	: Milli-Volt
mA	: Milli-Amper
m Ω	: Milli-Ohm
MHz	: Mega Hertz
mHz	: Milli-Hertz
kHz	: Kilo-Hertz
ρ	: Specific Resistance
k	: Oxygen Surface Exchange Coefficient
D	: Diffusion Coefficient
k_{chem}	: Chemical Oxygen Surface Exchange Coefficient
D_{chem}	: Chemical Diffusion Coefficient
E_k	: Kinetic Energy
E_B	: Photoelectron Binding Energy
h	: Planck's Constant
ν	: Frequency
ϕ	: Work Function
σ_i	: Conductivity
mm	: Milli-Meter
Θ	: Angle
eV	: Electro Volt
n	: Degree of Circularity

f	: Frequency
h_f	: Thickness of the Solid Film
ω	: Spinning Speed
h_c	: Critical Thickness for Crack Formation
K_{IC}	: Critical Stress Intensity
σ	: Shrinkage Stresses
Ω	: A Function That Depends on the Ratio of the Elastic Modulus of the Film and Substrate
113	: Mole Ratio of LaCoO ₃
214	: Mole Ratio of La ₂ CoO ₄
A	: Surface Area
AC	: Alternative Current
AFC	: Alkaline Fuel Cell
ASR	: Area Specific Resistance
BSE	: Backscattered Electron
C	: Centigrade
DC	: Direct Current
DMFC	: Direct Methanol Fuel Cell
E	: Nernst Potential
E	: Standard Electrode Potential
ECR	: Electrical Conductivity Relaxation
EDS	: Energy-Dispersive X-Ray Spectroscopy
EIA	: Energy Information Administration
EIS	: Electrochemical Impedance Spectroscopy
F	: Faraday Constant
FWHM	: Full Width at Half-Maximum
GDC	: Gallium Doped Ceria
GI-XRD	: Grazing Incidence X-Ray Diffraction
HF	: High Frequency
IT	: Intermediate Temperature
IT-SOFCs	: Intermediate Temperature Solid Oxide Fuel Cells
K	: Kelvin
K	: Reaction Constant
L	: Inductance

L	: Thickness
LCC	: (La,Ca)CoO ₃
LCC02	: 20% Ca Doped LaCoO ₃
LCC02-700	: 20% Ca Doped LaCoO ₃ Pre-Calcined at 700 °C
LCC02-800	: 20% Ca Doped LaCoO ₃ Pre-Calcined at 800 °C
LCC02-900	: 20% Ca Doped LaCoO ₃ Pre-Calcined at 900 °C
LCC04	: 40% Ca Doped LaCoO ₃
LCC04-800	: 40% Ca Doped LaCoO ₃ Pre-Calcined at 800 °C
LF	: Low Frequency
LSC	: (La,Sr)CoO ₃
LSC02	: 20% Sr Doped LaCoO ₃
LSC04	: 40% Sr Doped LaCoO ₃
LSCF	: Sr Doped A-site and Co Doped B-site LaFeO ₃
LSCM	: Sr Doped A-site and Mn Doped B-site LaCrO ₃ Perovskite
LSF	: (La,Sr)FeO ₃
LSM	: Sr Doped LaMnO ₃
MCFC	: Molten Carbonate Fuel Cell
Me	: Metal
MIECs	: Mixed Ionic and Electronic Conductors
Ni-YSZ	: Nickel- Yttria Stabilized Zirconia Composite
OCV	: Open Circuit Voltage
O-R	: Orthorhombic to Rhombohedral
ORR	: Oxygen Reduction Reaction
PAFC	: Phosphoric Acid Fuel Cell
PCFC	: Protonic Ceramic Fuel Cell
PEM	: Proton Exchange Membrane
PEMEC	: Proton-Exchange Membrane
PLD	: Pulse Laser Deposition
Q	: Charge in Coulombs
Q	: Constant Phase Component Fitting Parameters
R	: Gas Constant
RC	: Resistor and Capacitor
RP	: Ruddlesden-Popper

rpm	: Revelution Per Minute
SAFC	: Sulfiric Acid Fuel Cell
SDC	: Samaria Doped Ceria
SE	: Secondary Electron
SEM	: Scanning Electron Microscopy
SO	: Solid Oxide
SOFC	: Solid Oxide Fuel Cell Fuel Cell
SZO	: SrZrO ₃
T	: Temperature
TEC	: Thermal Expansion Coefficient
TPB	: Three Phase Boundary
TPPA	: Total Pore Perimeter Per-Image Area
XPS	: X-ray Photoelectron Spectroscopy
XRD	: X-Ray Diffraction
YSZ	: Yttria Stabilized Zirconia
Z	: Imagery Impedance

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1. INTRODUCTION

Energy is critical for satisfying fundamental human requirements. It is necessary for human health, daily life, communication, and mobility, as well as for the socio-economic development and well-being of society world in general [1]. The world's energy requirements have risen significantly in recent years and are anticipated to continue to do so as population expands, and economic and technological advancements continue [2]. By 2050, it is estimated that the world's population would reach roughly 9 billion. In accordance with the United States Energy Information Administration (EIA), worldwide energy ingesting is projected to growth nearly by % 50 up to 2050 [3]. Since the industrialization, hydrocarbons have come to be the major supply of energy, with consumption reaching nearly 10,000 million tons of oil equivalent. In 2010, fossil fuels generated almost 80% of all energy production globally [4], and they have been anticipated to continue to do so in the coming to fulfill global energy demands [3]. In 2040, it is predicted that 78% of the energy used worldwide would come from fossil fuels [5]. However, with the energy gain because of the combustion of hydrocarbons during the use of fossil fuels, CO₂ gas, which causes global warming, is released into the nature. World average temperatures have climbed at a pace of around 0.6°C per century on last century. This tendency has accelerated in recent years, with temperature increases of 2.3, 1.3, and 1.7 °C, respectively, according to well-recognized institutions evaluating this circumstance, namely Princeton in the United States of America, Hamburg in Germany, and the IPCC United Kingdom in London [6].

The emission of hazardous gases in the environment during the burning up of fossil-fuel, along with an inadequate source of fossil fuels, has accelerated the development of energy conversion technologies used in place of this conventional method of energy generation. Due to the pressing demand for a clean alternative energy source, several options have appeared. Saving energy with greater energy efficiency, a reduction in the use of fossil fuels, and an increase in demand for ecologically acceptable energy sources such as fuel cells and renewable sources are among these choices.

1.1. Fuel Cells

Fuel-cell is an energy transformation system that uses a chemical energy contained in fuel for generate electricity and heat not including the necessity of an intermediate burning step, led to significantly higher power conversion efficiency than standard thermomechanical systems. Fuel cells, like batteries, generate energy by mixing a fuel gas (hydrogen) with oxidizing gas (oxygen from the surrounding environment) via cathodes and an anion delivering electrolyte. A fuel cell never runs out of power or has to be recharged, apart from a battery. The fuel cell may operate with little environmental effect if both the fuel and the oxidant are supplied to the electrodes.

The chemical characteristics of the electrolyte which is employed as ionic conductors of the cell are quite often utilized to classify fuel cells, including sulfuric acid (SAFC), direct methanol (DMFC), phosphoric acid (PAFC), alkaline (AFC), molten carbonate (MCFC), proton-exchange membrane (PEMEC), protonic ceramic (PCFC), and solid oxide fuel cell (SOFC). Its first five kinds identified with relatively low operating temperatures (50–210°C) and poor energy production efficiency (40–50% by using easily accessible fuels like hydrocarbons and methanol, 50% in case of utilizing pristine fuel that obtained from hydrogen). The processing temperature (600–1000°C) of the latter three forms differ from each other. The ability to utilize methane successfully in fuel cells, and therefore relatively high productivity obtained (45–60% for conventional fuels like natural gas, 90% with heat enhancement) [6]. Although less common, other types of fuel cells could be useful in the time to come. Sodium amalgam cells, air-depolarized cells, regenerating cells, alkali metal-halogen cells, inorganic redox cells, and biochemical fuel cells are a few instances [6].

Fuel cells are already a reality in certain specific purposes due to advances in materials science. Solid Oxide (SO) cell and proton exchange membrane (PEM) stacks have stimulated the most research interest throughout the world. PEMs are a sort of advanced fuel cell that may be used in autos and public transit., SOFC technology is the most intensive, and it is being investigated for its considerable commercial competition, from a materials aspect as;

- SOFCs are now being studied as among the most competitive (fuel supply to energy output) fuel cell energy makers in the earth.
- SOFCs offer a broad variety of fuel sources, including petroleum fuels such as natural gas.
- Owing to its higher efficiency, SOFC technology is best useful for high in the distributive production (i.e., permanent power) industry, where fuel prices are greater owing to extensive fuel delivery systems.
- SOFCs possess a flexible, solid-state design with no moving components, making them suitable for indoor use.
- SOFCs generate a significant heat waste that may be employed for co-generation or combined cycle applications thanks to their elevated operation temperature.
- SOFCs do not include noble metals, which might create a difficulty in terms of available resources and cost in great volume production.
- Electrolyte management is not a concern for SOFCs (liquid electrolytes, such as, are caustic and hard to handle).
- Of the most effective and environmentally methods for creating energy from natural gas, hydrogen, and other alternative energies is the SOFC.
- Because they completely remove the danger of carbon monoxide in combustion products, SOFCs have extraordinarily low outputs because any CO formed is transformed to CO₂ in the elevated operation condition.
- SOFCs have the capacity for an extended lifespan than the other fuel cells [6].

1.1.1. Solid Oxide Fuel Cells

A prominent and newly "developed" elevated temperature technology of fuel cell is SOFCs. It might be immensely helpful in significant, high-energy uses, including whole industrial facilities and sizable power plants. Some fuel cell inventors believe that SOFCs might be used in autos. In a SOFC system, the electrolyte typically consists of solid ceramic and runs at elevated temperatures (600–1000 °C). The elevated running temperatures promotes individual regeneration while also promoting fast electrocatalysis with non-prized metals and generates higher emission heat for co-generation. This kind of fuel cell can operate at reaching to 70% efficiency, with an extra 20% efficiency being recoverable as heat. Because of the long time it takes for

SOFCs to achieve working temperatures, they are suitable for power generation in utility applications [6].

Their potential to perform on hydrogen as a fuel allows them to be independent of finite fossil fuel supplies. Furthermore, since no carbon is necessary in the electrochemical process, no CO_2 is being released during operation. They are promising as energy conversion options since they can run on hydrogen or hydrocarbon gases. In the case of hydrocarbon fuels, the SOFCs' high yield would make it possible for energy transformation with such a significantly smaller quantity of fuel, resulting in decreased CO_2 emissions.

Even though the benefits of SOFCs outlined above, there are critical concerns that need to be resolved for technology to succeed. The ability to turn down and start up with no degradation, long-time stability, and a cheaper price per unit of produced power are a few of these advantages. Many of these issues are material-related, and they provide materials scientists fascinating problems.

SOFCs are distinct from conventional fuel cell technologies in several ways. To begin with, they are made entirely of solid-state items. Another, cells may perform at up to 1000°C , which is much higher than any other main fuel cell category. Third, since all SOFC components are solid state, there are no basic limitations on cell configuration. Tubular cells and rolling tubes are the two most common cell shapes.

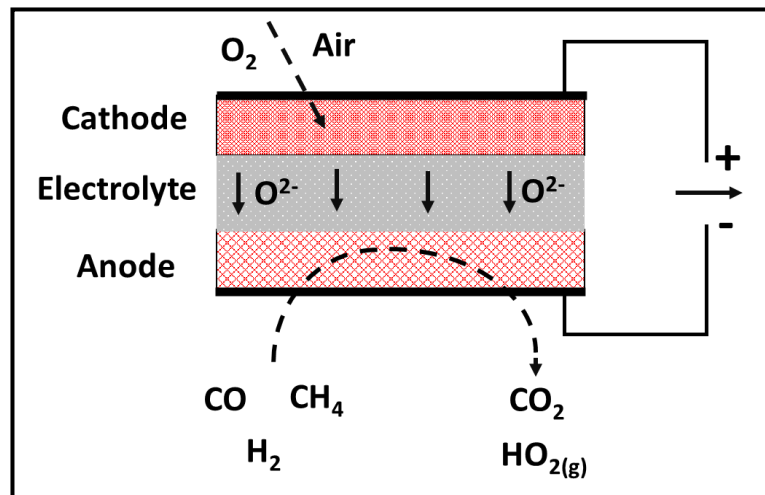
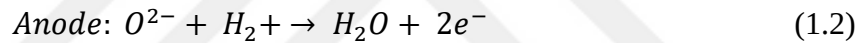
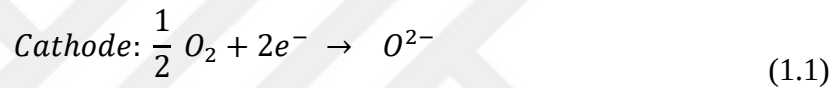


Figure 1.1. Schematic presentation of SOFC cell.

A SOFC is composed of two electrodes inserted by a strong ceramic electrolyte, for instance zirconia (Fig. 1.1). The fuel cell's anode takes hydrogen fuel, whereas the

cathode takes oxygen in the air. Fuel that included the hydrogen burn up on interlayer of anode and electrolyte, reducing the levels of oxygen. By interacting with the burned fuel, oxygen ions on this region will be able to leave the electrolyte and produce electrons (e⁻). On the opposite side of the cell that is subjected to atmosphere, an oxygen level difference throughout the electrolyte is produced, drawing oxygen anions from the air/cathode side, or cathode, to the fuel/anode side. When the electrodes are electrically connected, oxygen ions may move from the cathode to the anode, preserving the equilibrium of the total electric charges and allowing the burning of fuels to produce usable electrical power. Electrons can also move from the fuel electrode to the air electrode, sustaining a steady source of oxygen anions (O₂) for the electrolyte. Only heat and a natural water molecule (H₂O) are generated as seen in Fig. 1. The electrode reactions are given as;



Open circuit voltage (OCV) is the electrochemical potential variation throughout the electrolyte results in a change in oxygen partial pressures between the fuel electrode and air electrode. This voltage is obtained from the Nernst formula, which may be deduced from the Gibbs free energy of H₂O synthesis from its component, as below:

$$\Delta G = \Delta G^\circ + RT \ln(K) \quad (1.3)$$

$$\Delta G = -\Delta W_{\text{electrical}} = -EQ = -\eta FE \quad (1.4)$$

$$-\eta FE = -\eta FE^\circ + RT \ln(K) \quad (1.5)$$

Rearranging the terms;

$$E = E^{\circ} + \frac{RT}{\eta F} \ln(K) \quad (1.6)$$

where;

$$K = \frac{PH_2O}{pO_2^{0.5}pH_2} \quad (1.7)$$

R represents gas constant, T represents temperature, K represents reaction constant, ΔW represents electrical work, E represents Nernst potential, Q represents charge in Coulombs, F represents Faraday constant, E° represents standard electrode potential, and η represents amount of mole of electrons.

1.1.2. Components and Materials of Solid Oxide Fuel Cell

A solid oxide fuel cell (SOFC) consists of a solid air electrode/cathode, an fuel electrode/anode, and an oxygen ion conductor/electrolyte. The fuel remains indeed a key characteristic, and it is unrelated to the others because it is usually transformed to hydrogen. Highly pure hydrogen is a fuel usable in SOFC, which utilizes oxygen ion transport, however it is not necessary since it is costly to generate and challenging to manage. The basic role of the electrode is to initiate a chemical reaction between the the electrolyte and reactant (fuel or oxygen) without being consumed. The three components of the fuel gas, solid electrolyte, and electrodes themselves must also be combined. Electrons from the fuel cell's anode are employed as reliable power in the exterior circuit by distributing hydrogen gas uniformly over its surface. The oxygen reduction process requires electrons to be sent from the circuit to the cathodes through charge transfer. An additional need for ionic conductivity is that the cathode must be capable of transporting all of the electrons generated of the oxygen reduction process to the electrolyte, which then delivers the electrons to the anode. The electrolyte prevents the anode or cathode from generating electrical connection by regulating the fuel cell's operational temperature. Further, it allows chargeable ions to pass from cathode to the anode, ensuring that the entire electric charge stability is maintained. It may be an oxygen ion performer or even a proton performer, but the key distinction is which side of the fuel cell generates H_2O : the fuel side in oxygen-ion fuel cells and the

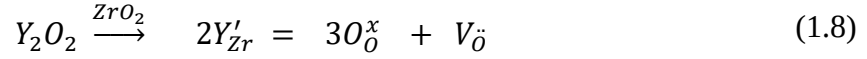
oxidizing side in proton-conductor fuel cells generates H_2O . Since each component of the SOFC performs many roles, it must fulfill specific requirements, like as;

- Optimal strength (chemical, phase, morphological, and dimensional)
- Optimal conductivity
- To be compatible with other components in terms of chemical composition
- To prevent fracturing when the cell is operating, a similar thermal expansion is used.
- To avoid gas mixing, use a dense electrolyte.
- Electrodes with pores to permit gas to flow to the reaction site
- Properties of high-strength and durability
- Processability
- Adaptable to a variety of manufacturing situations
- Compatibility with ceramic structures manufactured at higher temperatures
- Cost-effective

1.1.2.1. Electrolyte

The greatest electrical conductivities are found in materials like substituted lanthanum gallate, substituted bismuth oxide, and substituted ceria throughout a wide temperature range. Structural instability and high electrical conductivity, on the other hand, limit the greatest open circuit voltage that can be achieved with all these materials. As a result of its comparatively high electrical conduction (0.02 S/cm at 800 °C), significant electric conduction, chemical, and dimensional stability, yttria stabilized zirconia (Y_2O_3 -stabilized ZrO_2 or YSZ, $(\text{ZrO}_2)_{0.92}(\text{Y}_2\text{O}_3)_{0.08}$) having the structure of fluorite is the extreme generally favored electrolyte solid [7]. Each zirconium ion in the crystal lattice of ZrO_2 has two oxide ions. However, there are just 1.5 oxide ions per each yttrium ion in Y_2O_3 . The absence of oxide ions causes vacancies in the crystal structure. As a result, cathode oxide ions jump from vacancy to vacancy up to the attain the anode. In addition, ZrO_2 possesses monoclinic crystal structure in its pure form, which has a poor electrical conductivity (2.9×10^{-5} S/cm in air at 800 °C). At 1170° C, the monoclinic structure becomes tetragonal, and at 2370° C, it becomes fluorite. At ambient temperature, Y_2O_3 additions over 6 mol % stabilize

the fluorite lattice, which is a relatively free frame suited for ion carriage. Extrinsic oxygen vacancies are generated when ZrO_2 is doped with Y_2O_3 , allowing oxygen ions to pass through. The Kroger-Vink notation of YSZ is given as;



As a result of equation (1.8), the vacancy ratio, which presents the charge carrier, has a linear relation with the yttria ratio. However, whereas ionic conductivity rises to 8-9 mol percent yttria substituting, electric conductivity reduces when the yttria concentration exceeds this level. In this situation, the interaction between yttria and oxygen vacancies leads to the creation of complexes, which reduces the oxygen vacancies' mobility [8].

1.1.2.2. Anode

For the associated electrochemical process of fuel oxidation, the anode must be catalytically active (Eq. 1.2). The anode must have adequate electrical conductivity to capture electrons produced during fuel oxidation. Metals may be employed as SOFC anode owing to the general reducing circumstances of the fuel gas. Moreover, since the content of the gasoline varies throughout the performance of the system, these metals should not react with oxygen. SOFC anodes are composed of a mixture of composite powder of electrolyte (YSZ, GDC, or SDC) and nickel oxide NiO (the nickel oxide is then nickel ion take electron to form nickel metal prior to use), which prevents metal particles from sintering, exhibiting a wider TPB distance than single-phase Ni and a thermal expansion coefficient comparable to certain other cell components [9].

It is obvious that the parameters for SOFC anodes include chemical stability under the oxidative circumstances, chemically to be compatible with the electrolyte, adequate thermal expansion coefficient with the electrolyte, and sufficient porous for straightforward oxygen gas transmission. Redox uncertainty of Ni-YSZ anodes, which has become a major issue for materials scientists, has become another significant challenge. The commercial SOFC is expected to undergo several redox (reduction-oxidation) cycles because of the targeted or incorrect cessation of fuel supply. SOFCs

must thus be able to withstand redox cycling. On the other hand, the Ni-YSZ composite fails mechanically as a consequence of the Ni phase expanding during oxidation (69 vol. percent) [10], which causes fractures in the anode matrix. The creation of innovative anode materials has been the focus of several studies as a viable treatment for the redox instability issue. $\text{Sr}_{0.86}\text{Y}_{0.08}\text{TiO}_{3-\delta}$ (82 S/cm at 800 °C and $p\text{O}_2=10^{-9}$) [11] and $(\text{La}_{0.75}\text{Sr}_{0.25})_{1-x}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_3$ (LSCM) [12] have been presented as potential ceramic products not suffer from reduction/oxidation and have good conductivity in anode settings.

1.1.2.3. Cathode

To achieve oxygen reduction reaction (ORR), an oxygen electrode must have strong electrical and ionic conductivity [13] as well as high catalytic activity [14]. Sr-substituted lanthanum-manganite ($\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, LSM [15]) and YSZ are by far the most widely utilized oxygen electrodes in the past. LSM works as an electrical conductor and ORR catalyst in this electrode, whereas YSZ functions as an ionic conductor. The active sites of LSM/YSZ cathodes are restricted to the triple phase boundaries (TPB) within YSZ, the gas and LSM phase which is poor in ionic conduction, because the ORR needs both electrons and oxygen vacancies. By design of materials with both oxygen ion and electronic conductivity are mostly suggested to widen the reaction zone. Mixed ionic and electronic conductors (MIECs) are commonly perovskite or perovskite-like structures with a wide range of compositions and characteristics. Sr-doped lanthanum-cobaltite and ferrites ($\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_3$) have been the most prevalent. New MIEC materials having higher catalytic characteristics have been developed up to now. Perovskites like $(\text{Ba}_{0.5}\text{Sr}_{0.5})(\text{Co}_{0.8}\text{Fe}_{0.2})\text{O}_3$, double perovskites like $\text{PrBaCo}_2\text{O}_5$, and Ruddlesden-Popper materials like LaNiO_4 are only a few of the prominent examples.

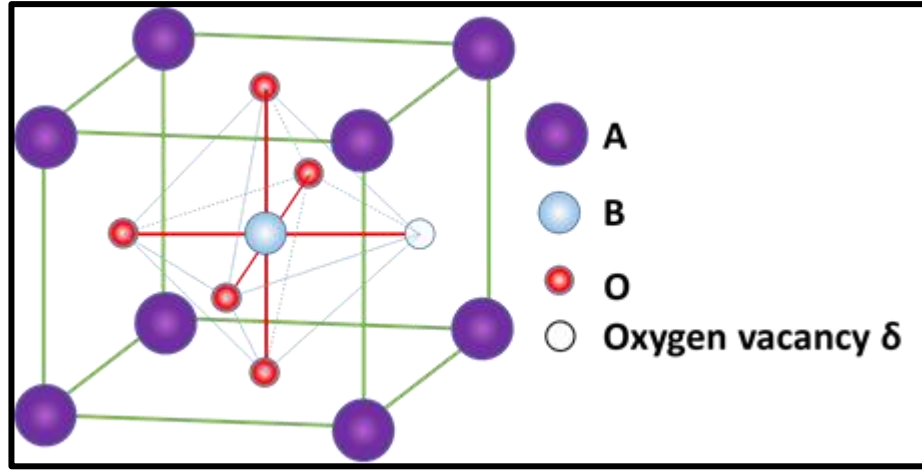
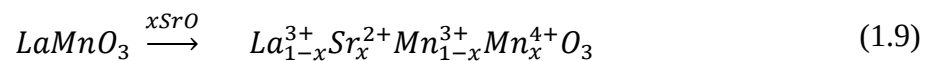


Figure 1.2: Schematic representation of unit cell of perovskite type compounds.

The most appropriate set of substances for SOFC air electrode uses has been discovered to be perovskite materials (Fig. 1.2). Strontium substituted lanthanum manganite ($\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$, LSM) is the most widely used type of lanthanum manganite thanks to the high electronic conductivity (120 S/cm at 800 °C), adequate catalyst behavior for the oxygen reduction reaction (ORR [16]–[18], and a thermal expansion coefficient (TEC) comparable to 8 mol percent Ytria stabilized zirconia (TEC_{LSM} : $12.4 \times 10^{-6} \text{ K}^{-1}$; TEC_{YSZ} : $10.5 \times 10^{-6} \text{ K}^{-1}$) [8]. LSM has a predominantly electronic conductivity rather than ionic conductivity (ionic conductivities of LSM are $5.9 \times 10^{-8} \text{ S/cm}$ in the partial pressure of oxygen fluctuate from 10^{-1} – 10^{-3} atm , at 800 °C) [19]. Because of variations in the Mn valence, LaMnO_3 -type cathodes mostly have intrinsic p-type conduction. Electric conductivity is additional improved by substituting La^{3+} with reduce valence of positive ions (e.g., Sr^{2+}), owing to the creation of charged holes that function as the charge carrier when the La^{3+} ion is replaced with Sr^{2+} ion in order to sustain electroneutrality. This can be expressed in the following way:



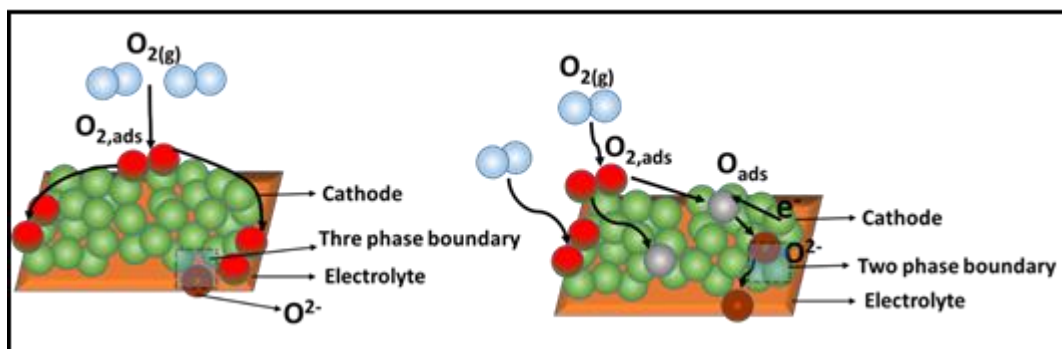


Figure 1.3: Shematic illustration of a) electronic and b) mixed ionic and electronic conductor (MIEC).

The ORR can only take place in case of the electrons, oxygen ions and oxygen gas interacted. Since LSM functions almost exclusively as an electrical conductor, an ionically conductive material must provide oxygen ions to the areas where oxygen gas and electrons interact. Thus, processes are restricted to the TPBs in the event of a pure phase LSM electrode (where oxygen gas, electrons, and ions encounter). The oxygen reduction process may occur at the surface of the cathode if a MIEC (like $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_3$, LSCF) is employed in place of an LSM (Fig. 1.3).

1.1.2.3.1. Methods for Enhancing Electrode Performance

Solid oxide cell application is limited by deterioration over long-term operation and significant operating costs. Performance in the so-called intermediate range of temperature (500-750°C) might considerably lower the latter, allowing for using less expensive materials for external components (e.g., interconnects, sealings). However, the electrocatalytic activity of SOCs is also extremely sensitive to temperature since the electrode processes and ionic conductivity of the electrolyte display Arrhenius type dependence. Reduced thickness of the electrolyte may result in a decrease in ionic conductivity, but significant overpotentials can balance sustained electrochemical activity, which aggravate degradation. Due to the higher ORR/OER activation energies, this is especially relevant for the cathode. Conversely, at reduced temperatures, air electrode degradation has a bigger impact on cell performance than fuel electrode degradation. The SOC society has spent a lot of time studying how to improve the electro-chemical properties of the oxygen electrode. Reduced overpotentials and, as a result, reduced rate of degradation would be possible with

improved electrode performance. There are several ways for improving performance, such as:

- Chemical composition of the bulk is being changed - Varying the cation concentration influences catalytic activity toward ORR/ OER, but it also impacts the material's thermodynamic stability and mechanical features.
- Composite cathodes - by combining substances with high ionic/electronic conductivity and catalytic features, one may get both properties at the same time, as well as deeper kinds of interaction.
- Adjustment of surface /infiltration- A little quantity of an infiltrating agent (usually nitrate of metals) is able to be placed on the cathode, resulting in a surface coated with minute particles following thermal treatment, thereby enhancing catalytic activity.

1.1.2.3.2. Fabrication of Solid Oxide Fuel Cell Electrodes

Sintering is a conventional process for making composite cathodes, which are widely employed in solid oxide fuel cells. The electrocatalyst and ionic conductive materials are mixed in powder form, and then a solvent-binding ingredient is added to the powder combination to make a liquid sludge. The resulting liquid sludge is usually silk-printed onto the electrolyte and sintered at high temperatures (1000-1300°C). Temperature-dependent coarsening of the microstructure and consequently shortening of the triple phase boundary happens in the generated electrode material due to the high sintering temperatures used in this process. For example, in a study in the literature, single-phase LSM and composite LSM-YSZ cathode were produced by sintering powders. High sintering temperatures might also cause undesirable secondary phases to develop in the structure. As the sintering temperature increases, the LSM particles and pores get larger. LSM cathodes sintered at 1200, 1250, and 1300 °C had cathode polarization resistances of 0.39, 0.85, and 1.20.cm², respectively, when measured at 800 °C. The expansion of LSM particles and, as a result, the active TPBs shortened as sintering temperatures increased. Sintering LSM and YSZ together at high temperatures has been reported to create secondary phases of La₂Zr₂O₇ (LZO) and SrZrO₃ (SZO) with high electrical resistance [20]-[23]. Because these secondary

phases have extraordinarily high resistivities, even a little quantity can block critical processes at TPBs, resulting in substantial long-term degradation.

1.1.2.3.3. Fabrication of Electrode by Thin Films Methods

New production techniques are developed in order to avoid the challenges produced by the previous production method's high temperature. In the manufacturing of SOFC cathodes, a preferred technique is to employ thin-film coating technologies that do not require a high heat treatment temperature. The methods utilized to make thin films include sputtering and pulsed laser deposition (PLD), both of which are physical vapor deposition procedures [24]. The substrate and the target material are placed in a vacuum chamber containing inert gas during the sputtering process (usually argon). A particular voltage is given the target that accelerates the Ar^+ ions. Momentum transfer creates a plasma by impinging the accelerated ions on the substance. During the processing, the plasma is placed on the substrate at the proper angle and distance from the target.

In comparison to sputtering and PLD methods, thin-film fabrication techniques utilizing liquid solutions require cheaper costs and easier setups. As a result, fabrication thin-film electrodes for SOFCs are more beneficial. Since the thin films produced by sputtering and PLD are denser, the active regions where the ORR take place decrease and high cathode polarization resistances can be increase. Low polarization resistances have also been achieved from thin film electrodes fabricated by PLD. On the other hand, PLD is less beneficial than others since it necessitates the purchase of a costly system. Because the microstructure of the cathodes fabricated by sintering, the borders of the active triple phase are shortened, resulting in high electrode resistances. The techniques are depicted in figure 1.4 that use liquid solutions stand out among the manufacturing methods due to a simple and low-cost system.

Basic techniques such as spray, dip, and spin coating can be used to apply liquid solutions to surfaces. Dip and spin coating processes are commonly used to create thin ceramic films on a variety of substrates, and these procedures can be utilized a wide range of precursor chemicals.

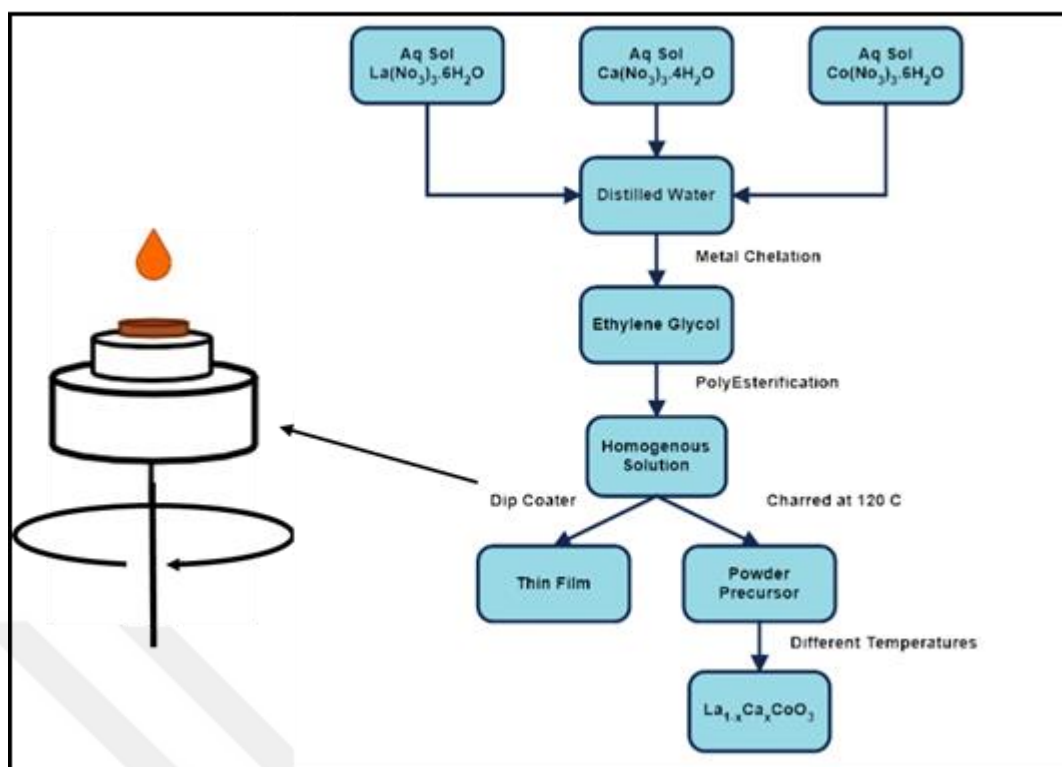


Figure 1.4: The schematic representation of preparation polymeric precursors and production of thin films and powder precursors.

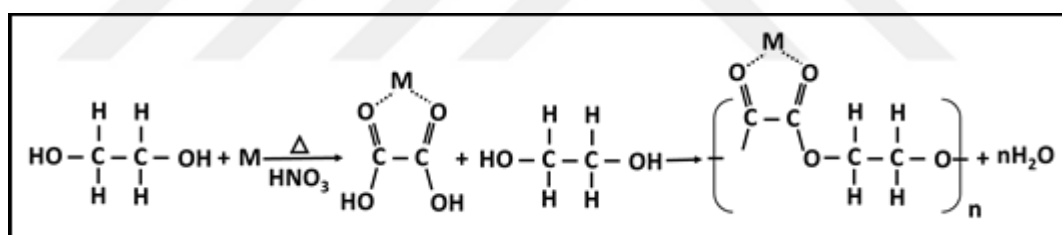


Figure 1.5: Chemical processes that occur during the formation of polymeric solutions are shown schematically [25].

The Pechini technique represented in (Fig. 1.5) that relies on the creation of a chelate between metal cations dissolved in water and a hydroxycarboxylic acid (usually citric acid). After the cations have been chelated (complex ring-shaped compounds generated around metal cations), the chelates are cross-linked with polyalcohols (typically ethylene glycol), and gels are created as a result of esterification. Organics are evaporated to produce nano-sized crystalline particles. The Pechini technique was popularized in the 1970s by H. U. Anderson, who used it to synthesis perovskite powders. In addition, he demonstrated in a 1986 research that a modified version of this process may be used to prepare a far broader spectrum of

oxides than Pechini predicted [26]. The Pechini technique was used to demonstrate that thin, polycrystalline metal oxide films may be created to be utilized as solid oxide fuel cell electrolyte or electrode in a work patented by H. U. Anderson in 1996 [25]. Solid oxide fuel cell electrodes were first manufactured at low working temperatures utilizing ethylene glycol-based polymeric solutions in totally liquid form, thanks to this study, which was patented by H. U. Anderson. The manufacture of ethylene glycol-based solutions in Anderson's work involves dissolving cations in a liquid solution including water and ethylene glycol, then heating the solution to polymerize. Nitrate acid is formed when nitrate ions from metal salts dissolved in water. Oxalic acid is generated when nitric acid reacts with ethylene glycol, and the resultant oxalic acid offers a polyester with metal cations. Without the need of external nitric acid, polymerization may always be accomplished with nitric acid derived from metal salts.

1.2. Methodology

Electrochemical Impedance Spectroscopy were used to monitor oxygen exchange activities throughout the thesis (EIS). To study the surface chemistry, photoelectron X-ray spectroscopy (XPS) was performed.

1.2.1. Electrochemical impedance spectroscopy

Electrical impedance spectroscopy is a handy method for analyzing electrochemical systems in real time. Impedance is the ratio of voltage to current that reflects a circuit's capacity to resist current flow. Impedance is a broader concept than Ohm's law's basic resistance. In addition to resistance, impedance also takes into account the behavior of other circuit components like capacitors and inductors (L). A circuit consisting of resistors, capacitors, and inductors will have complex resistance as its overall response to alternating current (AC) due to capacitor and inductor phase difference.

$$Z = \frac{E(t)}{I(t)} = \frac{E_0 \cdot \sin(wt)}{I_0 \cdot \sin(wt + \varphi)} \quad (1.10)$$

Impedance spectroscopy uses a small-amplitude periodic alternating current (a few mV or mA, based on whether the experiment is current-operated or voltage-operated) to disturb an electrochemical performance in non-equilibrium or equilibrium. The impedance responses of oscillating current are evaluated at various frequencies (usually between 1 mHz and 1 MHz), providing information on activities with variable relaxation periods. The the Nyquist plot (Z_{ideal} vs. Z_{real}) and Bode plot (Z vs. frequency) are two of the most frequent ways to illustrate impedance data, as presented in Figure 1.6. The study of impedance spectroscopy findings comprises of fitting the collected information with an equivalent circuit made up of basic parts like resistors, capacitors, and inductors, as well as electrochemical circuit elements like the Warburg and Gerischer elements.

From the Ohm' s law the resistance is given as;

$$R = \rho \frac{L}{A} \quad (1.11)$$

Here, $R(\Omega)$ is resistance, $\rho(\Omega.\text{cm}^2)$ is specific resistance, $L(\text{cm})$ is thickness, $A(\text{cm}^2)$ is surface area, R_1 is electrolyte resistance and R_2 is cathode resistance.

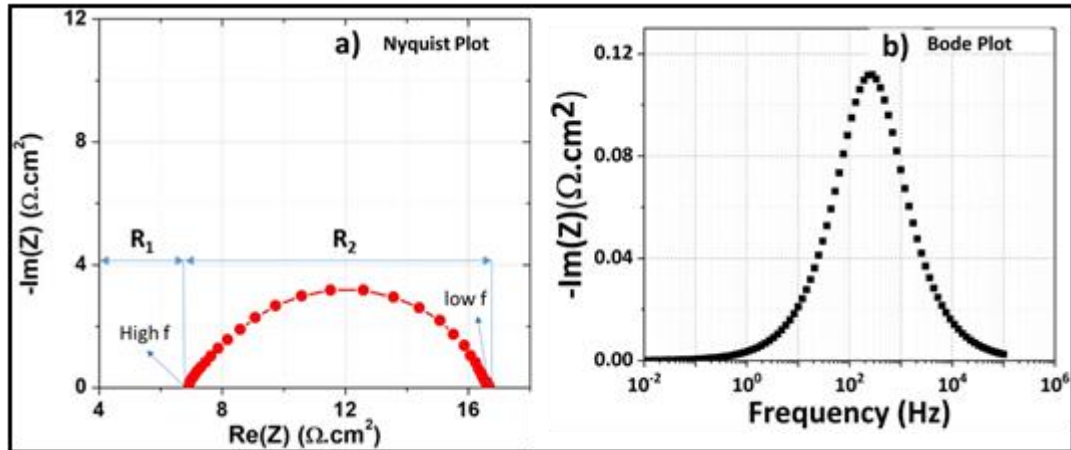


Figure 1.6: Generated impedance spectrum of an analogous circuit with a series resistor and an RC component (capacitor and resistor linked in parallel) displayed in two types: a) Nyquist plot and b) Bode plot.

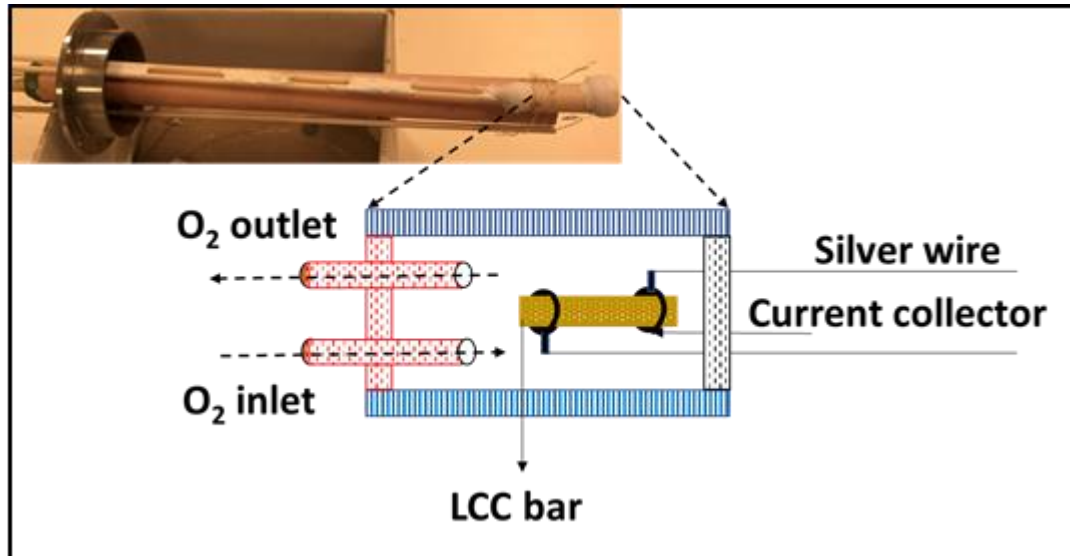


Figure 1.7: Represent figure of sample holder and its schematic cross-section image.

1.2.2. Electrical Conductivity Relaxation

The oxygen exchange kinetics at the gas/solid interfaces is examined using electrical conductivity relaxation (ECR), which involves detecting variations in sample characteristics after applying a chemical concentration difference to the sample's surface (Fig. 1.7). Upon a gradual variation in the environment oxygen partial pressure, the ECR method measures the time variation of the electrical conductivity of a specimen. Predicting oxygen surface exchange (k) and bulk diffusion coefficients, a relationship between an average conduction and the related non-stoichiometry was constructed (D). ECR allows to obtain the surface exchange coefficient (k_{chem}) and the bulk chemical diffusion coefficient by trying to fit the recorded conductivity (or alter in optical and mass characteristics) correlation with the diffusion model and choosing the ideal k and D values for a well-defined geometric shapes workpiece (D_{chem}) [27]–[31].

$$\frac{\sigma_{\infty} - \sigma_t}{\sigma_{\infty} - \sigma_0} = (x + a)^n = \sum_{p=1}^{\infty} \frac{2L_x^2 \cdot \exp\left(\frac{\beta_{p,x}^2 D_{chem}^2 t}{a}\right)}{\beta_{p,x}^2 (\beta_{p,x}^2 + L_x^2 + L_x)}$$

$$x \sum_{q=1}^{\infty} \frac{2L_y^2 \cdot \exp\left(\frac{\beta_{q,y}^2 D_{chem}^2 t}{b}\right)}{\beta_{q,y}^2 (\beta_{q,y}^2 + L_y^2 + L_y)} x \sum_{r=1}^{\infty} \frac{2L_z^2 \cdot \exp\left(\frac{\beta_{r,z}^2 D_{chem}^2 t}{c}\right)}{\beta_{r,z}^2 (\beta_{r,z}^2 + L_z^2 + L_z)} \quad (1.12)$$

The positive roots of the relevant equation are shown by β_s ;

$$\beta_{p,x} \cdot \tan \beta_{p,x} = L_x \quad (1.13)$$

$$\beta_{q,y} \cdot \tan \beta_{q,y} = L_y \quad (1.14)$$

$$\beta_{r,z} \cdot \tan \beta_{r,z} = L_z \quad (1.15)$$

Furthermore, a, b, and c represent half of a rectangular sample's dimensions and are utilized to calculate the dimensionless parameters:

$$L_x = \frac{a \cdot k_{chem}}{D_{chem}} \quad (1.16)$$

$$L_y = \frac{b \cdot k_{chem}}{D_{chem}} \quad (1.17)$$

$$L_z = \frac{c \cdot k_{chem}}{D_{chem}} \quad (1.18)$$

Eq. 1.12 may be reduced to a 2D or 1D expression by ignoring the diffusion along any sample dimension that is noticeably greater than all the others (for example, a, b, or c). The sensitivity of predicting k_{chem} and D_{chem} is directly determined by the variable L (Eq. 1.5-1.7). If L is big, for example, estimating k_{chem} gets challenging, and the analysis is in the diffusion-restricted region. Small L , but at the other hand, indicates more challenging D_{chem} estimate and a surface-controlled regime. The analysis is in the mixed-control system for intermediate levels, $0.03 L \leq L \leq 30,19$, and both k_{chem} and D_{chem} may be measured appropriately. This study utilizes the MATLAB tool ECRex to fit ECR data.

1.2.3. X-ray Photoelectron Spectroscopy

The kinetic energy of photoelectrons is measured through an approach for near-surface characterization known as X-ray photoelectron spectroscopy (XPS). A photoelectron is produced once an inner-shell electron is knocked off by an energetic enough X-ray photon (Fig. 1.8). The kinetic energy of the emitted electron (E_k) is linked to the photoelectron binding energy (E_B) in the following way.

$$E_B = h\nu - E_k - \Phi \quad (1.19)$$

Here, h presents Planck's constant, ν presents frequency, and Φ presents work function, all of which are affected by the spectrometer and material. Because each element has a distinct identity, knowing the binding energy facilitates chemical investigation. Surface sensitivity is the most essential element of XPS. Due to their comparatively low kinetic energies, the generated photoelectrons can only leave from the surface layers' topmost layers (10 nm or fewer) (typically 20-1100 eV). Quantitative analysis is also possible using XPS. The relative atomic fractions of the surface layers can be calculated by comparing the peak regions related to different elements.

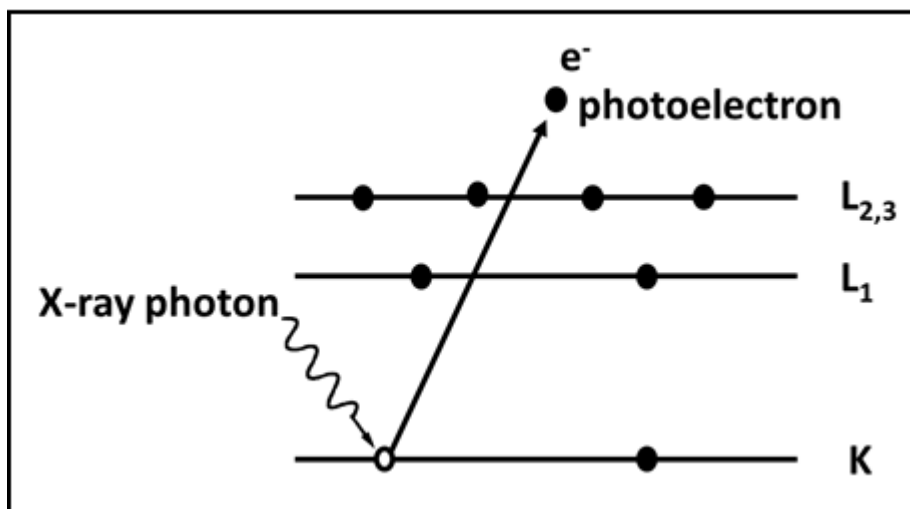


Figure 1.8: The representation of the photoelectron emission mechanism.

1.3. The Scope and Main Goal of the Thesis

With this effort, we want to provide clarity on how oxygen conductors in solid oxide fuel cells (SOFCs) interact with solid and gas phases. In order to improve cell efficiency, it is vital to understand how to make cathode that are both extremely efficient and stable. A quick oxygen exchange (ORR) between oxides and the environmental conditions, including oxygen sensors, separation membranes and metal-air battery, is also crucial. Surface composition as well as cathode efficiency, including both respect of chemical interaction and prolonged stability, will be examined extensively in this dissertation. Research in this area relies mostly on (La,Ca)CoO₃, a well-known perovskite MIEC exhibiting excellent stability in both oxidizing or decomposition environments.

A particular emphasis will be given during the thesis on the relationships between surface chemical composition and air electrode performance, both in terms of electrochemical performance and prolonged time stability. The study's primary reference material is (La,Ca)CoO₃, a conventional perovskite MIEC with high stability in both reducing and oxidizing atmospheres and a popular cathode for SOFC.

The thesis is concluded in Chapter 4. The project's primary scientific findings are included in the subsequent chapters. They have been created as stand-alone texts. Bulk electrodes (dense rectangular bars) are the subject of Chapter 2, whereas thin film

electrodes are the focus of Chapters 3 and 4. The benefit of utilizing electrodes made from polymeric precursors was assessed, along with how deposition parameters, surface chemistry, and surface area might affect observed performance.

Chapter 2 focused on the determination of phase evolution, ionic conductivity and oxygen exchange properties of (La,Ca)CoO₃ and (La,Sr)CoO₃ perovskite type mixed ionic and electronic conductors. The prolonged electrochemical performance of polymeric precursor-derived (La,Ca)CoO₃ (LCC) and (La,Sr)CoO₃ (LSC) perovskite membranes were examined in this chapter with a sudden change in oxygen partial pressure utilizing electrical conductivity relaxation to obtain surface oxygen exchange coefficient and diffusion coefficient.

Chapter 3 dedicated on the long time efficiency and stability of thin film (La,Ca)CoO₃ SOFC cathodes: association of phase, microstructure, and surface chemistry development. The long-term electrochemical efficiency of thin films that obtained from polymeric precursor of LaCoO₃ substituted with Ca²⁺ (LCC), rather than the larger Sr²⁺, which accumulates at the cathode surface and forms oxides/hydroxides.

Chapter 4 focused on influence of solution deposition parameter on the electrochemical performance stability. To enhance the electrochemical activity of 40% doped LCC pre-calcined at 800 °C, that exhibits the lowest polarization resistance, in this chapter we focused on the different deposition parameters of this LCC cathode. The long-term electrochemical performance of polymeric precursor-derived films of Ca²⁺-substituted LaCoO₃ (LCC) was examined by varying deposition parameters.

2. DETERMINATION OF PHASE EVOLUTION, IONIC CONDUCTIVITY AND OXYGEN EXCHANGE PROPERTIES OF (La,Ca)CoO₃ AND (La,Sr)CoO₃ PEROVSKITE TYPE MIXED IONIC AND ELECTRONIC CONDUCTORS

Abstract: The prolonged electrochemical performance of polymeric precursor-derived (La,Ca)CoO₃ (LCC) and (La,Sr)CoO₃ (LSC) perovskite membranes were examined in the current study with a sudden change in oxygen partial pressure utilizing electrical conductivity relaxation to obtain surface oxygen exchange coefficient and diffusion coefficient. It was revealed that the k_{chem} and D_{chem} values of Ca-doped LaCoO₃ samples were generally greater than those of Sr-doped ones. The 20% doped LaCoO₃ samples were more stable than the 40% series, despite the fact that the 40% doped LaCoO₃ samples produced higher k_{chem} and D_{chem} values. Throughout prolonged heat treatment, D_{chem} levels seemed to remain steady. X-ray diffraction, energy-dispersive X-ray spectroscopy mapping, and scanning electron microscopy examinations revealed that impure CaO and CoO_x phases precipitated on the grain boundaries of the 40% Ca doped LaCoO₃ sample before and after heat treatment. Heat treatment of these precipitates induced the grain to expand, which lowers k_{chem} because the active phase ratio on the surface is likewise diminished. The $\text{Ca}_{\text{non-lattice}}$ and $\text{O}_{\text{surface}}$ ratios, which produce an isolating CaO layer on the surface and reduce oxygen reduction reaction by trapping $\text{O}_{\text{terminations}}$, hardly changed after heat treatment. SEM examination identified random point-shaped particles and transparent amorphous-like platelets that partly covered grain surfaces in 40% Sr doped LaCoO₃. Platelets cover the Sr-doped LaCoO₃ phase's surface, reducing the active phase ratio and lowering k_{chem} . Following heat treatment, the $\text{Sr}_{\text{non-lattice}}$ and $\text{O}_{\text{surface}}$ ratios, which produce an isolating SrO layer on the surface and lower oxygen reduction reaction by blocking $\text{O}_{\text{terminations}}$, rose considerably.

2.1. Introduction

Mixed ionic–electronic conductors (MIECs) are widely considered for the application of oxygen separation membranes and air electrodes for solid oxide

fuel/electrolysis cells (SOFCs/SOECs) [32]. In the MIECs family, the most extensively examined electrode to date are the perovskite-structured ABO_3 type oxides, such as; (La, Sr) $CoO_{3-\delta}$ (LSC) [33], (La, Sr) $FeO_{3-\delta}$ (LSF) [34], (La, Sr)(Co, Fe) $O_{3-\delta}$ [29],[35]. The commonly applied A-site substitution of La^{3+} by Sr^{2+} in the ABO_3 type perovskite oxides serves to generate a charge imbalance, aiming to form oxygen vacancies and p-type electronic charge carriers. This, in turn, results in high ionic and electronic conductivity.

However, a disadvantage in the case of these compositions is the ionic radii mismatch between the host La^{3+} (ionic radius for 12 coordination =1.36 Å) and dopant Sr^{2+} (ionic radius for 12 coordination =1.44 Å). The larger Sr ion in the La sublattice generates tensile stresses, inducing Sr^{2+} segregation at the surface and grain boundaries in the form of $SrO/Sr(OH)_2/SrCO_3$, depending on the gas atmosphere, upon exposure to high temperatures during fabrication or device operation [36],[37]. This phenomenon decreases the performance of the MIECs because i) the segregated Sr-compounds are resistive and thus, inactive for oxygen reduction/evolution reactions and ii) A-site doping effect becomes diminished.

Demirkal et al. reported that upon long-term annealing of porous LSF thin films fabricated by polymeric precursors, significant Sr^{2+} ions accumulation took place at the top surface, creating $SrO/Sr(OH)_2/SrCO_3$, which was accompanied by a decrease in the SOFC cathode activity [38]. Oh et al., on the other hand, studies the Sr-segregation behavior of LSCF and reported that after long-term annealing, SrO species precipitated on the exposed grain surfaces in the form of submicron-sized particles [39]. They used bulk, dense LSCF ceramics for this investigation, which proved extremely beneficial due to the simplicity of the sample geometry for facile microstructural and chemical analysis and the relatability of the results to oxygen separation membrane applications.

In this work, we propose to replace the larger Sr^{2+} dopant with the smaller, Ca^{2+} (ionic radius for 12 coordination =1.34 Å), to eliminate elastic strain, and thus dopant segregation, while retaining all the benefits of divalent doping. Phase and surface chemistry evolution of Sr or Ca doped $LaCoO_3$ upon long-term exposure to the SOFC and oxygen separation membrane operating temperature of 700 °C were investigated in dense, bulk ceramics, which provided a simple geometry for facile characterization and direct applicability of results for oxygen separation membranes.

These chemical and structural changes upon long-term annealing were then correlated to how the surface oxygen exchange coefficient and bulk oxygen diffusion coefficient varied under the same conditions.

2.2. Experimental

2.1.1. Sample Preparation

Polymeric precursors were applied to generate the ceramic powder of $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ (LCC02), $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ (LCC04), $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ (LSC02) and $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ (LSC04). Polymeric (La, Ca)CoO₃ (LCC) and (La, Sr)CoO₃ (LSC) precursors were prepared by mixing appropriate amount of clear solutions of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Fluka, >99%), $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Merck, >99%), $\text{Sr}(\text{NO}_3)_2$, $\geq 99\%$, Sigma-Aldrich) $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar, > 99.9%), ethylene glycol and distilled water at 80 °C to enable for polymerization to occur. The molar rate of the positive ions to the ethylene glycol was held at 0.05:1. After polymerization, the solution gradually was heated up to 180°C to obtain dried gels. To acquire the pure LCC and LSC powders by decomposing the organics, the dried gels were calcined at 700 °C for 3 hours, in the atmosphere. The powders have been pressed to shaped as pellets without any binder and sintered in air at 1200°C for 4 hours.

2.1.2. The Characterization of Structure, Microstructure, and Surface Composition

X-ray diffraction (XRD) measurements were achieved before and following a 100-hour subjected to 700 °C in atmosphere in order to specify the phase development of the LCC and LSC dense samples following extended time operation. A copper radiation source ($\text{CuK}\alpha 1$, $\lambda = 0.15406$ nm, Rigaku Dmax 2200) was utilized to analyses XRD measurements in the 2θ range of 20°–80°. The difference in microstructure of LCC and LSC dense samples after 100-hour subjected to 700 °C was carried out by scanning electron microscopy (SEM, Philips XL30 SFEG), operating backscattered electron imaging, while the elemental distribution on the surface and

cross-section were performed via energy-dispersive x-ray spectroscopy (EDX- EDAX Amatek Apollo XPP) measurement.

2.1.3. Electrical Conductivity Relaxation

The LCC and LSC samples were manufactured by grinding and cutting the obtained dense LCC and LSC pellets into a bar specimen with estimated dimensions of $15 \times 1.0 \times 1.0 \text{ mm}^3$ in order to perform the electrical conductivity relaxation (ECR). Only the cutting surfaces were ground and polished using silicon carbide papers (P800/P1200). A four-probe DC technique was utilized to gather records on ECR. Two silver wires with 0.25 mm radii were wound around both ends of the sample for the current delivery. And also, two additional silver wires were wound 1 mm far away from the current electrodes to perform as voltage probes. An in-house silver current collector paste was put to the sample surface precisely below the silver wires to ensure excellent engagement between the silver wires and the bar. The sample was attached to a container and positioned in an alumina sample containment reactor. Air, and mixing dried oxygen and helium gas streams were created in the desired ratios, with a flowrate of 300 ml/min. and $p\text{O}_2$, using mass flow regulators. One of the air or gas flows was provided via the reactor by using an instantaneous two-way valve that operated pneumatically. In response to $p\text{O}_2$ oxidation and reduction step variations between 0.02 and 0.21 atm, transient electrical conductivity measurements were gathered. The chemical diffusion coefficient D_{chem} and the surface exchange coefficient k_{chem} were defined via fitting the transient conductivity to the proper analyses of Fick's second law applying for a non-linear least-squares program. A comprehensive definition of the ECR method and the model utilized for parameter fitting is specified elsewhere [48–50]

2.2. Results and Discussion

2.2.1. Phase Formation

To determine the phase evolution of dense LCC and LSC samples throughout prolonged operation, analyses of X-ray diffraction (XRD) were performed in air before

and after 100-hour exposure to heat treatment at 700°C (Fig. 2.1). LCCO2 and LSC pellets consisted solely of the intended rhombohedral structure (PDF: #36-1388) (Fig.2.1a and c) before and after heat treatment. In the literature, similar to our results, Cherepanov et al. reported that $\text{La}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$ shows a single phase with the composition of ($x=0.1$ and 0.2) even upon 150 hours at 1100 °C temperature [43]. Also they stated that for same condition, $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ - exhibits a single phase with the composition between $x=0.1-0.8$ [43]. Another study showed that the rhombohedral deformed ($x=0.0-0.5$) $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ perovskite phase transforms into the cubic ($x=0.55-0.7$) phase [44]. Correspondingly, Wong-Ng et al. stated that the extent of Ca solubility in LaCoO_3 is 20 % at 885 °C in air [45]. Besides, in the case of 20 % Ca substituted LaFeO_3 , it has been reported that orthorhombic (Pbnm) to rhombohedral (R-3c) (O-R) structural phase change exists at 738 °C in 20% O_2 and % 80 argon atmosphere [46]. Similarly, Song et al. pointed out that this transition occurs at 775 °C in 21 % O_2 and 79 % nitrogen atmosphere [47].

To increase the Ca content to 40% of A-site, on the other hand, induced not only the formation into orthorhombic structure, but also the formation of minor impurity phases (Fig. 2.1a). More detailed analyses indicated that these impurity phases were cubic CaO (PDF#82-1691), cubic Co_3O_4 (PDF#43-1003), and cubic CoO (PDF#48-1719) (Fig. 2.1b). Upon being subjected to 700 °C for 100 hours, CoO phase disappeared, while the other minority phases were retained. Cherepanov et al. reported that the homogeneity range of $\text{La}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$ in air at 1100 °C is $0 < x < 0.3$. In the case of $x \geq 0.4$ multiple other phases existed even after 480 hours of annealing. They also reported that to rise the dopant content in $\text{La}_{1-x}\text{Me}_x\text{CoO}_{3-\delta}$ ($\text{Me} = \text{Ca}, \text{Sr}, \text{Ba}$) perovskite resulted in the ordering of oxygen vacancies, which limited the solid solubility of Ca in a familiar plane, generating intergrowths of the perovskite [43]. Meanwhile, Woermann and Muan indicated that in the CaO-Cobalt oxide phase equilibria in atmosphere, cobalt is existing mainly in the divalent state as CoO with CaO phase at higher temperatures, whereas below the 926 or 1026 °C, it is present predominantly in the trivalent state as Co_3O_4 with CaO phase [48]. Kubicek et al. also reported that the CoO_x phase generated at $2\theta \approx 37^\circ$ and 42° on $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ thin films fabricated by PLD on single crystalline (100) YSZ substrates at comparatively lower temperatures of 625-800 °C, was ascribed to Co_3O_4 or CoO phase [49]. These findings are consistent with the present study.

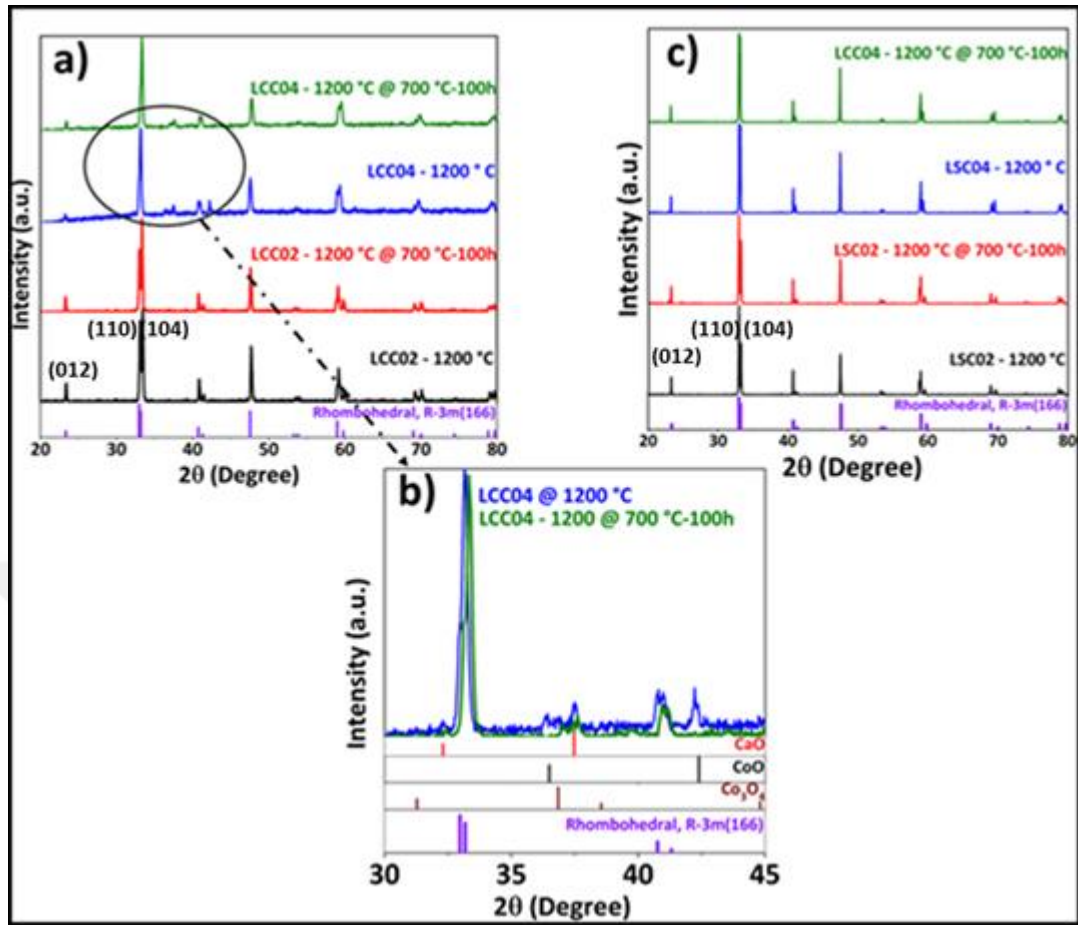


Figure 2.1: X-ray diffraction (XRD) patterns taken from (a) LCC samples, (b) a focused analysis of LCC004, and (c) LSC, before and following heat treatment at 700 °C for 100 h, in atmosphere.

Overall, increasing the Ca content to $x=0.4$ in LCC ceramics, induced the generation of the orthorhombic phase, while also increasing the amounts of CaO and CoO_x related minority phases.

Tai et al. indicated that increasing the Sr content in the $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_3$ decreases the orthorhombic-rhombohedral and rhombohedral-cubic (R-C) phase transition temperature [50]. However, in the present study, only the rhombohedral phase is observed in Sr-doped ceramics prior to and after heat treatment. This discrepancy could be related to the additional Fe content in the perovskites mentioned in [56].

2.2.2. Microstructure, and Surface Composition Evolution

Microstructural and surface chemistry changes in LCC and LSC ceramics are likely to have a considerable influence on the overall stability of the rate of oxygen exchange and its bulk diffusion, which are parameters that define the performance of these materials in SOFC/SOEC air electrode and oxygen separation membrane applications. SEM-EDX analyzes were carried out in all samples before and after prolonged exposure to operating temperature, so as to identify the effects of microstructural development and to estimate whether any segregated phase exists.

Figures 2.2 and 2.3 display the microstructures and surface compositions of LCC membranes before and following subjected to 700 °C, respectively. LCC02 has exhibited a dense microstructure with no impurity phases on its surface detectable by EDX, prior to the heat treatment (Figure 2.2). However, to increase the Ca content to % 40, the top surface of LCC generating heterogeneously distributed grains and Ca-rich or Co-rich impurity phases which were formed at the grain boundary (Fig. 2.2 and Fig 2.3). On the cross-section surface of LCC04 the same impurity phases existed, while those phases existed in LCC02, barely (Fig. 2.2 and Fig 2.3). The grain boundary is mostly a favorable source for heterogeneous nucleation, but growth even within the grain body is often more uncommon [51]. From the EDS analysis at the upper surface of the LCC, these phases were usually precipitated in contact with each other. These impurity phases were attributed to the CoO_x and CaO phases, respectively (Fig. 2.2 and Fig. 2.3). However, upon heat treatment at 700°C, the impurity phases ratio increased both on the surface and cross-section area of LCC02 (Fig. 2.2). The fact that those impurity phases were not revealed in XRD measurement (Fig. 2.1a) indicates that the generated phases are amorphous or out of the detection limit of XRD. Similarly, we reported in our recent study, the surface cation ratio of LCC02 which was heat-treated at 700 °C, became close to the theoretical value upon extended time operation [52].

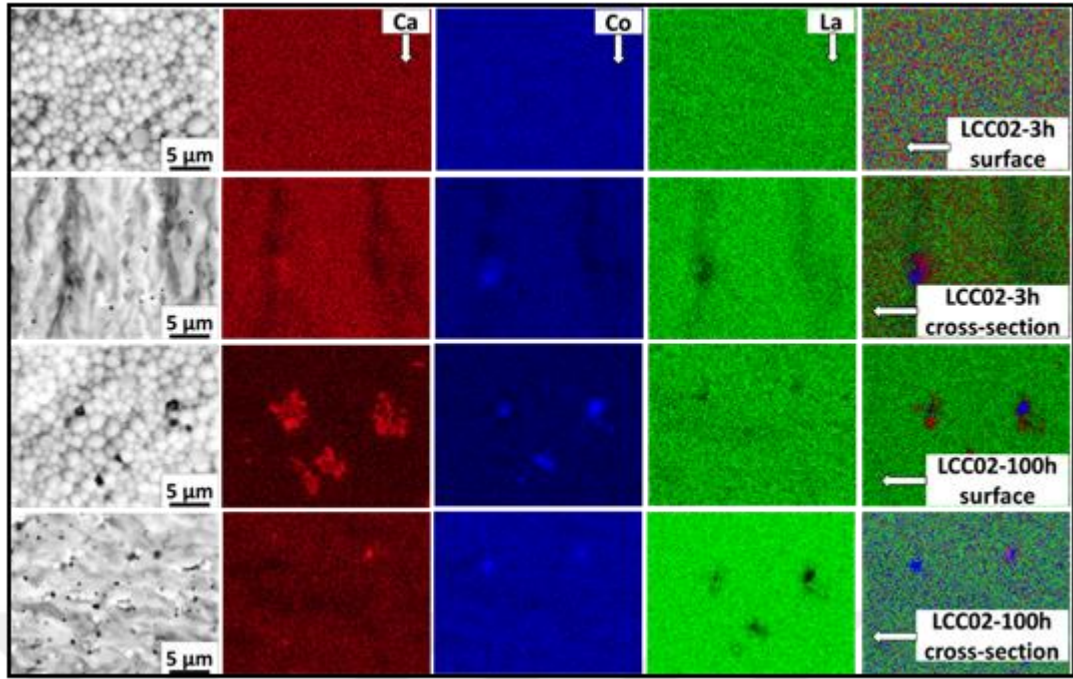


Figure 2.2: Elemental distribution on the surface and cross section of LCC02 prior to and following heat treatment is indicated on the EDS mapping.

Cherepanov et al. also reported that no impurity phases were observed within the $\text{La}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$ perovskite after 150 and 300 hours of exposure to 1100 °C in air, with $x = 0.2$ and 0.3 , respectively [43]. However, in the case of enhancing the amount of Ca up to $x=0.4$, Cherepanov et al. also observed multiple impurity phases after annealing, in agreement with our present results [43]. While no changes were observed in the CoO_x phase after long-term heat treatment, the grains of the CaO phase enlarged on the surface (Figure 2.3).

Figures 2.4 and 2.5 show the microstructures and surface compositions of LSC membranes before and after being subjected to 700 °C for 100 hours. In contrast to the LCC pellets, no impurity phase was observed in the EDS analysis collected from the surface of the LSC02 and LSC04 pellets before and after heat treatment.

While the EDS analysis in Fig. 2.2, 2.3, 2.4 and 2.5 provides a general idea of the surface elemental distribution, the chemical composition of the top surface, which should be detrimental to the oxygen exchange at the surface, is unknown.

Figures 2.6 displays an evaluation of microstructures of LCC and LSC pellets before and following heat treatment at 700 °C. Evidently, similar to the EDS analyses, no residual phase is observed in the BSE analyses of the LCC02 surface prior to heat

treatment. To increase the Ca content to % 40, on the other hand, impure phases indicated by EDS analyses were also detected by BSE analyses (Figure 2.6).

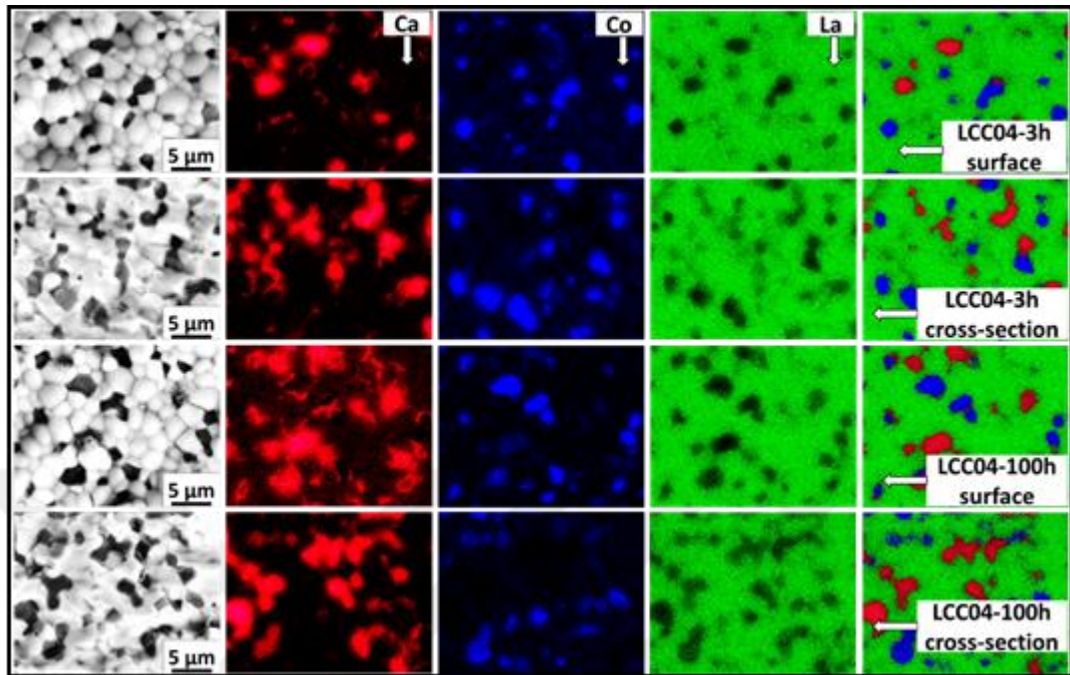


Figure 2.3: The EDS mapping presents the locations of elements on the surface and cross section of LCC04 before and after heat treatment.

In LSC series, however, impure phases were observed as transparent platelets and a tiny number of point-shaped particles. As a result of the heat treatment, the ratios of these phases rise, and the phases enlarged. Tripković et al. reported the phase segregation on the LSC and LSF that a overlayer of SrO or associated undesirable secondary phases just covers specimens at low temperatures and is reformed into either a perovskite or perovskite-like phase with such an enhanced rate of Sr at high temperatures (e.g. Rudlesden-Popper phase) [53]. In our recent study, we report that from the XPS measurement, following extended time subjected to 700 °C, LCC02 and LCC04 that pre-calcined at 800 °C, suffered significant Ca segregations, at the surface. We proposed a surface evolution model that the LCC surface is typically enclosed by a thin CaO overlayer at the operating temperature of 700 °C [52], which is probably the case here. Similarly, in the literature, SrO_x-like segregating phases have been reported in La_{1-x}Sr_xCoO_{3-δ} perovskite [54].

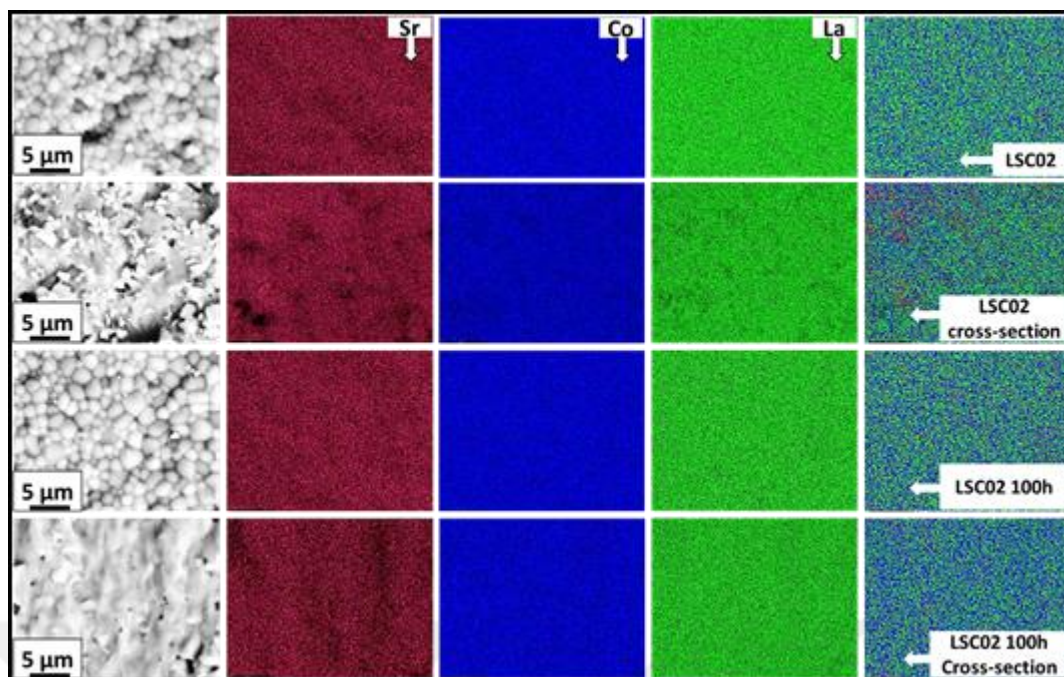


Figure 2.4: The cross section and surface of LSC02 are illustrated with the positions of the elements before and after heat treatment using the EDS mapping.

Overall, transparent platelets covered the grains enclosing the CaO and CoO_x phases in LCC samples. Due to the absence of these impure phases in the LSC samples, the transparent phase randomly covered the grain surface more, notably in the LSC04 sample following heat treatment. Importantly, the particle-shaped phase is only not detected on the surface of the LCC04 sample. However, this phase was noticed as small particles on the LCC02 sample surface following heat treatment. On the other hand, it was appeared in tiny quantities on the surfaces of LSC samples before to the heat treatment, while expanded significantly following the heat treatment and its ratio on the surface increased.

We also concluded that the size of the grains in each sample did not change before and after heat treatment. But it can be emphasized that the samples with 40% doping have larger grains than the others, both before and after heat treatment.

A basic notion of surface element distribution may be gained from the EDS analysis in Figures 2.2, 2.3, 2.4 and 2.5, but it is not enough to identify what the top surface content is. Another factor that may affect the electrochemical performance and prolonged stability is the surface composition. Prolonged variability in the comparative cation concentrations at the top surface of the LCC and LSC samples have been monitored because the cation concentrations at the membrane'

surface offer data on the kinds of varieties associated with the gas environment and therefore the oxygen reduction activity. Before and following extended time subjected to 700°C, samples underwent XPS examinations and the appropriate fittings, for this goal (Fig. 2.7). Initially, LCC04 had a Ca-rich (Fig. 2.7a) surface accompanied by La deficiency (Fig. 2.7b) with Co (Fig. 2.7c) which was quite near to the stoichiometric value. Following the heat treatment, however, the Ca and La ion ratios approached the stoichiometric values, whereas the Co ion ratio increased on the surface. Also, in addition to the orthorhombic phase, prior to heat treatment the

CaO, CoO and Co₃O₄ phases had been detected in XRD (Fig. 2.1a and b), while after heat treatment only CoO phase disappeared. CoO_x and CaO precipitated phases detected in EDS analysis are consistent with this finding, as well. Overall, the surface of LCC04 sample is thus expected to be rich in the CaO and CoO_x phases.

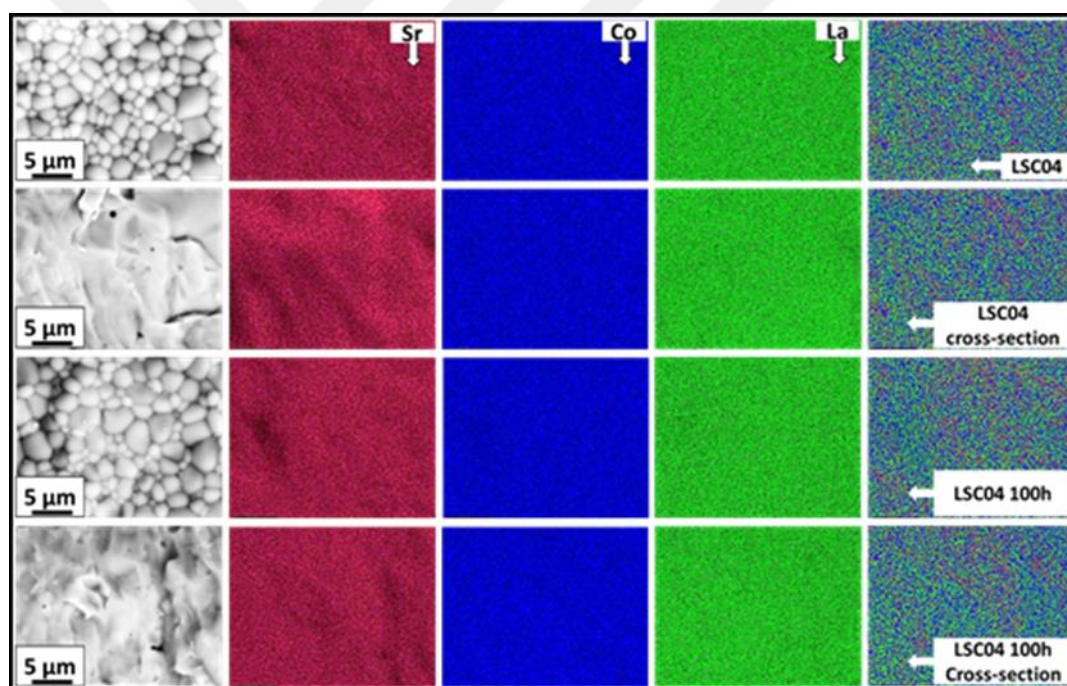


Figure 2.5: Using EDS mapping, the cross section and surface of LCSC04 are indicated together with the locations of the components before to and following heat treatment.

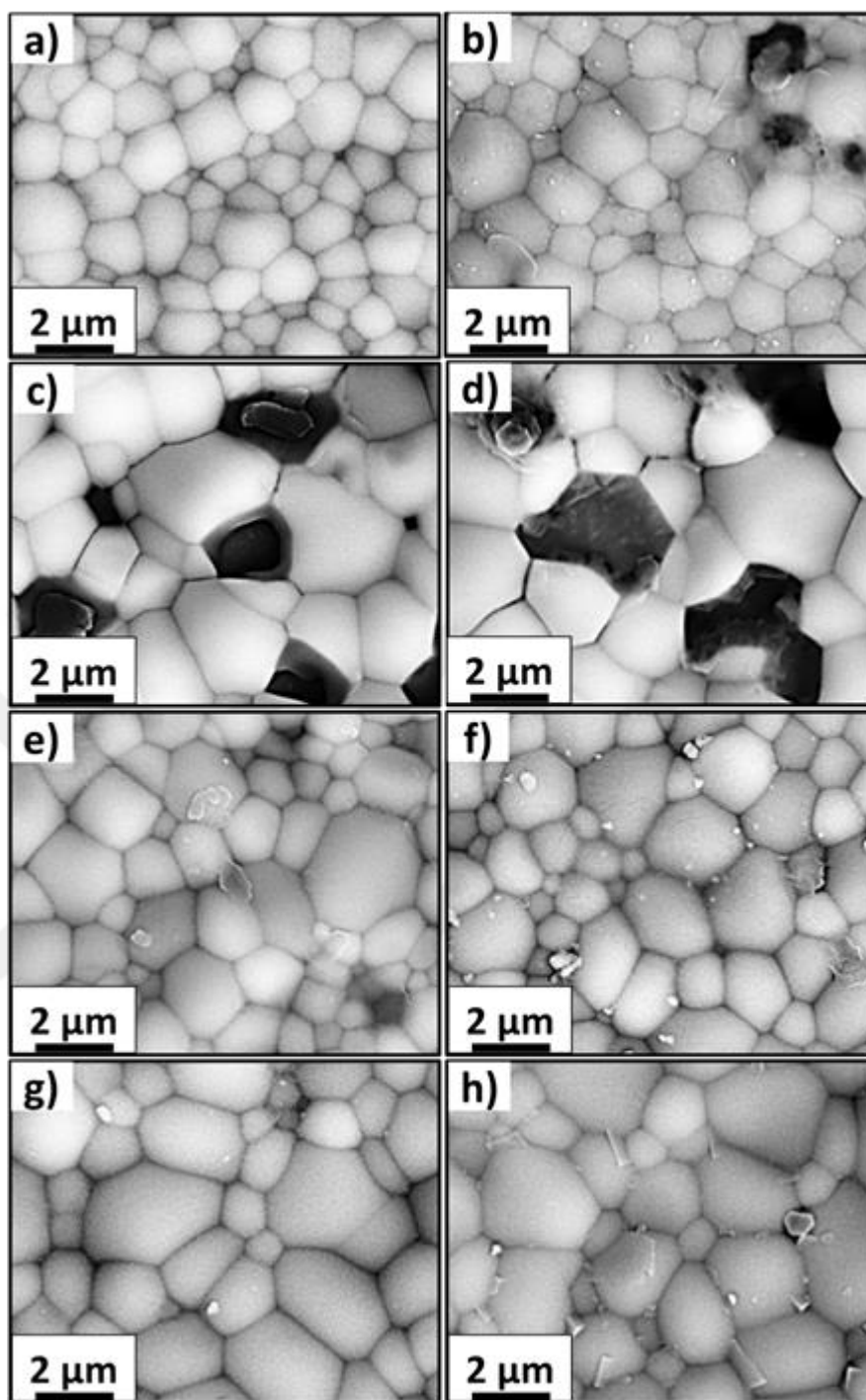


Figure 2.6: Indicate the backscatter images of a) LCC02, c) LCC04, e) LSC02 and g) LSC04 before, and b) LCC02, d) LCC04, f) LSC02 and h) LSC04 surface after heat treatment.

On the other hand, LCSC04 exhibited a Sr-rich surface (Fig. 2.7a) with a La (Fig. 2.7b) and Co deficiency prior to heat treatment (Fig. 2.7c). While the Sr and La ion ratios remained almost constant upon heat treatment, the Co ion ratios reduced slightly. As previously stated, in the XRD analysis (Fig. 2.1c) no phase separation was

observed, and in the EDS analysis (Fig. 2.5) no Sr-rich cluster was detected on the surface of LSC04, as well. However, as previously stated, although transparent platelet and spot-shaped particle impurities were identified on the surface in BSC pictures, they could not be detected in XRD analysis due to being beyond the XRD detection limit or being amorphous phases. Oh et al. analyzed the characteristics of elemental concentration on the surface of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF) [39]. They noticed that following heat treatment, submicron-sized precipitates appeared on grain surfaces. Their morphologies seemed to be oriented along the surface directions of the underneath grains, similar to our findings in Fig. 2.6h. They also used Auger electron spectroscopy and transmission electron microscopy to determine that the precipitation phase was composed of strontium (Sr) and oxygen (O). As a consequence, Sr ions recorded in XPS analysis before and after heat treatment, as well as impure phases observed in BSC imaging, likely represent amorphous SrO/Sr(OH)_2 phases.

The ion concentrations reveal only a small supply about the development of surface chemical properties. Hence, a detailed examination of the components to the O 1s, Ca 2p, and Sr 2p spectra offers important insight into the nature of the segregating component. There have been reports of oxygen taking three different types at the outer surface of perovskite-type oxides; as a result, the peak fits have been conducted in accordance with these findings [55]-[62]. The O1s peak that is placed at 529 eV is thought to be related with the lattice oxygen ($\text{O}_{\text{lattice}}$) in the perovskite, whilst the O1s peak that is sited at 529.8–531.5 eV is thought to be connected with the oxygen atoms that are placed at the termination layer of the perovskite ($\text{O}_{\text{termination}}$). Zhi et al. [58] used XPS to analyze $(\text{La,Sr})\text{MnO}_3$ microcubes and attributed the oxygen component to oxygen adsorbed onto electrochemically active surface vacancy locations with binding energies of about 531.5 eV [60]-[62].

During the data fitting procedure, additional contribution from the oxygen ions that are attached to surface oxide/hydroxide compounds and/or adsorbates ($\text{O}_{\text{surface}}$) [61],[62] has so far been considered. This contribution occurs at binding energies of 532–533 eV. On the other hand, the Ca 2p or Sr 2p photoelectron core level peaks at the electrode surface define the atomic concentration of Ca or Sr, as well as the development of the Ca or Sr binding environments in the perovskite structure and non-lattice phases. At smaller binding energies, the photoelectron spectrum records for Ca 2p or Sr 2p were taken from the perovskite lattice-bound ascribed to $\text{Ca}_{\text{lattice}}$ or $\text{Sr}_{\text{lattice}}$,

and at higher binding energies, from the surface-bound $C_{\text{anon-lattice}}$ or $Sr_{\text{non-lattice}}$. The Ca or Sr chemical environment of the perovskite LCC04 and LSC04 were attributed to the data acquired from the Ca_{lattice} or Sr_{lattice} . The creation of species such as CaO, $Ca(OH)_2$, SrO, or $Sr(OH)_2$ might be attributed to the chemical environment of $Ca_{\text{non-lattice}}$ or $Sr_{\text{non-lattice}}$.

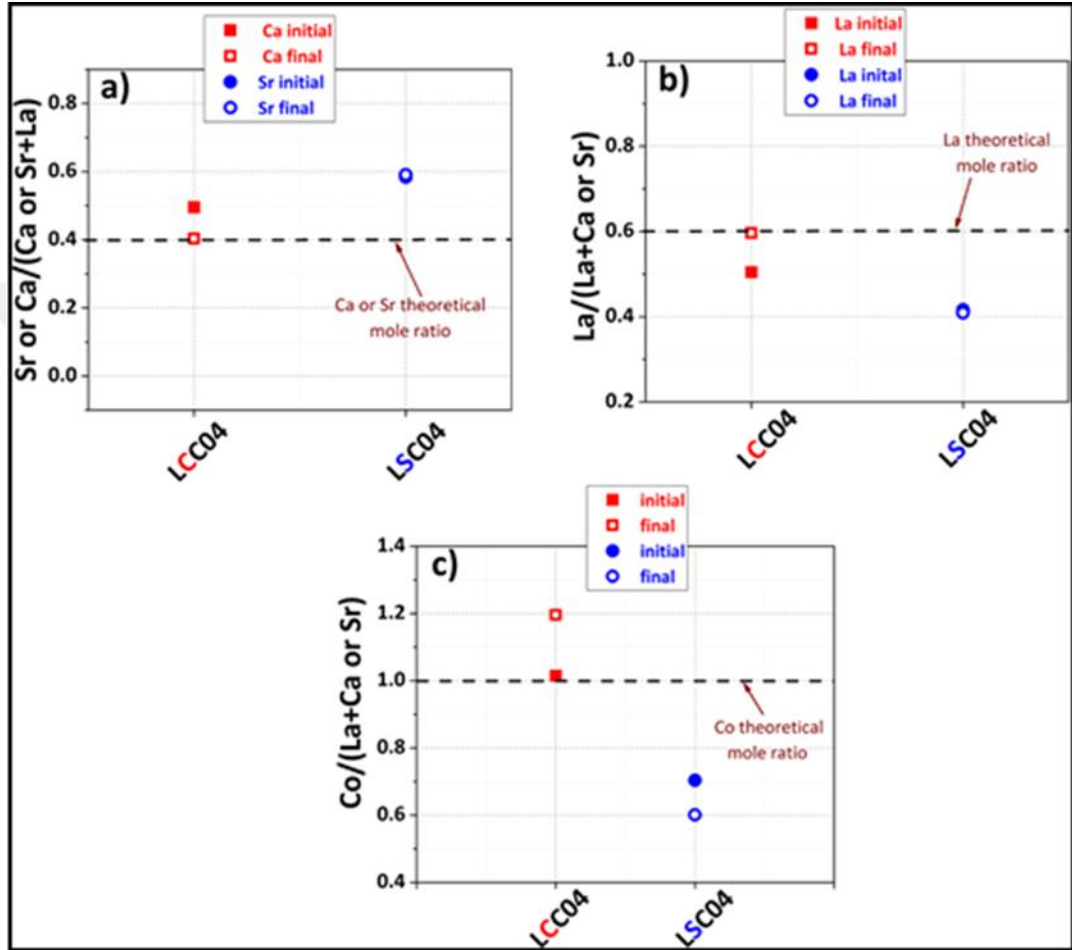


Figure 2.7: Variations in the quantities of (a) Ca or Sr, (b) La, and (c) Co at the surfaces of LCC and LSC membranes prior to and following prolonged operation at 700 °C in atmosphere.

Upon heat treatment, the $O_{\text{termination}}$ value in LCC04 fell somewhat. The O_{lattice} ratio, on the other hand, increased slightly while the O_{surface} value stayed the same. The ratios of Ca_{lattice} and $Ca_{\text{non-lattice}}$ virtually didn't alter while examining at the Ca components on the surface. The O_{lattice} ratio increased in response to a minor reduction in the $O_{\text{termination}}$ rate on the surface.

Overall, it can be concluded that following the heat treatment, the surface of LCC04 did not covered by $CaO/Ca(OH)_2$ species due to constant ratio of O_{surface} and

$\text{Ca}_{\text{non-lattice}}$. However, CaO and CoO_x impurity phases precipitated on the grain boundary of the LCC04 phase prior to and after heat treatment, according to XRD and EDS analyses. Similarly, the deficient La cation ratio in XPS examination revealed that the surface was rich in Ca and Co cation. The existence of CoO_x phase on the surface was verified by the Co-rich cation ratio upon heat treatment. Furthermore, the existence of oxide phases was supported by the presence of $\text{Ca}_{\text{surface}}$ and $\text{O}_{\text{surface}}$ species on the surface. As a result, the $\text{O}_{\text{surface}}$ ratio did not change much following the heat treatment. However, the coarsening of the oxide phase grains formed on the grain boundaries of the LCC04 phase after heat treatment revealed that the ratio of these phases increased relative to the LCC04 phase, as evidenced in the EDS analyses. Then, $\text{O}_{\text{termination}}$ may be reduced slightly. The poor coverage of the transparent platelets on LCC04 phase grains detected in BSC and EDS analyses solely in the immediate vicinity of the impurity phases may be one of another explanation for the reduction in this oxygen species.

$\text{O}_{\text{lattice}}$ reduced following heat treatment in LSC04, as it did in $\text{O}_{\text{termination}}$, but the $\text{O}_{\text{surface}}$ ratio increased almost threefold. The $\text{Sr}_{\text{non-lattice}}$ ratio increased when the $\text{Sr}_{\text{lattice}}$ ratio reduced. It's worth noting that following heat treatment, both the $\text{Sr}_{\text{non-lattice}}$ and $\text{O}_{\text{surface}}$ ratios increased. These findings indicate that following heat treatment, the LSC04 surface contains separate SrO/Sr(OH)_2 impurity phases. Similarly in the literature, Kubicek et al. previously observed cation segregation tendency in single crystals of pulsed laser-deposited zirconia [63]. As a consequence of Sr surplus particles following thermal annealing, they reported the creation of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ coating cathodes on YSZ chemically heterogeneous surfaces. Likewise, Cai et al. discovered a Sr-enriched surface in a $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ thin coating formed by a pulsed layer. Utilizing locally resolved AES, they decisively reveal the existence of SrO/Sr(OH)_2 species on the surface [64].

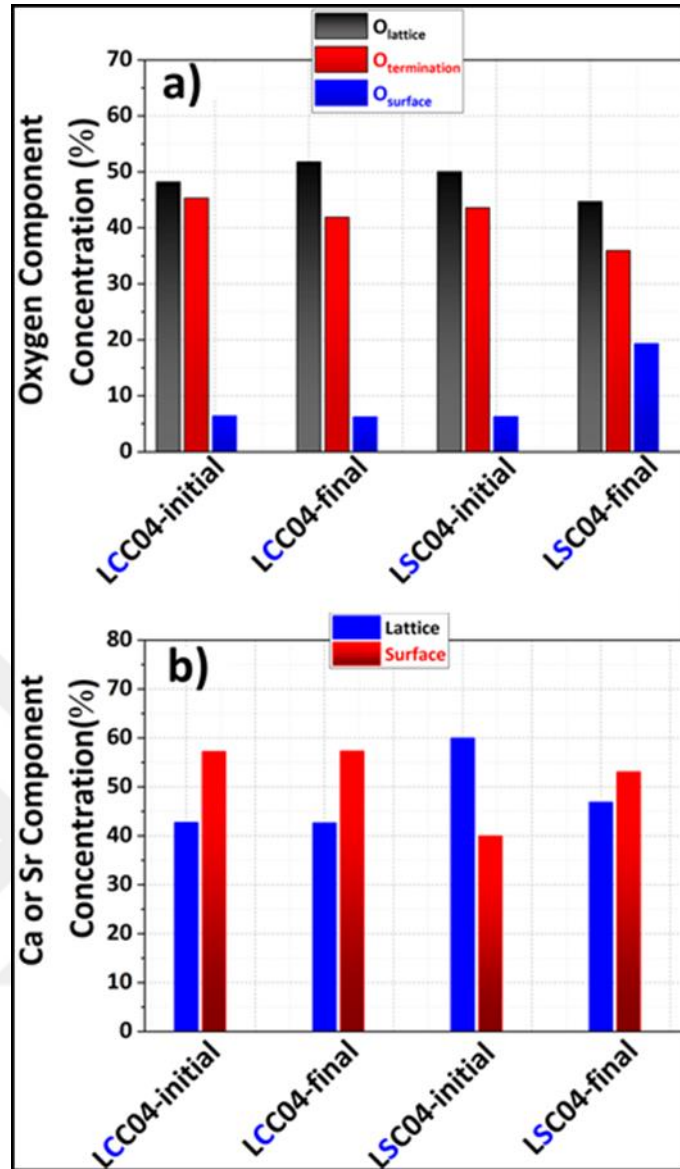


Figure 2.8: Schematic representation of the distribution of (a) oxygen species and (b) dopant element species on the membrane surface.

One of the reasons of elemental enrichment and precipitation on the surface of doped perovskite type ABO_3 is the defect structure and particularly the occurrence of point defects. Because LCC04 and LSC04 have a significant oxygen deficiency, oxygen vacancies might play a role in Ca-O or Sr-O precipitation. Although oxygen vacancies promote the oxygen reduction process on the surface and oxygen diffusion in the lattice, they decrease the structure's stability by improving repulsive interactions between similar atoms. Wang et al. proved the influence of oxygen vacancies on bonding strength in an experiment. They discovered that when the oxygen vacancy concentration rises, the elastic modulus of ceria drops dramatically [65]. This is

because oxygen vacancies weaken the attracting forces. Lee stated the other reason of the substituted cation segregation et al. Their findings showed that the elastic and electrostatic energy contributions were both present in the process substituted cation on perovskite oxides [36]. It was shown that the amount of dopant segregation could be reduced, and more stable cathode surfaces could be achieved by chemically enlarging the lattice and reducing the size mismatch between the host and substituted cations. Overall, CaO and CoO_x phases formed on the membrane surface and in the bulk as a consequence of the Ca cation's poorer solubility in the LaCoO_3 phase. These precipitates do not tend to cover the membrane surface due to generating at grain boundaries. However, the grains of these precipitates expand following heat treatment, this resulted in a reduction of ORR because the active phase ratio on the surface is reduced slightly. In LSC, on the other hand, since the Sr cation's solubility in the LaCoO_3 phase is great, there was no precipitate phase in the bulk structure or on the surface. The Sr cation, however, segregated to the film surface and covers the ORR-active film surface according to the processes explained above, resulting in reduced ORR activity.

2.3. Electrical conductivity relaxation

Electrical conductivity relaxation (ECR), which includes detecting alterations in sample properties after applying a chemical concentration difference to the sample's surface, is employed to examine the kinetics of oxygen exchange at gas/solid interfaces. The ECR technique analyzes the temporal variation of a specimen's electrical conductivity in response to a progressive variation in the atmosphere oxygen partial pressure. A link between an average conductivity and the associated non-stoichiometry was built in order to determine oxygen surface exchange (k) and bulk diffusion coefficients (D). ECR allows the determination of k and D by attempting to fit the recorded conductivity correlations via MATLAB tool ECRex code with the diffusion model and determining the optimum k and D values for a well-defined geometric shaped workpiece. Simultaneous fitting of surface k_{chem} and bulk D_{chem} has been demonstrated in several studies to make correct estimation of both quantities from ECR measurements difficult [66].

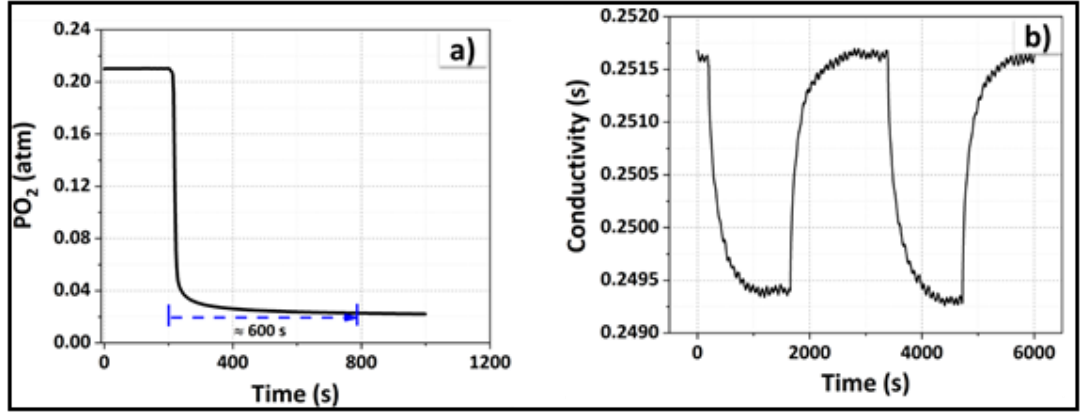


Figure 2.9: a) The variation of the oxygen gas pressure used during the ECR measurement versus time after the alter of the gas partial pressure, and b) the display of the graph of the current passing through the sample against time due to this partial gas change at the time of measurement.

The experimental results and theoretical curves are quite well aligned. The oxygen pressure changes from 0.21 to 0.02 versus time and a conductivity vs time trace on a sample at 700°C after a sudden shift in pO_2 from 0.21 to 0.02 atm is shown in Fig. 2.9a and b, respectively. Fig. 2.10 shows typical conductivity relaxation spectra, as well as the fitting results, for both D and k as the adjustable parameters. The standard deviation (R^2) of the experimental data from the best fit line, which is given as a variation by the fitting software, was used to determine the error in fitted data, depicted on the plots. In comparison to the 04 series, the standard deviation was larger in the 02 series. The possible explanation is that the current changes less than the 04 series when compared to that series' time for the current to normalize upon a rapid change in oxygen partial pressure. Fluctuation in temperature results in an increase of oscillation in current that leads to increase the standard deviation in these samples. The experimental results and theoretical curves are quite well aligned. The determined surface exchange coefficient and oxygen diffusion coefficient were clearly dependent on the various replacement cations with varied doping amounts, as shown in Fig. 2.10.

To test the impact further, all samples were subjected to a second series of conductivity relaxation experiments extending 100 hours. Following the cool-up, electrical conductivity become stable in less than one hours, although the samples were given another couple of hours to equilibrate before the first ECR analysis. Prior to pO_2 variations linked to ECR measurements were enforced, the samples were equilibrated with regard to oxygen at the operating temperature. In general, Ca-doped $LaCoO_3$

samples had higher k and D values than Sr-doped one. (Fig. 2.11). Although, the 0.4 doped LaCoO_3 samples, on the other hand, yielded greater k and D values than the 0.2 doped ones, 0.2 doped series were more stable than those of 0.4 series. D values appeared to be stable during long-term heat treatment. k and D values are influenced by surface chemistry, surface microstructure, dopant ratio, furnace environment, and temperature. In this study, all samples had the same temperature and surrounding environment. In the next chapter, it will be addressed how various variables affect k and D values.

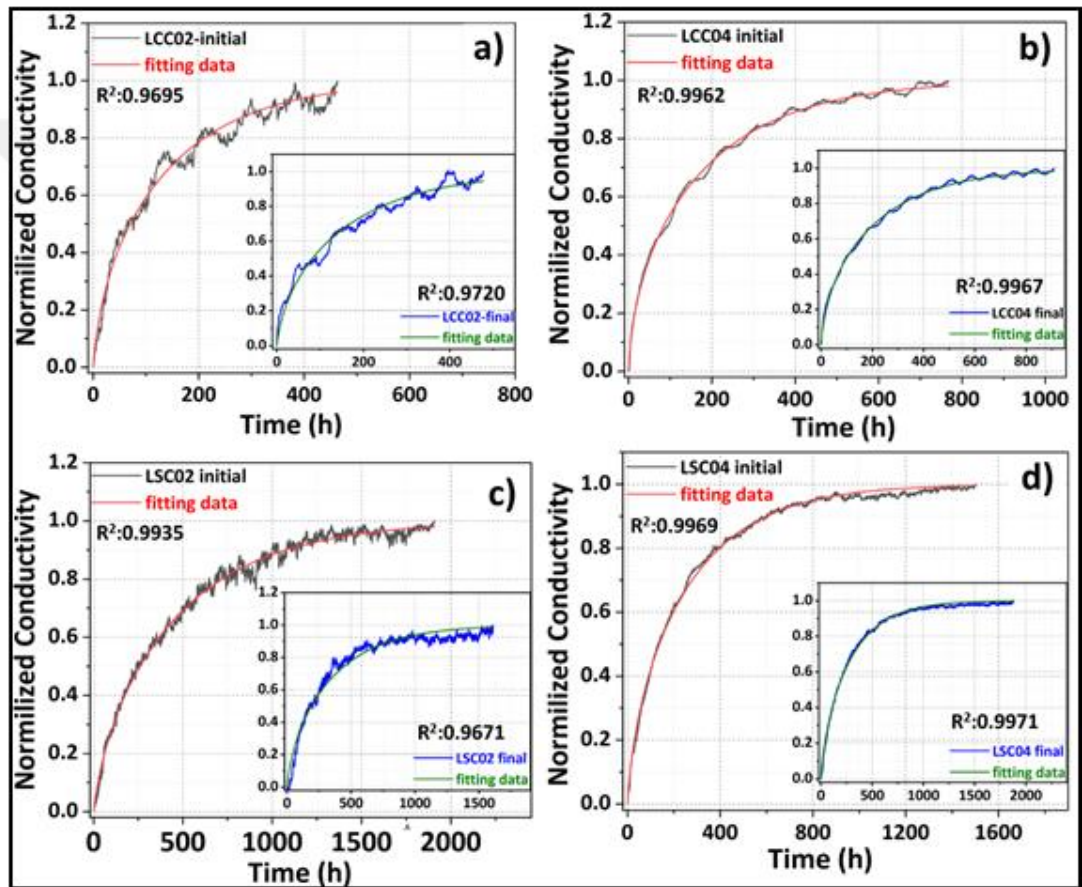


Figure 2.10: Electrical conductivity relaxation (ECR) collected from sample prior to and following (inset) heat treatment, 100 hours subjected to 700 °C, for a) LCC02, b) LCC04, c) LSC04, and d) LSC04 represented in normalized conductivity vs time along with the fitting lines.

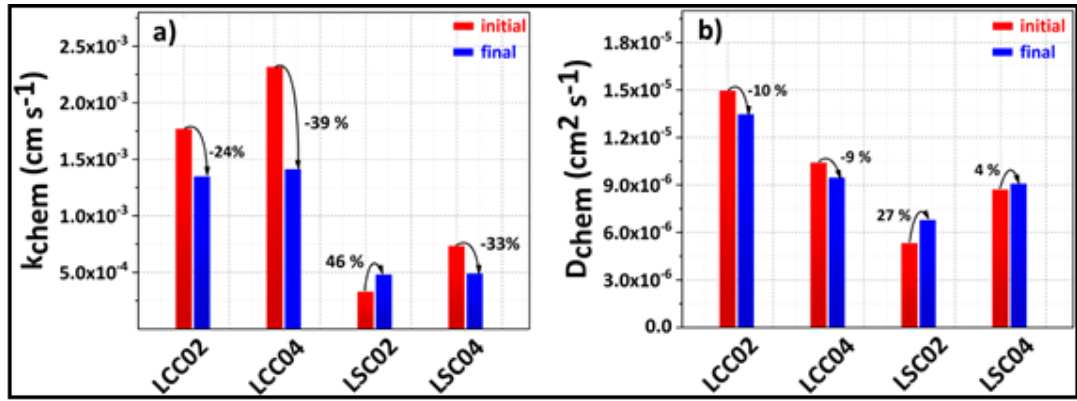


Figure 2.11: Presentation of a) oxygen exchange (k_{chem}) and b) diffusion coefficient (D_{chem}) before and after heat treatment for 100 hours at 700 °C in air, taken from fitting ECR data from all samples.

2.4. The Effect of Surface Evolution on the Long-Term Electrical Conductivity Relaxation

To achieve oxygen reduction reaction (ORR), an oxygen electrode or separator must have strong electrical and ionic conductivity as well as high catalytic activity. Since material supplies an active site for reduction at the surface as well as a pathway for oxygen ion diffusion throughout the bulk, the kinetics of oxygen reduction should be improved. The charge-transfer process takes place at the electrode or membrane surface following oxygen molecule adsorption, converting the adsorbed atoms into oxygen ions that are immediately integrated into the electrode or membrane material (Fig. 2.12). The oxygen surface exchange coefficient k ($cm.s^{-1}$) and the oxygen diffusion coefficient D ($cm^2.s^{-1}$) represent the integration of oxygen ions into the electrode or membrane and the transit of oxygen ions inside the bulk, respectively. Kilner et al. discovered that k and D had a substantial relationship [67]. As a result, it is possible that excellent oxygen ion conductors have strong oxygen exchange characteristics as well. Another study of perovskites indicated that k is influenced by oxygen non-stoichiometry [27]. This means that the existence of vacancies in the oxygen sublattice affects both surface exchange and diffusion. However, in order to achieve high oxygen-exchange activities and oxygen diffusivity, the compositions must have high oxygen-exchange rates for facile integration of oxygen ions into their sites and greater oxygen diffusivity for quick transit of oxygen ions across the lattice. In this study, the examined (La,Ca/Sr)CoO₃ perovskite have MEIC properties. When Ca and Sr cations were doped at varying rates to the electrode or membrane in the

LaCoO₃ perovskite structure, varied k and D values were achieved. Both the k and D values were higher in 04 series than those of 02. This discrepancy can be linked to the high oxygen vacancy ratio. Namely, in order to preserve the charge equilibrium, any replacement of cations in the perovskite ABO₃ with cations that have smaller oxidation state would generate oxygen vacancies. To increase the dopant rate in the structure results in a high oxygen vacancies rate which contribute to high k and D values. For example, doping LaInO₃ with 10 % Sr²⁺ expands the ionic conductivity from 7.3×10^{-5} S/cm for LaInO₃ to 1.8×10^{-3} S/cm for La_{0.9}Sr_{0.1}InO_{2.95} [68]. However, having several vacancies may lead to structural deformations, or the vacancies can potentially become integrated, as in brownmillerite structures [69], which reduces ionic conductivity.

On the other hand, k and D values calculated for Ca doped LaCoO₃ were bigger than those of Sr doped LaCoO₃. This finding may be linked to lower Ca cation mass (40) than that of the Sr (87.62). Mogensen et al. stated that the length of the thermal oscillation of the metal ions is increased when the mass of the metal ions is reduced, which improves the oxygen ionic conductivity [70]. The larger lattice free volume in the unit cell may be the other reason of higher oxygen ion conductivity of the Ca-doped LaCoO₃ perovskite structure than that of the Sr-doped one. Sammells et al. propose the lattice free volume, V_f , which is derived by subtracting the volumes of the component ions from the total volume of the unit cell [71]. Clearly, a greater free volume allows more area for mobile ions to freely jump, hence decreasing the energy barrier for anion movement [72]. Hayashi et al. also established the particular free volume (free volume dividing by the unit cell volume) to evaluate different types of perovskite oxides [73]. To produce greater oxygen ion conductivity, bigger specific free volumes are required.

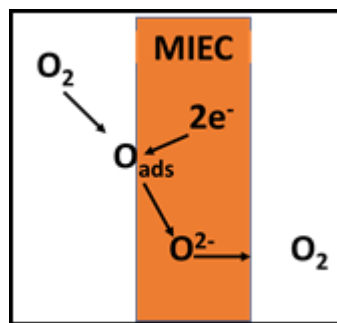


Figure 2.12: Represent the O₂ molecule pathway in air, on the surface and bulk of the oxygen separation membrane.

The crystal structure also influences oxygen conductivity in doped perovskites. Cubic perovskites have the greatest oxygen conductivity which diminishes as the distortion in cubic symmetry increases. Also, deviation from the cubic symmetry leads to stress in the structure. Aforementioned from XRD analysis we observed that LCC02 and LSC pellet consisted solely of the intended rhombohedral structure (PDF: #36-1388) (Fig. 2.1a and c) before and after heat treatment. However, to increase the Ca content to 40% of A-site, on the other hand, endorsed not only the formation of the orthorhombic structure but also with some impurity phases (Fig. 2.1a). Evidently, distortion in LSC peaks was more apparent than in that of LCC02, prior to and following heat treatment. However, the LCC04 peaks showed the lowest distortion. Lower k and D values in Sr doped samples may be related to a larger deviation in cubic symmetry. Mogensen et al. focused for other ways to describe how perovskites deliver ions [70]. They concluded that a lattice with no stress is the most important thing for rapid oxygen ion conductors. Cubic symmetry makes stress-free lattices that make oxygen sites the same [73]. When the lattice distortion gets worse, oxygen sites have a high level of anisotropy, which makes it hard for oxygen ions to move. As the ideal cubic symmetry is moved away from, the conductivity goes down [69]. So, cation replacements must be handled carefully, for example, the difference in diameter between the host atoms and the dopant being replaced must be reduced to a minimum so that the structure does not change too much. A small average values of metal–oxygen bond formation energy [69] of the whole structure and little polarizability of the place to move by the structure [71] are also thought to promote high ionic conductivity.

D values appeared to be stable, on the other hand, during long-term heat treatment. This likely means that during the heat treatment, the chemical composition and overall bulk structures of all samples remained essentially unaltered. Similarly, Tripković et al. stated that bulk properties of $(\text{La}_{0.6}\text{Sr}_{0.4})_{0.99}\text{CoO}_{3-\delta}$ (LSC) and $(\text{La}_{0.6}\text{Sr}_{0.4})_{0.98}\text{FeO}_{3-\delta}$ (LSF), such as electrical conductivity and the oxygen chemical diffusion coefficient stay unchanged even following 250 hours at 650 °C [53].

Overall, surface elements and surface chemistry have a greater impact on the k value. We found that impure CaO and CoO_x phases precipitated on the grain boundaries on the surface and bulk of the LCC04 sample prior to and after heat treatment, as described above, as a result of XRD, EDS mapping, and BSC analyses.

However, the grains of these precipitates enlarged following heat treatment, this leads to a slightly reduction of ORR that results in a decrease in k value, because the active phase ratio on the surface is reduced slightly. Another crucial point to note is that, as was already indicated in the XPS analysis, following heat treatment, $\text{Ca}_{\text{non-lattice}}$ and $\text{O}_{\text{surface}}$ ratios, which generate an isolating CaO layer on the surface and reduce ORR by trapped the active $\text{O}_{\text{terminations}}$, almost did not change.

On the other hand, the BSC analysis revealed that there were also point-shaped particles that were spread randomly, and particularly transparent amorphous-like platelets that partly covered the grain surfaces and multiplied over the heat treatment period in LSC04. However, since these platelets cover the surface of the Sr-doped LaCoO_3 phase, the active phase ratio on the surface is lowered, which likely results in a drop of ORR and a fall in k value. This finding may be related to what the XPS study previously showed, which is that after heat treatment, $\text{Sr}_{\text{non-lattice}}$ and $\text{O}_{\text{surface}}$ ratio, which produce an isolating SrO layer on the surface and lower ORR by trapping the active $\text{O}_{\text{terminations}}$, significantly increased.

2.5. Summary

MIEC perovskites are a desirable electrode material for intermediate temperature (in the range of 500-700°C) solid oxide fuel cells (IT-SOFC) and oxygen separation membrane operations due to their high oxygen reduction reaction (ORR) electro-catalytic performance, electronic and ionic conductivities, and compatibility with other cell components. By appropriately substituting alkaline-earth metals, the transport properties of these materials, including $(\text{La}, \text{A})(\text{Co}, \text{Fe})\text{O}_3$ ($\text{A} = \text{Sr}, \text{Ca}, \text{Ba}$), are significantly enhanced. Though, when these materials are exposed to high temperatures, the surface physical and chemical properties and kinetics of the ORR significantly decline due to the AO-like insulated phases at the surface. Such oxides block paths for oxygen exchange and charge transport, which causes a lack of dopants close to the surface. Electrode or membrane instability results from electrochemical degradation over time. In this study, we have concentrated on the impact of phase, microstructure, and surface chemistry evolving on oxygen exchange and diffusion coefficient of the $(\text{La}, \text{Ca})\text{CoO}_3$ (LCC) and $(\text{La}, \text{Sr})\text{CoO}_3$ (LSC) samples that were made

from the polymeric precursor of metal-nitrate salt at 1200 °, before and after subjected to 700 °C for 100 hours, in stagnant air.

The oxygen exchange coefficient (k_{chem}) and diffusion coefficient (D_{chem}) values are more influenced by surface chemistry and surface element distribution. From the X-ray diffraction (XRD), energy-dispersive x-ray spectroscopy (EDS) mapping, and scanning electron microscopy (SEM) BSE investigations, we discovered that impure CaO and CoOx phases precipitated on the grain boundaries on the surface and bulk of the LCC04 sample before and after heat treatment. However, the heat treatment of these precipitates caused the grains to grow, which causes a minor drop in ORR and a consequent fall in k_{chem} value since the active phase ratio on the surface is also somewhat lowered. Another important thing to keep in mind is that, as presented by the X-ray photoelectron spectroscopy (XPS) study, the $\text{Ca}_{\text{non-lattice}}$ and $\text{O}_{\text{surface}}$ ratios, which provide an isolating CaO layer on the surface and lower ORR by trapping the active O terminations, virtually did not alter as a result of heat treatment.

However, the BSE analysis also found particles that were dispersed randomly, and in particular translucent amorphous-like platelets that partially covered the grain surfaces and proliferated during the heat treatment time in LSC04. However, since these platelets cover the Sr-doped LaCoO_3 phase's surface, the active phase ratio is reduced, which is probably what causes the ORR and k value to decrease. The X-ray photoelectron spectroscopy (XPS) analysis revealed that following heat treatment, $\text{Sr}_{\text{non-lattice}}$ and $\text{O}_{\text{surface}}$ ratio, which generate an isolating SrO layer on the surface and reduce ORR by trapping the active O terminations, dramatically increased.

3. THE LONG TIME EFFICIENCY AND STABILITY OF THIN FILM (La,Ca)CoO₃ SOFC CATHODES: ASSOCIATION OF PHASE, MICROSTRUCTURE, AND SURFACE CHEMISTRY DEVELOPMENT

Abstract. The present work focused on the prolonged electrochemical efficiency of thin films that obtained from polymeric precursor of LaCoO₃ substituted with Ca²⁺ (LCC), rather than the larger Sr²⁺, which accumulates at the cathode surface and forms oxides/hydroxides. According to the findings, pre-calcination at 800 °C (20 % Ca-doped LCC-800) led to greater electrochemical performance but weaker prolonged stability than pre-calcination at 700 °C (20 % Ca-doped LCC -700) or 900 °C (20 % Ca-doped LCC -900). Increased Ca²⁺ concentration (40 % Ca-doped LCC -800) resulted in a small increase in initial electrochemical performance, but at the expense of significantly reduced long-term stability. The results of the microstructural evolution assessments indicated that, while it had a certain effect on the beginning and extended efficiency of LCC cathodes, the most crucial thing to take into account was not it. According to the results of XPS evaluations, the creation of CaO and CaO + La₂O₃ films at the 20 % Ca-doped LCC-800 and 40 % Ca-doped LCC -800 surfaces, respectively, associated with reductions in the percentage composition of adsorbed oxygen kind (relating to surface oxygen defects), induced an accelerated performance loss in these examples than in samples that had been pre-calcined at 700 or 900 °C. It was only after a long period of operation that the surface ion rate of 20 % Ca-doped LCC-700 reached near to that predicted by theoretical one.

3.1. Introduction

Extended operation degradation in solid oxide fuel cells (SOFCs) must be minimized if they are to be economically feasible. Working temperatures in the 500 to 700°C range are generally recommended for prolonged permanence of SOFC equipment in order to reduce degradation processes as the corrosion of steel connections and grain densification, which occur at 800 °C [74]-[76]. In contrast, lowering the operating temperature also causes a slowdown in electrochemical

activities, in particular at the SOFC cathode's oxygen reduction reaction (ORR) [75],[76]. As a result, the improvement of cathode efficiency at 500-700 °C has received considerable attention. At moderate temperatures, mixed ionic-electronic conducting (MIEC) electrode materials as well as elevated oxygen surface exchange coefficients, including $\text{La}_x\text{Sr}_{1-x}\text{CoO}_{3-\delta}$ (LSC), have demonstrated reduced electrode resistances [77]. For instance, Januschewsky et al. [78] stated a cathode resistance of 0.1 cm^2 at 600 °C with LSC electrodes created utilizing pulsed laser deposition (PLD), whereas Evans et al. [79] obtained 3.7 cm^2 at 550 °C. Instead, Benel et al.[79], [79] produced LCS electrodes on YSZ electrolyte covered by a CGO interlayer using a spray pyrolysis technique and achieved an electrode polarization resistance of 0.32 cm^2 at 650 °C. Hayd et al. [80] devised a rather reasonably priced way to fabricating LSC electrodes, reporting electrode resistances as small as 0.023 cm^2 at 600 °C in samples obtained by deposition process.

Notwithstanding its excellent ORR properties, the advantage of LSC electrodes did not exhibit prolonged stability [81]-[83]. Cai et al. [64] demonstrated that PLD-grown LSC cathodes display considerable Sr accumulation on the surface, generating $\text{SrO}/\text{Sr}(\text{OH})_2$ pairs and hence inhibiting electro-chemically active areas. Lee et al. [36] suggested that the Sr accumulation at perovskite type cathode surfaces was prompted by i) the elastic strain induced via Sr^{2+} enormously sizable ionic radius comparing to the host cation, La^{3+} , and ii) the electrostatic interaction between the positively charged oxygen vacancies ($V_{\text{O}}^{\bullet}$) display at the surface and the negative charges Sr'_{La} species.

To make IT-SOFCs practical, a great specific surface area LaCoO_3 electrode generated economically and with adequate long-term stability is very essential. To inhibit the substituted A-site atom from accumulating at the top surface of the perovskite electrodes over time, a divalent cation that has a diameter close to that of the host (La^{3+}), including Ca^{2+} , must be utilized instead of the normally employed Sr^{2+} . The purpose of this study is to construct Ca^{2+} substituted LaCoO_3 (LCC) cathodes with improved electrochemical performance using a reasonably priced polymeric precursor coating technique and to understand the reasons underlying their extended-time performance reduction, if there are any. The fabrication and electrical conductivity of Ca^{2+} substituted LaCoO_3 (LCC) have already been explored in the literature [84],[85], also its mechanical behavior [86]. Furthermore, the electrochemical performance of LCC was examined solely in alkaline solutions [87], and to our knowledge, no

investigations on the extended-time strength of LCC under SOFC electrode settings occur.

In this chapter, we discuss on the microstructure, phase composition, and surface chemistry changes in $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ (LCC) after prolonged subjected to IT-SOFC requirements (i.e., 700 °C). We provide a link between these features and the extended time stability of LCC's ORR performance for the first time in the literature.

3.2. Sample Preparation

Die-pressed yttria stabilized zirconia (YSZ) powders (TOSOH, TZ-8Y) were sintered at 1400°C for 4 hours in atmosphere to create dense electrolyte substrates. To eliminate the production of undesirable phases at the YSZ/ $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ interface, a dense YSZ ceramic was covered with just a samaria substituted ceria (SDC) film by polymeric precursor deposition. To create a polymeric SDC precursor, distilled water and ethylene glycol were dissolved in $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar, > 99.9 %) and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar, > 99.9 %) salts. The proportion of Sm to Ce cations was maintained constant at 1:1, whereas the mole fraction of the positive ions to ethylene glycol was maintained at 0.05:1. At 80 °C, this aqueous solution was agitated while waiting for the entire water is removed and polymerization happened. The mixture was subsequently diluted 1:1 by 2-butoxyethanol and ethylene glycol to decrease the total surface stress and so increase substrate wetting. The polymeric SDC precursors were placed on top of a YSZ pellet surface through a spin coating method (VTC-100 Vacuum Spin Coater, 3000 rpm). To vaporize the diluent and eliminate the organics, the wet layer was heated at 350 °C. The spin-coating/break-up operations were repeated period take five circles to completely coat the YSZ substrate surface. SDC layers were grown on YSZ pellets surface and then pre-calcined for 3 hours at 800 °C.

The LCC thin film electrodes were similarly fabricated using polymeric precursor deposition. Polymeric LCC precursors have being produced via agitating clear mixture of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Fluka, >99%), $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Merck, >99%), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar, > 99.9%) liquids, distilled H_2O , and ethylene glycol at 80 °C to promote polymerization. The mole fraction of the metal ions to the ethylene glycol remained at 0.05:1, and 2-butoxyethanol was supplied to enhance surface wetting. Polymeric LCC precursors were coated on two sides of SDC/YSZ/SDC pellet

surfaces using spin coater at 3000 rpm and dried at 350 °C on a hot plate. Following optimization (data not shown), it was established that coatings formed by repetition the spinning/dry up periods take 30 times (equivalent to a typical coating width of approximately 4 m in all experiments) produced the smallest cathode resistances. As a result, all the LCC cathodes used in this study were constructed in this manner. Three hours at 700, 800, or 900 °C were used to heat treat the achieved symmetrical LCC/SDC/YSZ/SDC/LCC half-cells architecture.

3.2.1. Structure, Microstructure and Surface Chemistry Characterization

To characterize the phase development of polymeric precursor-originated LCC electrodes over time, X-ray diffraction (XRD) studies were conducted before to and following a 100-hour subjected to 700 °C in atmosphere. To prevent any contribution from the substrates to the XRD pattern, the current investigation used LCC powders produced by calcining gels prepared by polymeric precursors at 700, 800, or 900 °C for 3 hours then following prolonged subjected to 700 °C. A copper radiation source (CuK1, $\lambda = 0.15406$ nm, Rigaku Dmax 2200) was used to perform XRD examinations in the 2θ range of 20-80°.

The microstructure of LCC thin films was monitored throughout a 100-hour subjected to 700°C using scanning electron microscopy (SEM, Philips XL30 SFEG) with secondary electron image. Total pore perimeter per-image area (TPPA) is indeed a semi-numerical measure of the electro-chemically active surface area of LCC cathodes that was obtained for every sample before and after sufficient period of time using ImageJ image processing software.

X-ray photoelectron spectroscopy (XPS) has been employed to detect variations in the top surface constituent/chemical composition of LCC electrodes after prolonged time pre-calcined at 700 °C. The XPS studies were conducted in an ultrahigh vacuum environment with a base pressure of 10⁻¹⁰ mbar. The chamber is integrated by a SPECS Phoibos 150 hemispherical charged-particle analyzer and a 300 W SPECS X-ray origin XR 50. The XPS data was analyzed using an Al K (1486.61 eV) X-ray sources in the fixed analyzer transmission mode at a 50 eV pass energy. The photoemission lines of Au 4f_{7/2} (84.1 eV) were utilized to calibrate the spectrometer in connection with the Fermi level. Au4f_{7/2} had a full width at half-maximum (FWHM)

of 1.5 eV. After subtracting a Shirley background function [88], the XPS records were mounted on a pseudo-voight function employing a mix of Lorentzian and gaussian distributions of around 30% and 70%, respectively.

3.2.2. The Analysis of Electrochemical Performance

Electrochemical impedance spectroscopy (EIS) data were measured at 500-700 °C in atmosphere (Biologic, SP150), in a frequencies the interval of 50 mHz - 50 kHz, with only an applied voltage of 10 mV, according to open circuit circumstances. Such parameters were measured employing cells with such a geometric size of 0.5 x 0.5 cm² and electrodes with an area of 0.25 cm². Intermittent EIS analyses were utilized to determine the extended time stability of the LCC cathodes following a 100-hour subjected to 700°C. To match the acquired EIS data using the EC-Lab program, an analogous circuit type was employed. To conduct the EIS analyses, a proprietary Ag current collector paste was put on face of a symmetrical half-cell, lead to an Ag/LCC/SDC/YSZ/SDC/LCC/Ag construction. To use a Ceramabond 552 (Aremco) adhesive paste, silver wires were connected to the current collector films.

3.3. Results and Discussion

3.3.1. Extended-Time Stability of the Electrochemical Performance

On symmetrical half-cells, electrochemical impedance spectroscopy (EIS) data were measured to examine the variations in the oxygen reduction efficiency of the LCC air electrodes for a 100-hour duration at 700 °C. The Nyquist and Bode graphs produced from 20 % doped Ca LCC pre-calcined at 700, 800, and 900 °C (shortened as 20 % doped Ca LCC-700, 20 % doped Ca LCC -800, and 20 % doped Ca LCC - 900) and from 40 % doped Ca LCC pre-calcined at 800 °C (20 % doped Ca LCC - 800), gathered at 700 °C, are presented in Figure 3.1a and the accompanying insertion. The ohmic losses resulting mostly from ionic transportation through the SDC/YSZ substrate were deleted from graphs to facilitate data comparability (Fig. 3.1a). Since all samples in Fig. 3.1a exhibit just one semi-circle, an equivalent circuit made up of two resistors, one of them is connected in collinear to a constant phase component

($R_{ohmic}-R_{LF}/Q_{LF}$, Fig. 3.1a) was employed to match the EIS records. R_{ohmic} and R_{LF} denote, correspondingly, the ohmic and polarization resistances of two cathodes with low point summit frequencies. Divide the final amount by two to attain the polarization resistance of a single air electrode ($ASR_{cathode}$).

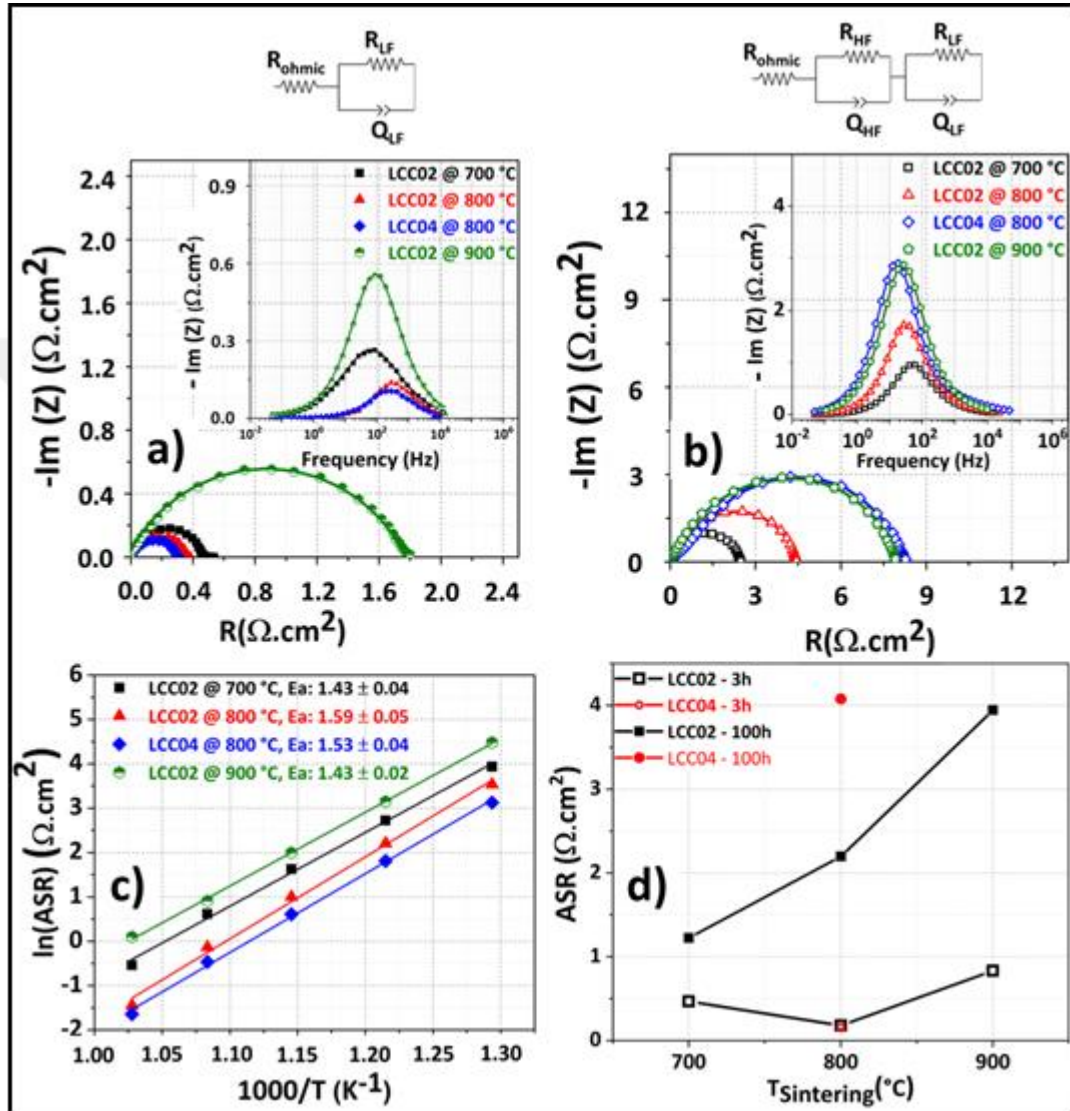


Figure 3.1: a) and b) Bode and Nyquist graphs of electrochemical impedance spectroscopy information taken from all specimens prior to and following subjected to 700 °C, respectively, together with the fits depicted in solid lines and the equivalent circuit model being utilized to fit the records, c) Temperature dependency of the area specific polarization resistances of all specimens; and d) Variations in the area specific polarization resistance for electrode with heat treatment temperature before and after 100 hours at 700 °C in atmosphere.

Fig. 3.1b shows the EIS data gathered from all samples following a 100-hour subjected to 700 °C. The Nyquist and Bode graphs indicate that $ASR_{cathode}$ values grew

dramatically in all samples, whereas summit frequencies declined (Fig. 3.1b). Acceptable fits of equivalent circuits to the EIS data recorded following prolonged annealing of the samples were possible only when an equivalent circuit comprised of RQ elements ($R_{ohmic} - R_{HF}/Q_{HF} - R_{LF}/Q_{LF}$) relating to one high-frequency range and one low-frequency range process was utilized (Fig. 3.1b).

Resistance, capacitance, and peak frequency quantities retrieved from equivalent circuit fittings are listed in Table I. Entire samples had ohmic resistances in the interval of $5 \Omega \cdot \text{cm}^2$, which is nearly equivalent to the resistance to ionic transmission thorough a 0.8 mm thick YSZ substrate at 700 °C. The capacitance (C) amounts were calculated by substituting $C = (R^{(1-n)} Q)^{(1/n)}$ for the resistance (R) and constant phase component (Q) fitting parameters, where n is the degree of circularity, with values scale from zero to 1.

The oxygen reduction ratio at the initial of the experiment is determined by a single electrochemical process happening at low frequencies in all samples. After extensive annealing, an extra high frequency process emerges observable, but it contributes only a modest amount to the total impedance (less than 15%). Capacitance levels in the 10^{-3} F/cm^2 range are related with the dominating low frequency process (Table I). This number is too low to indicate lattice contribution in the oxygen reduction process, which would result in faradaic capacitances to as many as 1 Farad/cm² [16],[89]. On the other side, oxygen adsorption on the surfaces of Pt and (La, Sr)FeO₃ cathodes was connected with capacitances in the 10^{-3} F/cm^2 array [16],[90], which is most certainly the situation here. Oxygen reduction at (La, Sr)CoO₃ cathode has also been shown to be constrained by surface oxygen exchange [91],[92].

After 30 minutes of subjected to the prolonged heat treatment temperature of 700 °C, activation energies ranging from 1.43 to 1.59 eV were obtained by analyzing the temperature dependency of $ASR_{cathode}$ values (equivalent to half of R_{LF}) measured from all samples (Fig. 3.1c). There is no published research on the electrochemical efficiency of LCC air electrodes. Moreover, contradictory $ASR_{cathode}$ activation energy values for LSC air electrodes have been published, which may be deemed similar to the LCC electrode used in this work. Baumann et al. observed a 1.3 eV activation energy for La_{0.6}Sr_{0.4}CoO₃ electrodes produced through pulsed laser deposition (PLD) [93]. Peters et al., and from the other hand, achieved a 1.07 eV activation energy for La_{0.5}Sr_{0.5}CoO₃ thin film electrodes produced by metal organic coating [94]. Given that

the rate-limiting oxygen reduction process was ascribed to oxygen exchange at the surface both in the LSC and the current LCC experiments, the dispersed activation energy values could be attributed to various cathode manufacturing processes. The differing surface chemistries of the PLD and metal organic precursor-originated electrodes are likely to have generated in distinct oxygen exchange activation energies at the surface.

Table 3.1: Resistance, peak frequency, capacitance, and "n" values were retrieved from fits to EIS data acquired from the whole specimens prior to and during prolonged operation at 700°C in atmosphere.

	R_{ohmic} ($\Omega.cm^2$)	R_{LF} ($\Omega.cm^2$)	R_{HF} ($\Omega.cm^2$)	C_{LF} (F/cm^2)	C_{HF} (F/cm^2)	$f_{LF, summit}$ (Hz)	$f_{HF, summit}$ (Hz)	n_{LF}	n_{HF}
LCC02 700-3h	5.17	1.01	-	3.75×10^{-3}	-	42	-	0.93	-
LCC02 700-100h	4.97	0.38	2.13	1.5×10^{-3}	1.72×10^{-3}	307.6	1504.75	0.89	0.5
LCC02 800-3h	5.13	0.36	-	1.37×10^{-3}	-	326	-	0.83	-
LCC02 800-100h	6.02	0.51	3.93	1.3×10^{-3}	1.0×10^{-3}	185.31	1822.57	0.89	0.63
LCC04 800-3h	4.94	0.30	-	2.02×10^{-3}	-	260	-	0.8	-
LCC04 800-100h	6.85	0.92	7.38	1.3×10^{-3}	1.6×10^{-4}	101.08	6525.71	0.84	0.54
LCC02 900-3h	4.94	1.80	-	9.80×10^{-4}	-	90	-	0.71	-
LCC02 900-100h	5.68	1.06	6.83	0.9×10^{-3}	1.7×10^{-3}	150.33	533.48	0.84	0.66

The high-frequency process observed in EIS records after prolonged heat treatment at 700 °C is closely related with capacitance levels in the 10^{-4} - 10^{-3} F/cm² array (Table I). High frequency activities have been attributed to oxygen ion transport at the cathode/electrolyte boundary in investigations on La_{1-x}Sr_xCo_{1-x}Fe_xO₃ and La_{1-x}Sr_xCoO₃ cathodes with capacitances in the 10^{-5} to 10^{-2} F/cm² array[95],[96]. Other side, a current research on La_{1-x}Sr_xFeO₃ cathodes ascribed the high frequency process resulting in a capacitance of about 10^{-3} F/cm² to oxygen diffusion at the cathode surface [90]. Considering that oxygen diffusion is rapid in LCC electrodes (as it is in

(La,Sr)CoO₃), it is regarded further probable that the high-frequency impedance circle is caused by oxygen ion migration at the cathode/substrate interface.

The data for electrode ASR of LCC at heat treatment temperature following calcination at various temperatures are shown in Fig. 3.1d. Obviously, the pre-calcined LCC02 electrode with an ASR_{cathode} value of 0.18 Ω.cm² had the smallest ASR_{cathode} value among the LCC02 electrodes. Raising the Ca²⁺ concentration (40 % Ca doped LCC-800) led in a modest decrease in the ASR_{cathode} value, down close to 0.15 Ω.cm², attaining the European SOFC600 project's goal cathode polarization resistance value of 0.15 Ω.cm² [97]. In light of current study, in the literature on the impact of Sr accumulation at the top surface of LSC electrodes [64], one of the primary objectives of the current study is to assess the extended-time stability of LaCoO₃ substituted with Ca²⁺ rather than the greater Sr²⁺. The Fig. 3.2a–d illustrate the variations in ASR values caused by high and low frequency processes, and the overall ASR, for 20 % Ca doped LCC-700, 20 % Ca doped LCC-800, 40 % Ca doped LCC-800, and 20 % Ca doped LCC-900, respectively. The high frequency process appears obvious in all samples following 20-30 hours of subjected to 700 °C and is very constant over the course of the prolonged studies (Fig. 3.2a-d). As previously indicated, the high frequency procedure has a negligible effect on the entire impedance spectrum, and hence the total resistance loss trend in all samples follows the ASR_{LF} profile (Fig. 3.2a-d). The comparison in Fig. 3.2e shows the variations in the total ASR after extended subject to 700 °C. To appropriately comparison performing degradation ratios, it is necessary to assess variations in the cathode resistance unconnected of the beginning performing. To this aim, the total ASR values collected over the prolonged testing period were matched to the sample's original ASR value (Fig. 3.2d). Clearly, 20 % Ca doped LCC-700 and 20 % Ca doped LCC-900 degraded at similar ratio, however 20 % Ca doped LCC-800 increased ASR_{cathode} at a quicker rate (Fig. 3.2d). By increasing the Ca²⁺ concentration from x=0.2 to 0.4 in pre-calcined LCC cathodes at 800 °C, the ASR_{cathode} degradation rate was considerably increased (Fig. 3.2d).

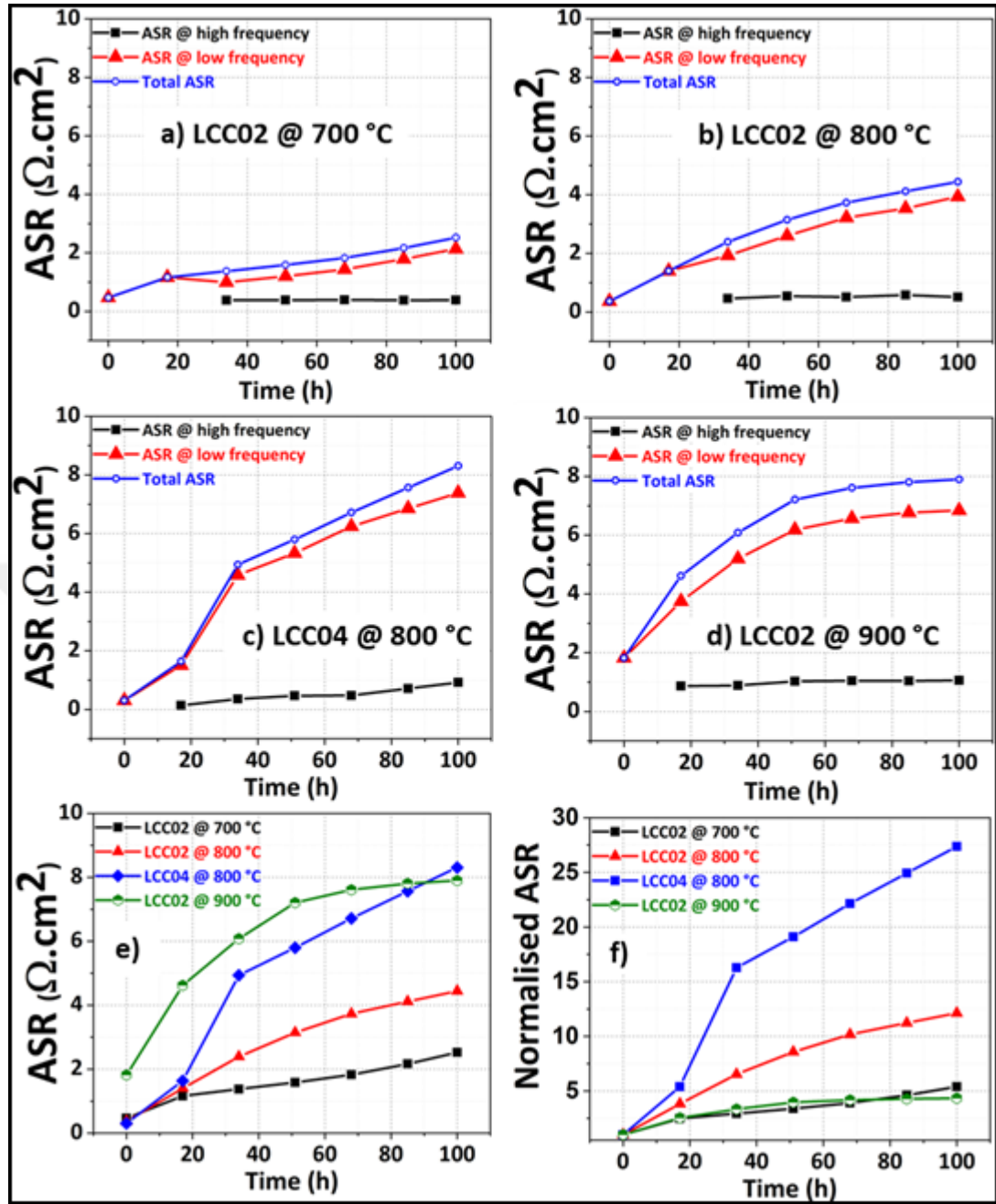


Figure 3.2: Variations in the area specific polarization resistance (ASR), which is recovered via fitted as high or low frequency, of a) 20 % Ca doped LCC-700, b) 20 % Ca doped LCC-800, c) 40 % Ca doped LCC-800, and d) 20 % Ca doped LCC-900, e) the actual ASR, and f) the normalized area ASR results of all specimens after extended subjected to 700 °C in atmosphere.

3.3.2. Phase Evolution

To decide exactly if the polymeric precursor way produced the intended rhombohedral phase and to monitor phase development over time at the upper extend of the intermediate temperature (IT) process about to 700 °C, X-ray diffraction (XRD) findings were conducted on gels dehydrated from the polymeric LCC precursors upon thermal treatment (Fig. 3.3). Heat treatment of dried 20 % Ca doped LCC gels at 700 °C resulted in the production of the anticipated rhombohedral structure (PDF:#36-1388), as well as certain undesirable phases (Fig. 3.3a). A more comprehensive investigation indicated that one of these undesirable phases was cubic Co_3O_4 (Fig. 3.3b, PDF:#42-1467). Moreover, the peak at XRD pattern collected from 20% Ca doped LCC-700 in its as-produced form.

$2\theta=31.92^\circ$ did not correspond to any of the chemicals in our database (Fig. 3.3b). Nonetheless, it has been observed that in the event of Sr-substituted LaCoO_3 , along with the rhombohedral $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ structure, Co_3O_4 interacted with a tetragonal $(\text{La,Sr})_2\text{CoO}_4$ Ruddlesden-Popper phase [77]. Given that the greatest sharp peaks of La_2CoO_4 takes place at $2\theta = 31.36^\circ$ (PDF:#34-1081) and that substituting the A-site with Ca – a positive ion with a lower ionic strength than La – shifts the peak to upper 2θ degrees, the peak at $2\theta = 31.92^\circ$ is linked to the tetragonal $(\text{La,Ca})_2\text{CoO}_4$ Ruddlesden-Popper phase (Fig. 3.3b). By contrast, calcination at 800 and 900 °C formed just the rhombohedral phase (Fig. 3.3a). Contrary to what we saw here, the tetragonal Ruddlesden-Popper phase is anticipated to occur at elevated temperatures in ABO_3 -type perovskite materials [97]. This mismatch is most likely due to the production approach based on polymeric precursors that we use here. Hayd et al. also detected the formation of the Ruddlesden-Popper phase during a low-temperature fabrication of La – Sr – Co – O cathodes with metal organic precursors [80]. The phase diagrams they gained indicated that the Ruddlesden-Popper phase formed more readily under conditions of high temperature and low $p\text{O}_2$. They indicated that the low $p\text{O}_2$ levels that developed locally near the deposited layer as a result of organic breakdown triggered the creation of the Ruddlesden-Popper phase [80], which is probably the scenario here.

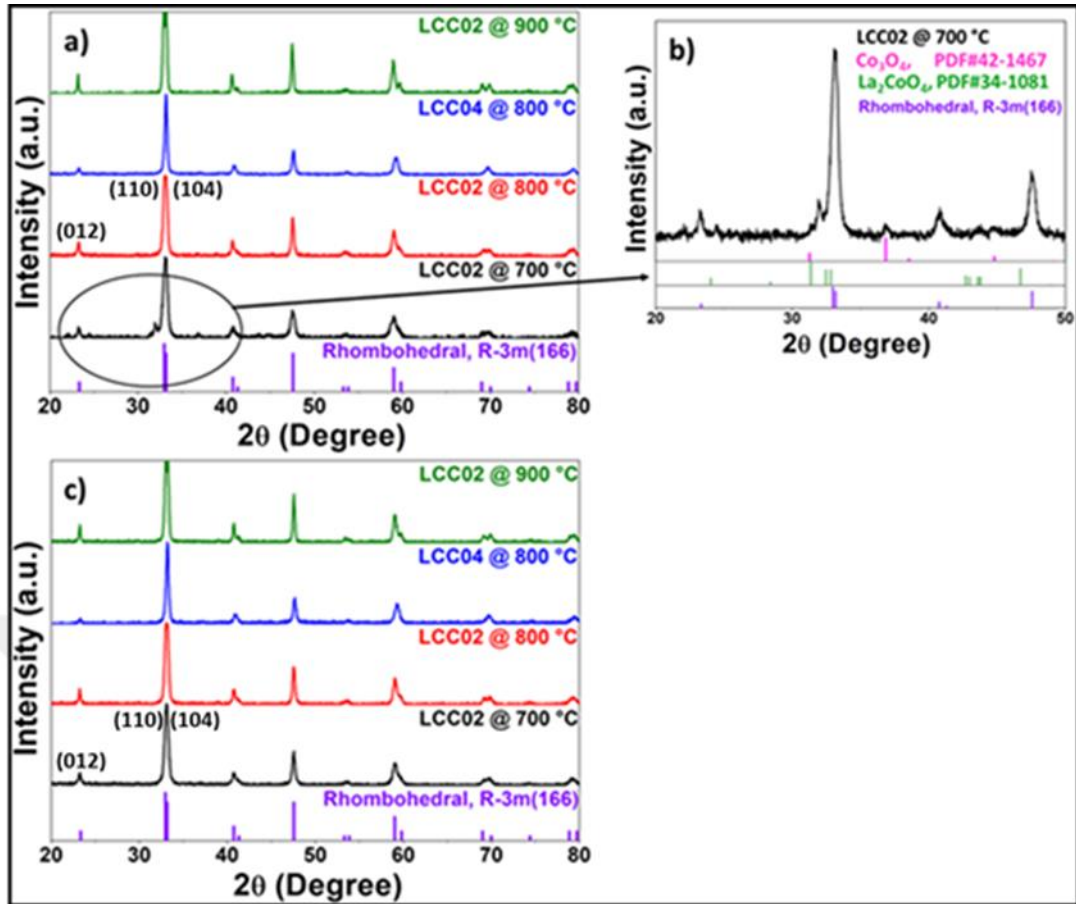


Figure 3.3: X-ray diffraction (XRD) profiles of all specimens acquired a) before, c) following heat treatment at 700°C for 100 hours in atmosphere, and b) a focused inspection of the XRD arrangement collected from 20 % Ca doped LCC-700 in its as-constructed form.

Long term subjected to 700°C (100 hours), ended up 20 % Ca doped LCC electrodes with the rhombohedral structure, irrespective the calcination temperature (Fig. 3.3c). Following extended time subjected to 700 °C, the phase change of 40 % Ca doped LCC-800 remained stable to that of 20 % Ca doped LCC-800, i.e., clear rhombohedral structure was seen not only before but also following to prolonged time subjected to heat treatment temperature (Fig. 3.3a and c).

In general, it is obvious that the only phase transitions occurs in LCC02-700 during prolonged operation, when minor quantities of $(\text{La,Ca})_2\text{CoO}_4$ and CoO_x phases existed at beginning dissipate to provide a fully rhombohedral structure (Fig. 3.3). The presence of rhombohedral ABO_3 and minor quantities of tetragonal A_2BO_4 phases has been shown to enhance the oxygen reduction efficiency of perovskite-type electrodes in the literature [97]-[100]. The strong electrochemical activity of $\text{ABO}_3/\text{A}_2\text{BO}_4$ patterned electrode has been attributed to the exceptionally rapid

oxygen reduction occurring at their phase boundaries [97]. However, this improvement was observed to be confined to the presence of trace levels of A_2BO_4 phase [101], whereas excessive concentrations of A_2BO_4 were revealed to inhibit oxygen reduction activity [101]. Given that calcination at 700 °C produced trace quantities of tetragonal A_2BO_4 phase in addition to the rhombohedral ABO_3 matrix, but not at elevated temperature, it may be concluded that 700 °C is advantageous for achieving high electrochemical activity. Additionally, the elimination of the tetragonal A_2BO_4 with prolonged subjected to 700 °C must result in a loss of extremely active ABO_3/A_2BO_4 phase boundaries, resulting in some electrochemical activity loss. Moreover, the fact that 20 % Ca doped LCC-800 had more performance than 20 % Ca doped LCC-700 (Fig. 3.1a) indicates that the influence of phase composition alone on electrochemical performance and stability is not simple to comprehend. Therefore, more clarification is to be offered later in the text in combination with the microstructure and surface chemical development data.

3.3.3. Microstructural Evolution

Microstructure development of the LCC electrodes can have a significant effect on their prolonged electrochemical performance stability. For instance, Wang et al. [102] demonstrated that the performance degradation of SOFC electrodes fabricated by infiltration of $La_{1-x}Sr_xFeO_3$ (LSF, another MIEC electrocatalyst) into permeable YSZ scaffolds over a extended period of operation at 700 °C was closely associated to sintering-provoked loss in LSF surface area. SEM analysis of all samples exposed to 700 °C for varied periods was used to examine the impact of microstructural development on the prolonged performance loss efficiency of the LCC cathodes.

The microstructures of LCC electrodes before and after a prolonged time subjected to 700°C are shown in Fig. 3.4. According to an examination of the LCC02 samples, raising the calcination temperature ended up a denser initial microstructure with larger grains (Fig. 3.4a, c and g). On the other hand, raising the Ca concentration ended up a reduction in the mean grain dimension of LCC cathodes calcined at 800 °C (Fig. 3.4c and e). Generally, extended time subjected to 700 °C results in the

production of coarser and denser microstructures, irrespective of the Ca concentration or pre-calcination temperature (Fig. 3.4b, d, f and h).

Whereas the SEM study in Fig. 3.4 gives some insight into the microstructural development, it does not ensure enough evidence to provide an obvious evaluation of its effect on performing stability. To get a better interpretation of the amount of microstructural change and its potential influence on electrochemical performance, ImageJ software was used to undertake semi-measurable analysis of SEM pictures taken by the LCC cathodes before and following prolonged operation time. More precisely, we computed the total perimeter per image area (TPPA), which is indicative of the surface area per volume in two dimensions, supposing that oxygen reduction is confined to oxygen exchange at the cathode surface in lanthanum cobaltite class cathodes [91],[93],[94]. Fig. 3.5a and b illustrate the pore detection technique using a specimen SEM image and its binary representation. Fig. 3.5c illustrates the evolution of the calculated TPPA values over time at 700 °C for the entire LCC electrodes. Apparently, raising the annealing temperature ended up smaller TPPA values in 20 % Ca doped LCC samples, however an analysis of 20 % Ca doped LCC-800 and 40 % Ca doped LCC-800 indicates comparable original TPPA values (Fig. 3.5c).

When exposed to 700 °C for an extended period, 20 % Ca doped LCC cathodes revealed analogous TPPA loss ratios in the 52-62 % interval (Fig. 3.5c). Whereas 40 % Ca doped LCC-800 had a much more stable microstructure than 20 % Ca doped LCC electrodes, this result indicates that Ca concentration has a greater effect on microstructural stability during prolonged operation time than calcination temperature (Fig. 3.5c).

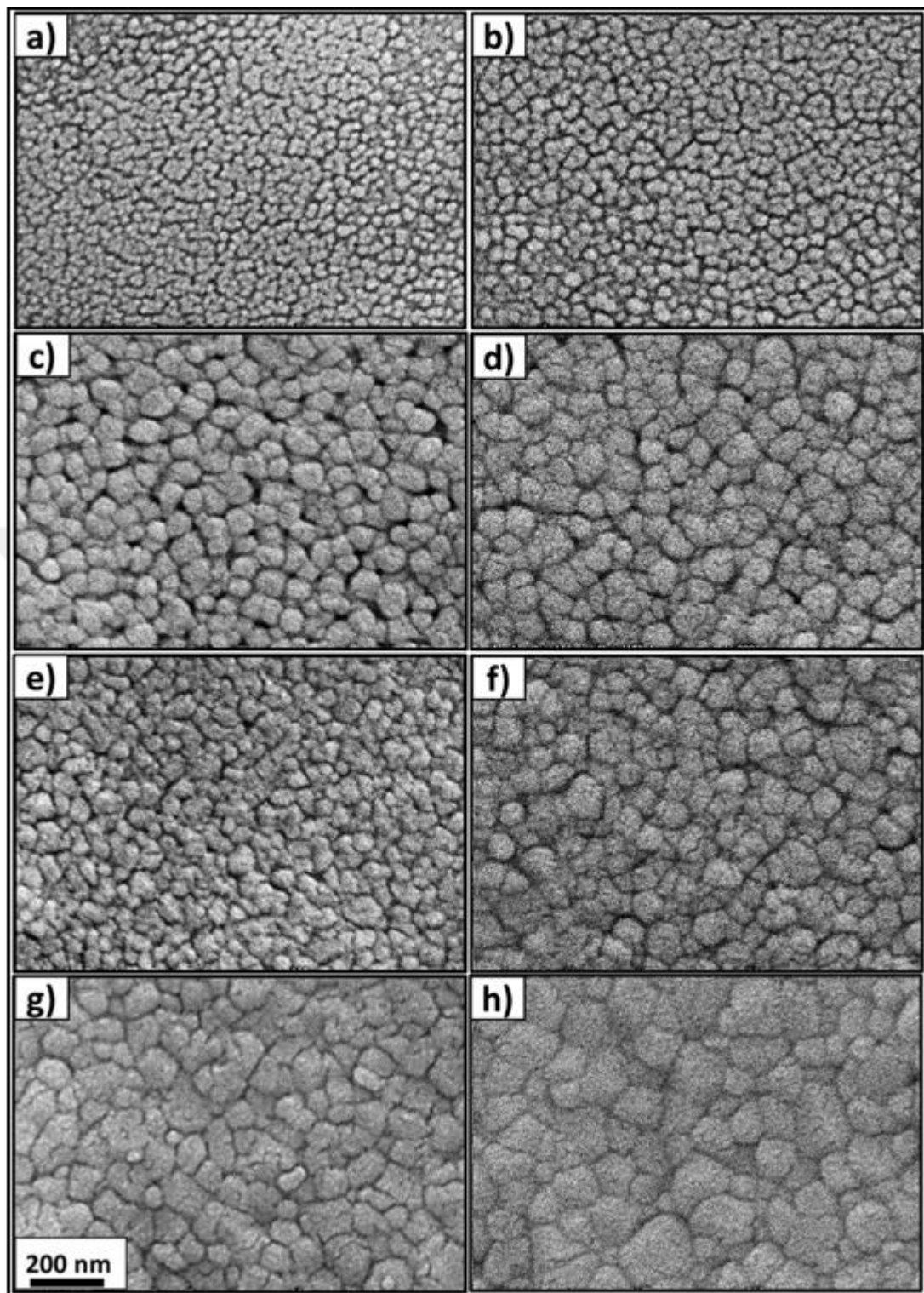


Figure 3.4: Scanning electron microscopy pictures of the outer surface of a) 20 % Ca doped LCC-700, c) 20 % Ca doped LCC-800, e) 40 % Ca doped LCC- 800, and g) 20 % Ca doped LCC-900 before, b) 20 % Ca doped LCC-700, d) 20 % Ca doped LCC-800, f) 40 % Ca doped LCC-800, and h) 20 % Ca doped LCC-900 following extended heat treatment subjected to 700 °C for 100 hours in atmosphere.

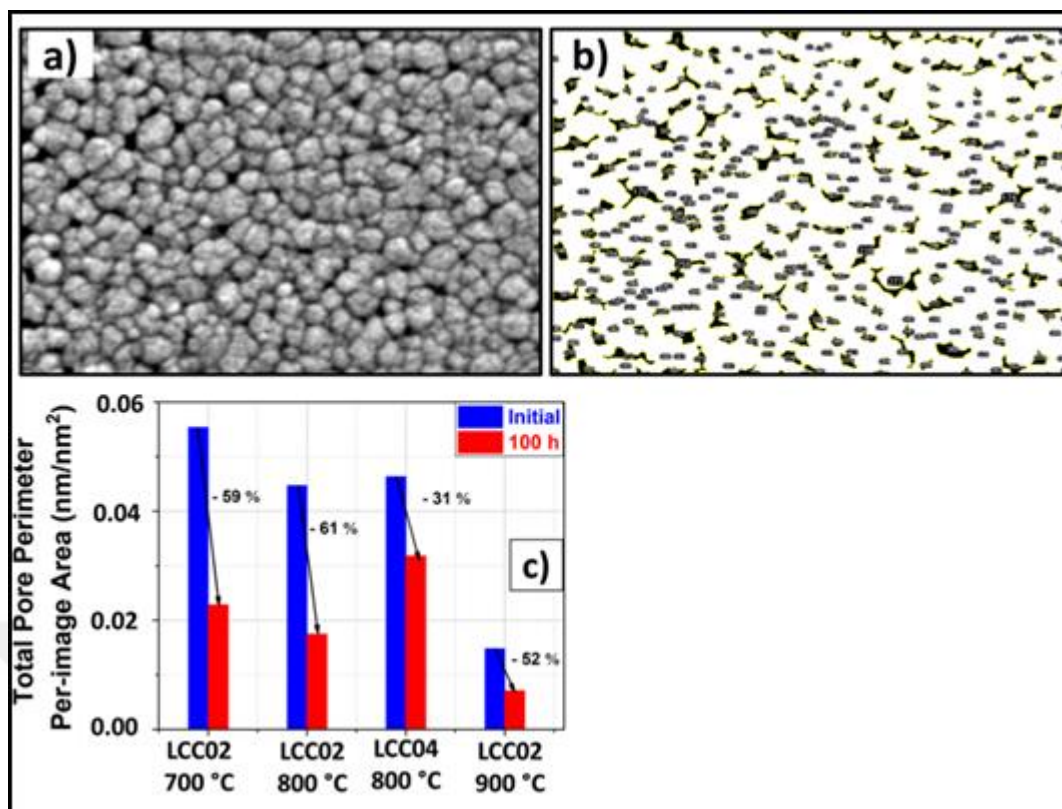


Figure 3.5: a) A usual scanning electron microscopy picture of the upper surface of an 20% Ca doped LCC film, b) its ImageJ-processed form displaying the binary mode of the picture along with the calculated pore perimeters, and c) variations in the total pore perimeter per picture area (TPPA) values of the LCC cathodes following a 100-hour subjected to 700 °C in atmosphere.

Consequently, in fact the greatest TPPA values achieved in 20 % Ca doped LCC-700 (Fig. 3.5c), along with a more desirable phase composition compared to other samples (Fig. 3.2a and b), did not result in the greatest electrochemical performance (Fig. 3.1) indicates that these factors had no the greatest effect on the electrochemical performance. However, because the weakest electrochemical performance was achieved in 20 % Ca doped LCC -900 – the example with the smallest TPPA value – a level of microstructure effect on the electrochemical performance cannot be ruled out.

3.3.4. Surface Chemistry Evolution

Another factor which may have an effect on the electrochemical performance and prolonged stability under the working circumstances is the surface chemistry. Because the positive ion ratios at the surface of the SOFC cathodes offer knowledge

on the entity's interaction with the gas mixture and thus the oxygen reduction activity, we monitored depends on the comparative positive ions substances at the surface of the LCC cathodes over time (Fig. 3.6). This was accomplished by performing X-ray photoelectron spectroscopy (XPS) observations and fits on specimens prior to and following a extended time subjected to 700 °C. Originally, 20 % Ca doped LCC-700 has a Co-rich surface but lacked La and Ca (Fig. 3.6a-c). In the as-calcined form, XRD studies of 20 % Ca doped LCC-700 indicated the presence of Co_3O_4 , rhombohedral perovskite, and an A_2BO_4 – type Ruddlesden – Popper phase (Fig. 3.3). The surface then is likely to be rich in the Co_3O_4 phase. After prolonged operation, cation ratio on the surface of 20 % Ca doped LCC- 700 approached stoichiometric levels (Fig. 3.6a-c).

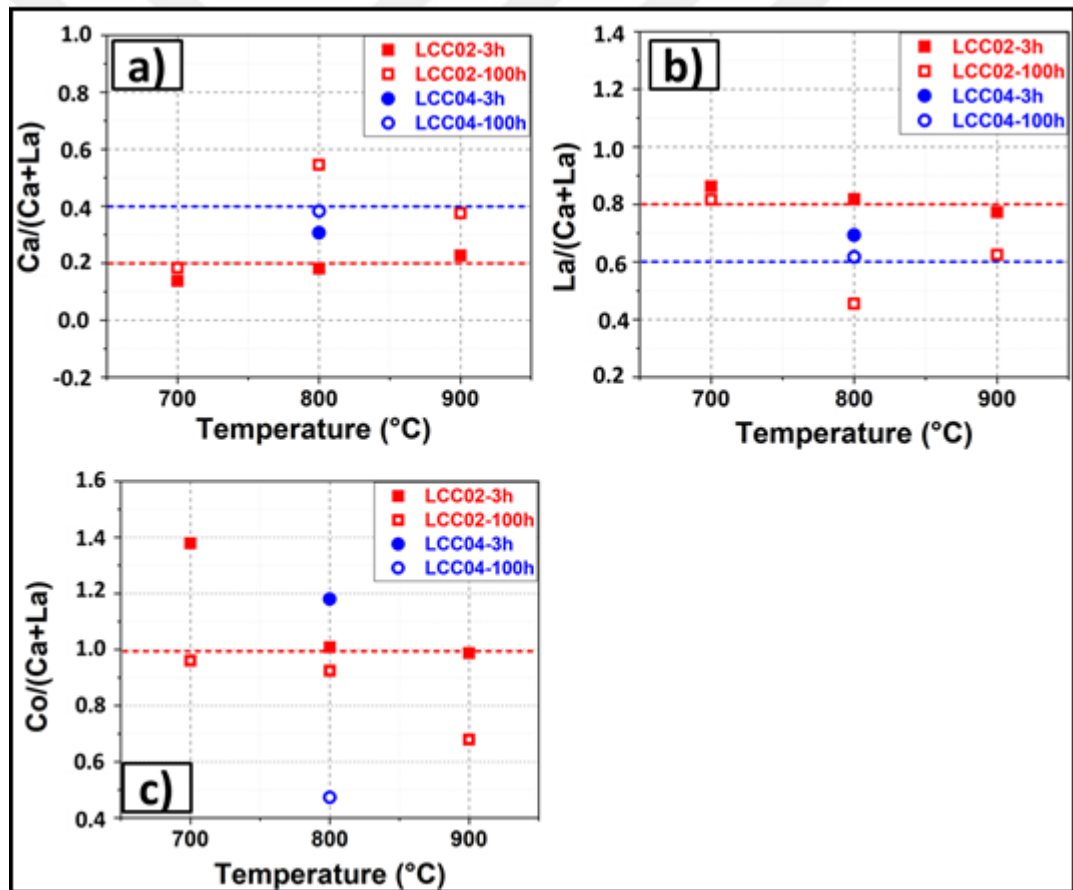


Figure 3.6: Variations in the comparative quantities of a) Ca, b) La, and c) Co with pre-calcination temperature at the surfaces of LCC cathodes prior to and during prolonged operation at 700 °C in atmosphere.

20 % Ca doped LCC-800 exhibited a surface positive ion stoichiometry that was near to theoretical values, however the rise in the Ca concentration of the polymeric precursor to obtain 40 % Ca doped LCC-800 influenced the surface cation rates (Fig. 3.6a-c). Although 40 % Ca doped LCC-800 had a greater comparative Ca level than 20 % Ca doped LCC-800, its surface remained modestly deficient in Ca in comparison to predicted positive ion rates (Fig. 3.6a and b) but was abundant in Co. (Fig. 3.6c). After prolonged subjected to 700 °C, 20 % Ca doped LCC-800 and 40 % Ca doped LCC-800 exhibited considerable Ca and A-site (La and Ca) segregation at the top surface, respectively (Fig. 3.6a-c). At the same time, the surface of 20 % Ca doped LCC-900 originally exhibited positive ion rates similar to those of the bulk, but thereafter developed deficient in Co (Fig. 3.6c), whilst the Ca/(Ca+La) ratio rose after a extended time subjected to 700 °C (Fig. 3.6a-c).

The positive ion ratios give just a restricted amount of data on how the surface chemical composition evolved. Hence, a careful investigation of the supplements to the O1s spectrum might offer important details about the segregating species. Since oxygen can exist in three different forms on the surfaces of perovskite type cathodes, the pattern fits conducted correspondingly [55]-[62]. The O1s pattern at 529 eV has been ascribed to the oxygen atoms in the perovskite's lattice (O_{lattice}), whilst the peak at 529.8-531.5 eV has been assigned to the oxygen atoms in the terminated overlayer of the perovskite ($O_{\text{termination}}$) [60]-[62]. At binding energies of 532-533 eV, an additional input from oxygen atoms bound to surface oxide/hydroxide species and/or adsorbates (O_{surface}) [61],[62] was also included during the fitting method.

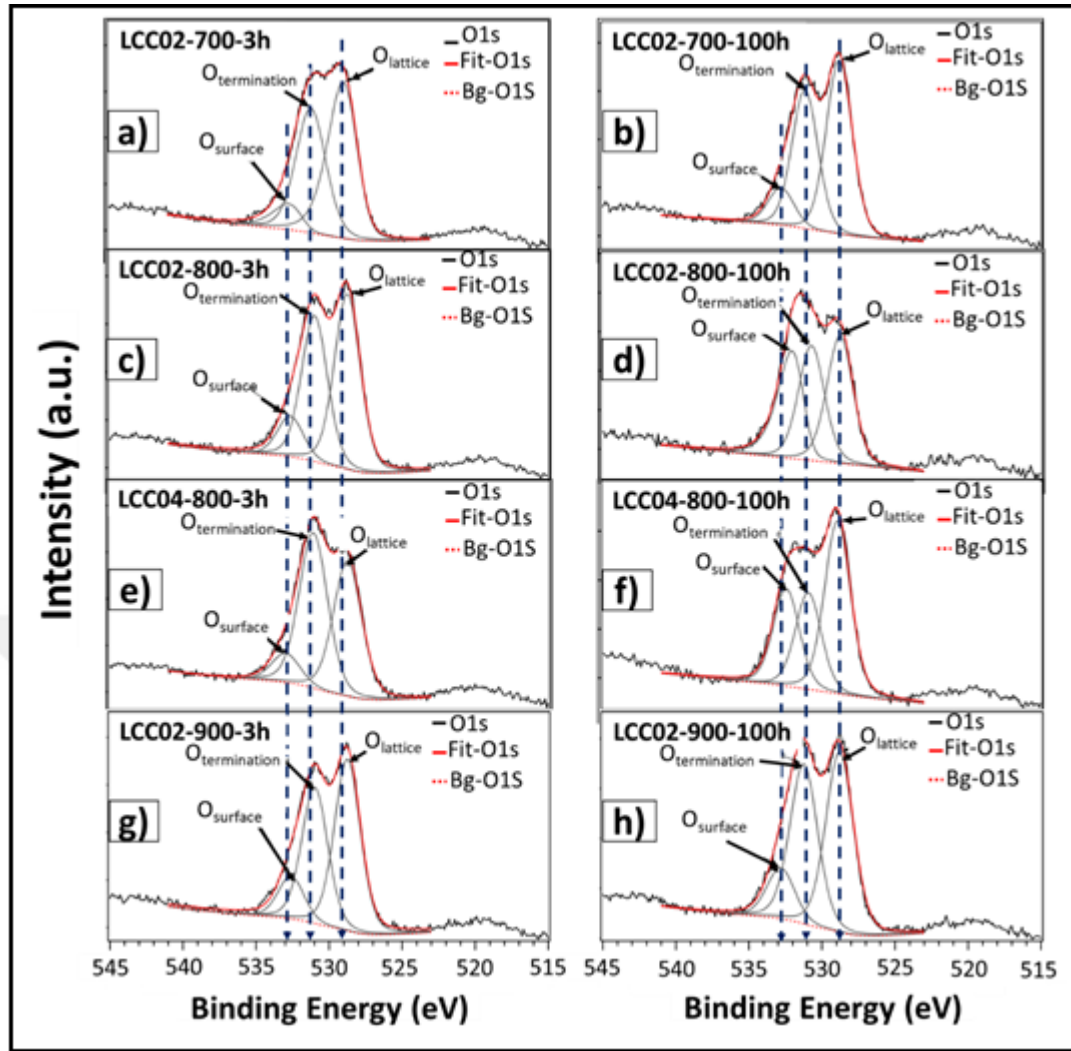


Figure 3.7: O1s core level x-ray photoelectron spectra of a) 20 % Ca doped LCC-700, c) 20 % Ca doped LCC-800, e) 40 % Ca doped LCC-800, and g) 20 % Ca doped LCC-900 before, b) 20 % Ca doped LCC-700, d) 20 % Ca doped LCC-800, f) 40 % Ca doped LCC-800, and h) 20 % Ca doped LCC-900 following long-term subjected to 700 °C for 100 hours in atmosphere. Related fittings are included.

Table 3.2: the relative contributions of oxygen species provide in segregated oxide/surface adsorbed, surface termination, and perovskite lattices (O_{surface} , $O_{\text{termination}}$, and O_{lattice} , respectively).

	02 700 3h	02 700 100h	02 800 3h	02 800 100h	04 800 3h	04 800 100h	02 900 3h	02 900 100h
O_{lattice}	50.9	49.7	48.4	36.5	42.3	47.1	48.9	46.0
$O_{\text{termination}}$	40.7	39.6	40.6	32.8	48.7	26.4	38.9	40.9
O_{surface}	8.4	10.7	11.0	30.7	9.1	26.6	12.2	13.1

Before extended time subjected to 700 °C, the calcination temperature had no effect on the $O_{\text{surface}}: O_{\text{termination}}: O_{\text{lattice}}$ ratios (Fig. 3.7a, c and g). When 20 %Ca doped LCC-800 is compared to 40 %Ca doped LCC-800, it is shown that raising the Ca-doping level results in a rise in $O_{\text{termination}}$ but a drop in O_{lattice} values (Fig. 3.7c and e). Crumlin et al. [61] showed that increasing the Sr content at the surface of LSC cathodes made through PLD enhanced the $O_{\text{termination}}$ supplement to the O 1s spectra, implying that the $O_{\text{termination}}$ element represents electrochemically active vacancy locations following oxygen dissociation. Zhi et al. [58] used XPS to analyze (La, Sr)MnO₃ microcubes and assigned the oxygen element with bonding energies of around 531.5 eV to oxygen attached on an electrochemical active surface vacancy locations. This result agrees with the larger $O_{\text{termination}}$ supplement to the O 1s spectrum produced by the greater Ca substituting concentration in 40 % Ca doped LC-800 compared to 20 % Ca doped LCC-800 (Fig. 3.7) and the resulting, somewhat improved performance of the previous one (Fig. 3.1). $O_{\text{surface}}: O_{\text{termination}}: O_{\text{lattice}}$ in the instance of 20 % Ca doped LCC-700, the O_{lattice} ratios remained constant (Fig. 3.7a and b). However, after extended heat treatment of specimens calcined at 800 °C (20 % Ca doped LCC-800 and 40 % Ca doped LCC-800), a reduction in $O_{\text{termination}}$ but a rise in O_{surface} was found (Fig. 3.7 c-f). In the event of LCC02-800, these alterations were followed by a drop in O_{lattice} , but an enhancement in the case of 40 % Ca doped LCC-800. Meanwhile, after extended time subjected to 700 °C, the original $O_{\text{surface}}: O_{\text{termination}}: O_{\text{lattice}}$ ratio was preserved in 20 % Ca doped LCC-900. Remarkably, specimens that degraded the fastest (20 % Ca doped LCC-800 and 40 % Ca doped LCC-800) had a considerable drop in $O_{\text{termination}}$ (is equivalent to a reduction in active surface vacancy intensity) during prolonged operation (Fig. 3.7).

3.3.5. Extended-Time Electrochemical Performance and the Hypothesized Surface Development Model

Fig. 3.8 illustrates graphically a hypothesis of surface development that we suggest, depending on the surface positive ions (Fig. 3.6) and $O_{\text{surface}}: O_{\text{termination}}: O_{\text{lattice}}$ ratios (Fig. 3.7), that clarifies the mechanisms underlying the prolonged performance deterioration of various LCC cathodes. As noted, before in the text, XRD examination

(Fig. 3.3) indicates that co-segregation at the 20 % Ca doped LCC-700 surface (Fig. 3.6) results in the generation of Co_3O_4 and $(\text{La}, \text{Ca})_2\text{CoO}_4$ near to the surface.

Muturo et al. [103] and Choi et al. [104] reported that when Co_3O_4 is deposited on the surface of LSC electrodes, the electrochemical performance decreases. Rupp et al. [105], on the other hand, asserted the opposite, claiming that Co_3O_4 deposition ended up an improvement in electrochemical performance. Given that 20 % Ca doped LCC-700 with its Co_3O_4 -rich surface showed minor electrochemical performance than, for instance, 20 % Ca doped LCC-800, which also has a surface component similar to that of bulk (Fig. 3.2d) but a smaller surface area than 20 % Ca doped LCC-700, it is deduced that Co_3O_4 is electrochemically passive for oxygen reduction.

The Co-rich 20 % Ca doped LCC-700 surface exhibited a comparable $O_{\text{surface}}: O_{\text{termination}}: O_{\text{lattice}}$ ratio to the 20 % Ca doped LCC-800 surface, indicating that its composition was identical to that in bulk. The consistency in $O_{\text{termination}}$ and O_{lattice} values indicates that Co_3O_4 in LCC02-700 i) didn't even cover a significant portion of the cathode surface and ii) was not thick adequate to prohibit O_{lattice} signal (Fig. 3.7a and c). Supposing that the LCC and $(\text{La}, \text{Ca})_2\text{CoO}_4$ phases existing in 20 % Ca doped LCC-700 contain comparable quantities of surface oxygen vacancies [100], it is able to be concluded that Co_3O_4 species developed primarily at the surface termination of the LCC / $(\text{La}, \text{Ca})_2\text{CoO}_4$ phase borders, as diagrammatically indicated in Fig. 3.8. Because the $\text{ABO}_3/\text{A}_2\text{BO}_4$ interphases are reported to be more active than the stark surfaces of those two phases [98]-[100], the creation of the passive Co_3O_4 at these interphases most probably inhibited 20 % Ca doped LCC-700 from achieving good electrochemical performance.

After prolonged subjected to 700 °C, the surface positive ion rates of 20 % Ca doped LCC-700 approached those of the bulk (Fig. 3.6), whereas impurities in the structures observed by XRD in the prepared condition dissipated (Fig. 3.3c). Thus, we suggest the formation of a homogenous $(\text{La}, \text{Ca})\text{CoO}_3$ phase (Fig. 3.8). The O_{surface} 's stability: O_{lattice} ratios observed on the 20% Ca doped LCC-700 surface throughout prolonged annealing (Fig. 3.7a and b) are compatible with the transition of $(\text{La}, \text{Ca})_2\text{CoO}_4$ and interphase-bound Co_3O_4 into $(\text{La}, \text{Ca})\text{CoO}_3$. Moreover, it has been observed that oxygen exchange occurs by oxygen interstitials instead than oxygen vacancies in A_2BO_4 – type compounds [97], thereby rendering some oxygen vacancies (related undirectly to the $O_{\text{termination}}$ in Fig. 3.7) in the prepared condition of 20% Ca

doped LCC-700 passive for oxygen reduction. Hence, despite equal $O_{\text{surface}}: O_{\text{termination}}: O_{\text{lattice}}$ rates in the prepared and prolonged heat-treated specimens, the oxygen vacancies are much more actively employed in oxygen reduction in the latter circumstance. Consequently, surface chemical composition and phase formation had to have beneficial effect on the electrochemical performance of 20% Ca doped LCC-700 during prolonged heat treatment, leaving surface area loss as the primary cause of performance decline. The surface positive ion rates are similar to those in the bulk (Figure 6) and there are no detectable impurity phases (Fig. 3.3a), implying an uniform (La,Ca)CoO₃ surface in the prepared 20% Ca doped LCC-800 (Fig. 3.8), which, as reported earlier, is probably responsible for the sample's relatively high electrochemical performance. Ca accumulation was detected in 20% Ca doped LCC-800 following extended time subjected to 700 °C, which was associated by a rise in O_{surface} but a reduction in $O_{\text{termination}}$ and O_{lattice} . Additionally, based on the increased surface species of the Ca 2p spectra (Fig. S1), it is claimed that 20% Ca doped LCC-800 generated a CaO and/or Ca(OH)₂ species overlaying the bulk of the surface during prolonged annealing (Fig. 3.8). Given that Ca(OH)₂ decomposes into CaO at 512 °C [106]47, the surface is anticipated to be substantially occupied by CaO at operational temperature of 700 °C. The absence of phase precipitation in XRD measurements (Fig. 3.3b) indicates that the resulting CaO oxide overlayer is amorphous. Since CaO is a deactivated electrochemical compound [107] and a well-recognized isolator, its prolonged heat treatment stimulated production at the surface should have resulted in a large performance degradation. Thus, the accelerated degradation of performance seen in 20% Ca doped LCC-800 in contrast to 20% Ca doped LCC-700 (Fig. 3.2d) is a result of the related impacts of CaO production at the surface and surface area reduction in the previous (Fig. 3.5).

The somewhat Co-rich surface of 20% Ca doped LCC-800 in its calcined condition is thought to match the surface of 20% Ca doped LCC-700, i.e., the Co₃O₄ phase most probably developed at the (La, Ca)₂CoO₄ / (La,Ca)CoO₃ phase boundaries (Fig. 3.8). The absence of the Co₃O₄ and (La, Ca)₂CoO₄ phases in the XRD results (Fig. 3.3) is probably owing to their lower abundance in 40% Ca doped LCC-800 than in 20% Ca doped LCC-700, which were previously noticeable in the latter's XRD analysis (Fig. 3.3). The better electrochemical performance of LCC20% Ca doped LCC-800 than 20% Ca doped LCC-800 can be attributed to the greater Ca

substituting ratio, which resulted in a higher concentration of surface oxygen vacancies, as demonstrated by the greater overall $O_{\text{termination}}$ content (Fig. 3.7).

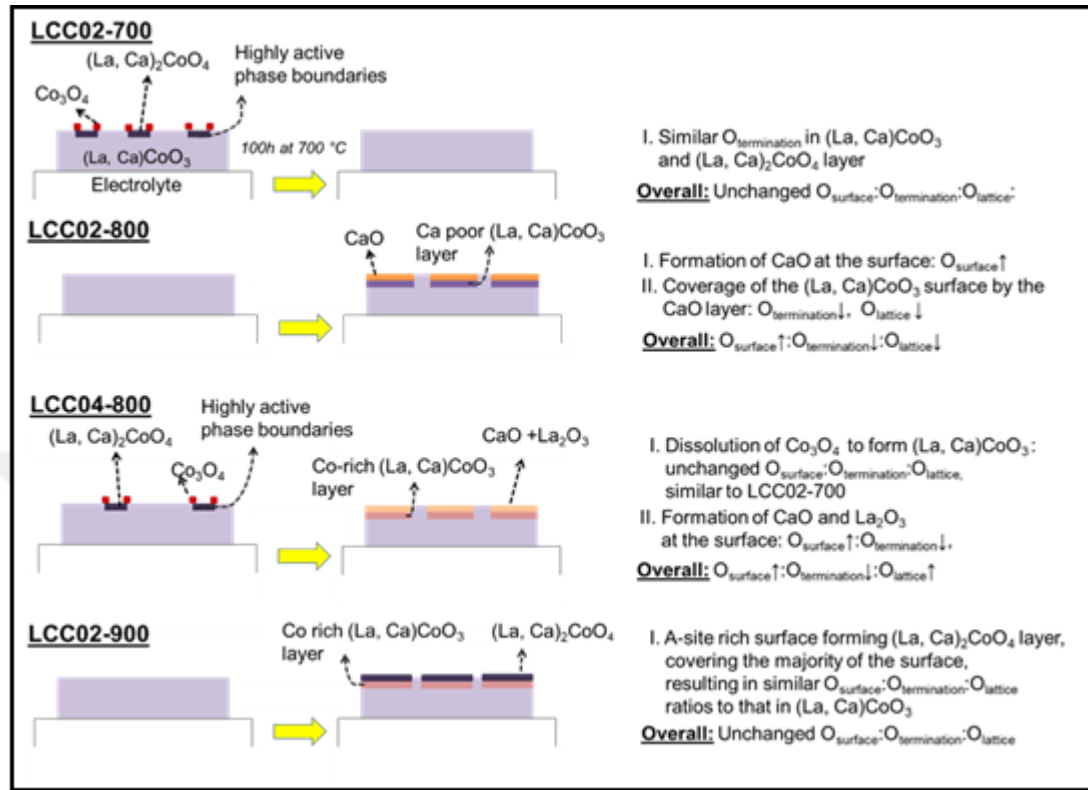


Figure 3.8: A schematic example illustrating the link between the generation of surface positive ion rates and the chemical atmosphere of surface oxygen species.

The segregation of the A-sites ($\text{La} + \text{Ca}$) that occurred throughout prolonged heat treatment at the cost of Co is hypothesized to generate $\text{CaO}/\text{Ca}(\text{OH})_2$ and $\text{La}_2\text{O}_3/\text{La}(\text{OH})_3$ layers that occupy the active vacancies existing at the $(\text{La, Ca})\text{CoO}_3$ surface (Fig. 3.8). The rise in the O_{surface} species of the $\text{O}1\text{s}$ spectra at the cost of $O_{\text{termination}}$ supports this theory (Fig. 3.7). The increased supplement of the $\text{Ca}2\text{p}$ spectra to the surface is likewise consistent with this evaluation (Fig. S1). Due to the fact that the breakdown temperatures of $\text{Ca}(\text{OH})_2$ and $\text{La}(\text{OH})_3$ into CaO and La_2O_3 , respectively, are lower than the heat treatment temperatures (700°C) [106],[108], it is probable that CaO and La_2O_3 are the dominant types at the surface throughout operation, creating an oxygen vacancy-isolating overlayer (Fig. 3.8), thereby significantly contributing to prolonged performance loss (Fig. 3.2d).

While investigating why 40% Ca doped LCC-800 degrades more rapidly than 20% Ca doped LCC-800, it is worth noting that the degree of performance

deterioration links strongly with the degree of $O_{\text{termination}}$ decline. CaO and La_2O_3 created on the 40% Ca doped LCC-800 surface probably enclosed a bigger region than the Ca oxide overlayer developed on the 20% Ca doped LCC-800 surface, so preventing a greater number of active surface vacancies. The $(\text{La}, \text{Ca})\text{CoO}_3$ surface with no segregation calcined 20% Ca doped LCC-900 became deficient in Co, while the $\text{Ca}/(\text{Ca}+\text{La})$ rate rose (Fig. 3.8). (Fig. 3.6). In contrary to 40% Ca doped LCC-800, these alterations in positive ion rates were followed by constant $O_{\text{surface}}: O_{\text{termination}}: O_{\text{lattice}}$ ratios (Fig. 3.6 and 7), indicating that the segregated A-site positive ions did not react to create $\text{CaO}/\text{Ca}(\text{OH})_2$ and $\text{La}_2\text{O}_3/\text{La}(\text{OH})_3$. Presuming equal oxygen vacancy amount on the surface of the ABO_3 and A_2BO_4 – kind cobaltites [100], the creation of a $(\text{La}, \text{Ca})_2\text{CoO}_4$ overlayer enclosing the bulk of the surface appears to be the solely left realistic option for the surface development of the 20% Ca doped LCC-900 electrodes (Fig. 3.8). The emergence of the $(\text{La}, \text{Ca})_2\text{CoO}_4$ impure phase at the surface might elevate electrochemical activity via creating $(\text{La}, \text{Ca})\text{CoO}_3/(\text{La}, \text{Ca})_2\text{CoO}_4$ interphases, whereas going to cover the active $(\text{La}, \text{Ca})\text{CoO}_3$ surface with $(\text{La}, \text{Ca})_2\text{CoO}_4$ may lead to a decline in electrochemical activity, being subject to the degree to which the $(\text{La}, \text{Ca})\text{CoO}_3$ surface is covered by $(\text{La}, \text{Ca})_2\text{CoO}_4$. However, by comparing the extended time activity deterioration profiles of 20% Ca doped LCC-900 and 20% Ca doped LCC-700 (Fig. 3.2d) and the identical surface area degradation in these two specimens (Fig. 3.5), it seems that 20% Ca doped LCC-900 likewise suffers from a microstructural evolution-conquered activity loss mechanism. In general, the studies conducted in this work indicate that the development of the surface chemical composition gives a bigger effect on the prolonged performance stability of LCC cathodes than the surface area loss caused by microstructural coarsening. Although there was a clear tendency toward increasing the $\text{Ca}/(\text{La}+\text{Ca})$ and decreasing the $\text{Co}/(\text{La}+\text{Ca})$ ratios in polymeric precursor-derived LCC electrodes, the degree of these occurrences and the chemical composition of the ions that developed at the surface following prolonged testing were largely dependent on the pre-calcination conditions. Cai et al. studied the influence of pre-calcination condition on the prolonged performance stability of LSC cathodes manufactured using PLD [64] in the literature. They found that specimens pre-calcined at 650 °C degraded at a faster rate than samples pre-calcined at 450 °C at 600 °C [64]. They hypothesized that the LSC thin film pre-calcined at 450 °C was amorphous, enabling the Sr^{2+} cation to be

accommodated more simply without segregating at the surface [64]. However, none of the LCC samples in this example were amorphous, even though they displayed varying degrees of segregation. Thus, the precise origin of the influence of pre-calcination condition on the development of the surface chemical composition are still unknown.

A rather more fundamental conclusion from this study is that replacing the A-site substituted from Sr^{2+} to Ca^{2+} , a smaller positive ion, did not inhibit its segregation at the surface of the LaCoO_3 following extended heat time subjected to 700 °C. Upon extended time annealing, all samples, save 20 % Ca substituted LCC-700, displayed Ca or La+Ca accumulation at their top surfaces. This finding appears to contradict the results of Lee et al that Ca dopant generated in a significantly more stable surface chemical composition than Sr dopant in PLD-derived LaMnO_3 thin film cathodes [36]. However, given the possibility that the electrode creation technique influenced the surface chemical composition, phase, and microstructure development of the LCC electrodes, further study will focus on the surface chemical composition development/prolonged activity loss of Ca-substituted LaCoO_3 thin film electrodes prepared using the same polymeric precursor technique.

3.3.6. Summary

To make solid oxide fuel cells (SOFCs) economically workable, the loss of performance triggered by extended time operation at intermediate temperatures (700 °C) should be removed. In spite of the very favorable electrode polarization resistances gained from the LSC mixed ionic electronic conductor (MIEC) electrode materials, they display rapid activity loss, owing primarily to the segregation of the sizable Sr^{2+} positive ion at the surface, resulting in the formation of electrochemically blocked SrO/Sr(OH)_2 on the exterior surface. We examined the phase, microstructure, and surface chemical composition development of LaCoO_3 thin film cathodes substituted with the smaller Ca^{2+} cation (LCC) rather than Sr^{2+} and the effect on the rate of performance deterioration at 700 °C.

Electrochemical impedance spectroscopy (EIS) examinations on symmetrical half-cells heated to 700 °C found that the beginning performance and prolonged stability were substantially dependent on the pre-calcination temperature,

at 800 °C resulting in the smallest electrode polarization resistance (20% Ca doped LCC-800 and 40% Ca doped LCC-800). Meanwhile, specimens as-calcined at 800 °C revealed a greater rate of performance degradation when exposed to 700 °C for an extended period than samples as-calcined at 700 or 900 °C. Enhanced Ca concentration in LCC-800 ended up an even more rapid loss of performance.

With the exception of 20% Ca doped LCC-700, which included Co_3O_4 and $(\text{La,Ca})_2\text{CoO}_4$ impurities in the as-calcined condition, XRD analysis indicated that all specimens had only rhombohedral $(\text{La,Ca})\text{CoO}_3$ before to and following to extended subjected to 700 °C. Considering that oxygen reduction across the LaCoO_3 type MIEC electrodes is restricted by oxygen exchange at the surface, the total pore perimeters per unit area (TPPA) values were determined to assess microstructural development and its likely influence on the electrochemical activity and stability. These values are indicative of the surface area created by porosity per unit volume as determined by scanning electron microscopy (SEM) images processed with the ImageJ software. As predicted, raising the calcination condition resulted in a drop in surface area, while raising the calcium content resulted in an increase in surface area. Prolonged exposure to 700 °C ended up equal TPPA losses independent of the pre-calcination condition, although raising the Ca concentration (40 % Ca doped LCC-800) ended up a substantially more stable microstructure.

X-ray photoelectron spectroscopy (XPS) studies were employed to track the formation of the surface chemistry. Appropriate fitting approaches were used to detect the difference in cation concentrations at the surface and the proportionate quantities of H_2O , adsorbed, and lattice-bound oxygen to the $\text{O}1\text{s}$ spectra ($\text{O}_{\text{surface}}$, $\text{O}_{\text{termination}}$, and $\text{O}_{\text{lattice}}$, respectively). At first, the surfaces of 20 % Ca doped LCC-700 and 40 % Ca doped LCC-800 were cobalt-rich and most certainly included Co_3O_4 produced at the $(\text{La,Ca})\text{CoO}_3$ / $(\text{La,Ca})_2\text{CoO}_4$ phase interfaces. Despite the overall tendency toward more Ca-rich and Co-deficient LCC surfaces seen across entire specimens, the chemical composition of the surface species was temperature dependent. CaO and $\text{CaO} + \text{La}_2\text{O}_3$ species, for e.g., created on the surfaces of 20 % Ca doped LCC-800 and 40 % Ca doped LCC-800, respectively, which were the just two specimens to display a reduction in oxygen vacancy ratios while also experiencing the most pronounced electrochemical performance degradation after extended time subjected to 700 °C.

In general, it was found that the generation of the surface chemical composition had a greater effect on the electrochemical activity and prolonged stability. The fabrication of (La,Ca)CoO₃ electrodes using reasonably priced polymeric precursor technologies that demonstrate both improved electrochemical activity and prolonged stability may necessitate specific refinements, including surface modification to retard surface segregation.



4. INFLUENCE OF SOLUTION DEPOSITION PARAMETERS ON THE ELECTROCHEMICAL PERFORMANCE STABILITY OF LCC ELECTRODE FILMS

Abstract: In the current study, the prolonged electrochemical performance of polymeric precursor-derived films of Ca^{2+} -substituted LaCoO_3 (LCC) was examined by varying deposition parameters. It was determined that to increase the spinning rate results in a lower polarization resistance and a better long-term stability. Although surface morphology development had considerable effect on the initial and long-term performance of LCC electrodes, it was not the most significant factor. It was revealed by XPS measurement that a platelet shaped impure CoO_x phase forms on the top surface due to the transport of cobalt in the gas phase. This phase determines the electrochemical performance route prior to and after 100 hours of heat treatment at 700 °C. Furthermore, a decline in the comparative quantities of adsorbed oxygen types (matching to surface oxygen vacancies) triggered performance loss in the 1000 rpm rate, while an increase in that of 3000 rpm results in stable condition. The performance of samples fabricated with 1000 and 3000 rpm were affected not only by the CoO_x phase and surface morphology, but also by the kind of oxygen that is absorbed to the surface. The performance of that of 2000 rpm was simply affected by the CoO_x phase and surface morphology.

4.1. Introduction

Mixed ionic and electronic conducting (MIEC) perovskites with the ABO_3 stoichiometry are appealing electrode materials for intermediate temperature (below 700 °C) solid oxide fuel cell (IT-SOFC) operations, due to their high electrocatalytic performance for oxygen reduction reaction (ORR) [109]-[111]. Substitution of the trivalent A-site host (La in most cases) with a suitable divalent cation, most frequently, Sr, significantly improves the transport properties of such materials, including, LaCoO_3 , LaFeO_3 and $\text{La}(\text{Co,Fe})\text{O}_3$, [38],[52],[64],[77]. However, when these electrodes are exposed to operating temperatures, the surface chemistry and consequently ORR kinetics deteriorate significantly. Lee et al. postulated that the Sr

segregates at perovskite surfaces because of the elastic strain generated by the exceptionally large ionic radius of Sr^{2+} in comparison to that of the host cation, La^{3+} [36]. In addition, the electrostatic interaction between the positively charged oxygen vacancies ($\text{V}_{\text{O}}^{\bullet\bullet}$) present at the surface and the negatively charged Sr^{2+} species was another driving force for the surface segregation of Sr [36], which formed insulating phases, such as oxides/hydroxides/carbonates, hindering oxygen exchange at the surface [38],[52],[64],[77]. Further, the bulk of the electrode becomes deficient of divalent doping, which deteriorates transport properties. All of these events caused by Sr segregation at the surface, results in long-term performance instability of the SOFC cathodes.

To enhance the stability of electrodes, modification of the electrocatalyst surfaces has been examined in several studies. For example, Rupp et al. decorated the surface of LSC with the constituent oxides of LSC electrode by pulse laser deposition. It was stated that small amounts of SrO (ca. 4 % of a monolayer) coated on an LSC surface resulted in a drastic deactivation of the surface, while Co, induced re-activation [105]. Mutoro et al. decorated the surface of microelectrode LSC by oxide of constituents via pulse laser deposition. The surface exchange coefficient, k_p , of the LSC was increased by an order of magnitude after decoration of the surface with SrO nanoparticles with a surface coverage of 50 - 80 % [103]. Meanwhile, decoration of the surface with La or Co-oxides resulted in no alteration in k_p [103]. On the other hand, Tsvetkov et al. modified the surface of $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ (LSC) with transition metal cations that were either more or less reducible than Co of the B site of LSC [92]. It was found that the less reducible cations with oxidation states of 4+ prevented Sr accumulation by lowering $\text{V}_{\text{O}}^{\bullet\bullet}$ concentration and thereby reducing the electrostatic driving force [92].

In the previous chapter, to enhance the long-term performance stability of the LSC cathode, we employed Ca^{2+} , a divalent cation with a radius closer to that of the host (La^{3+}), as the A-site dopant, instead of the often-used Sr^{2+} [53],[54],[61]-[63],[76],[78],[80],[83],[92],[98],[103],[105],[112]-[116]. This way, elimination of the elastic strain that triggers Sr segregation was aimed. To obtain an enhanced cathode performance, we adopted a low-temperature electrode fabrication route that involves the spin-on deposition of ethylene glycol-based polymeric precursors [52], which is also much more cost-effective in comparison to the widely used pulsed laser deposition

method. Our experiments showed that i) surface chemistry evolution was the main cause of long-term performance degradation, ii) pre-heat treatment temperature had a strong influence on the initial surface chemistry, which, in turn, was detrimental to the long-term performance stability and iii) higher amounts of Ca doping induced faster performance degradation [52].

Having established that the initial state (surface chemistry and etc.) of the electrode is closely related to the long-term performance degradation behavior, our next target is to determine the how changes in fabrication parameters other than pre-heat treatment temperature influence the initial state of the electrode material and, consequently, long-term performance degradation.

An important fabrication parameter when fabricating oxide films via spin-coating of liquid precursors onto dense substrates is spinning speed as it determines the amount of solution that is kept on the substrate surface. Amount of remnant solution influences the amount of carbonaceous gas emission and strain during drying, which determines the main microstructural characteristics of the films, such as; film adhesion, presence/absence of cracks/porosity [109] and, as will be discussed in detail in this study, surface chemistry.

In this work, long-term electrochemical performances of $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ (LCC) films deposited by cost-effective polymeric precursor deposition with spinning at 1000, 2000 and 3000 rpm were investigated. Different numbers of deposition/drying cycles were employed to obtain films that have been deposited by different spinning speeds, but with similar thicknesses. Microstructure, phase, surface chemistry evolution of the polymeric precursor derived electrodes upon long-term exposure to 700 °C were determined by scanning electron microscopy (SEM), x-ray diffraction (XRD) and x-ray photoelectron spectroscopy (XPS) analyses.

4.1. Experimental

Dense electrolyte yttria stabilized zirconia (YSZ) substrates and samaria doped ceria (SDC) coated on substrate to prevent phase formations that may occur at the interface of $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ (LCC) and YSZ electrolyte, and LCC polymeric precursor were set up as in our previous study. Polymeric LCC precursors were spin-coated onto each side of SDC/YSZ/SDC substrates at speeds of 1000, 2000, and 3000 rpm, and

then dried at 350 °C on a hot plate. It was revealed that the same thicknesses could be achieved by spinning at 1000 rpm/drying cycles for 15, 2000 rpm/drying cycles for 23, and 3000 rpm/drying cycles for 55 times. In all samples, this corresponds to an average film thickness of around 6-7 μm . The gained symmetrical LCC/SDC/YSZ/SDC/LCC half-cells were pre-calcined for 3 h at 800 °C. Grazing X-ray diffraction (XRD) examinations with 1° were achieved before and after a 100-hour experience of LCC cathodes to 700 °C in stagnant air to examine the phase evolution of the polymeric precursor generated LCC cathodes. A copper radiation source ($\text{CuK}\alpha$, $\lambda = 0.15406 \text{ nm}$, Rigaku S-Lab diffractometer) was used to make XRD examinations in the 2θ range of 20° - 80° .

Using secondary electron imaging and scanning electron microscopy (SEM, Philips XL30 SFEG), the variations in the microstructure of LCC electrodes after heat treatment at 700 °C were recorded.

X-ray photoelectron spectroscopy (XPS) was used to detect alterations in the surface composition/chemistry of LCC electrodes upon exposure to 700 °C for 100 h. The experimental set up of XPS is the same as our recent study.

Electrochemical impedance spectroscopy (EIS) tests were done at the range of 500°C – 700°C in stagnant air (Biologic, SP150), at a frequency 50 mHz–50 kHz, with an excitation voltage of 10 mV, under open circuit circumstances to assess the electrochemical operation of LCC electrodes. The experimental set up of EIS is the same as our recent study.

4.2. Results and Discussion

4.3.1. Microstructure and Phase Evolution

Our recent work had shown that the initial surface chemistry of the polymeric precursor-derived SOFC cathode coatings, dictated by the pre-heat treatment temperature, had a detrimental effect on how these electrodes would perform during long-term operation [52]. Here, we expect that the spin-coating rate used to deposit the LCC electrode coating would have a considerable effect on the initial properties of the LCC electrode films, which, in turn, would have a detrimental effect on the long-term electrochemical performance. For example, it is well-known that spinning rate

determines the thickness of the deposited liquid via $h_f \sim \omega^{-1/2}$ where, h_f and ω are final thickness of the solid film and spinning speed, respectively [117]. The deposited film thickness should influence the amount and rate of carbonaceous gas emitted during the drying stage, which influences the presence/absence of cracks/porosity in the as-fabricated metal oxide film microstructure [109]. In addition, amount of carbonaceous gas emissions would influence the local oxygen partial pressure around the film, which could influence the stability of the perovskite phases [77].

In this work, properties of the LCC electrodes fabricated from polymeric precursors via spin coating at different spinning speeds prior to and after long-term exposure to the IT-SOFC operating temperature of 700 °C are compared. A correlation between the changes in these properties and the long-term performance stabilities was sought for. For a sound comparison, LCC electrodes with similar thicknesses were aimed. For this purpose, 1000 rpm deposition/drying cycles were repeated for 15 cycles, which corresponded to a thickness of ca. 6.5 μm (Fig. 4.1a). To achieve similar thicknesses, 2000 and 3000 rpm deposition rates required the repetition of the deposition/drying cycles for 23 and 55 times, respectively (Fig. 4.1b and c). Assuming roughly linear increase in thickness with the number of deposition/drying cycles; deposition rates of 1000, 2000 and 3000 rpm corresponds to dried thicknesses of 400, 260 and 110 nm per deposition/drying cycle, respectively.

Fig. 4.1a-c also revealed the presence of large spherical pores. Pores of similar shape and size have been observed in coatings prepared by similar methods [118],[119]. Eksioglu et al. reported that the root cause of formation of these pores was an abrupt discharge of organic content in gas form during drying [120]. It was reported that these pores could be eliminated when the film thickness was reduced to below 1 μm , due to shorter distance required for the gas discharge [120]. Evidently, with increasing spinning speed and number of deposition/drying cycles, pores reduced in size, but grew in numbers (Fig. 4.1a-c).

Low magnification SEM images of the top surfaces of LCC coatings fabricated by deposition at different spin rates are provided in Figures 1d, e, and f. In general, two kinds of microstructural features, namely, i) macro cracks and ii) large pores with spherical shapes (same ones that were also visible in the cross-sectional images in Fig. 4.1a-c) were observed (Fig. 4.1a, c, and e).

Surfaces of 1000 rpm samples had numerous macro cracks with openings up to a few microns (Fig. 4.1d). One of the main reasons for macro crack formation is that the film thickness obtained at each deposition/drying cycle is higher than the critical thickness for crack formation (h_c) [117]. During the drying stage, the deposited film shrinks in volume. As the heat treatment continues, the solidified film continues to shrink to densify. Films with thicknesses larger than h_c cannot accommodate the shrinkage and crack [117]. For films that adhere well to the substrate, h_c is given by Eq. 4.1. Here, K_{IC} is critical stress intensity, σ is shrinkage stresses and Ω is a function that depends on the ratio of the elastic modulus of the film and substrate [121]. It is very likely that the film thickness obtained per deposition/drying cycle exceeded h_c in the case of 1000 rpm sample and macro-cracks formed at every deposition cycle (Fig. 4.1d).

$$h_c = (K_{IC}/\sigma\Omega)^2 \quad (4.1)$$

Increasing the deposition rate to 2000 rpm and the number of deposition/drying cycles to 23 yielded a surface that is almost free of macro cracks (Fig. 4.1e). The absence of macro cracks was because the film thickness obtained per deposition/drying cycle dropped below h_c and thus, the shrinkage stresses were accommodated.

A further increase of the spinning rate up to 3000 rpm and the number of deposition/drying cycles to 55 resulted in the appearance of macro cracks (Fig. 4.1f). However, this time, in comparison to the 1000 rpm sample, the macro cracks were much fewer in numbers and narrower (Fig. 4.1f). Considering that the thinner films formed per deposition cycle, it is unlikely that shrinkage stresses were the origin of these cracks. In Fig. 4.1a-c, it was observed that the number of gas discharge induced large pores increased with increasing spinning speed, which was accompanied by a decrease in their size. It is possible that the increase in the number of pores allowed for their percolation, which resulted in crack formation. Soo et al also reported that an increased number of pores resulted in the formation of cracks in sol-gel deposited ZrO_2 films.

Higher magnification SEM images showed that, in addition to macro cracks, the surface of LCC electrodes also contained large pores (Fig. 4.1g-h), similar to those observed in the cross-sectional images (Fig. 4.1-c). Evidently, the number of these

pores increased with spinning speed and number of depositions (Fig. 4.1g-h), which indicates that these pores are the same ones that are generated by the carbonaceous gas burnout during the drying of the polymeric precursors.

A more detailed analysis revealed that all LCC surfaces contain plate-like particles that appear to be embedded into the coating (Fig. 4.1i-k). While it was not possible to accurately measure the size of these particles due to their perpendicular position with respect to the detector, it can generally be stated that the particles at the 3000 rpm surface were smaller in size, in comparison to the particles on other samples (Fig. 4.1i-k). Our efforts to determine the composition of these plate-shaped particles via energy dispersive x-ray spectroscopy failed due to large interaction volume of the technique (data not shown).

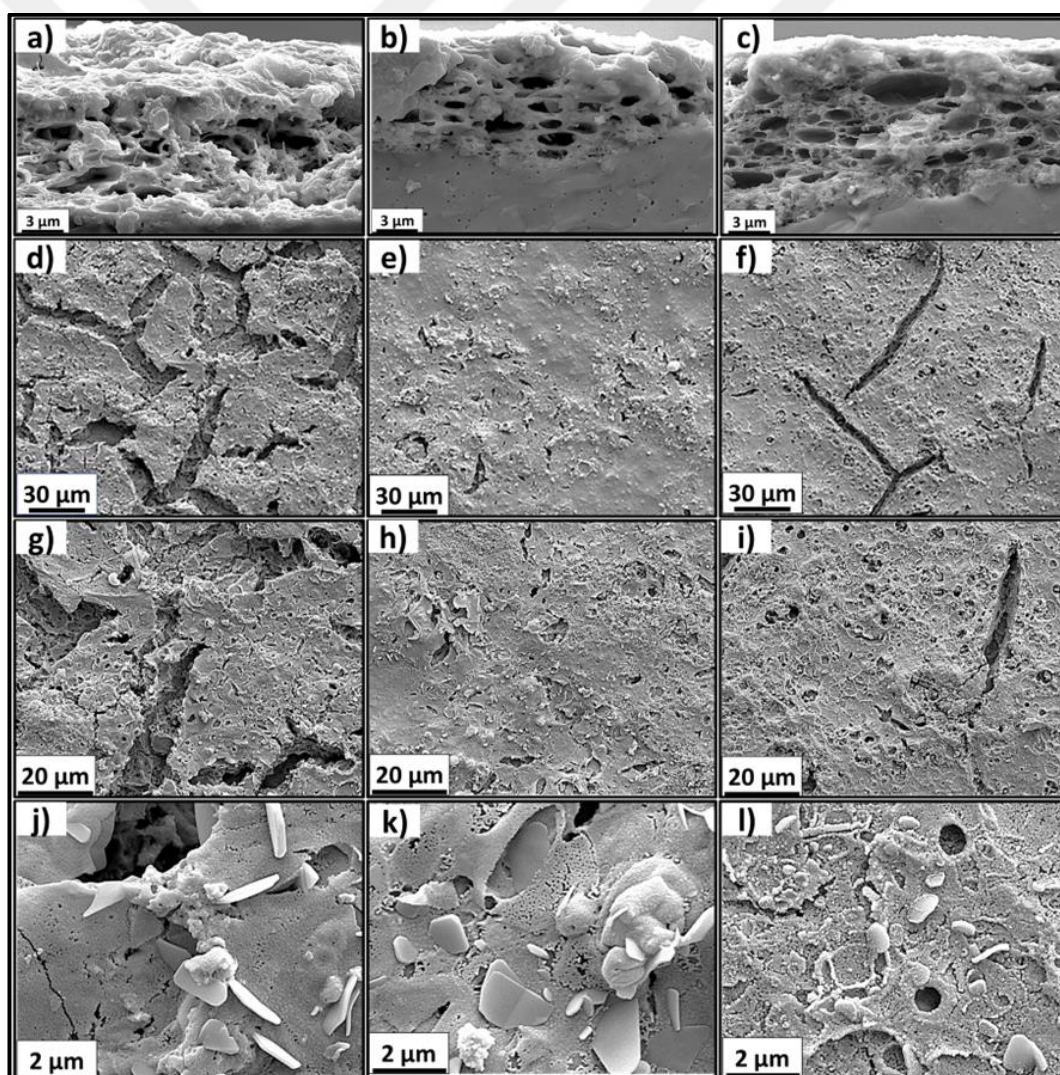


Figure 4.1: Cross-section and surface microstructure images of pre-calcined sample that deposited with different rotation speed represented by scanning electron microscopy (SEM) measurement with different magnification rate.

Cross-sectional images of LCC electrodes collected after 100-hour exposure to 700 °C depicted that the coatings underwent notable densification (Fig. 4.2a-c). Top surface images showed that in 1000 rpm sample, the large cracks shrank notably upon long-term annealing (Fig. 4.2d). Densification has been shown to contribute to crack healing in ceramics in the literature [122]. The surfaces of the other samples remained virtually unchanged in terms of pore and crack development (Fig. 4.2e and f). Higher magnification images indicated that the plate-like particles were still present after long-term annealing (Fig. 4.2g-i). The particles on 1000 and 2000 rpm samples shrank, while those on 3000 rpm sample seemed to have grown in size (Fig. 4.2i).

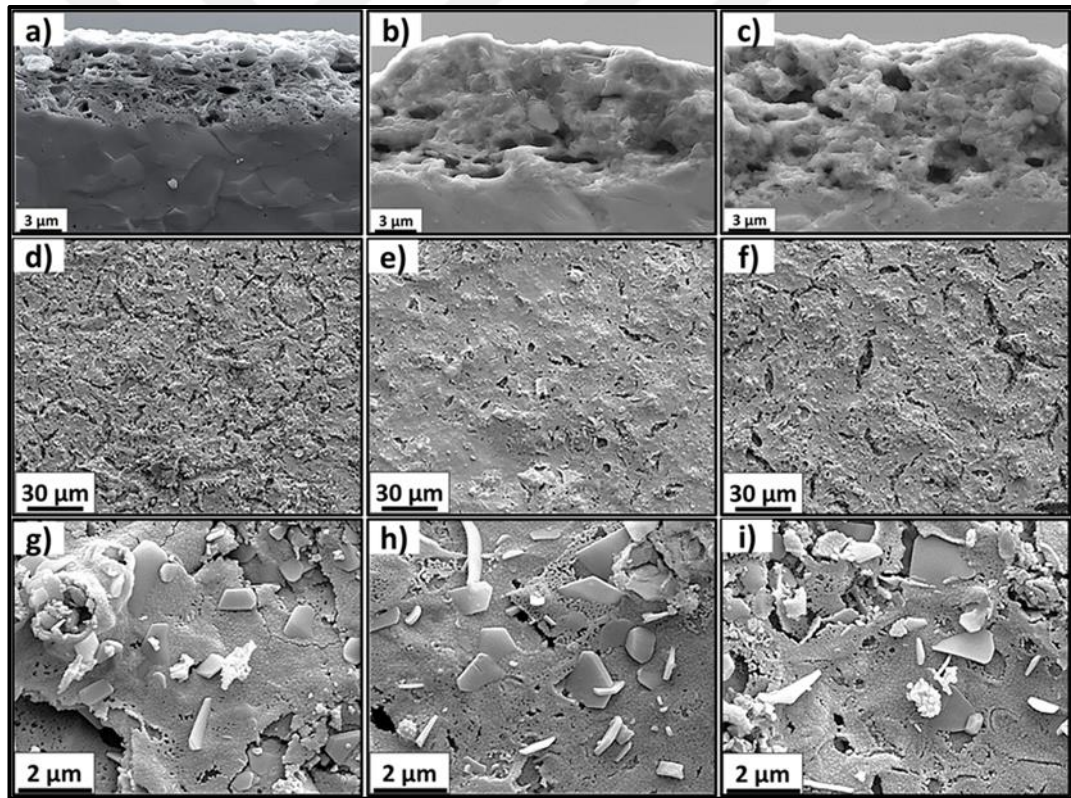


Figure 4.2: Cross-section and surface microstructure images of heat-treated sample that deposited with different rotation speed represented by scanning electron microscopy (SEM) measurement with different magnification rate.

Grazing incidence x-ray diffraction (GI-XRD) analyses were conducted on the films with 1° incident beam angle, to evaluate if the polymeric precursor approach

provided the desired rhombohedral phase and to trace the phase development after prolonged exposure to 700 °C (Fig. 4.3). The predicted rhombohedral (La,Ca)CoO₃ phase (PDF: #36-1388 – will be referred to as the 113 phase from here on) is observed in all of the films, prior to and after the heat treatment exposure to 700 °C for 100h. Our earlier analyses on dried gels that were heat treated at 700 °C, revealed Co₃O₄ (PDF:#42-1467, Fig. 4.4) and (La,Ca)₂CoO₄ Ruddlesden-Popper impurity phases (will be referred to as the 214 phase from here on) due to the low Po₂ atmosphere generated by the carbonaceous gas discharge from the gels [77]. The difference between these results could be ascribed to the surface sensitivity of the GI-XRD.

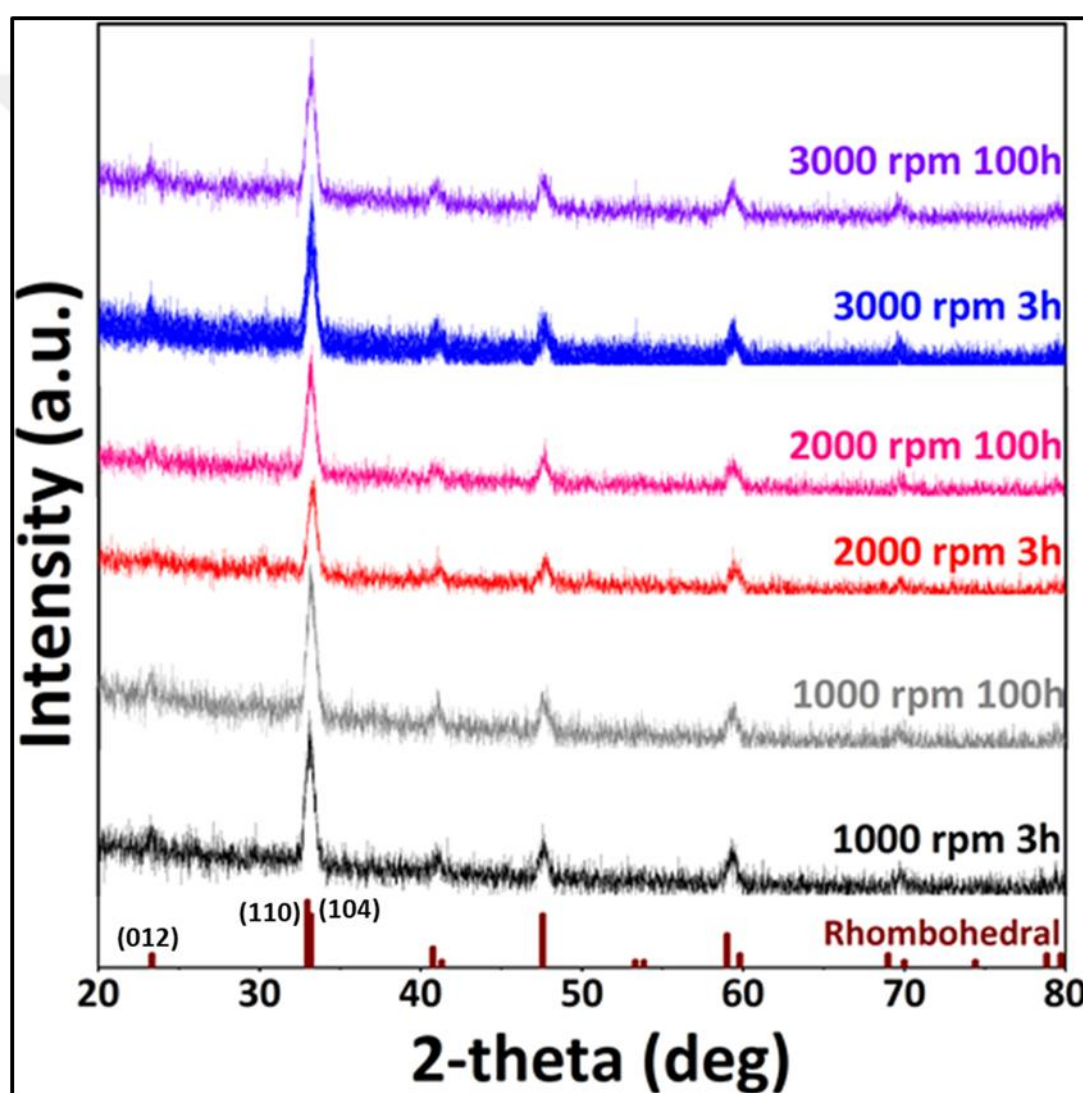


Figure 4.3: Grazing X-ray diffraction (XRD) patterns of all samples collected prior to and after annealing at 700 °C for 100 h, in air.

4.2.2. Surface Chemical Composition

As shown in the previous chapter, oxygen reduction reaction rate is limited by the rate of oxygen exchange at the surface; therefore, the chemistry of the near surface region is detrimental to the electrochemical efficiency and stability of LCC electrodes under operating conditions. X-ray photoelectron spectroscopy (XPS) analysis performed on LCC electrodes fabricated via spin-coating rates of 1000, 2000 and 3000 rpm prior to and after 100 hours exposure to 700 °C indicated that none of the specimens contained any impurities. Variations in relative cation concentrations at the surface of LCC electrodes upon prolonged operation were calculated through curve fittings, (Fig. 4.5). All the samples were Co-rich at the surface after pre-calcining at 800 °C for 3 hours (Fig. 4.5c), which is consistent with our previous study [52]. Two main reasons are considered here for the formation of Co-rich surfaces, both of which are closely related with the fabrication parameters. First possible reason is the decomposition of the 113 phase into Co_3O_4 and 214 phases, caused by the locally formed low $p\text{O}_2$ atmosphere generated by the carbonaceous gas discharge during drying, with Co_3O_4 being located at the outer surface [77]. The other possibility is the transport of Co through carbonaceous gas phase during drying, as reported for LSC electrodes prepared through the deposition of metal organic precursors [109].

Co-rich surfaces revealed by XPS also suggests that the plate-like particles observed on the top surfaces of all samples prior to and after exposure to heat treatment at 700 °C (Fig. 4.1 and 4.2), were Co_3O_4 . Interestingly, despite the Co-rich surfaces, such surface particles were not observed in polymeric precursor-derived LCC electrodes discussed in the previous chapter. It is possible that the slower spinning speeds of 1000 and 2000 rpm left larger amounts of liquid precursor on the electrolyte surface and, upon drying, larger amounts of carbonaceous gases evolved, causing lower $p\text{O}_2$ locally after each deposition step. Lower $p\text{O}_2$ generated locally in the present case resulted in surfaces even richer in Co in comparison to the sample discussed in the previous chapter, thereby forming the plate-shaped particles. The spinning speed of the 3000 rpm sample was the same as the samples described in the previous chapter. However, this time, deposition/drying cycles were repeated almost twice as many times. The numerous repetitions likely caused entrapment of

carbonaceous gases, which, eventually was discharged in large amounts, causing lower pO_2 locally in comparison to the earlier sample and thus, a surface richer in Co [52].

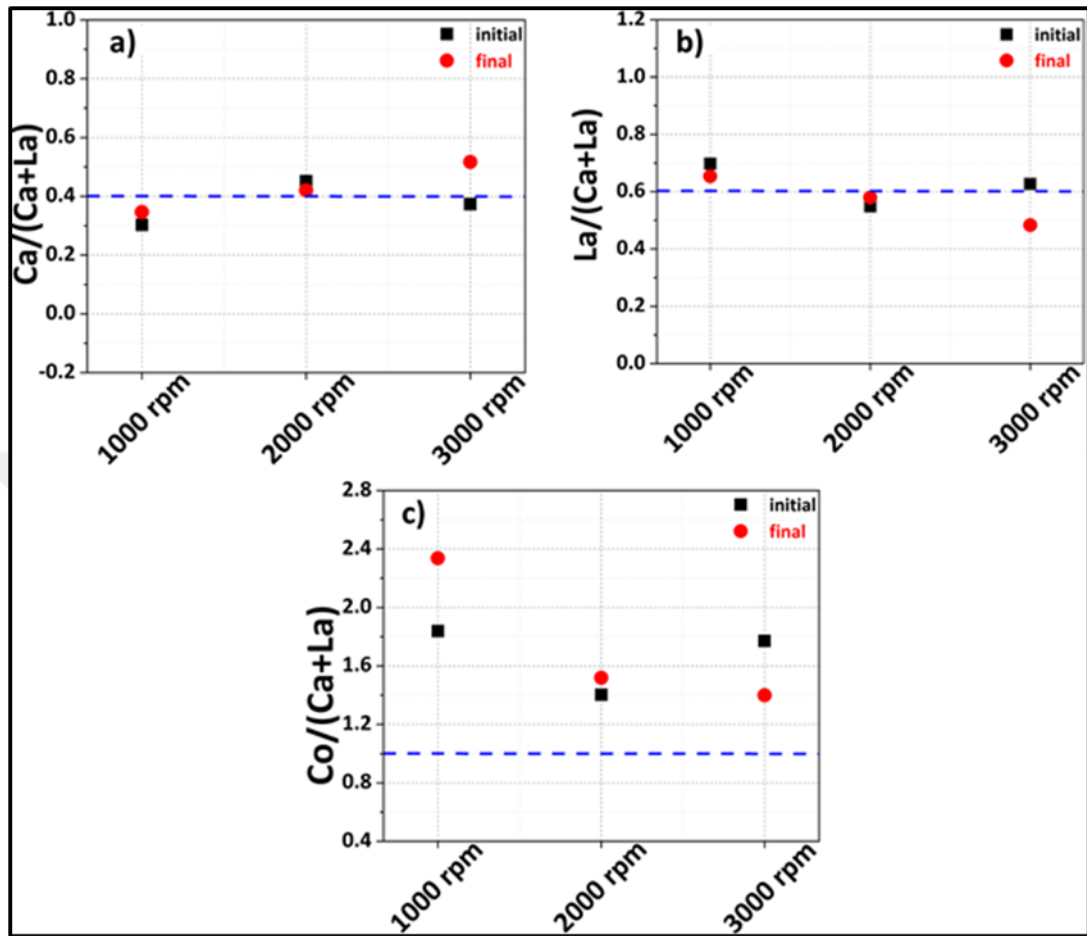


Figure 4.4: Variations in the relative amounts of (a) Ca, (b) La, and (c) Co at LCC film surfaces prior to and after prolonged operation at 700 °C in air.

There is only limited information that can be obtained from the cation ratios. A detailed analysis of the O1s spectrum may offer useful information about the nature of the species that are segregated on the film surfaces. Peak fittings revealed three kinds of oxygen at the surfaces of perovskite oxides [55]-[62]. O1s peak at 529.8–531.5 eV was ascribed to the perovskite's lattice oxygen ($O_{lattice}$), whereas, the one at 529.8–531.5 eV was linked to the perovskite's termination layer ($O_{termination}$) atoms [60]-[62]. These terminal oxygen atoms have been suggested to desorb easily at SOFC operating temperatures to generate surface oxygen vacancies, which facilitate oxygen reduction reaction by acting as oxygen adsorption sites. The peak at binding energies of 532–

533 eV originated from oxygen atoms attached to surface oxide/hydroxide compounds and/or adsorbates (O_{surface}) [61],[62].

Upon pre-calcination at 800 °C for 3 hours, the O_{surface} , $O_{\text{termination}}$ and O_{lattice} ratio was not significantly influenced by the deposition parameters (fig. 6, table 1). On the other hand, exposure to heat treatment at 700 °C for 100 hours affected the three types of samples differently. For example, a decrease in $O_{\text{termination}}$ accompanied by an increase in O_{lattice} was observed when 1000 rpm sample was exposed to 700 °C for 100 hours (Fig. 4.6, Table 4.1). Considering also that the decrease in $O_{\text{termination}}$ upon long-term heat treatment was accompanied by an increase in Co concentration (Fig. 4.5c), it can be suggested that the Co cations replaced terminal oxygens. The fact that O_{surface} remained unchanged indicates that the surface segregating Co did not form additional surface oxides (Fig. 4.6, Table 4.1).

Contributions to the O1s spectra remained almost unchanged in the 2000 rpm sample (Fig. 4.6, Table 4.1), which is a result of stable cation ratios at the surface (Fig. 4.5). In the case of 3000 rpm sample, a significant decrease in O_{surface} and a concomitant increase in $O_{\text{termination}}$ was observed upon long-term exposure to 700 °C (Fig. 4.6, Table 4.1). This finding suggests that some surface oxides dissolved back to generate additional surface oxygen vacancies. Since this process was accompanied by a decrease in Co content at the surface, it can be suggested that surface Co-oxides (that had formed as a result of either gas phase transport during drying or due to decomposition of 113 phase) dissolved back into the lattice forming the oxygen vacancy bearing perovskite.

It should be noted that in the previous chapter, we had reported that LCC electrode fabricated through 30 deposition/drying cycles using 3000 rpm spinning speed underwent a dramatic decrease in Co content at the surface upon long-term annealing while changing the spinning rate and number of depositions dramatically affected the initial surface chemistry and its evolution. The root cause of this phenomenon is suggested to be enhanced the amount of carbonaceous gases emitted during drying when the spinning rate is reduced.

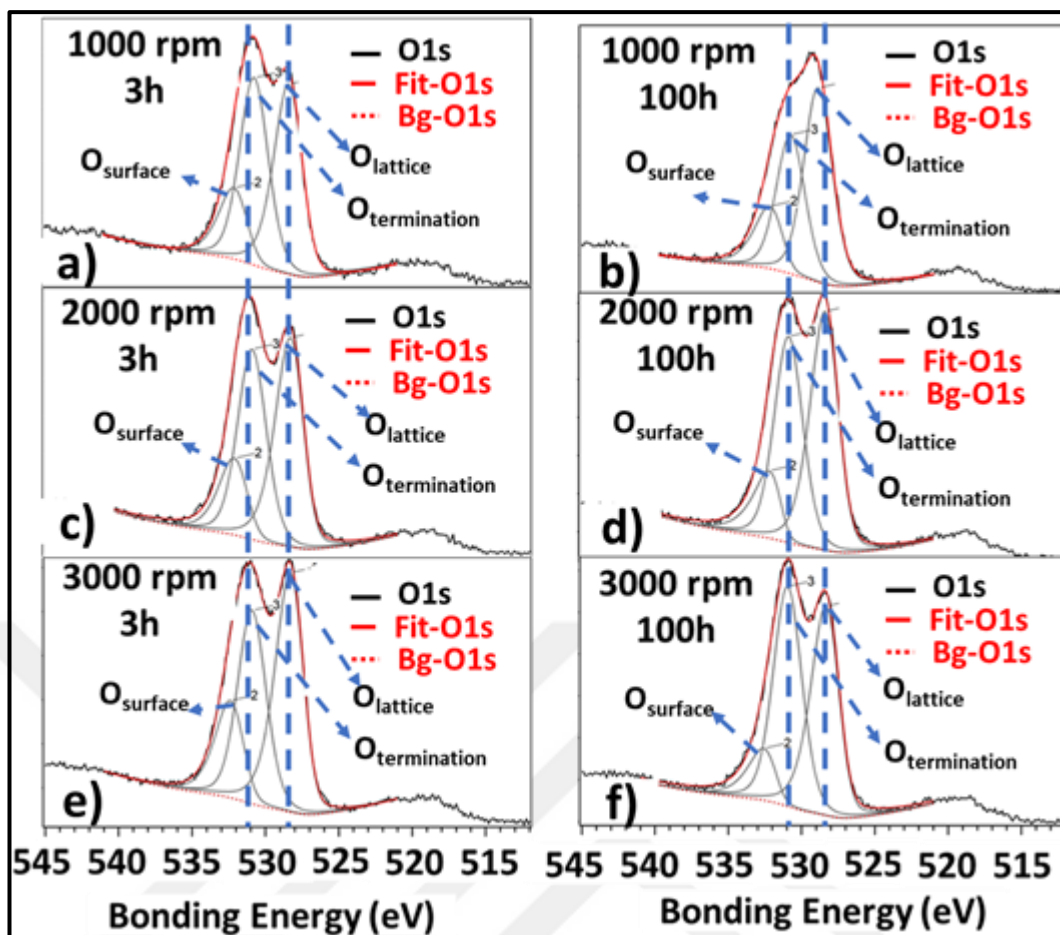


Figure 4.5: O1s core level X-ray photoelectron spectra of the top surface of LCC electrodes deposited at the spinning rate of a) 1000 rpm, c) 2000 rpm and e) 3000, before exposure to heat treatment, and b) 1000 rpm, d) 2000 rpm and f) 3000 rpm, after prolonged exposure to 700 °C for 100 h, in air, respectively. Relating fittings are also supplied.

Table 4.1: Relative findings from the oxygen species that were detected in the near-surface areas of specimens prior to and after they were exposed for an extended period to 700 °C.

	O _{lattice}	O _{termination}	O _{surface}
1000 rpm initial	42	42	16
1000 rpm final	49	35	16
2000 rpm initial	44	40	16
2000 rpm final	47	40	13
3000 rpm initial	45	37	18
3000 rpm final	44	46	10

The variations in the oxygen reduction ability of the LCC films, which were fabricated through different coating rates, were measured using electrochemical

impedance spectroscopy (EIS) on symmetrical half-cells, with the LCC/SDC/YSZ/SDC/LCC architecture. Fig. 4.6a and b, and its related inset represent the Nyquist and Bode plots, respectively, prior to and after long-term operation at 700 °C. The area specific electrolyte resistances and any extra current collecting losses were denoted as ASR_{ohmic} . For the purpose of making, it easier to compare the electrochemical activities, these resistances were omitted from the Nyquist plots. In this case the distance from the origin to the horizontal intercept is considered as the total polarization resistance of the two electrodes (ASR_{total}). This value should be divided by two to obtain the polarization resistance per one electrode ($ASR_{cathode}$). As stated in the first chapter, rate of oxygen reduction over LCC-type MIEC electrodes is limited by a surface adsorption process [89], [16], [90] which is assumed as the case here. Activation energies of ASR_{total} ranging from 1.23 to 1.48 eV obtained here (Fig. 4.6c) are also in agreement with oxygen surface exchange processes [52].

It was clear that the coating rate had a substantial influence on the Initial electrode resistance, $ASR_{cathode}$. At 700 °C, the $ASR_{cathode}$ values were obtained to be 0.43, 0.16, and 0.12 $\Omega \cdot cm^2$ at 1000, 2000, and 3000 rpm, respectively. The thinner version of our 3000 rpm sample yielded an $ASR_{cathode}$ value of 0.15 $\Omega \cdot cm^2$ at 700°C. It can be suggested that increasing the thickness did not increase the initial performance significantly.

$ASR_{cathode}$ data were gathered every ten hours during 100-hour soaking time to investigate the influence of deposition with varying spinning rates on the stability of LCC cathodes (Fig. 4.6d). $ASR_{cathode}$ values raised considerably in samples manufactured at 1000 rpm and 2000 rpm but remained almost steady at 3000 rpm after prolonged annealing at 700°C.

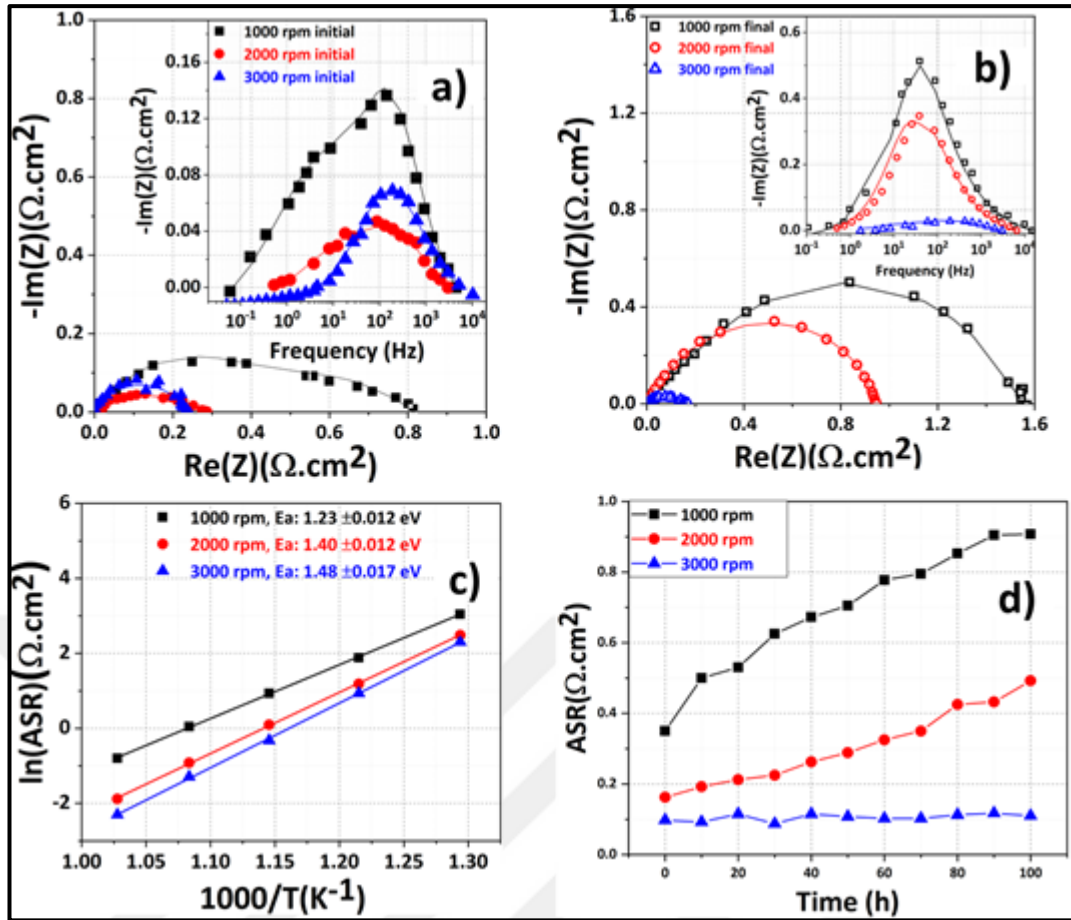


Figure 4.6: Nyquist and Bode (insets) graphs gathered from electrochemical impedance spectroscopy analysis collected from LCC samples a) pre-calcined at 700 °C, b) heat treated for 100 h at 700 °C, and temperature dependence of the total polarization resistances and area specific resistance obtained from per 10 hours during the long-term measurement at 700 °C of all samples are provided in (c) and (d), respectively.

4.3. Correlation of the Long-Term Performance Stability to Spin-Coating Rate

Initial microstructure and surface chemistry of polymeric precursor-derived LCC electrodes are dictated by the spin-coating rate through which they are fabricated. It is reasonable to propose that the unique crack and pore structures obtained in the case of different spinning speeds are strongly correlated to the initial surface chemistry of the electrodes, and hence, their long-term performance stabilities. For example, it is possible that formation of the large cracks in the 1000 rpm sample during drying allowed for facile transport of Co to the surface via carbonaceous gases, resulting in a highly Co-rich surface. The reduced stresses by thinner film deposition via 2000 rpm

reduced the amount of large cracks and gaseous phase Co transport took place through the large pores generated by abrupt gas discharge, and hence less severe Co enrichment was observed at the surface. 3000 rpm sample was fabricated through a cumbersome 55 deposition/drying cycles, leaving entrapped gasses, which was discharged through both pore and crack formation. The additional Co-containing gas discharge route likely yielded a surface richer in Co in comparison to that of 2000 rpm sample.

Despite the stability of both relative amounts of cations and O1s components, the electrochemical performance of the 2000 rpm sample degraded notably upon long-term operation. This could be ascribed to the densification of the film microstructure, reducing the effective electrode surface area. On the other hand, further enrichment of the surface with Co in the 1000 rpm sample resulted in a decrease in surface oxygen vacancies and an increase in surface oxygen. This could be ascribed to the formation of electrochemically inactive Co_3O_4 phase [52], blocking the surface vacancies and thereby reducing the electrochemical performance. On the other hand, the Co content in the 3000 rpm sample decreased upon long-term annealing, this, in turn, increased surface oxygen vacancy concentration. The combination of sintering-induced surface area loss and enhancement of surface oxygen vacancy concentration resulted in a stable electrochemical performance.

4.4. Summary

In this chapter we have investigated the effect of spin-coating parameters on the performance stability of polymeric precursor-derived LCC electrodes. 1000 rpm sample had macro-cracks at its surface, originating from the inability to accommodate shrinkage stresses, while 2000 rpm sample had a thinner film layer after each coating, which allowed for crack-free film formation. All samples (1000, 2000 and 3000 rpm) also had spherical pores at their surfaces and throughout their bulk, which has recently been ascribed to abrupt discharge of carbonaceous gases during drying. In addition to these, 3000 rpm sample also had cracks (morphologically dissimilar to those observed in 1000 rpm sample), which are likely caused by the higher number of deposition/drying cycles applied in comparison to other samples to reach similar thicknesses. The films appeared to have densified upon long-term exposure to 700°C.

The different surface microstructures yielded different surface chemistries. For example, cracked surfaces allowed for facile gaseous transport of Co to the top surface, resulting in highly Co-rich surfaces. 1000 rpm had its surface further enriched in the electrochemically inactive Co_3O_4 , while the surface oxygen vacancy concentration decreased. This resulted in fast electrochemical performance decay. On the other hand, the Co-concentration decreased at the surface of 3000 rpm sample, which was concomitant to an increase in the surface oxygen vacancy content. The combined effect of oxygen vacancy concentration increases and surface area loss via sintering resulted in stable electrochemical performances.

This study clearly showed that long-term performance stability is directly affected by the fabrication parameters of polymeric precursor derived LCC electrodes.



5. CONCLUSIONS AND RECOMMENDATIONS

The world's energy needs have increased dramatically in recent years and are expected to keep rising as the population grows and economic and technological progress is maintained. Hydrocarbons have replaced fossil fuels as the main source of energy since the industrial revolution, with usage now approaching 10,000 million tons of oil equivalent annually. However, the energy gained from burning hydrocarbons while using fossil fuels results in the emission of CO₂ gas into the environment, which contributes to global warming. The need for a clean alternative energy source is urgent, hence there are now many possibilities available. These options include reducing the use of fossil fuels, increasing the demand for environmentally friendly energy sources like fuel cells and renewable sources, and maximizing energy efficiency. Fuel-cell technology, which generates electricity and heat using the chemical energy in fuel without the need for an additional burning phase, has a substantially greater power conversion efficiency than traditional thermomechanical systems. In contrast to batteries, fuel cells never need to be recharged or run out of electricity. If the electrodes are supplied with both the fuel and the oxidant, the fuel cell may function with little environmental impact. SOFCs are a well-known and recently "developed" high temperature fuel cell technology. Significant, high-energy users, such as whole industrial complexes and huge power plants, may benefit much from it. SOFCs may be employed in automobiles, according to certain fuel cell innovators. The electrolyte in a SOFC system normally is made of solid ceramic and operates at high temperatures (600–1000 °C). The higher operating temperatures encourage individual regeneration, quick electrocatalysis with common metals, and increased cogeneration heat output. This particular fuel cell may function at up to 70% efficiency, with an additional 20% efficiency being recovered as heat. They are appropriate for power production in utility applications since SOFCs take a while to reach operational temperatures. Application of solid oxide cells is limited by long-term degradation and high running expenses. Air electrode deterioration affects cell performance more significantly than fuel electrode degradation at low temperatures. To improve the cathode performance, the stability and performance of perovskite-based thin film cathodes for solid oxide fuel cells was investigated in this dissertation. To do this, we suggested substituting Ca²⁺ (ionic radius for 12 coordination = 1.34 Å) for the bigger Sr²⁺ dopant in order to prevent elastic

strain and subsequently dopant segregation while maintaining all the advantages of divalent doping. With relation to surface chemistry in particular, the purpose of this dissertation was to get a deeper knowledge of the processes occurring at the gas-solid interface on the oxygen electrode of solid oxide cells. The nature of common MIEC materials' surfaces was demonstrated throughout the dissertation to be dynamic, clearly distinct from the bulk, and most notably major element of the rate of oxygen exchange kinetics.

Chapter 2 deal with ECR. The oxygen exchange coefficient (k_{chem}) and diffusion coefficient (D_{chem}) values are more influenced by surface chemistry and surface element distribution. We discovered that impure CaO and CoO_x phases precipitated on the grain boundaries on the surface and bulk of the 40% Ca doped LCC sample before and after heat treatment. However, the heat treatment of these precipitates caused the grains to grow, which causes a minor drop in ORR and a consequent fall in k_{chem} value since the active phase ratio on the surface is also somewhat lowered. Another important thing to keep in mind is that, the $\text{Ca}_{\text{non-lattice}}$ and $\text{O}_{\text{surface}}$ ratios, which provide an isolating CaO layer on the surface and lower ORR by trapping the active O terminations, virtually did not alter as a result of heat treatment.

However, particles that were dispersed randomly, and in particular translucent amorphous-like platelets that partially covered the grain surfaces and proliferated during the heat treatment time in 40% Sr doped LSC. Since these platelets cover the Sr-doped LaCoO_3 phase's surface, the active phase ratio is reduced, which is probably what causes the ORR and k value to decrease. Following heat treatment, $\text{Sr}_{\text{non-lattice}}$ and $\text{O}_{\text{surface}}$ ratio, which generate an isolating SrO layer on the surface and reduce ORR by trapping the active O terminations, dramatically increased.

Chapter 3: The initial performance and prolonged stability were substantially dependent on the pre-calcination temperature, at 800 °C resulting in the smallest electrode polarization resistance (20% Ca doped LCC-800 and 40% Ca doped LCC-800). Meanwhile, specimens as-calcined at 800 °C revealed a greater rate of performance degradation when exposed to 700 °C for an extended period than samples as-calcined at 700 or 900 °C. Enhanced Ca concentration in LCC-800 ended up an even more rapid loss of performance.

With the exception of 20% Ca doped LCC-700, which included Co_3O_4 and $(\text{La,Ca})_2\text{CoO}_4$ impurities in the as-calcined temperature. All specimens had only

rhombohedral (La,Ca)CoO₃ before to and following to extended subjected to 700 °C. Considering that oxygen reduction across the LaCoO₃ type MIEC electrodes is restricted by oxygen exchange at the surface, the total pore perimeters per unit area (TPPA) values were determined to assess microstructural development and its likely influence on the electrochemical activity and stability. These values are indicative of the surface area created by porosity per unit volume as determined by scanning electron microscopy (SEM) images processed with the ImageJ software. As predicted, raising the calcination condition resulted in a drop in surface area, while raising the calcium content resulted in an increase in surface area. Prolonged exposure to 700°C ended up equal TPPA losses independent of the pre-calcination condition, although raising the Ca concentration (40 % Ca doped LCC-800) ended up a substantially more stable microstructure.

At first, the surfaces of 20 % Ca doped LCC-700 and 40 % Ca doped LCC-800 were cobalt-rich and most certainly included Co₃O₄ produced at the (La,Ca)CoO₃/(La,Ca)₂CoO₄ phase interfaces. Despite the overall tendency toward more Ca-rich and Co-deficient LCC surfaces seen across entire specimens, the chemical composition of the surface species was temperature dependent. CaO and CaO + La₂O₃ species, for e.g., created on the surfaces of 20 % Ca doped LCC-800 and 40 % Ca doped LCC-800, respectively, which were the just two specimens to display a reduction in oxygen vacancy ratios while also experiencing the most pronounced electrochemical performance degradation after extended time subjected to 700 °C.

In general, it was found that the generation of the surface chemical composition had a greater effect on the electrochemical activity and prolonged stability. The fabrication of (La,Ca)CoO₃ electrodes using reasonably priced polymeric precursor technologies that demonstrate both improved electrochemical activity and prolonged stability may necessitate specific refinements, including surface modification to retard surface segregation.

Chapter 4: The top surface of LCC films generated at different spinning rates have two types of characteristics: i) pores created by gas discharge; ii) macro cracks on the top surface of the films induced by shrinkage strains. Also, the cross-sectional images show that the thickness of films are 6-7 micrometers with a presence of pores inside the films. Platelets are concentrated in locations where microcracks and pores are tightly packed together, according to images acquired from all sample surfaces.

Prior to and after extensive heat treatment, all of the specimens appear to be Co-rich on the surface. This is most likely due to the fact that cobalt is transported in the gas phase by carbonaceous gases. It also implies that the hexagonal platelets seen on the top surface of all samples before and after heat treatment at 700°C are Co-oxide. The O_{surface} , $O_{\text{termination}}$, and O_{lattice} ratio were essentially unaffected by the deposition parameters after 3 hours of pre-calcination at 800 °C. After 100 hours of heat treatment at 700°C, $O_{\text{termination}}$ stayed unchanged in the sample generated by 2000 rpm, reduced in this of generated by 1000 rpm, and rose in that of generated by 3000 rpm.

The spinning deposition rate had a significant impact on the initial performance and long-term stability. The sample formed by 3000 rpm has the lowest cathode polarization resistance and is the most stable film. It can be concluded here that to increase the spinning rate during the deposition processes of LCC films that derived from polymeric precursors, the ASR_{cathode} value decreases. The sample generated at 3000 rpm would be suitable for use as a cathode with intermediate temperature (below 700°C) in solid oxide fuel cells (IT-SOFC). To best of our knowledge, no cathode has ever been developed in the literature that is stable for this long term-operation (100 hours).

This research has shown that Ca-doped LaCoO_3 perovskites are more stable than Sr-doped LaCoO_3 perovskites, which are widely utilized as cathode materials in SOFC applications. However, it is vital to examine into these cathodes' long-term stability before using them as cathode material in SOFC cells (eg 1000 hours). The performance of cathodes with increased geometric surface area should also be manufactured and tested. These cathodes should also be used in SOFC stacks, and the performance of such stacks should be evaluated.

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BIOGRAPHY

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APPENDICES

1. Supplementary Information

1.1. The area specific polarization resistances

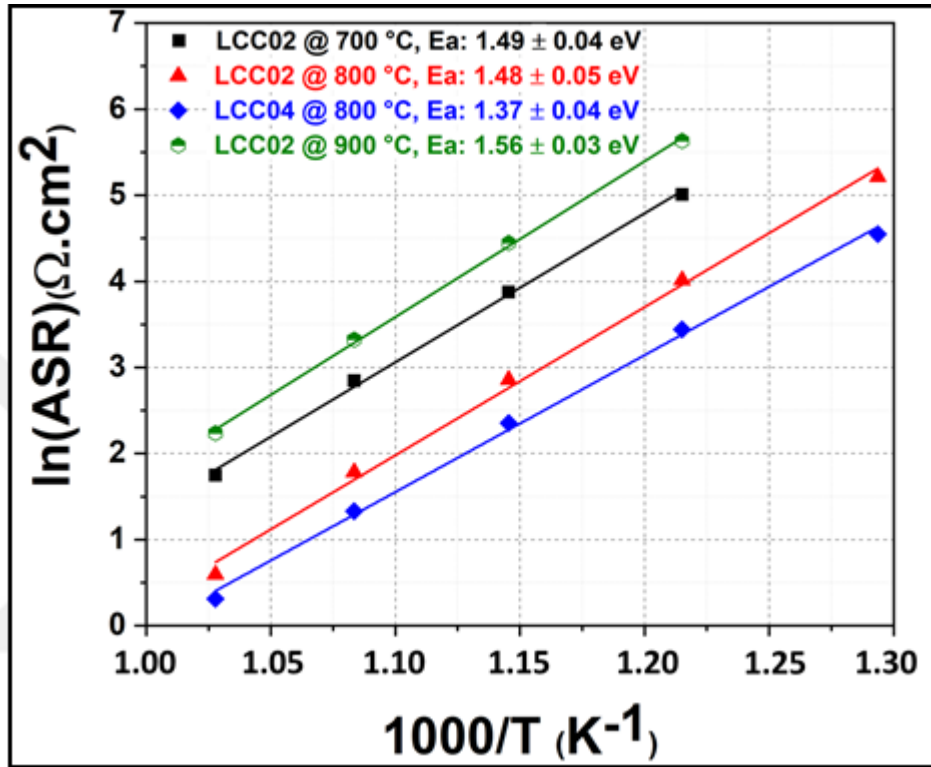


Figure A.1: Temperature dependency of area-specific polarization resistances for all specimens after 17 hours of subjected to 700 °C.

Electrochemical impedance spectroscopy (EIS) studies at temperatures ranging from 700 to 500 °C in air (Biologic, SP150), at a frequency interval of 50 mHz to 50 kHz, with an excitation voltage of 10 mV, were used to determine the electrochemical performance of LCC electrodes. Alternating EIS measurements achieved after a 17-hour subjected to 700 °C were employed to assess the LCC cathodes' extended time activity. The temperature dependency of $ASR_{cathode}$ values was investigated, and activation energies ranging from 1.37 to 1.56 eV were found.

1.2. X-ray Photoelectron Spectra of LCC Thin Films

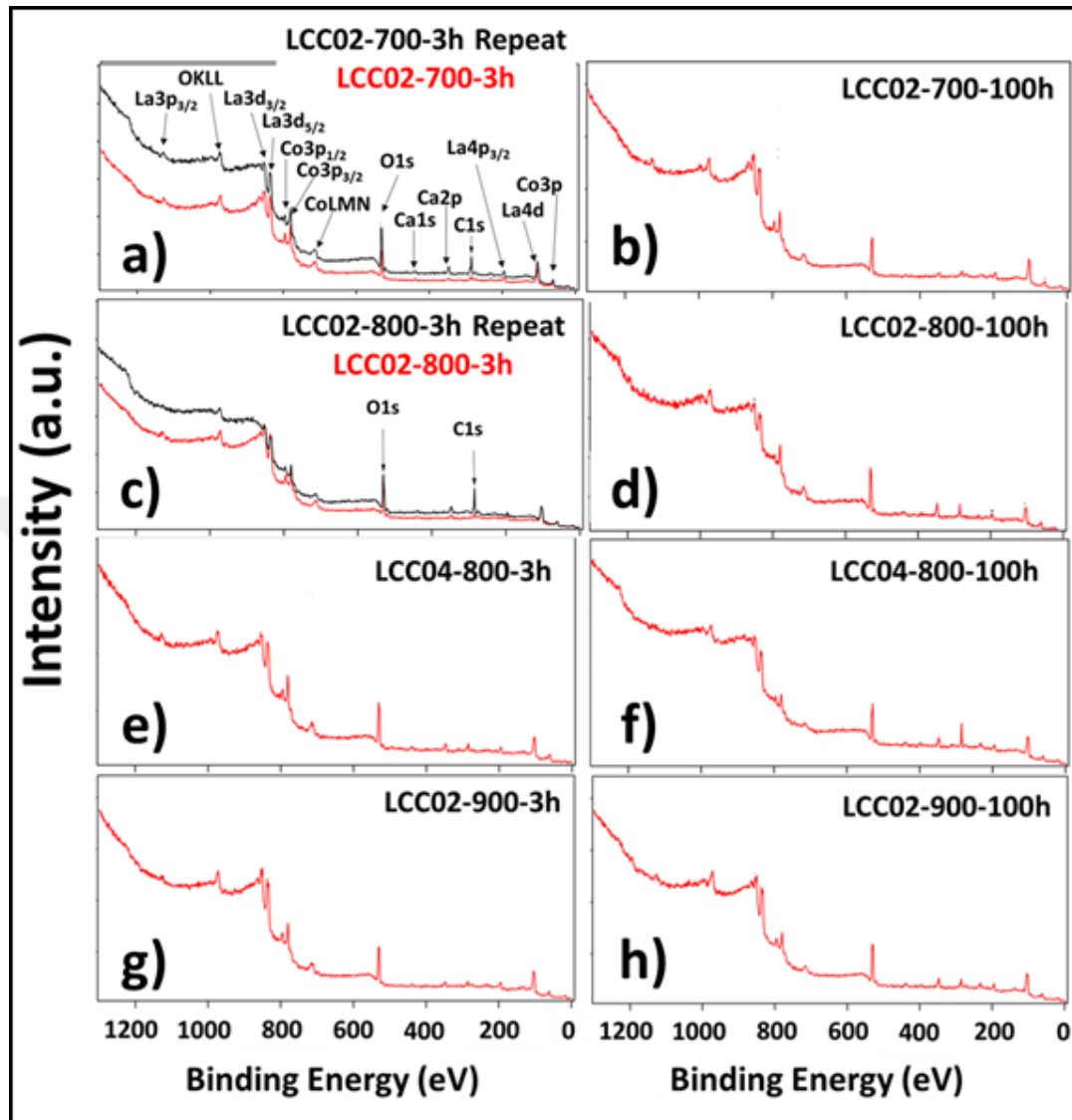


Figure A.2: X-ray photoelectron spectra of a) and c) the first and second analysis of 20 % Ca doped LCC-700 and 20 % Ca doped LCC-800, respectively, e) 40 % Ca doped LCC-800 and g) 20 % Ca doped LCC-900 before, b) 20 % Ca doped LCC-700, d) 20 % Ca doped LCC-800, f) 40 % Ca doped LCC-800, h) 20 % Ca doped LCC-900 following long-term subjected to 700 °C, in atmosphere.

By using x-ray photoelectron spectroscopy, we were able to identify variation in the surface composition/chemical composition of LCC thin films after prolonged heat treatment at 700 °C (XPS). The XPS analysis was conducted in an ultrahigh vacuum environment with a base pressure of 10⁻¹⁰ mbar. The chamber is attached with a SPECS Phoibos 150 hemispherical charged element analyser and a SPECS XR 50 300 W X-ray source. The XPS measurement was conducted in static analyzer transmission

type using an Al K (1486.61 eV) x-ray source at a pass energy of 50 eV. The photoemission lines of Au 4f_{7/2} (84.1 eV) were utilized to calibrate the Fermi level spectrometer. Au4f_{7/2} possessed a full width at half maximum (FWHM) of 1.5 eV. Meanwhile, whereas the cation percentages on the surface of the SOFC cathodes supply data on the component in touch with the ambient air and thus the oxygen reduction activity, we followed the variations in the virtual positive aion insides on the surface of the LCC cathodes over time. Extents of x-ray photoelectron spectroscopy (XPS) were determined on samples before and following extended time subjected to 700°C.

1.3. Analysis of Ca 2p Spectra

The Ca atomic concentration and development of the Ca binding environment in the crystal lattice and in the non-lattice phase are governed by the Ca 2p photoelectron core level peak at the cathode surface, as shown in Figure 1S. Ca 2p photoelectron spectra data were acquired from perovskite lattice-bound Ca_{lattice} at low binding energies and surface-bound Ca_{non-lattice} at high binding energies. The results gathered from the Ca_{lattice} were attributed to the perovskite LCC's Ca chemical environment. Canon-chemical lattice's environment might be attributed to the creation of species such as CaO or Ca(OH)₂.

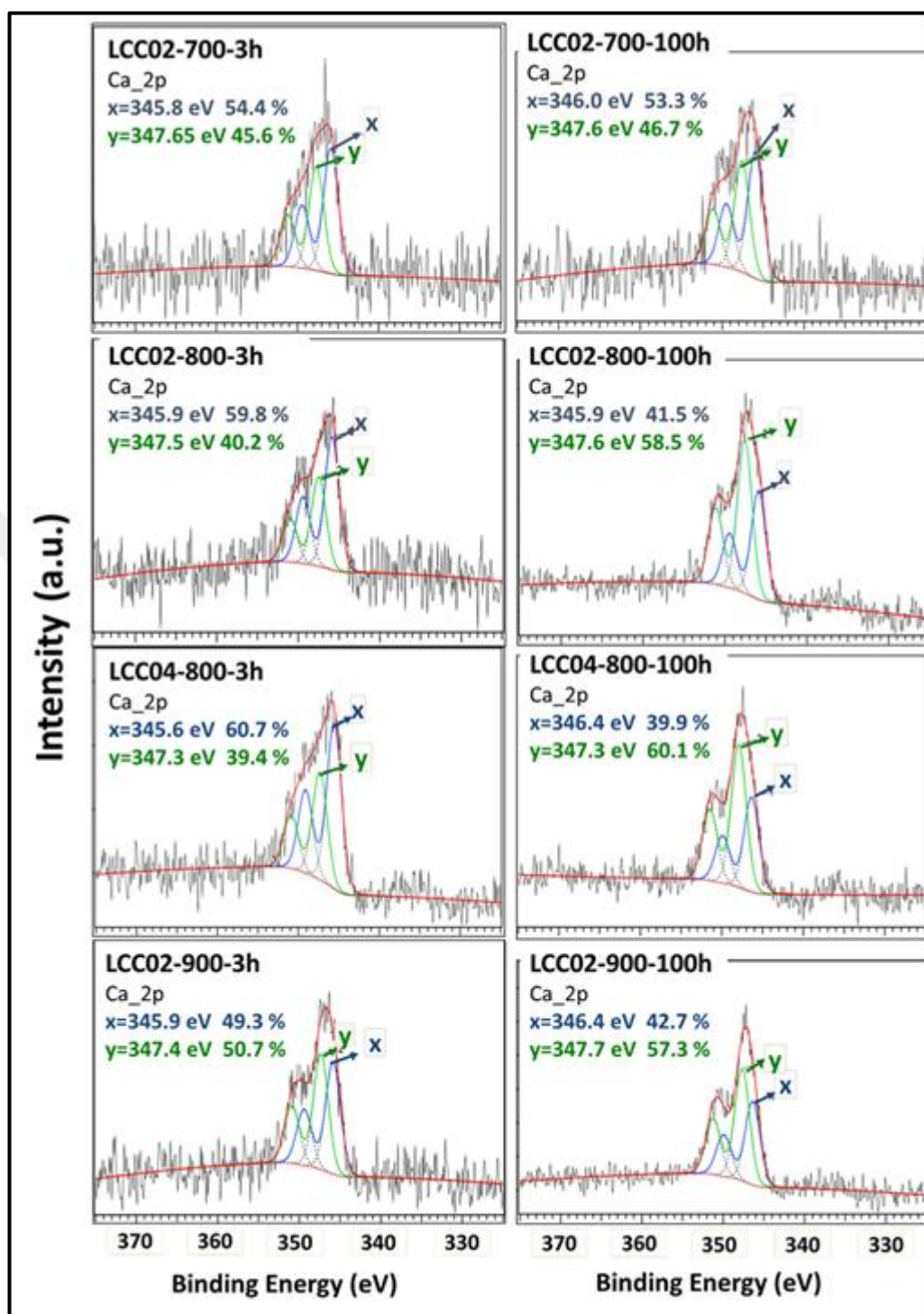


Figure A.3: Displays the Ca 2p x-ray photoelectron spectra recorded from the surface of electrodes before and following extended time operation at 700 °C in atmosphere. (x denotes Ca_{lattice}, y denotes Ca_{surface})