

**T.R.**  
**GEBZE TECHNICAL UNIVERSITY**  
**GRADUATE SCHOOL**

**DEVELOPMENT OF A-SITE DOPANT-FREE PEROVSKITE**  
**AIR ELECTRODES FOR SOLID OXIDE CELLS**

**ÖMER FARUK AKSOY**

**A THESIS OF MASTER OF SCIENCE**  
**DEPARTMENT OF MATERIALS SCIENCE AND**  
**ENGINEERING**

**ADVISOR: ASSOC. PROF. ALİGÜL BÜYÜKAKSOY**

**FEBRUARY 2025**

**T.R.**  
**GEBZE TECHNICAL UNIVERSITY**  
**GRADUATE SCHOOL**

**DEVELOPMENT OF A-SITE DOPANT-FREE  
PEROVSKITE AIR ELECTRODES FOR  
SOLID OXIDE CELLS**

**ÖMER FARUK AKSOY**

**A THESIS OF MASTER OF SCIENCE  
DEPARTMENT OF MATERIALS SCIENCE AND  
ENGINEERING**

**ADVISOR: ASSOC. PROF. ALİGÜL BÜYÜKAKSOY**

**FEBRUARY 2025**

**T.C.**  
**GEBZE TEKNİK ÜNİVERSİTESİ**  
**LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ**

**KATI OKSİT HÜCRELERİ İÇİN A-POZİSYONU**  
**KATKISIZ PEROVSKİT HAVA ELEKTROTLARININ**  
**GELİŞTİRİLMESİ**

**ÖMER FARUK AKSOY**

**YÜKSEK LİSANS TEZİ**  
**MALZEME BİLİMİ VE MÜHENDİSLİĞİ**  
**ANABİLİM DALI**

**DANIŞMAN: DOÇ. DR. ALİGÜL BÜYÜKAKSOY**

**ŞUBAT 2025**



## **MASTER of SCIENCE JURY APPROVAL FORM**

A thesis submitted by Ömer Faruk AKSOY, defended on 14/02/2025 before the jury formed with the 03/02/2025 date and 2025/08 numbered decision of the GTU Graduate Administration Board, has been accepted as a MASTER of SCIENCE thesis in the Department of Materials Science and Engineering.

### **JURY**

MEMBER

(THESIS ADVISOR) : Assoc. Prof. Aligül BÜYÜKAKSOY

MEMBER : Assist. Prof. Dr. Büşra GÜNHAN

MEMBER : Assist. Prof. Dr. Kerem Özgür GÜNDÜZ

### **APPROVAL**

Gebze Technical University Graduate Administration Board  
...../...../..... date and ...../..... numbered decision.

SIGNATURE/SEAL

## ABSTRACT

The need for energy in the global world is increasing day by day and solid oxide cells (SOCs) are promising devices that generate electricity or produce hydrogen (depending on the need) with extremely high efficiencies of up to %80. However, SOCs are associated with several problems, which need to be resolved to produce economically viable devices. Most of these problems arise from the relatively high operation temperatures of 600-800 °C, which induce materials degradation and, consequently, performance loss. One particular issue is the cation segregation in ABO<sub>3</sub>-type perovskite structured oxygen electrocatalysts. Sr has been used for decades to substitute the A-site La cation partially to generate oxygen vacancies and/or electron holes to enhance their electrochemical performance. However, due to the large cation size of Sr in comparison to that of La and the electrostatic attraction between Sr and the surface oxygen vacancies, Sr de-mixes and segregates to the perovskite surface. These segregations of oxides, carbonates and/or hydroxides of Sr are insulative and block oxygen exchange at the perovskite surface. Segregation in Sr doped electrodes are degradation mechanisms, thus cell performs poorly due to blocking of oxygen adsorption on the electrode surface.

The hypothesis of this work is, assuming that Sr segregation is extensive and is inevitable even at the electrode fabrication stage, Sr-free, perovskite-based electrodes may also be viable for SOC applications. To test this hypothesis, both undoped and Sr-doped LaMnO<sub>3</sub> - Sm-doped CeO<sub>2</sub> (SDC) composite films deposited on yttria-stabilized zirconia (YSZ) electrolyte substrates using the spin-coating deposition technique with polymeric liquid precursors were studied. The impact of Sr doping on long-term performance stability assessed through electrochemical impedance spectroscopy (EIS) were conducted on symmetrical electrode/electrolyte/electrode half-cells. Surface chemistry, phase, and microstructure evolution analyzed using x-ray photoelectron spectroscopy, x-ray diffraction, and scanning electron microscopy, respectively.

Undoped LaMnO<sub>3</sub> – SDC composite film demonstrated promising electrochemical performance in both short-term and long-term tests, exhibiting a reduced activation energy of 1.19 eV and an ASR of 0.45 Ω·cm<sup>2</sup> at 700 °C after 100 hours testing in EIS. These results indicate that Sr-free LaMnO<sub>3</sub>-SDC composite electrodes outperformed highly Sr-doped composites and were competitive against moderately doped ones. The higher performance of the Sr-free electrodes was linked to the homogeneous phase and surface chemistry they had.

**Keywords:** SOC, Perovskites, Air Electrode, Energy, Spin-coating, Deposition

## ÖZET

Küresel dünyada enerjiye olan ihtiyaç her geçen gün artmaktadır ve katı oksit hücreleri (KOH) %80'e varan çok yüksek verimliliklerle elektrik üreten veya hidrojen üreten (ihtiyaca bağlı olarak) umut verici cihazlardır. Ancak, KOH'lerin, ekonomik olarak uygulanabilir olması için çözülmesi gereken çeşitli sorunları vardır. Bu sorunların çoğu, malzemelerin bozulmasına ve sonuç olarak performans kaybına neden olan 600-800 °C gibi nispeten yüksek çalışma sıcaklıklarından kaynaklanmaktadır. En özel sorunlardan biri, ABO<sub>3</sub> tipi perovskit yapılı oksijen elektro katalizörlerindeki katyon ayrışmasıdır. Sr, on yıllardır A-pozisyonu La katyonunun yerine kısmen oksijen ve/veya elektron boşlukları oluşturmak ve böylece elektrokimyasal performanslarını artırmak için kullanılmıştır. Ancak, Sr'nin La'ya kıyasla daha büyük katyon boyutu ve Sr ile yüzey oksijen boşlukları arasındaki elektrostatik çekimler nedeniyle, Sr perovskit yüzeyine difüze olur ve ayrışır. Bu ayrışan ve oluşan oksitler, karbonatlar ve hidroksitler yalıtıcıdır ve perovskit yüzeyinde oksijen değişimini engeller. Bozunma mekanizması, Sr katkılı elektrotlarda stronsiyum ayrışması, dolayısıyla elektrot yüzeyindeki oksijen adsorpsiyonunun engellenmesi nedeniyle hücrenin zayıf performans göstermesi kaçınılmazdır.

Bu çalışmanın hipotezi, Sr ayrışmasının kapsamlı olduğunu ve elektrot üretim aşamasında bile kaçınılmaz olduğunu varsayarak, Sr içermeyen, perovskit bazlı elektrotların da KOH uygulamaları için uygun olabileceğidir. Bu hipotezi test etmek için hem katkısız hem de Sr katkılı LaMnO<sub>3</sub> - Sm katkılı (%20 mol) CeO<sub>2</sub> (SDC) kompozit filmler, polimerik sıvı öncüllerle döndürme-biriktirme tekniği kullanılarak itriya ile stabilize edilmiş zirkonya (YSZ) elektrolit alt tabakaları üzerine biriktirilmiştir. Elektrokimyasal empedans spektroskopisi (EIS) ile değerlendirilen Sr katkılanmasının uzun vadeli performans kararlılığı üzerindeki etkisi, simetrik elektrot/elektrolit/elektrot yarı hücrelerinde gerçekleştirildi. Yüzey kimyası, faz ve mikroyapı değişimi sırasıyla x-ışını fotoelektron spektroskopisi (XPS), x-ışını kırınımı (XRD) ve taramalı elektron mikroskobu kullanılarak (SEM) analiz edildi.

Katkılanmamış LaMnO<sub>3</sub> – SDC kompozit filmi hem kısa hem de uzun vadeli testlerde umut verici elektrokimyasal performans gösterdi, EIS'de, 700 °C'de 100 saatlik testten sonra 1,19 eV'lik azaltılmış bir aktivasyon enerjisi ve 0,45 Ω·cm<sup>2</sup>'lik bir ASR gösterdi. Bu sonuçlar, Sr içermeyen LaMnO<sub>3</sub>-SDC kompozit elektrotlarının yüksek oranda Sr katkılanmış kompozitlerden daha iyi performans gösterdiğini ve orta derecede katkılanmış olanlarla rekabet ettiğini göstermektedir. Sr içermeyen elektrotların daha yüksek performansı, sahip oldukları homojen faz ve yüzey kimyasıyla bağlantılıdır.

**Anahtar Kelimeler:** KOH, Perovskit, Hava Elektrodu, Enerji, Spin-kaplama, Biriktirme

## ACKNOWLEDGEMENTS

I would like to thank my supervisor Assoc. Prof. Aligül BÜYÜKAKSOY who steered me in to right direction and taught valuable learnings throughout my bachelor and master education.

I also would like to thank Ahmet NAZIM for SEM images, Adem ŞEN for XRD analysis, Dr. Ali Şems AHSEN for XPS results and Dr. Büşra Tuğba Çamiç and Dr. Selçuk Birdoğan.

I would like to thank my laboratory colleagues and friends in the department who helped me and spent great time with, especially Dr. Mustafa Ünsal ÜNVER who always helped me and stood right next to me. I am so grateful that my family supported me for everything that I have done in this journey.

This thesis is financially supported by TÜBİTAK 2210-C (2023/2) and YÖK ADEP (2024-A-113-02) projects, I would like to thank them.

# TABLE OF CONTENTS

|                                                                                                                 | <b><u>Page</u></b> |
|-----------------------------------------------------------------------------------------------------------------|--------------------|
| ABSTRACT                                                                                                        | v                  |
| ÖZET                                                                                                            | vi                 |
| ACKNOWLEDGEMENTS                                                                                                | vii                |
| TABLE OF CONTENTS                                                                                               | viii               |
| LIST of SYMBOLS and ABBREVIATIONS                                                                               | ix                 |
| LIST OF FIGURES                                                                                                 | x                  |
| LIST OF TABLES                                                                                                  | xii                |
| <br>                                                                                                            |                    |
| 1. INTRODUCTION                                                                                                 | 1                  |
| 1.1. Energy Issue                                                                                               | 1                  |
| 1.2. Solid Oxide Cells                                                                                          | 2                  |
| 1.2.1. Working Principle of SOCs                                                                                | 3                  |
| 1.2.2. Fabrication of Solid Oxide Cells                                                                         | 5                  |
| 1.2.3. Materials for SOCs                                                                                       | 7                  |
| 1.2.4. Challenges of SOCs                                                                                       | 12                 |
| 1.2.5. Proposed Solutions in the Literature                                                                     | 14                 |
| 1.3. Aim of This Work                                                                                           | 15                 |
| 2. EXPERIMENTAL                                                                                                 | 17                 |
| 2.1. Fabrication                                                                                                | 18                 |
| 2.1.1. Electrolyte                                                                                              | 18                 |
| 2.1.2. Air electrode                                                                                            | 19                 |
| 2.1.3. Electrical Contact and Connection Configuration                                                          | 20                 |
| 2.2. Characterization                                                                                           | 21                 |
| 2.2.1. Crystal Structure and Phase Analysis                                                                     | 21                 |
| 2.2.2. Scanning Electron Microscopy                                                                             | 22                 |
| 2.2.3. Focused Ion Beam Processing and Transmission Electron Microscopy                                         | 22                 |
| 2.2.4. X-Ray Photoelectron Spectroscopy                                                                         | 23                 |
| 2.2.5. Electrochemical Impedance Spectroscopy                                                                   | 25                 |
| 3. RESULTS AND DISCUSSION                                                                                       | 28                 |
| 3.1. Phase Analysis                                                                                             | 28                 |
| 3.2. Microstructural Analysis                                                                                   | 30                 |
| 3.2.1. Surface Chemistry                                                                                        | 34                 |
| 3.3. Electrochemical Analysis                                                                                   | 37                 |
| 3.3.1. Temperature Dependence of the ASR                                                                        | 38                 |
| 3.3.2. Long-term Stability of the ASR                                                                           | 40                 |
| 3.4. Correlation of Microstructure, Phase and Surface Chemistry Evolution to<br>the Electrochemical Performance | 42                 |
| 4. CONCLUSION                                                                                                   | 43                 |
| <br>                                                                                                            |                    |
| REFERENCES                                                                                                      | 44                 |
| BIOGRAPHY                                                                                                       | 50                 |
| APPENDICES                                                                                                      | 51                 |

## LIST of SYMBOLS and ABBREVIATIONS

|              |   |                               |
|--------------|---|-------------------------------|
| SOC          | : | Solid oxide cell              |
| OCV          | : | Open circuit voltage          |
| $E^0$        | : | Standard electrode potential  |
| R            | : | Gas constant                  |
| T            | : | Temperature                   |
| MEA          | : | Membrane electrode assembly   |
| TPB          | : | Triple phase boundary         |
| LMO          | : | Lanthanum Manganite           |
| LSM          | : | Lanthanum strontium manganite |
| SDC          | : | Samarium doped ceria          |
| YSZ          | : | Yttria stabilized zirconia    |
| GDC          | : | Gadolinium doped ceria        |
| $R_{pol}$    | : | Electrode polarization        |
| $R_{ohm}$    | : | Ohmic polarization            |
| ASR          | : | Area specific resistance      |
| HT           | : | Heat-treated                  |
| LT           | : | Long-term                     |
| $\eta_{act}$ | : | Activation polarization       |

## LIST OF FIGURES

|                                                                                                                                                                                                                                                                        | <u>Page</u> |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------|
| <b>Figure 1.1:</b> Global electricity generation by source                                                                                                                                                                                                             | 2           |
| <b>Figure 1.2:</b> Graphical representation of SOC with integration of other green energy technologies and needs                                                                                                                                                       | 3           |
| <b>Figure 1.3:</b> Cell voltage and power density based on polarization sources                                                                                                                                                                                        | 4           |
| <b>Figure 1.4:</b> Working Principle of SOC                                                                                                                                                                                                                            | 5           |
| <b>Figure 1.5:</b> Mixing of electrocatalytic and ionic powders and TPB representation                                                                                                                                                                                 | 6           |
| <b>Figure 1.6:</b> Oxygen Ionic conductivity of various electrolyte materials                                                                                                                                                                                          | 8           |
| <b>Figure 1.7:</b> Crystal structure of single perovskite cell with formula of $\text{ABO}_3$                                                                                                                                                                          | 10          |
| <b>Figure 1.8:</b> Partial cell structure with current collector layer, porous electrode and dense electrolyte layer with TPB model included.                                                                                                                          | 10          |
| <b>Figure 1.9:</b> Electron and oxygen ion paths for single phase perovskites and MIECs in oxygen reduction reactions                                                                                                                                                  | 11          |
| <b>Figure 1.10:</b> Sr in $\text{ABO}_3$ structure causes a) elastic strain, b) electrostatic attraction and segregation hence c) enrichment of SrO on the surface (AFM image)                                                                                         | 15          |
| <b>Figure 1.11:</b> Illustration of Sr segregation and formation of oxides and other compounds.                                                                                                                                                                        | 17          |
| <b>Figure 2.1:</b> Schematic of symmetrical SOC fabrication.                                                                                                                                                                                                           | 17          |
| <b>Figure 2.2:</b> Production of green YSZ pellets by uniaxial pressing.                                                                                                                                                                                               | 18          |
| <b>Figure 2.3:</b> Sintering regime of YSZ pellets.                                                                                                                                                                                                                    | 18          |
| <b>Figure 2.4:</b> Spin coating deposition schematic.                                                                                                                                                                                                                  | 20          |
| <b>Figure 2.5:</b> Various contact a), b) configuration of contact wires, c) connection setup to sample holder and c) graphical contact representation of the cell.                                                                                                    | 22          |
| <b>Figure 2.6:</b> Basic principles of a) FIB-SEM and b) TEM                                                                                                                                                                                                           | 23          |
| <b>Figure 2.7:</b> Schematic representation of photoelectron emission in band gap as XPS based of.                                                                                                                                                                     | 25          |
| <b>Figure 2.8:</b> Graphical representation of Nyquist plot with one single arc visible and corresponding polarizations.                                                                                                                                               | 27          |
| <b>Figure 3.1:</b> XRD patterns and selected references for a) single-phase and b) composite samples and c) zoomed sections between $22-36^\circ$                                                                                                                      | 29          |
| <b>Figure 3.2:</b> SEM images collected from the surfaces of single phase electrodes prior ((a) LMO HT, b) LSM82 HT, c) LSM64 HT) to and after (d) LMO HT 100h, e) LSM82 HT 100h and f) LSM64 HT) long-term exposure to $700^\circ\text{C}$ .                          | 31          |
| <b>Figure 3.3:</b> SEM images collected from the surfaces of nanocomposite electrodes prior ((a) LMO-SDC HT, b) LSM82-SDC HT, c) LSM64-SDC HT) to and after (d) LMO-SDC HT 100h, e) LSM82-SDC HT 100h and f) LSM64-SDC HT) long-term exposure to $700^\circ\text{C}$ . | 32          |
| <b>Figure 3.4:</b> FIB process as a) carbon deposition, b) milling of both sides of the 33 layer to be removed and c) atom probe attached to the thin specimen                                                                                                         | 33          |
| <b>Figure 3.5:</b> STEM analysis with EDS mapping of La (red), Ce (blue), Mn (green) and Sr (dark Green) for a) LMO-SDC HT and b) LSM64-SDC HT.                                                                                                                        | 34          |
| <b>Figure 3.6:</b> Normalized dopant ratio to total A-site cations of different electrode surfaces.                                                                                                                                                                    | 35          |
| <b>Figure 3.7:</b> O 1s spectrums of annotated samples                                                                                                                                                                                                                 | 36          |

|                                                                                                                                            |    |
|--------------------------------------------------------------------------------------------------------------------------------------------|----|
| <b>Figure 3.8:</b> Sr 3d spectrums of annotated samples.                                                                                   | 36 |
| <b>Figure 3.9:</b> Nyquist plots for a) single phase and b) composite symmetrical cells at 700 °C in stagnant air as initial state 0 hour. | 39 |
| <b>Figure 3.10:</b> ASR vs temperature plots of a) single phase and b) composite samples with activation energies calculated               | 40 |
| <b>Figure 3.11:</b> Electrode polarization of all samples with increasing operation time at 700 °C.                                        | 41 |

## LIST OF TABLES

|                                                                                                                                                                                                                                                                                                                                        |    |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| <b>Table 1.1:</b> Various common LaMOx materials as air electrodes for SOC                                                                                                                                                                                                                                                             | 12 |
| <b>Table 2.1:</b> Summary of types of samples, their code names and the corresponding explanations. When referring to the as-heat treated states of these samples, the code name will be followed by “HT” and to refer to the states of samples after exposure to air at 700 °C for 100 hours, the code name will be followed by “LT”. | 20 |
| <b>Table 3.1</b> Detected oxygen concentrations from XPS data for given samples.                                                                                                                                                                                                                                                       | 35 |

# 1. INTRODUCTION

## 1.1. Energy Issue

Today, the need for energy in the world is increasing, due to advancements in technology. The conventional method of energy production is the burning of fossil fuels, which is an inefficient process (up to ca. 33% efficiency for coal plants and up to ca. 40% for natural gas plants without combined-cycle methods.) [1], [2], [3]. Today, up to 60% (International Energy Agency) of electricity is generated from fossil fuels. Production of electricity based on source can be seen in **Figure 1.1**. One crucial problem associated with this approach is the diminishing reserves of fossil fuels. International Energy Agency estimates that by the year 2030, the world will reach “peak oil” and the exhaustion of fuel supplies will be upon us [4]. In addition, and maybe even more importantly, burning fossil fuels result in the emission of gases that are extremely harmful both for the environment and human health. For example, CO<sub>2</sub> emissions induced by conventional energy technologies constitute ca. 75% of the total CO<sub>2</sub> emissions, which is the main reason for the thickening of the greenhouse layer [5]. Global warming caused by the CO<sub>2</sub> emission-induced greenhouse layer thickening is considered to have devastating implications on humanity, such as; draught, famine, mass migrations and wild fires [6].

Renewable energy technologies, such as electricity production from sunlight (solar power) and motion of wind turbines (wind power) emerged as possible alternatives to the conventional energy conversion routes. However, the renewable resources are intermittent, i.e., the access to sunlight and wind is not continuous. Hence, the use of renewable energy technologies is limited.

Solid oxide cells (SOCs) are devices that can generate electricity and water vapor from hydrogen and oxygen (fuel cell mode) or produce hydrogen and oxygen from electricity and water vapor (electrolysis mode) at very high efficiencies (reaching ca. 90%) [7]. Hence, they are ideal candidates to be integrated to the renewable energy technologies to mitigate their intermittency issues.

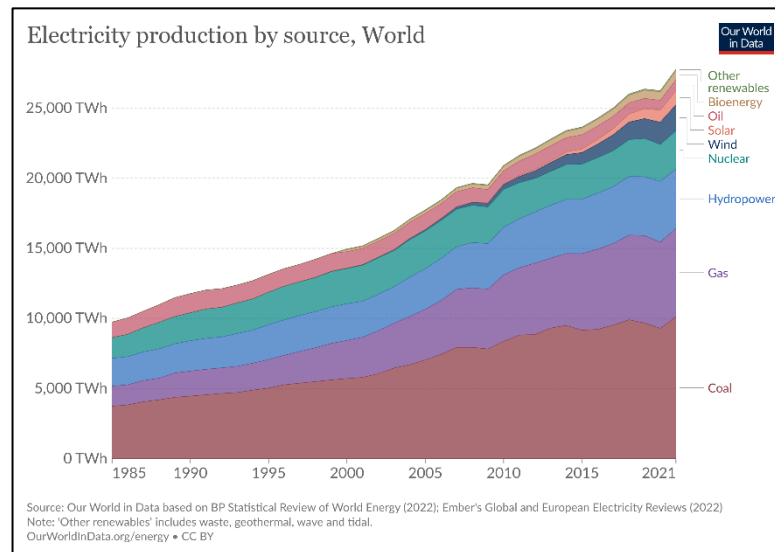


**Figure 1.1:** Global electricity generation by source [8].

## 1.2. Solid Oxide Cells

The importance of solid oxide cells is increasing day by day, especially in stationary applications [9]. SOC systems can exhibit up to ca. 80% efficiency, depending on the cell and stack design, used materials, operating temperature range, manufacturing process and the ability of the system to utilize excess heat [7]. With its high efficiency and ability to operate at zero carbon emissions it is a strong candidate to be both a powerful and sustainable solution. Early SOC's were designed to operate at elevated temperatures around 1000 °C, while recent developments in design, chemistry and fabrication techniques made SOC operation at 600-800 °C possible. SOC's can also be used in electrolysis mode to produce hydrogen from steam and electricity, at high efficiencies up to 99% with heat utilizations, owing to the high operating temperatures facilitating the breaking of bonds between the hydrogen and oxygen [3], [10]. The ability of SOC's to operate reversibly makes them very suitable to mitigate the intermittency of renewable energy technologies. For example, when there is plenty of sun/wind, SOC can be used in electrolysis mode and store hydrogen. In the absence of sun or wind, stored hydrogen can be used to run the SOC in fuel cell mode to provide electricity (**Figure 1.2.**).

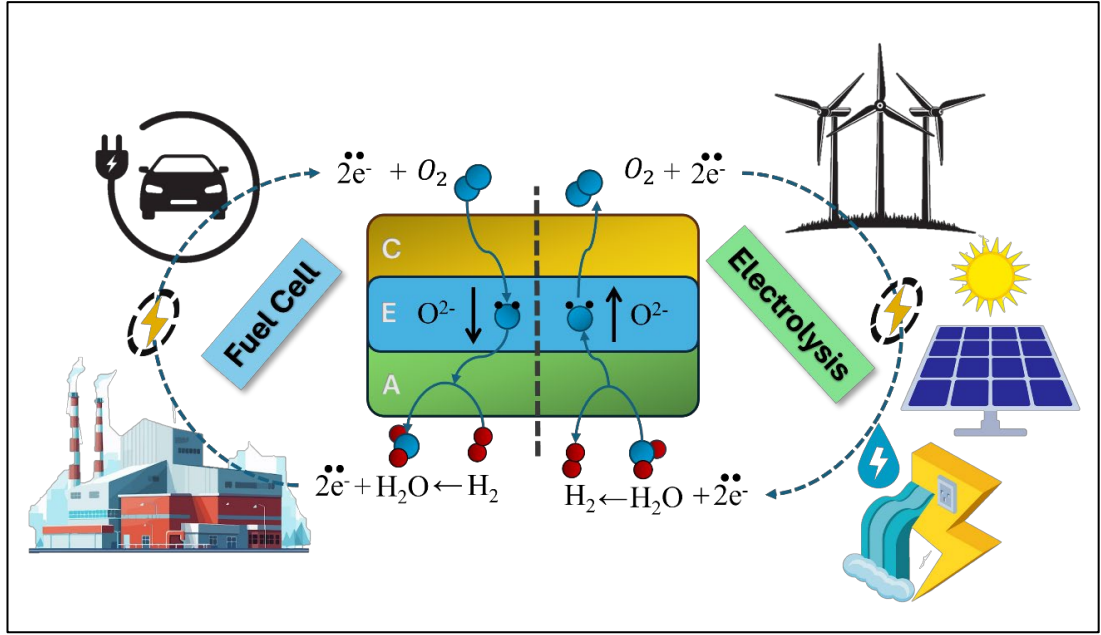


**Figure 1.2:** Graphical representation of SOC with integration of other green energy technologies and needs.

### 1.2.1. Working Principle of SOC

SOC structure consists of fuel and oxygen electrodes separated by an oxygen ion conductor electrolyte. In the fuel cell mode, air and fuel are supplied to oxygen and fuel electrodes respectively, while the system is kept at 600-800 °C. This generates an open circuit voltage (OCV), determined by the Nernst equation (**Equation 1.1**). OCV is 1.229 V under standard conditions at 273.15 K, and pressure of 1 atm.

$$E_{rev}(p, T) = E^0(T, p^0) - \frac{RT}{2F} \ln \left( \frac{x_{H_2O}}{x_{H_2} \cdot \sqrt{x_{O_2}}} \right) + \frac{RT}{4F} \ln p. \quad (1.1)$$

Where  $E^0$  is standard electrode potential,  $R$  is universal gas constant,  $T$  is temperature,  $F$  Faraday's constant, molar concentration  $x$  and air pressure  $p$ . Hence theoretical OCV can be calculated. In standard conditions, since  $p$  is 1 atm, right term diminishes.

However, the actual measured OCV is typically slightly lower than the theoretical reversible voltage ( $E_{rev}$ ) by an amount denoted as  $U_L$ , which accounts for potential losses caused by residual electronic conduction in the electrolyte and possibly gas crossover or leakage through cracks and defects in the electrolyte. The thermodynamically achievable cell voltage ( $V_{cell}$ ) at OCV which is calculated in

**Equation 1.2**, also depends on the type of fuel used, as well as the operating temperature and pressure. For instance, an atmospheric SOC running on hydrogen and oxygen has an OCV of approximately 0.908 V at 1,000 °C. When a current (I) is drawn, the voltage decreases further due to factors such as, ohmic resistance (IR),  $U_L$  for gas crossover-leakage, activation polarization ( $\eta_{act}$ ) and concentration polarization losses ( $\eta_{conc}$ ).

$$V_{cell} = E_{rev} - U_L - IR - (\eta_{act} + \eta_{conc}) \quad (1.2)$$

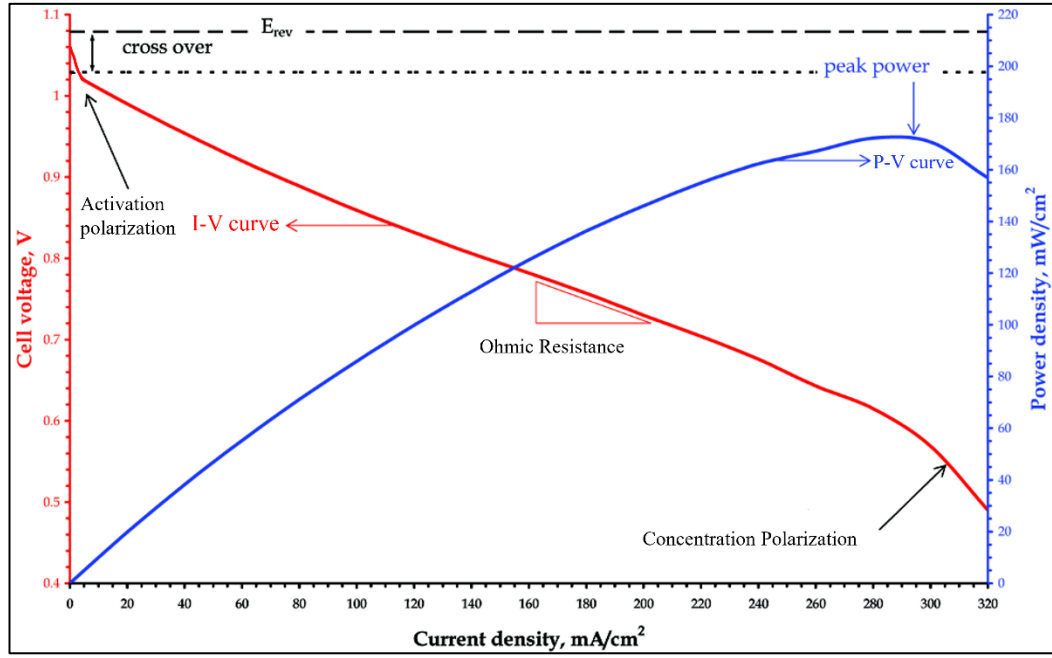


**Figure 1.3:** Cell voltage and power density based on polarization sources [11].

As can be seen in **Figure 1.3**, I-V curve behaves linearly in the middle except voltages near to OCV and below the 0.6 V. Ohmic resistance is directly related to internal resistance of the cell due to mostly thickness which is dominant and obeys Ohm's Law. Activation polarization is due to chemical factors such as limited activity of gases towards the electrode material and the electrode-electrolyte interface. Examples as limited reactivity due to the high activation energy of the gas/electrode reaction (i.e. oxygen reduction and fuel oxidation reactions) and the formation of unreacted species that saturate and eventually drown the electrodes. Concentration polarization however is in the simplest terms absence of reactants, oxygen or fuel.

When current is drawn from the cell, oxygen gas is reduced to oxygen ion at the oxygen electrode by gaining electrons and transported to the fuel electrode through the ionic conductor electrolyte. At the fuel electrode, oxygen ion combines with hydrogen to release electrons and steam, completing the circuit. Electrolysis in SOCs is a process where electrical energy is used to drive a chemical reaction to produce hydrogen. The electrolyte conducts oxygen ions ( $O^{2-}$ ) from the fuel electrode (where reduction occurs) to the air electrode (where oxidation occurs). At the fuel electrode, steam ( $H_2O$ ) molecules are reduced to release hydrogen ( $H_2$ ) and oxygen ions. At the air electrode, the oxygen ions release electrons and form oxygen gas. Overall, electricity splits water into hydrogen and oxygen. Schematic representations of two modes of SOC are given with reactions in **Figure 1.4**.

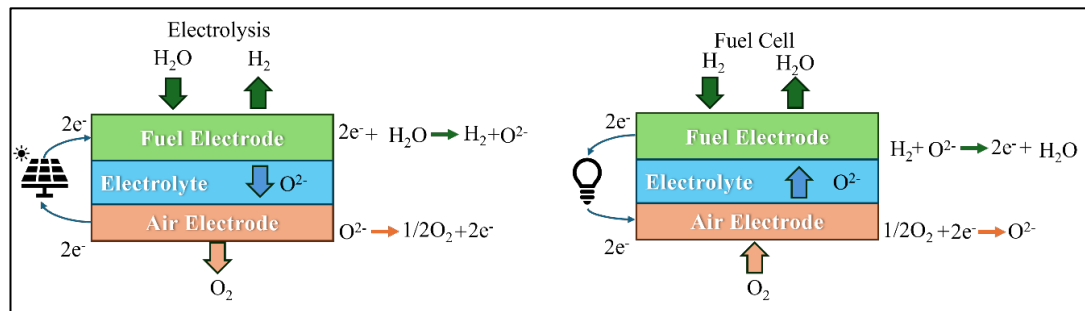


**Figure 1.4:** Working Principle of SOC.

### 1.2.2. Fabrication of Solid Oxide Cells

Solid oxide cells fabricated according to type of the cell e.g. planar or tubular, supporting structure of membrane electrode assembly (MEA), desired performance, working conditions and cost. MEA is the core structure of the cell which contains electrodes and electrolyte hence fabrication must be done very carefully.

Most common fabrication techniques are tape casting, solid-state powder synthesis, screen printing, depositions such as electrophoretic deposition, spin-coating, spray pyrolysis, sputtering, dip coating, atomic layer deposition, plasma spraying and lastly sol-gel or Pechini methods. Infiltration method which is based on capillary forces of porous backbone to absorb desired ionic or electronic phase as polymeric precursor to

form nano particles or thin-films is used to enhance further the electrocatalytic activity of the electrodes especially in air electrodes.

Sintering is the crucial part of fabrication of electrodes and electrolyte in SOC applications. Because bonding, density, mechanical integrity, particle size and reactions are directly affected by sintering. Studies about sintering behavior has been done in the literature [12], [13], [14]. Homogenous composite microstructure of electrodes can be achieved with mixing powders of both electrocatalyst and ionic conductor together after ball milling to achieve few microns of particle size. Mixing homogeneity is a crucial factor in the development of composite cathodes, homogeneity is influenced by the intrinsic properties of the starting powders, the quality of dispersion, and the packing structure. Alongside the maximum number of contacts between the same phase particles is desired as high as possible, intersection of electrocatalyst, ionic phase and porous structure is crucial for electrode performance of the cell, this structure is called Triple Phase Boundary (TPB) and explained further in latter chapters.

Powder mixing of both phases and TPB are shown in **Figure 1.5**. With conventional solid-state reactions eventually sintering involving, nano-scaled homogenous and small particle sized electrode structure is not attainable.

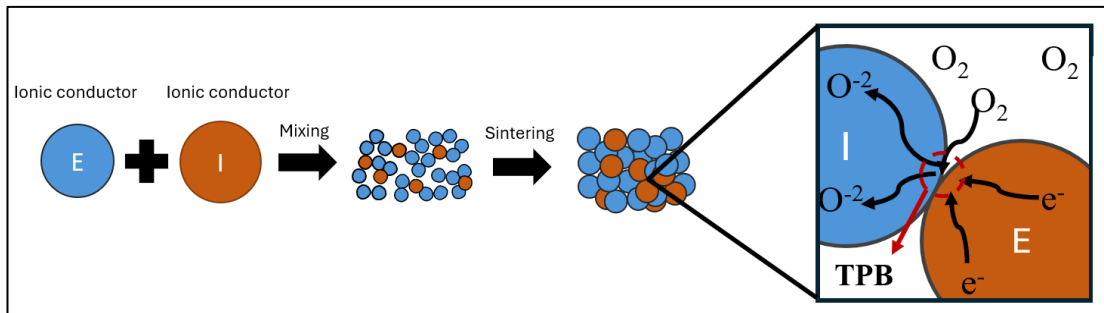


**Figure 1.5:** Mixing of electrocatalytic and ionic powders and TPB representation.

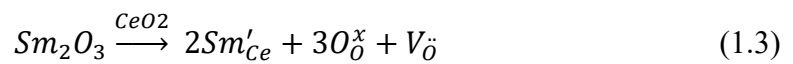
In the case of Pechini method, nano-structured composite porous electrode can be achieved at low cost compared to other deposition techniques such as atomic layer deposition (ALD) or solid-state reaction techniques such as powder synthesis which have lower homogeneity compared to Pechini. Electrocatalyst and ionic conductor materials brought together with mixing of solutions before the combustion of the pre-

cursors hence nanocomposite is obtainable. After combustion, calcination carries on to eliminate organics. Fabrication method in this study explained in **chapter 2.1.2**.

### 1.2.3. Materials for SOCs

#### 1.2.3.1. Electrolyte

As mentioned previously, electrolytes must be an oxygen ion conducting material, which also simultaneously must be an electronic insulator to prevent electron leakage between electrodes. Oxygen ion transport occurs via the thermally activated hopping of oxygen ions between neighboring crystal lattice sites. For this migration to occur, the crystal must have unoccupied sites (i.e., oxygen vacancies). Additionally, the energy required for an oxygen ion to migrate to an adjacent unoccupied site must be relatively low typically less than 1 eV [15]. At first glance, achieving such a low migration barrier might seem unlikely, given that oxygen ions are the largest constituents of the lattice, with an ionic radius of 0.14 nm. Intuitively, smaller metal ions would be expected to exhibit higher mobility within the lattice and thus contribute more significantly to current conduction. However, in certain crystal structures where oxygen defects dominate, oxygen ions become the primary mobile species, migrating under the influence of an electric field such as  $ZrO_2$ -,  $CeO_2$ -, and  $Bi_2O_3$  [16]. Oxygen vacancy formation of ceria by Sm doping can be seen in **Equation 1.3**.



Electrolyte layer must be very dense (gas-tight) to prevent gas mixing hence leakage of fuel and air from both electrode sides. In electrode or interconnect supported cells, electrolyte layer must be as thin as possible to obtain minimum ohmic resistance. Electrolyte thickness is generally between 10 $\mu$ m to 500 $\mu$ m, depending on the cell design. It is also common that barrier layers with different electrolyte materials (SDC, ScDC, GDC, YSZ) is applied to ensure chemical and mechanical stability between cathode and electrolyte layers. Main electrolyte materials used in SOCs mostly are fully stabilized zirconia with 8% mol doping of yttria for high-temperature SOC operation and GDC( $Gd_{0.1-0.2}Ce_{0.9-0.8}O_2$ ) or SDC ( $Sm_{0.2}Ce_{0.8}O_2$ ) for low temperature

SOC operations. **Figure 1.6** illustrates the oxygen ion conductivity of various selected oxides.

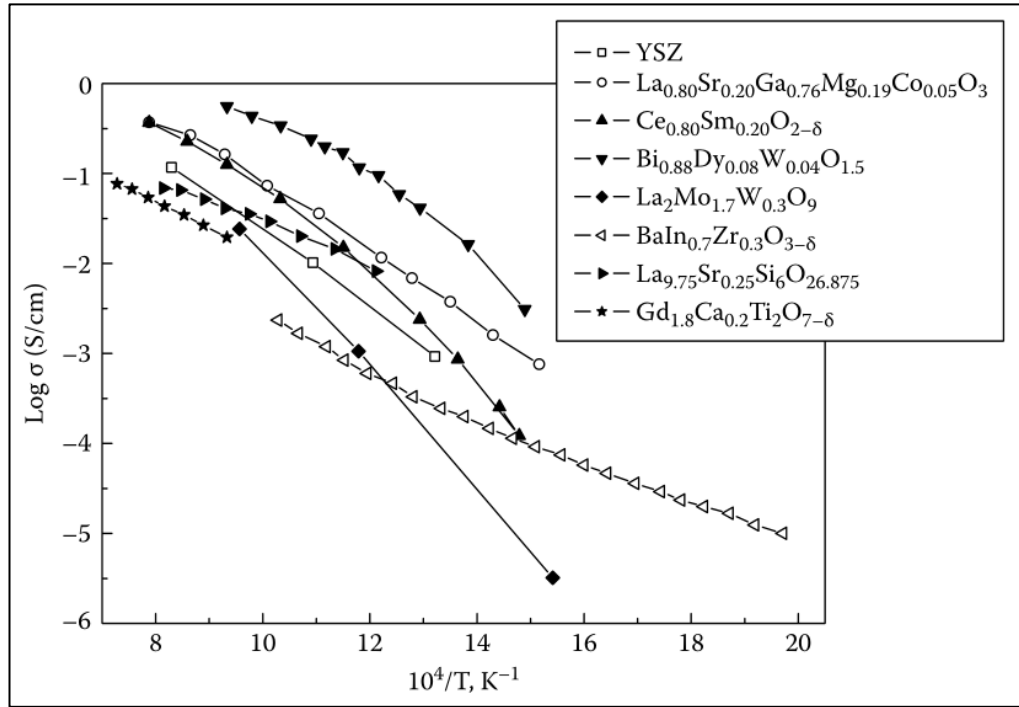


**Figure 1.6:** Oxygen Ionic conductivity of various electrolyte materials [17].

### 1.2.3.2. Fuel Electrode

The primary role of the fuel electrode in a SOC is to facilitate the electrochemical oxidation of fuels in fuel cell mode therefore anode is referred to as electrode. When a hydrocarbon fuel, such as methane, is utilized, the anode may also perform additional functions like internal reforming or partial oxidation of the fuel. These chemical and electrochemical reactions predominantly occur at TPBs. The resistance to these electrode processes, referred to as anode polarization, is influenced by factors such as the intrinsic catalytic activity of the surface for fuel oxidation and reforming, as well as the microstructure, morphology, and transport properties of the electrode materials.

A key challenge in designing an efficient anode is optimizing charge and mass transfer along surfaces, across interfaces, and through the bulk of the electrode. For an anode-supported SOC, the anode also serves as the structural backbone of the entire cell, making mechanical integrity a critical consideration.

There are reviews and studies for SOC anodes, covering aspects such as processing, fabrication, characterization, and electrochemical behavior, with a particular focus on nickel-yttria stabilized zirconia (Ni-YSZ) cermet anodes [18], [6]. Since Ni-YSZ is widely used and accepted standard material for anodes in SOC. Problems with Ni-YSZ are, Nickel tends to coarsen and captures carbon when using hydrocarbons as fuel. Sulphur poisoning also challenges Ni-YSZ anodes [19], [20].



### 1.2.3.3. Air electrode

Air electrode behaves as cathode when SOC is in fuel cell mode, in which reduction reaction of oxygen gas takes place to produce oxygen anions by receiving electrons from external the circuit (**Equation 1.4**). The cathode should be porous to allow gas flow, active for oxygen reduction, resistant to oxidation, and capable of ionic conduction. Gas conversion is the rate determining reaction which contributes most of the polarization within the cell. This is called cathodic polarization in fuel cell mode. Hence air electrodes are the thinnest layer among the most common SOC designs.



Perovskites, especially La-based ones are highly promising for air electrodes since they are versatile for doping with various transition metals. They are stable in both reducing and oxidizing environments and can be synthesized using flexible chemical methods like the Pechini method [22]. Since oxygen vacancies can be formed more easily than other ionic materials, they show ionic conduction and transition metals provide electronic conductivity by changing their oxidation states. Perovskites are oxides with general formula notation of  $ABO_3$ . An element can be alkaline-earth metals or lanthanide metals, B element can be first row of transition metals and O is oxygen. A-site in lattice is located at the corners of the unit cell, which is one atom shared with 8 unit cell, B site is located in center of the cell and oxygens located in octahedral space at face of the cell. Crystal structure of single perovskite shown in **Figure 1.7** [23]. A site cation is relatively larger than B site cation. A site or B site doping can be done for enhanced conductivity purposes. B-site element since it is a

transitional metal mostly responsible for charge carriage. If elements at the same type of site doping have significant difference in atomic radius depending on the valance state, perovskite can be reconstructed as double perovskite.

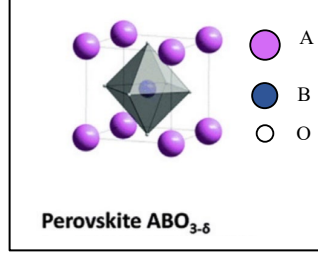


**Figure 1.7:** Crystal structure of single perovskite cell with formula of  $ABO_3$  [23].

Oxygen reduction takes place within the electrode at the active surface of the oxides where vacancy for oxygen is present via deficient due to stoichiometry. Electrochemical reaction follows as **Equation 1.5**. Formation of oxygen vacancies explained in latter chapters. Triple phase boundaries (TPB) are crucial structure mechanism for air electrodes where oxygen is reduced with the received electron and formed oxygen ion is transported through ionically conductive phase. TPB model and partial cell structure are represented in **Figure 1.8**.

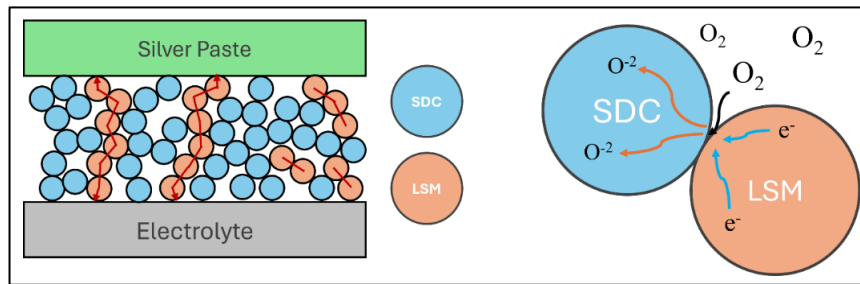
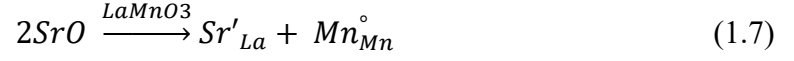
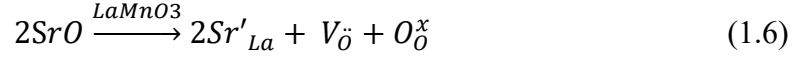


**Figure 1.8:** Partial cell structure with current collector layer, porous electrode and dense electrolyte layer with TPB model included.

Sr is a commonly doping element for La-based perovskites since addition of it increases oxygen vacancy concentration and electron hole concentration thus reducing activation energy for ion transport and charge transfer [11], [24]. Sr also hinders grain

growth within microstructure which favors in TPB length. Kröger-Vink notation for defect reactions in LSM due to Sr doping follows as:



Possible oxygen reduction routes in electronic conductor (e.g., LSM) and mixed ionic electronic conductor (MIEC, e.g., LSC) are provided schematically in **Figure 1.9**. Reduction of oxygen takes place at TPB both in single phase and composite electrode as shown.

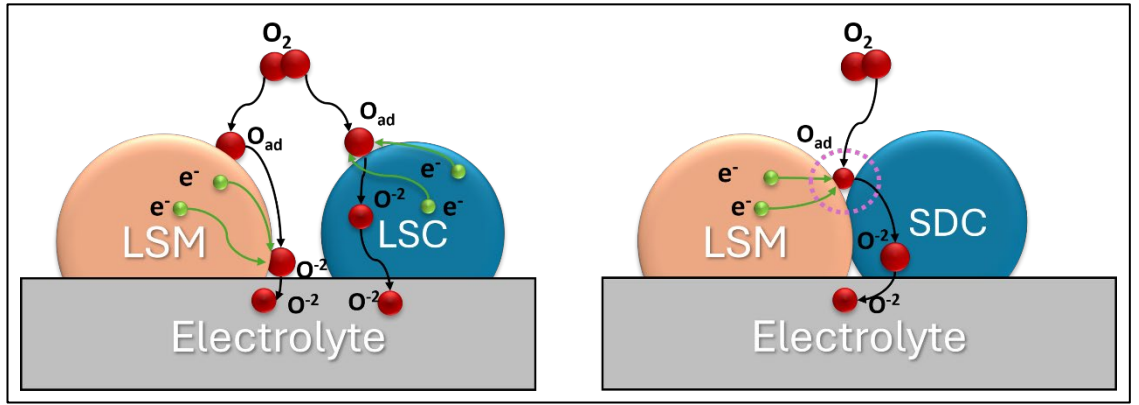


**Figure 1.9:** Electron and oxygen ion paths for single phase perovskites and composite perovskites in oxygen reduction reactions.

In the literature, common materials for air electrodes are LSM (LaSr,Mn), LSC(LaSr,Co), LSFC(LaSr,FeCo), LM (La,Mn), LC(La,Co) and LF (La,Fe) oxides due to perovskite type structure which enables transportation of oxygen ions via defect mechanisms, and mechanical and chemical stability with electrolyte material which is generally yttria stabilized zirconia (YSZ) or gadolinium doped ceria (GDC). In **Table 1.1**, various La-based ( $\text{LaMO}_x$ ) perovskite materials can be seen [16].  $D^*$  and  $k$  are oxygen chemical diffusion and surface exchange coefficients, respectively. The oxygen incorporation rate and the oxygen flux through the materials can be characterized with these two parameters. High  $D^*$  and  $k$  values are desired for better electrode performance. In this study LSM materials with different compositions are studied.

**Table 1.1:** Various common LaMO<sub>x</sub> materials with ionic conductivity  $\sigma_i$ , surface exchange coeff.  $k$  and diffusion coeff.  $D^*$  values as air electrodes for SOCs [16].

| Composition                                                                            | Temp. (°C) | $D^*(\text{cm}^2 \text{ s}^{-1})$ | $k(\text{cm s}^{-1})$ | $\sigma_i(\text{Scm}^{-2})$ |
|----------------------------------------------------------------------------------------|------------|-----------------------------------|-----------------------|-----------------------------|
| La <sub>0.8</sub> Sr <sub>0.2</sub> CoO <sub>3</sub>                                   | 900        | $4 \times 10^{-8}$                | $2 \times 10^{-5}$    |                             |
|                                                                                        | 800        | $2 \times 10^{-8}$                | $5 \times 10^{-6}$    |                             |
|                                                                                        | 700        | $1 \times 10^{-8}$                | $43 \times 10^{-6}$   |                             |
| La <sub>0.8</sub> Sr <sub>0.2</sub> MnO <sub>3</sub>                                   | 1000       | $6.60 \times 10^{-13}$            | $5.62 \times 10^{-8}$ | $\sim 10^{-4}$              |
|                                                                                        | 900        | $1.60 \times 10^{-13}$            | $1.78 \times 10^{-8}$ | $\sim 10^{-6}$              |
|                                                                                        | 800        | $4.00 \times 10^{-15}$            | $5.62 \times 10^{-9}$ | $\sim 10^{-7}$              |
| LaFeO <sub>3</sub>                                                                     | 1000       | $5.28 \times 10^{-12}$            | $1.67 \times 10^{-7}$ |                             |
|                                                                                        | 900        | $9.84 \times 10^{-13}$            | $3.89 \times 10^{-8}$ |                             |
| LaCoO <sub>3</sub>                                                                     |            | $5.31 \times 10^{-9}$             |                       |                             |
|                                                                                        | 800        | $2.41 \times 10^{-11}$            | $3.47 \times 10^{-7}$ |                             |
|                                                                                        | 700        | $9.20 \times 10^{-13}$            | $4.57 \times 10^{-9}$ |                             |
| La <sub>0.9</sub> Sr <sub>0.1</sub> CoO <sub>3</sub>                                   | 800        | $1.99 \times 10^{-10}$            | $1.54 \times 10^{-8}$ |                             |
| La <sub>0.9</sub> Sr <sub>0.1</sub> FeO <sub>3</sub>                                   | 900        | $2.65 \times 10^{-9}$             | $3.60 \times 10^{-7}$ |                             |
| La <sub>0.6</sub> Sr <sub>0.4</sub> CoO <sub>3</sub>                                   | 900        |                                   |                       | 1.2                         |
| La <sub>0.6</sub> Sr <sub>0.4</sub> Co <sub>0.8</sub> Fe <sub>0.2</sub> O <sub>3</sub> | 900        |                                   |                       | 0.18                        |
|                                                                                        | 900        | $3 \times 10^{-7}$                | $4 \times 10^{-5}$    |                             |
|                                                                                        | 800        | $1 \times 10^{-7}$                | $2 \times 10^{-5}$    |                             |
|                                                                                        | 700        | $2 \times 10^{-8}$                | $4 \times 10^{-6}$    |                             |
| La <sub>0.6</sub> Sr <sub>0.4</sub> Co <sub>0.8</sub> Cu <sub>0.2</sub> O <sub>3</sub> | 900        |                                   |                       | 2.00                        |
| La <sub>0.6</sub> Sr <sub>0.4</sub> Co <sub>0.8</sub> Ni <sub>0.2</sub> O <sub>3</sub> | 900        |                                   |                       | 3.16                        |
| LaGa <sub>0.6</sub> Co <sub>0.4</sub> O <sub>3</sub>                                   | 882        |                                   |                       | 0.0034                      |
| Y <sub>0.9</sub> Ca <sub>0.1</sub> O <sub>3</sub>                                      | 1000       |                                   |                       | 0.039 <sup>a</sup>          |
|                                                                                        | 900        |                                   |                       | 0.0043 <sup>a</sup>         |

• Measured by electron blocking technique.

#### 1.2.4. Challenges of SOCs

SOCs operate at elevated temperatures (600-800 °C), under oxidizing and reducing environments. This working environment is quite challenging, thus, results in chemical and microstructural degradation in cell components, which result in performance drop.

In fuel electrodes, common problems with conventional SOCs are carbon deposition and sulfur poisoning on Ni electrode surface when hydrocarbons are used, as well as Ni particle coarsening and migration. The carbon deposition and sulfur poisoning block the surface Ni sites, where the fuel gas molecules can attach to, diminishing the electrochemical activity of the electrode [10], [18], [19], [20], [25], [26]. Ni agglomeration occurs as a result of high Ni/YSZ interfacial energy and the tendency of Ni to reduce its overall surface energy. This, in turn, results in TPB shortening and thus, leading to performance loss [27], [28], [29].

In oxygen electrodes, Sr doping causes segregation at perovskite electrocatalyst surfaces of Sr, resulting insulative surface layers as oxides, carbonates and hydroxides, which is the major issue [27], [30]. Sr has been historically used as a dopant in ABO<sub>3</sub> – type perovskite electrocatalysts to substitute the A-site cation, La<sup>3+</sup>. to promote electrochemical performance. When Sr<sup>2+</sup> replaces La<sup>3+</sup> a negative effective charge is generated ( $Sr'_{La}$ ). To compensate for the negative effective charge, positively charged oxygen vacancies ( $V_{\ddot{O}}$ ) and/or an increase in the oxidation state of the transition metal cation from 3+ to 4+ ( $Mn_{Mn}$ ) takes place [7], [9], [16]. While the former enhances oxygen ion conductivity and provides additional surface sites for oxygen gas to adsorb onto, the latter enhances the electronic conductivity. Both of these mechanisms serve to enhance the electrochemical performance of the electrocatalyst [31], [32].

One major challenge with the Sr-doped LaMO<sub>3</sub> (M: Mn, Fe and/or Co) electrocatalysts is that Sr tends to segregate to electrode surface and forms oxide and hydroxide phases such as SrO, SrCO<sub>3</sub> and Sr(OH)<sub>2</sub> which is represented in **Figure 1.10** [33].

It has been suggested in several studies that the driving force of this segregation is the elastic strain caused by the %5.9 larger ionic radius of the doped Sr<sup>2+</sup> compared to the La<sup>3+</sup> present in the matrix and the electrostatic attraction between the abundant positively charged oxygen vacancies ( $V_{\ddot{O}}$ ) on the outer surface and the negatively charged Sr dopant located at the La site ( $Sr'_{La}$ ) [33], [34]. One of the dependencies of segregation according to study is oxygen pressure [33]. Low pO<sub>2</sub> reduces the extent of dopant segregation due either to the chemical expansion of the lattice and/or a reduction of the space charge (electrostatic effect) which is a layer just under the positively charged top surface with electron-rich dopant defect sites in the doped LaMnO<sub>3</sub> films. To compare and prevent segregation, they doped LaMnO<sub>3</sub> also with Ca and Ba. Sr performed mediocre compared the other two dopants since ionic radius relies between them, Ca had non-observable segregation while Ba segregated most according to atomic force microscopy (AFM) analysis thus correlation between cation size and Sr segregates by volume is deducted. Annealing or sintering temperature also affects the amount of segregation. LSM shows up Sr segregation at 630 °C which intensifies with increasing temperature. Annealing at different pO<sub>2</sub> has led to lattice parameter alteration. Higher oxygen pressure drives oxygen incorporation into the lattice, causing it to contract, whereas lower oxygen pressure results in oxygen loss,

leading to lattice expansion hence high  $pO_2$  causes cation segregation on the surface to minimize elastic strain caused by contraction. According to a previous study, scanning tunneling microscopy (STM) revealed that Sr rich phases resulting from Sr segregation are electronically more insulating than the rest of the film surface [33]. In another work, it is found that Sr segregation is greater on the sample that has been exposed to 72 hours of applied voltage, which supports that electrochemical processes contribute to Sr segregation [35]. It is also known in the literature that Sr reacts with zirconia-based electrolytes and forms  $SrZrO_3$  [36], [37]. Consequently, it can be said that segregation prevents oxygen adsorption and suppresses oxygen surface diffusion kinetics, hence increases cathodic polarization which eliminates the advantage of Sr doping where the goal is to create oxygen vacancies.

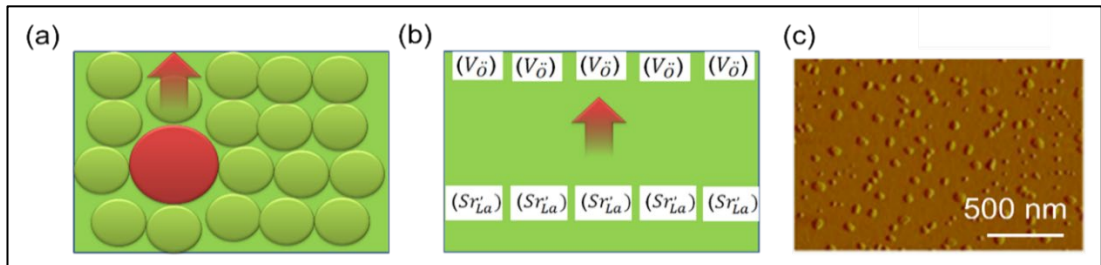


**Figure 1.10:** Sr in ABO<sub>3</sub> structure causes a) elastic strain, b) electrostatic attraction and segregation hence c) enrichment of SrO on the surface (AFM) [33].

### 1.2.5. Proposed Solutions in the Literature

Ba and Ca are common A-site doping elements to prevent Sr segregation. Ca is an alternative dopant to Sr which has a smaller ionic radius in La-based perovskites, enhancing surface exchange and diffusion kinetics while Ba possesses higher electrical conductivities at 500–800 °C and displays lower polarization resistances to oxygen adsorption and dissociation kinetics in  $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$  (LSCF) composition. Ba also has ~1.9 eV higher migration barrier than Ca both in the bulk and at the surface of  $LaMnO_3$ . Ba tends to migrate to the surface to minimize elastic energy; its high migration barrier slows down the segregation process [32]. However, Ca enrichment at the surface was detected by AES at elevated temperature despite its matching size to La cation. Furthermore, Ba cation is larger compared to La and also Ca; hence, except in low  $pO_2$  ( $<10^{-6}$  Torr) environments and low temperatures, it tends to form secondary

phases on the surface [33]. Low oxygen levels can cause concentration polarization. B-site doping is also another method to enhance electrode performance without Sr doping. A study on high-entropy perovskites, where transition metals like Cu, Ni, Fe, and Co are co-doped into La-based perovskites demonstrate enhanced electrochemical performance in air below 800 °C. This improvement is attributed to the coupling of five transition metal atoms at the B-site, leading to the transition of  $Mg^{3+}$  to  $Mn^{2+}$  and promoting oxygen vacancy formation [39]. Adding different kind of precious metals increases cost and fabrication process durations.

It is important point out that, Sr doping has benefits to LCO based electrodes in the literature [40]. Changing surface morphology via texturing has also been proposed prevent Sr-based challenges [41]. Keeping fabrication temperatures lower was reported to prevent crystallization of LSM and Sr segregation. Initial electrochemical performances of Sr containing composition was worse than that of LSM, however, at longer operation durations , i.e., up to 100h, LSM with 40% Sr had stable performance [34].

Another approach was replacing Sr with other divalent oxides with smaller ionic radii, such as; Ca. Ca-doped  $LaCoO_3$  materials have been studied in thin film and bulk forms. In both cases, formation of CaO, CoO,  $Co_3O_4$  and  $La_2O_3$  as secondary phases has been reported, which hindered oxygen kinetics [42], [43].

### **1.3. Aim of This Work**

A detailed literature survey suggests that Sr segregation in  $ABO_3$  - type perovskite electrocatalysts is almost inevitable and its prevention may only be achieved through cumbersome measures. In this work, it is hypothesized that perovskite surface enriched and blocked with Sr phases would be devoid of electrochemically active surface sites and yield Sr-deficiency in the bulk. It is known that  $LaMnO_3$  has been widely studied among different fuel electrode materials because of its high electronic conductivity, good chemical stability, and thermomechanical compatibility with solid electrolytes. Presence  $Mn^{3+}$  and  $Mn^{4+}$  states within LMO which is responsible for its electrical conductivity can alter with Sr doping to increase electronic conductivity but drawbacks are blatant and aforementioned in previous chapters [44]. Hence, Sr-free perovskites

should perform better upon long-term operation because they would have Sr-free surface and thus, easy access to the electrochemically active perovskite sites. This hypothesis is schematically shown in **Figure 1.11**.

Moreover, LMO exhibits phase transformation from orthorhombic to rhombohedral due to the oxidation of  $\text{Mn}^{3+}$  to  $\text{Mn}^{4+}$  at  $600^\circ\text{C}$ . This transformation reduces the energy that tends to produce long-ranged Jahn-Teller ordering which distorts crystal lattice and decreases electronic conductivity [45]. Thus, the crystallographic transitional temperature of LMO depends on the  $\text{Mn}^{4+}$  content, since A-site deficiency increases the concentration of  $\text{Mn}^{4+}$  in the  $\text{LaMnO}_3$  lattice hence there will be a decrease in the transformation temperature [7]. While  $\text{Mn}^{4+}$  ions provide more electronic conductivity, the incorporation of SDC phase with LMO perovskite will compensate ionic conductivity.

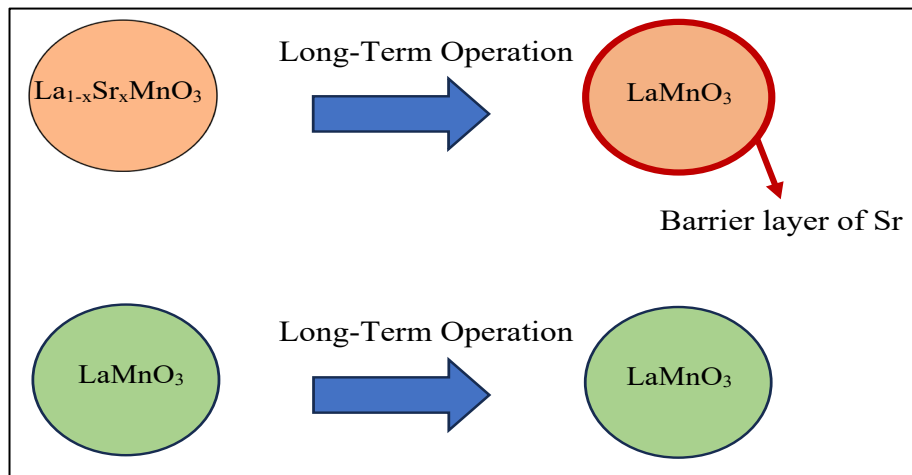


**Figure 1.11:** Illustration of Sr segregation and formation of oxides and other compounds.

To assess this, perovskite films of both undoped and Sr-doped  $\text{LaMnO}_3$  and Sm-doped (20% by mol)  $\text{CeO}_2$  composite deposited on yttria-stabilized zirconia (YSZ) electrolyte substrates using the spin-coating deposition technique with polymeric liquid precursors. The impact of Sr doping on long-term performance stability assessed through electrochemical impedance spectroscopy (EIS) conducted on symmetrical electrode/electrolyte/electrode half-cells. Surface chemistry, phase, and microstructure evolution analyzed using x-ray photoelectron spectroscopy, x-ray diffraction, and scanning electron microscopy, respectively.

## 2. EXPERIMENTAL

The SOC samples were produced as asymmetric cells with air electrode layer on both sides of thick electrolyte substrate, yttria-stabilized zirconia (YSZ) was used as the electrolyte material, LSM/LMO-SDC ( $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3\text{-Ce}_{0.8}\text{Sm}_{0.2}\text{O}_2$ ,  $x:0, 0.2, 0.4$ ) as the air electrode material and shows mixed ionic electronic conducting (MIEC) properties. The air electrode stoichiometries was chosen due to compare other studies including most common compositions which is why studied in this work. Silver paste (Alfa Aesar) is applied on air electrode surfaces and silver wires attached on top of cell surfaces with 2-probe electrode configuration for EIS measurements. EIS measurements were carried out in 700 °C for optimal performance in terms of electrochemical performance, microstructural and chemical stability. The flow chart of polymeric precursor solution preparation and electrolyte pellet fabrication is shown in **Figure 2.1**.

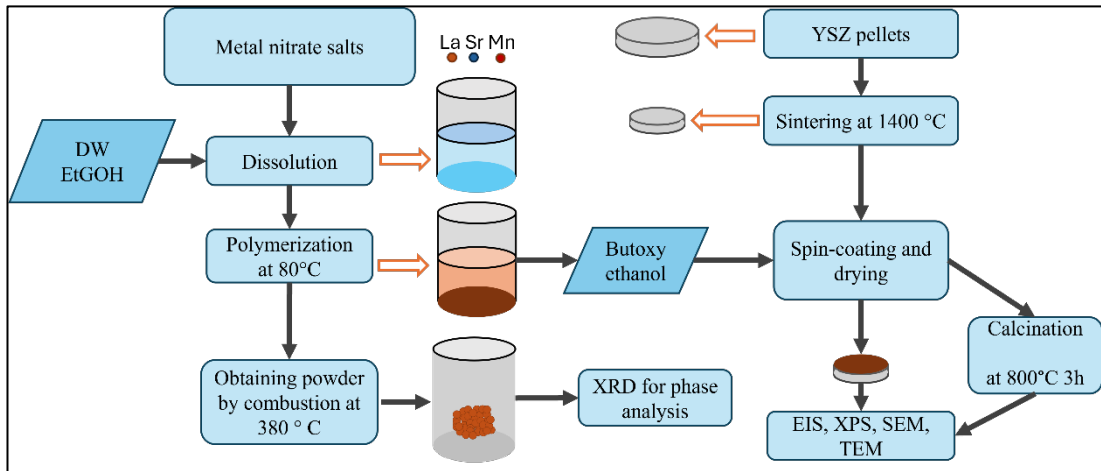


**Figure 2.1:** Schematic of symmetrical SOC fabrication.

## 2.1. Fabrication

### 2.1.1. Electrolyte

Commercially available yttria stabilized (8 mol%  $\text{Y}_2\text{O}_3$ ) zirconia ( $\text{Zr}_2\text{O}_3$ ) powders (TOSOH - Tosoh Corporation Nanyo Manufacturing Complex, Japan) is used as electrolyte in this work. After weighing the YSZ powders on a digital precision balance to 0.7 grams, poured them into the mold and pressed them under a load of 150 kilograms ( $\approx 4.71\text{MPa}$ ) for 20 seconds in a uniaxial pressing device in our laboratory. After each press, mold and stoppers were cleaned with ethyl alcohol. The samples coming out of mold are in the form of disk pellets which were approximately 1.2 mm in thickness (**Figure 2.2**).

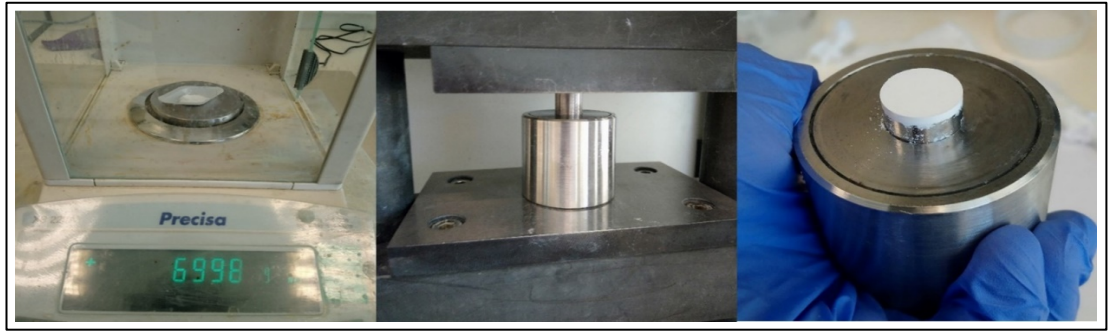


**Figure 2.2:** Production of green YSZ pellets by uniaxial pressing.

After pressing, green pellets are sintered to obtain mechanical strength and densification for cell stability and prevention of gas mixing respectively. Pellets were placed on alumina plates and sintered at  $1450\text{ }^\circ\text{C}$  for 7 h in a tube furnace (Protherm PTF 12/50/250, Türkiye). The sintering regime for YSZ pellets given in **Figure 2.3**.

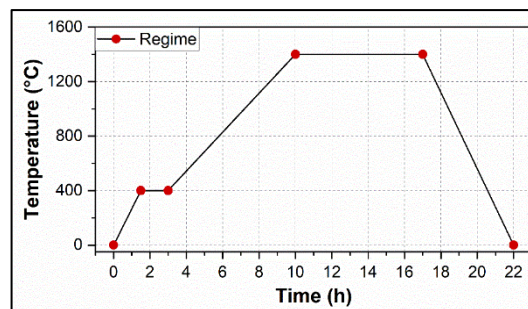


**Figure 2.3:** Sintering regime of YSZ pellets.

### 2.1.2. Air electrode

LSM-SDC composite solution and single phase LSM solution precursors prepared with similar to Pechini method using where x is 0, 0.2 and 0.4 [22]. A summary of sample codes along with their explanations is provided in **Table 2.1**. For x = 2 and x = 4 composition named as LSM82 and LSM64 respectively. When Sr is absent, composition will be referred as LMO from here on. In the case of composite samples, LSM or LMO to SDC ratio is 60:40 by volume, to ensure percolation of both the electrocatalyst and ionic conductor phases.

**Table 2.1:** Summary of types of samples, their nomenclature and the corresponding explanations. When referring to the as-heat treated states of these samples, the code name will be followed by “HT” and to refer to the states of samples after exposure to air at 700 °C for 100 hours, the code name will be followed by “100h”.

| Code Names  | LMO                             | LMO-SDC                                                                           | LSM82                                                             | LSM82-SDC                                                                                                           | LSM64                                                             | LSM64-SDC                                                                                                           |
|-------------|---------------------------------|-----------------------------------------------------------------------------------|-------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------|
| Explanation | Single phase LaMnO <sub>3</sub> | LaMnO <sub>3</sub> - Ce <sub>0.8</sub> Sm <sub>0.2</sub> O <sub>2</sub> composite | Single phase La <sub>0.8</sub> Sr <sub>0.2</sub> MnO <sub>3</sub> | La <sub>0.8</sub> Sr <sub>0.2</sub> MnO <sub>3</sub> - Ce <sub>0.8</sub> Sm <sub>0.2</sub> O <sub>2</sub> composite | Single phase La <sub>0.6</sub> Sr <sub>0.4</sub> MnO <sub>3</sub> | La <sub>0.6</sub> Sr <sub>0.4</sub> MnO <sub>3</sub> - Ce <sub>0.8</sub> Sm <sub>0.2</sub> O <sub>2</sub> composite |

Related material nitrate salts are added in distilled water and stirred with magnet pill until nitrates are fully dissolved. Ethylene glycol (EG) is added when mole ratio of total nitrates to EG is = 0.04 mole and solution is heated at 80 °C until water amount is vaporized. In the meantime, polymerization takes place. 2-butoxy ethanol (Acros Organics) is added as the equal amount of total solution precursor to enhance wetting ability of solution in spin coating process after the polymerization. Spin coating of solution precursors on YSZ pellets are done with spin coater with 2000rpm for 35 seconds, afterwards maximum heating at 350 °C on hot plate is done to obtain formation of nanoscale metal-oxides by evaporating the organic solvents. The whole spin coating and heating process repeated 6 times to achieve sufficient amount of electrode thickness (**Figure 2.4**).

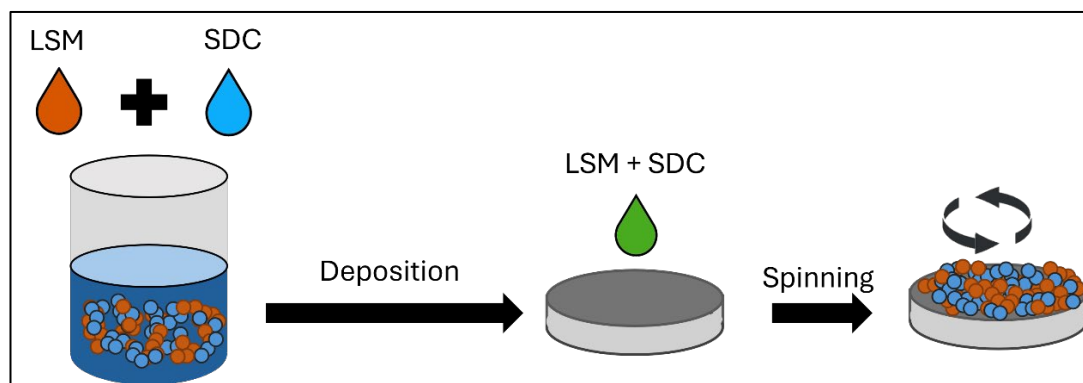


**Figure 2.4:** Spin coating deposition schematic.

Before the contact application, heat treatment at 800 °C for 3 hours is applied to all samples. When referring to the samples in this state, their code names will be followed by “HT”. These samples will also be subjected to 100 hours of long-term exposure to 700 °C in stagnant air to analyze the changes in their chemistry, structure and electrochemical performance. To refer to samples subjected to the long-term heat treatment, their sample code will be followed by “LT”.

### 2.1.3. Electrical Contact and Connection Configuration

In order to determine the electrochemical performance of air electrodes, a symmetrical cell configuration was used. In this configuration, both sides of pellets were deposited with air electrodes forming a half-cell. Contacts, essential for the analysis, were prepared according to the following procedure: Silver powder (Alfa Aesar) is mixed with 2-butoxy ethanol and  $\alpha$ -terpineol (Alfa Aesar) in certain proportions to achieve an applicable contact paste. After desired consistency, paste is applied on top of electrode surfaces of the cell with toothpick. To dry out organics in paste, half-cell is heated to 80 °C on top of hot plate. After drying, silver wires were glued on top of silver paste along with Ceramabond (552-VFG) ceramic-based heat-resistant glue and symmetrical cell connected to sample holder for EIS measurement in tube furnace. Symmetrical cell configuration and setup can be seen in **Figure 2.5**. The active surface area for electrochemical analysis is 0.45 cm<sup>2</sup>.

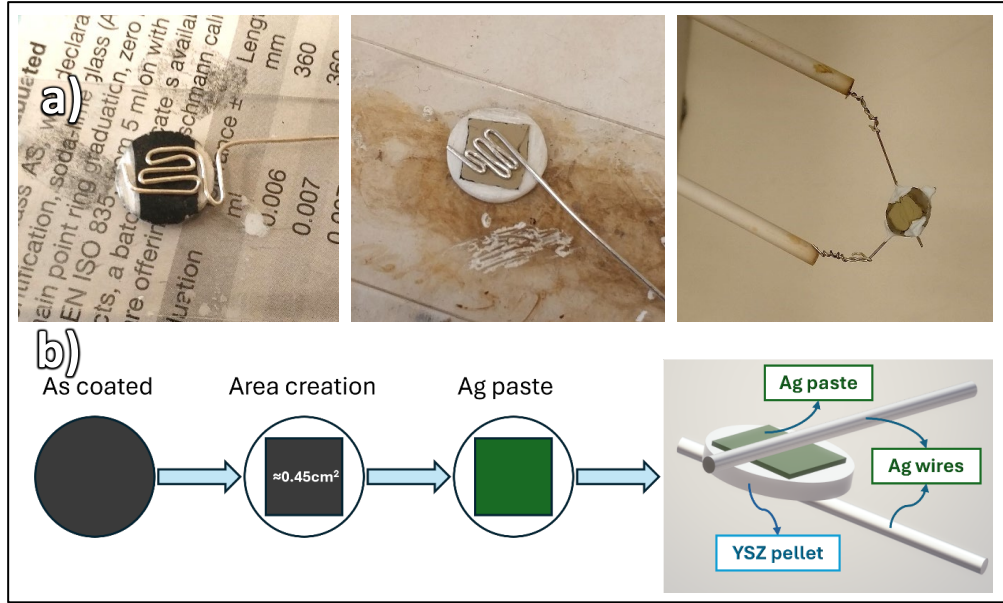


**Figure 2.5:** Various contact a), b) configuration of contact wires, c) connection setup to sample holder and c) graphical contact representation of the cell.

## 2.2. Characterization

### 2.2.1. Crystal Structure and Phase Analysis

X-ray Diffraction (XRD) is a powerful analytical technique used to study the structure, composition, and properties of crystalline materials. It is based on the diffraction of X-rays by the periodic arrangement of atoms in a crystal lattice.

XRD operates on the principle of Bragg's Law, which relates the wavelength of the incident X-rays  $\lambda$ , the angle of incidence  $\theta$  and the distance between atomic planes in the crystal  $d$ . **Equation 2.1** is given for Bragg's Law.

$$n\lambda = 2d\sin \theta \quad (2.1)$$

When the path difference between X-rays scattered by successive planes is an integer multiple of the wavelength, constructive interference occurs, producing a diffraction peak.

X-ray Diffraction Spectroscopy analysis was carried out with Bruker D8 Advance. Samples were scanned between 20 °- 80 ° with a step size of 0.02° and radiation of Cu

K $\alpha$  is used. Search match procedure was executed by using X'Pert Highscore 2 software with PDF-2 database. Air electrode material composition which are included and mentioned earlier synthesized with Pechini and combusted to obtain powder form of materials. After the combustion, calcination at 800 °C for 3 hours is applied to remove all of the organics and obtain crystal formation of the phases of related materials.

### **2.2.2. Scanning Electron Microscopy**

A Scanning Electron Microscope (SEM) works by generating a focused beam of high-energy electrons using an electron gun which is thermionic emitter like a tungsten filament or field emission gun, then electrons accelerated with electric field having 1 to 30 kV onto a sample through electromagnetic lenses. The beam scans the sample in a raster pattern, and as it interacts with the surface, it produces various signals such as secondary electrons (SE) for detailed surface imaging, backscattered electrons (BSE) for compositional contrast, and X-rays for elemental analysis (via Energy Dispersive Spectroscopy, EDS). These signals are detected and processed to form high-resolution grayscale images, where contrast depends on surface features and material composition. SEM offers advantages like nanometer-scale resolution, 3D-like imaging due to its high depth of field, and elemental characterization, making it widely used in materials science, biology, forensics, and semiconductor analysis.

Scanning electron microscopy (SEM) analyses were performed with Philips XL30S FEG. Cells used in SEM are the same cells but without the Ag paste current collector layer. Images taken from surface with 2000x, 5000x, 10000x and 20000x magnification. Secondary electrons are used for imaging in this study. Samples coated with Au layer to enhance imaging clarity and prevent overexposure due to electron accumulation from bombarding.

### **2.2.3. Focused Ion Beam and Transmission Electron Microscopy**

Transmission Electron Microscopy (TEM) with Focused Ion Beam (FIB) and Energy Dispersive X-ray Spectroscopy (EDS) is a powerful combination for high-resolution imaging, sample preparation, and elemental analysis at the nanoscale. TEM operates

by transmitting a high-energy electron beam (typically 60-300 kV) through an ultra-thin specimen (<100 nm), producing images based on mass-thickness contrast, diffraction contrast, and phase contrast. It provides detailed structural and crystallographic information at atomic resolution. When integrated with EDS, TEM enables elemental composition analysis by detecting characteristic X-rays emitted from atoms excited by the electron beam, making it essential for identifying impurities, phase distributions, and chemical compositions at nanoscales. FIB complements TEM by using a highly focused gallium ion beam (5-50 keV) to mill, cut, or modify materials through sputtering, allowing precise sample preparation for TEM analysis. FIB can also be used for direct imaging by collecting secondary electrons or ions emitted from the surface. The principle schematics of FIB and TEM can be seen in **Figure 2.6**.

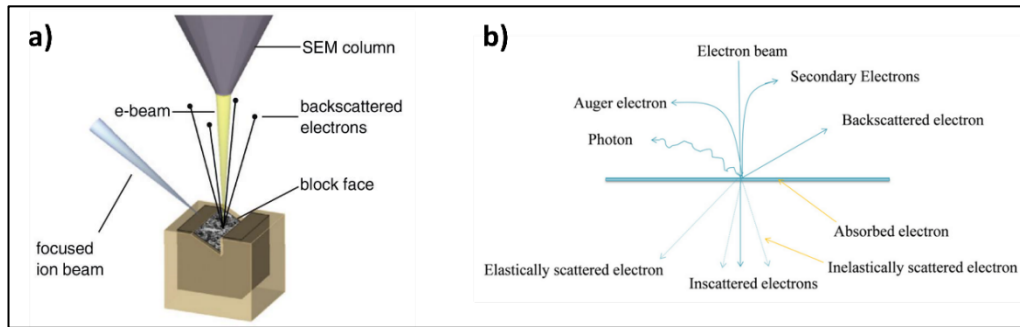


**Figure 2.6:** Basic principle of a) FIB-SEM and b) TEM [46], [47].

FIB and TEM analyses of samples were carried out with JEOL JIB-4601F MultiBeam and JEOL JEM-ARM 200 CFEG respectively at Sabancı University Nanotechnology Research and Application Center (SUNUM) with the contribution of Dr. Büşra Tuğba Çamiç and Dr. Selçuk Birdoğan.

#### 2.2.4. X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is an analytical technique where a sample is exposed to low-energy x-rays, causing electrons to be ejected from the atomic orbitals through the photoelectric effect which can be seen in **Figure 2.7**. XPS is typically limited to the top 1–10 nanometers of the sample surface. This range is determined by the mean free path of the photoelectrons within the material, which depends on the electron kinetic energy and the material's density. The resulting data, typically plotted

as the number of emitted electrons versus their binding energy, provides information about the atom and orbital from which the electrons originated. While valence electrons are involved in bonding, XPS primarily focuses on core electrons, which are characteristic of each element.

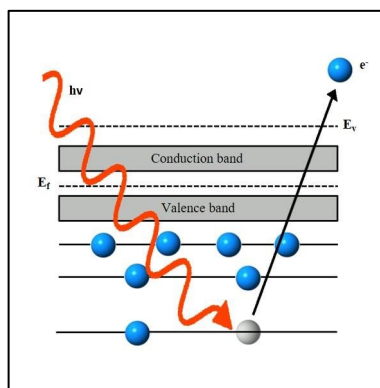


**Figure 2.7:** Schematic representation of photoelectron emission in band gap as XPS based of.

The kinetic energy of emitted photoelectrons  $E_k$  can be calculated with frequency of the incident beam  $h\nu$ , work function  $W$ , binding energy of photoelectron  $E_b$  (**Equation 2.2**).

$$E_k = h\nu - E_b - W \quad (2.2)$$

XPS is widely used for both qualitative and quantitative surface analysis, helping determine the elemental composition, chemical bonding, and oxidation states of surface atoms. For qualitative analysis, a low-resolution "survey scan" covering binding energies from 0 to 1250 eV reveals peaks corresponding to elements in the sample. Comparing these peaks in the spectra with standard spectra identifies the elements present.

Chemical shifts in peak positions provide insights into the chemical state of atoms. Higher-resolution scans of specific peaks reveal slight shifts in binding energy due to variations in valence electrons and bonding types. These shifts, typically a few electron volts, indicate changes in chemical bonding or oxidation state. For example, the 2p peak in silicon shifts between pure Si and SiO<sub>2</sub>, reflecting differences in chemical bonding. Comparing measured peak positions with reference data allows the determination of chemical bonding in surface atoms.

In our study, characterization of LMO, LMO-SDC, LSM64 and LSM64-SDC coated cells are tested for XPS. We aimed to provide support for cation ratio, element distribution within surface area of electrodes and Sr segregation phenomena as La(3d), Mn(2p), Sr(3d), Ce(3d), O(1s), Sm(3d5/2) photoelectron spectrums.

### 2.2.5. Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) is a powerful diagnostic technique used to study the electrochemical properties and performance of SOCs. It provides insights into the processes occurring within the cell, such as ion transport, charge transfer, and electrode reactions. EIS involves applying a small sinusoidal AC voltage or current to the SOC across a range of frequencies and measuring the resulting current or voltage response. The ratio of the voltage to the current gives the impedance, a complex quantity expression as in **Equation 2.3**.

$$Z(\omega) = Z'(\omega) + jZ''(\omega) \quad (2.3)$$

$Z'$  represents real impedance as resistive components.  $Z''$  represents capacitive or inductive components, and  $\omega$  is angular frequency of the applied signal. By analyzing the impedance as a function of frequency, one can deconvolute the various processes occurring in the fuel cell. Different processes in SOC, such as electrode reactions, gas diffusion, and ionic/electronic conduction, occur over different timescales (frequencies). EIS allows for separation and identification of these processes.

The cathode is often the performance-limiting component in SOCs due to slow oxygen reduction reactions. EIS helps in understanding reaction mechanisms and optimizing materials. The anode, especially when exposed to carbonaceous fuels, can experience degradation. EIS can detect changes in impedance due to carbon deposition, sulfur poisoning, or microstructural changes. EIS can measure ionic conductivity and identify defects or degradation in the electrolyte, such as cracking or reduced ionic conductivity. Over time, SOC components degrade due to thermal cycling, fuel contaminants, or mechanical stress. EIS can monitor these changes by tracking shifts in impedance spectra. EIS data can be fitted to equivalent electrical circuit models to

represent the physical processes in the cell. This modeling aids in optimizing materials and operational conditions.

Impedance spectra with x-axis being real impedance ( $Z'$ ) and y-axis being imaginary impedance ( $Z''$ ) which are mentioned. This plot is called Nyquist graph named after Harry Nyquist. Impedance arc represents the overall cell response under different frequencies at specified voltages. From left to right of the x-axis, frequency decreases. From origin to high frequency (HF) the starting point of the arc is the ohmic polarization ( $R_{ohm}$ ) due to electrolyte resistance related to thickness and resistivity of the material. Polarization due to electrode attributed  $Z'$  length from starting point (HF) of the arc to end (LF) of the arc which will be referred as  $R_{pol}$  afterwards. Graphical representation can be seen in **Figure 2.8**.

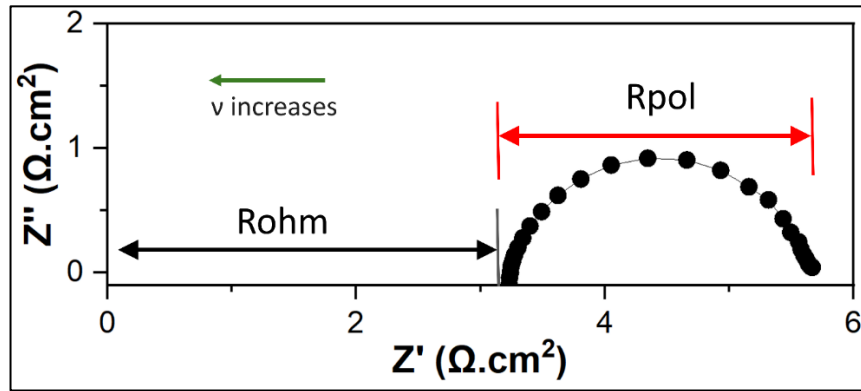


**Figure 2.8:** Graphical representation of Nyquist plot with one single arc visible and corresponding polarizations.

Electrochemical Impedance Spectroscopy analysis (EIS) is performed with Biologic-SP150 potentiostat at Gebze Technical University in Surface Modification Laboratory. Frequency range and excitation voltage are set to 0.05Hz to 0.5MHz and  $\pm 10$  mV, respectively. Setup for the cell is two electrode configuration and connected to silver wires of the device crocs. Samples placed in the tube furnace while EIS analyzing. Testing is done in two ways, with up-down operation and long-term regimes to obtain cell performance at different temperatures ranging from 450  $^{\circ}\text{C}$ -700  $^{\circ}\text{C}$  and 100 hours at 700  $^{\circ}\text{C}$  respectively in stagnant air. Both regimes are applied to all sample cells one after another.

Collected impedance data of the cells multiplied with active area ( $0.45 \text{ cm}^2$ ) of the air electrode to obtain area specific resistance (ASR) which has unit of  $\Omega.\text{cm}^2$ . Hence, we wanted to examine and compare one electrode surface since full cell has one anode and one cathode, we divided the ASR value with 2.

## 3. RESULTS AND DISCUSSION

### 3.1. Phase Analysis

**Figure 3.1** shows XRD patterns of single phase and composite electrodes. To avoid signals from the YSZ substrate and detect minority phases more easily, XRD analyses were performed on dried gels calcined at 800 °C for 3 hours, and those after 100 hours of exposure to 700 °C after calcination. In all samples, rhombohedral 113 phase was present (PDF:00-050-0308). Evidently, all the samples with Sr content had (La,Sr)<sub>2</sub>MnO<sub>4</sub> Ruddlesden-Popper tetragonal phase (214 - PDF-2: 01-083-1896), the amount of which increased with increasing Sr content (**Figure 3.1**). Upon long-term exposure to 700 °C, SrCO<sub>3</sub> phase appeared in Sr-containing LSM82 and LSM64 samples, whereas no changes were observed in LMO. The trend was also observed in the case of composite electrodes, only difference being the SDC phase formation, which suggests the successful synthesis of the electrocatalyst – ionic conductor composites (**Figure 3.1b**). The formation of SrCO<sub>3</sub> phase can be explained by the de-mixing (and possibly segregation) of the Sr dopant. Considering the studies reporting that Sr overlayer deposition onto (La,Sr)CoO<sub>3</sub> electrodes induced 214 phase formation [48], 214 formation observed here, in the Sr-containing samples can also be explained by the presence of de-mixed Sr. In other perovskite electrodes, such as; (La,Sr)CoO<sub>3</sub> [49], (La,Sr)FeO<sub>3</sub>, it is said that 214 phase has no detrimental effect on performance degradation rates [30]. It was reported that presence of optimal amounts of 214 phase where  $0.6 \leq x \leq 2.0$  stoichiometric range for (La<sub>2-x</sub>Sr<sub>x</sub>)MO<sub>4</sub>, along with the parent 113 phase was beneficial for electrochemical performance, as oxygen exchange at the 113/214 interface has been reported to be extremely fast [49], [50].

When we look at the zoomed sections of XRD patterns, it can be seen that composite samples have broader 113 peaks in comparison to those observed in the single phase samples while single phase peaks are sharper and smoother peak bases. It is also important to note that composite samples have higher SrCO<sub>3</sub> intensity than single phase counterparts. This may be due to SDC is blocking perovskite (LSM or LMO) formation while allowing SrCO<sub>3</sub>. When additional cations are added to the precursor

solution, they hinder the diffusion of other cations, thereby reducing their crystal size [51], [52].

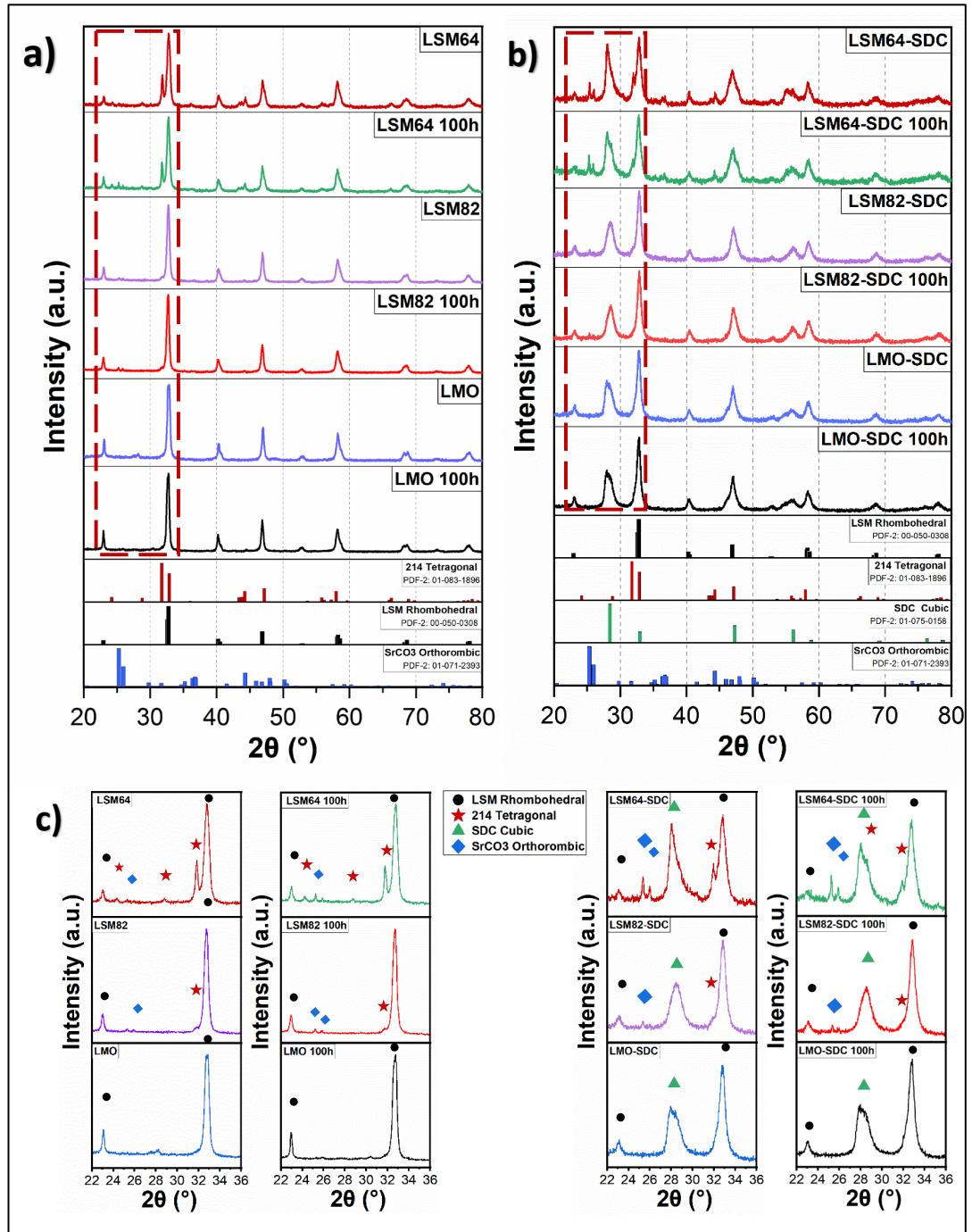


**Figure 3.1:** XRD patterns and selected references for a) single-phase and b) composite samples and c) zoomed sections between 22-36°.

### 3.2. Microstructural Analysis

Scanning Electron Microscope with secondary electron technique reveals that spin-on coating with all of solutions led to cohesive and nearly homogenous layer of electrode to electrolyte substrate. Surfaces of electrodes are porous rather than dense layers. In **Figure 3.2**, SEM images for samples without long-term operation shows that single phase samples have coarser grains and more porosity than composite samples. Porosity helps oxygen molecules to access and being adsorbed at active area sites which increases the rate of electrochemical conversion of oxygen into ion. In **Figure 3.2a**, LMO-HT shows cubic morphologies among the granular particles which can be  $\text{La}_2\text{O}_3$  or  $\text{MnO}_x$  cubic phases which are denoted in red circles although XRD did not reveal such phases. It is seen that crystal formation of different crystal phases within LSM64-HT marked in red circles and it may be  $\text{SrCO}_3$  phases in **Figure 3.2c**. In **Figure 3.2f**, in the absence of Sr, grains are rounder and bigger hence it can be said that Sr hinders grain growth by looking at the SEM images. Discrete formation of secondary phase SrO as bright areas can be seen in **Figure 3.3b** which is similar found in Lee et. al. study [33]. However, XRD has no evident to support SrO formation in our study. They also worked with the same stoichiometry of LSM with 0.2 Sr although our composition is composite and contains SDC. During calcination, organic solvents evaporate and this can leave crater-like structure behind which is obvious in **Figure 3.3c**.

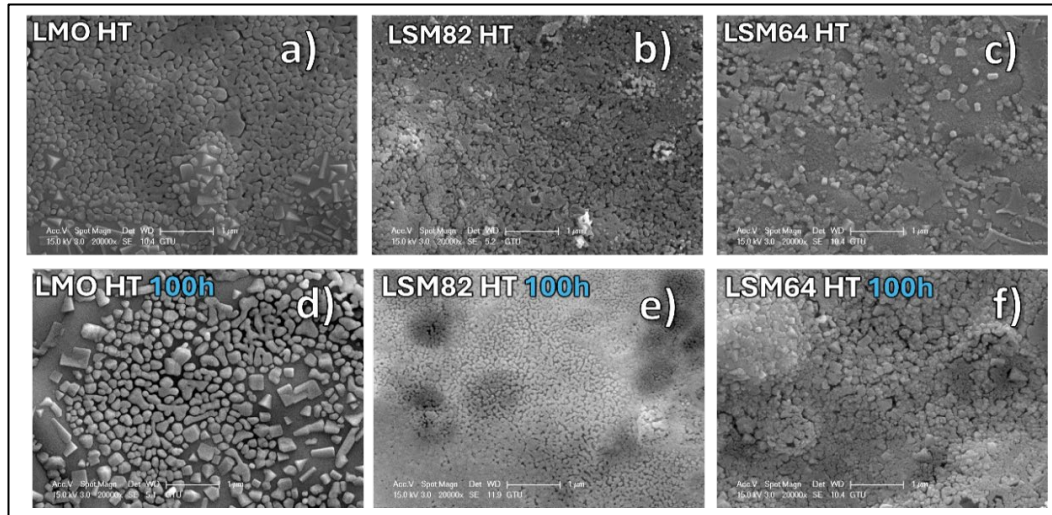
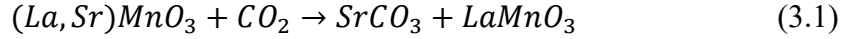


**Figure 3.2:** SEM images from the surfaces of single phase electrodes prior ((a) LMO HT, b) LSM82 HT, c) LSM64 HT) to and after ((d) LMO HT 100h, e) LSM82 HT 100h and f) LSM64 HT)) long-term exposure to 700 °C.

It is also important to note that there is blatant formation of  $\text{SrCO}_3$  in LSM64-SDC due to reaction of C in humid air and phase containing Sr on top of the electrode surface. Reaction for this formation follows in **Equation 3.1**. We have seen in  $\text{SrCO}_3$  phases SEM images which is proven by XRD analysis we mentioned earlier. This carbonate phase prevents oxygen to adsorb and dissociate to anion state hence increasing  $R_{\text{pol}}$ .



After the long-term testing at 700 °C, all of the microstructures of the samples showed relatively larger particle size. Especially in **Figure 3.2d**, particle size increased tremendously. In **Figure 3.2e**, microstructure has more homogeneous phase distribution. In **Figure 3.3f**, LSM64/SD-HT shows no sign of crater-like formation we have seen before LT, presumably that morphology vanished after long heat exposure at 700 °C. Again, this finding proves that Sr hinders crystallization, formation and homogeneity. As we can see in **Figure 3.3**, LMO-HT has the biggest particle size due to absence of Sr thus Sr lowers particle size and inhibits grain coarsening. LSM82-HT is very homogenous and well dispersed perovskite phase. It is clear that  $\text{SrCO}_3$  structures increased in size which can be related to exposure to lower temperature for longer duration, XRD results also support this deduction.

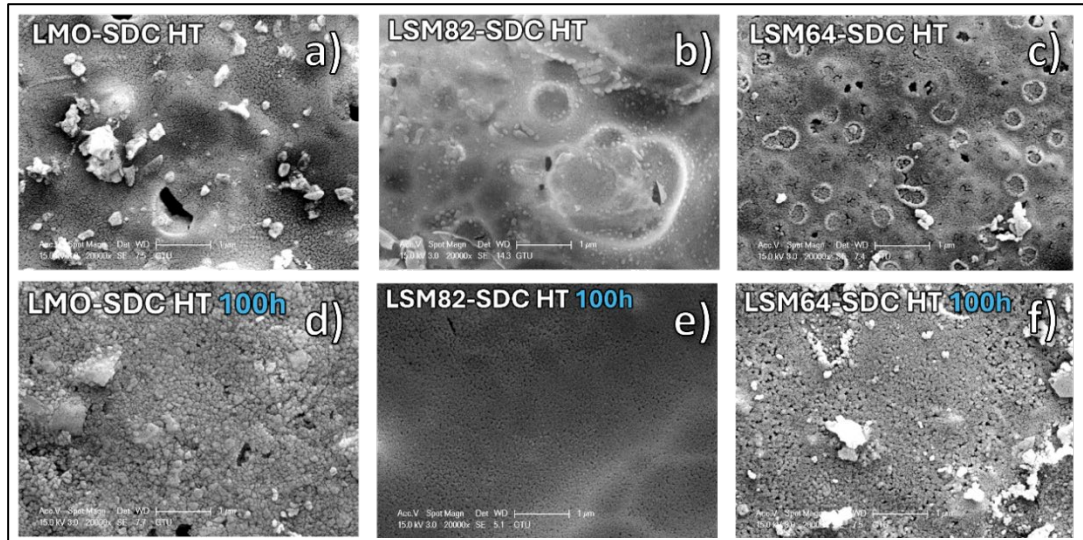


**Figure 3.3:** SEM images collected from the surfaces of nanocomposite electrodes prior ((a) LMO-SDC HT, b) LSM82-SDC HT, c) LSM64-SDC HT) to and after (d) LMO-SDC HT 100h, e) LSM82-SDC HT 100h and f) LSM64-SDC HT) long-term exposure to 700 °C.

Samples of LMO-SDC HT and LSM64-SDC HT were exposed to 700 °C for 100 hours in stagnant air used for FIB and TEM analysis. This way, accurate determination of elemental distribution in these samples was aimed. Electrodes were coated with gold-palladium coating (Cressington 108) prior to FIB and TEM to obtain to avoid charging. Carbon was deposited on top of samples during FIB to attach atom probe and prevent milling of electrode film above the electrolyte. After carefully extracting ultra-thin layers from samples using atom probe, samples were placed on the copper grid for TEM imaging. sing EDS ability of the device, STEM images revealed what elements are in the electrode film with distribution of them.

Step by step process of FIB can be seen in **Figure 3.4**. After depositing carbon on top of eligible spot of electrode surface (**Figure 3.4a**), front and back of the designated area was milled with Ga ion beam (**Figure 3.4b**). After that attaching atom probe with the carbon deposition has done and followed by cutting the thin sample (**Figure 3.4c**).

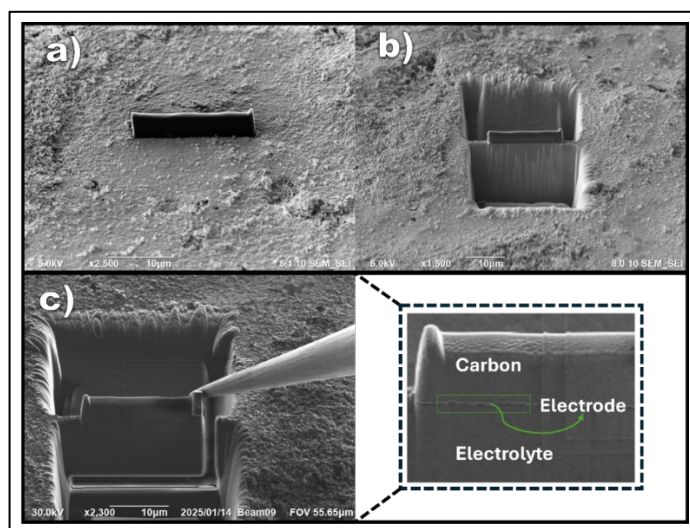


**Figure 3.4:** FIB process as a) carbon deposition, b) milling of both sides of the layer to be removed and c) atom probe attached to the thin specimen.

As seen in **Figure 3.5**, EDS mapping has been seen for La (red), Ce (blue), and Mn (green). The STEM image corresponding to the sections where EDS scan was acquired is provided to the right of the respective samples. Although the electrode thickness in the area where EDS was conducted is around 50-100 nm, there ere regions within the sample where the thickness reaches up to 200 nm. The dense YSZ electrolyte structure was observed on the far right of the microstructure. The bright coating seen on the left

section of the film, which follows the electrode morphology, is a gold-palladium coating. When examining **Figure 3.5a**, the element distribution of LMO-SDC is observed to be a highly homogeneous nanocomposite perovskite structure, with no signs of segregation or agglomeration. In LSM64-SDC (**Figure 3.5b**), however, heterogeneity in element distribution is observed in certain areas, particularly in regions where Ce is concentrated and La and Mn are found together. Sr is mainly detected near the surface which is denoted within red circle, confirming its segregation and supporting the XPS results. However, since the binding energy of Sr overlaps with Au-Pd, its proximity to this region might be misleading. Additionally, Sr also overlaps with the energy of Zr, that is why it is detected in electrolyte region also.

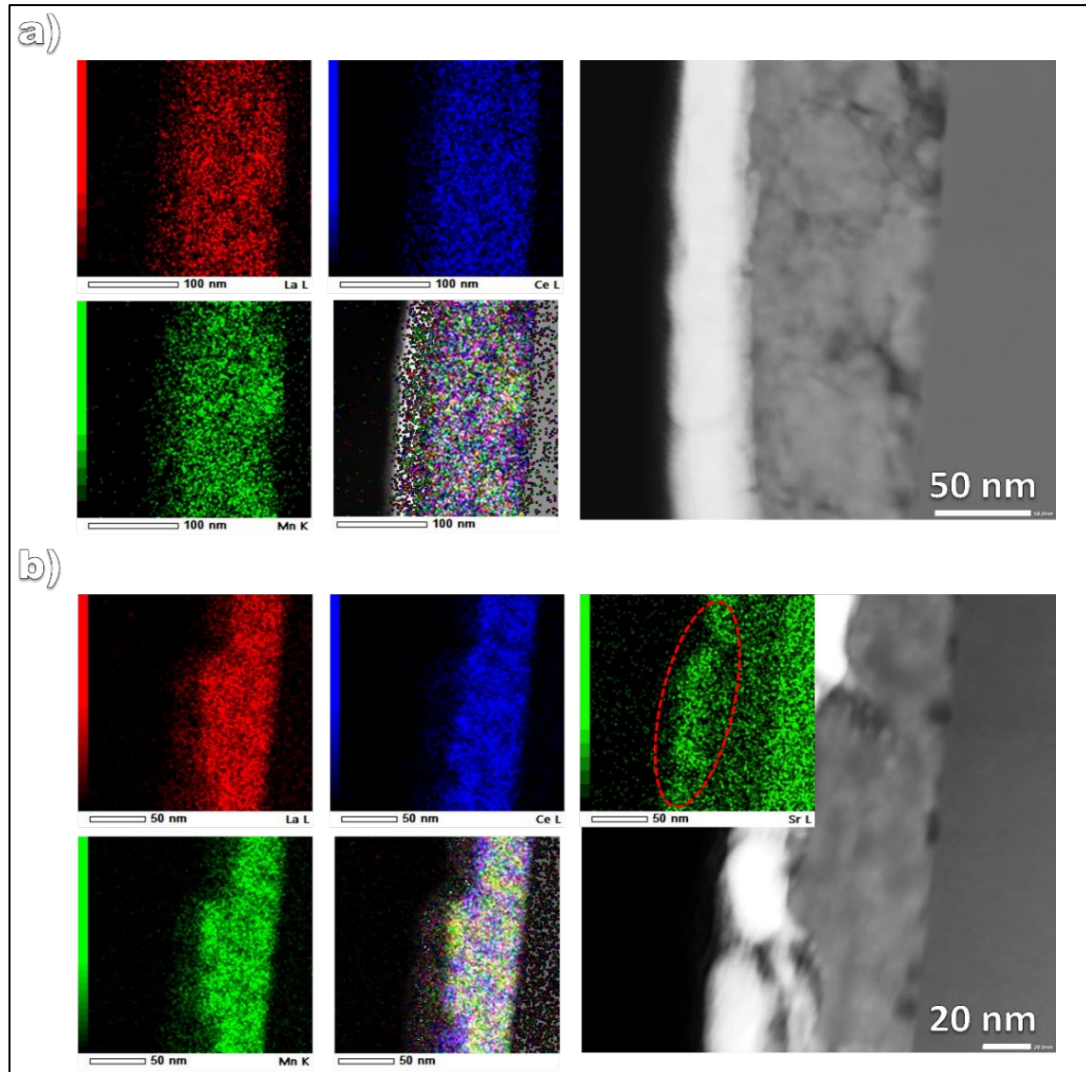


**Figure 3.5:** STEM analysis with EDS mapping of La (red), Ce (blue), Mn (green) and Sr (dark Green) for a) LMO-SDC HT and b) LSM64-SDC HT.

### 3.2.1. Surface Chemistry

XPS measurements were performed on LMO, LMO-SDC, LSM64 and LSM64-SDC electrode samples after 100 hours of exposure to 700 °C. This way, the effect of Sr on the surface chemistry evolution of the model single phase and composite technical electrodes will be evaluated.

In **Figure 3.6a**, it is shown that LSM 64 has a Sr/(La+Sr) ratio that is higher than the expected value, while in the case of LSM64-SDC, this value is close to the expected one that exhibits lower Sr 3d response which is close to theoretical stoichiometry ratios. All samples appear to have a higher ratio of total A site cations to B site cation Mn than stoichiometric ratio (**Figure 3.6b**). In addition, atomic ratio of total cations of the perovskite phase (La+Mn in the case of LMO-SDC and La+Sr+Mn in the case of LSM64-SDC) to the total cations of SDC is significantly larger than the expected value in the LSM64-SDC case, but closer to the expected value in the LMO-SDC case (**Figure 3.6c**). In the case of LSM64, Sr enrichment is evident, while mixing it with SDC renders the surface La+Sr rich (**Figure 3.6a**). Sm/(Sm+Ce) value is slightly higher than what is expected (**Figure 3.6d**).

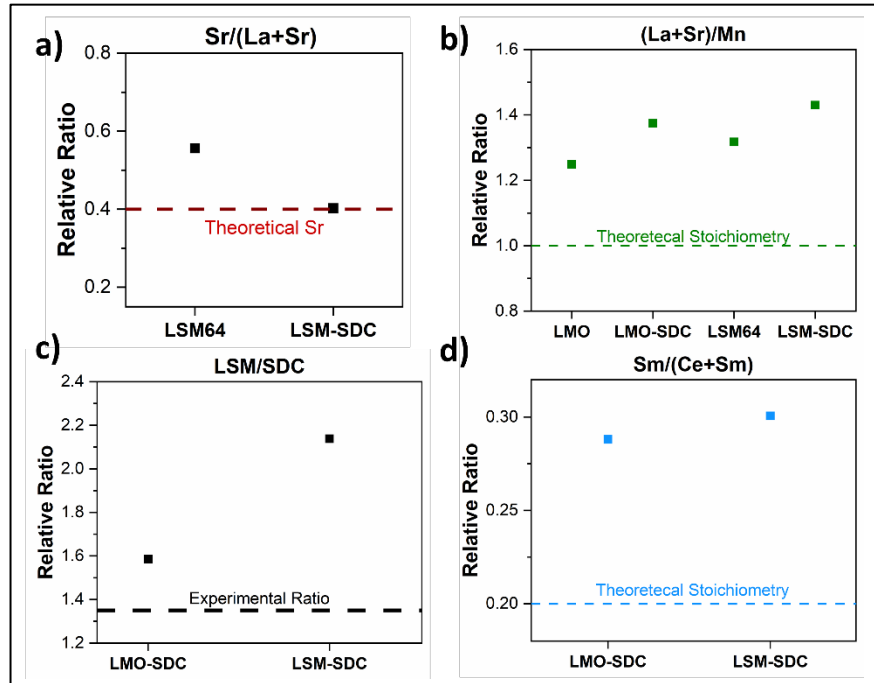


**Figure 3.6:** Normalized dopant ratio to total A-site cations of different electrode surfaces.

Dopant ratio is not enough only by itself to obtain a full understanding of the surface chemistry evolution. Analysis of the O 1s spectra has proven very useful for this purpose [33], [40], [53] (**Figure 3.7**). O 1s spectra obtained from the samples in this study consists of three components.  $O_{\text{lattice}}$  is oxygen within the lattice and is associated with a binding energy of  $\sim 529$  eV.  $O_{\text{ad}}$  is adsorbed oxygen can be related to the perovskite lattice termination oxygen, corresponding to surface oxygen vacancies at the operating temperatures and is at around  $\sim 531$  eV.  $O_s$  is surface oxygens associated with secondary phases, such as; carbonates, oxides or hydroxides at the surface and is found at binding energies of  $\sim 533$  eV [40]. However  $O_{\text{lattice}}$  and  $O_{\text{ad}}$  values are more determining parameters for our conclusion on surface chemistry. While the relative ratios of the O 1s components are provided as insets within the plots, these values are not normalized to the total amounts of oxygen each sample contains. The normalized values are provided in **Table 3.1**. Evidently, concentration of surface oxygen vacancies was slightly enhanced upon the addition of Sr (**Table 3.1**), consistent with the generic Sr substitution rationale.

**Table 3.1** Detected oxygen concentrations from XPS data for given samples.

| Composition | Normalized           |                 |          |
|-------------|----------------------|-----------------|----------|
|             | $O_{\text{lattice}}$ | $O_{\text{ad}}$ | $O_s$    |
| LMO         | 47.85636             | 21.77169        | 4.224357 |
| LMO-SDC     | 44.2494              | 22.60633        | 8.398356 |
| LSM64       | 36.44506             | 27.86814        | 4.192552 |
| LSM64-SDC   | 40.1045              | 28.35642        | 6.082764 |

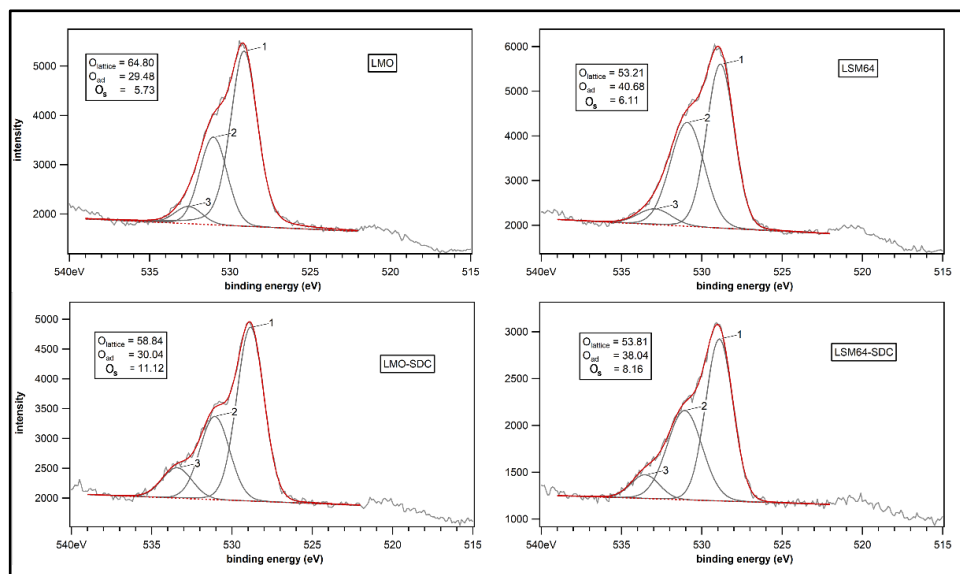


**Figure 3.7:** O 1s spectrums of annotated samples.

Sr3d peaks were also collected and fitted (**Figure 3.8**). Peak 2 is Sr response from bulk under the surface which has 132-133 eV binding energy and peak 1 is Sr response from surface. Both LSM64 and LSM64-SDC surfaces appear rich in Sr-related compounds, such as  $\text{SrCO}_3$ , in agreement with the XRD results. Thus we can also say that SDC addition increased  $\text{SrCO}_3$  response as peak 1.

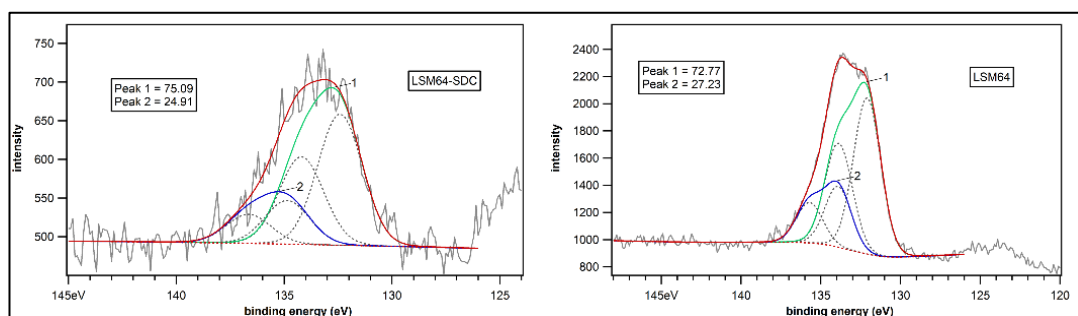


**Figure 3.8:** Sr 3d spectrums of annotated samples.

Overall, the XPS results indicate that the surfaces of LMO and LSM64 are La and Sr-rich, respectively. Meanwhile, the larger amounts of surface oxygen vacancies in the latter indicate that, despite the presence of insulating  $\text{SrCO}_3$  phases at the surface, there is still a certain amount of Sr dissolution into the perovskite structure, which should render LSM64 more active than LMO. The smaller particle size of the former should also further enhance this difference.

Comparison of composite samples is not so straight-forward. LSM64-SDC appears to have a significantly larger amount of LSM64 than that of SDC. Meanwhile, in LMO-SDC, LMO/SDC ratio at the surface appears closer to the expected value. Considering that 60:40 perovskite:ionic conductor volume ratio set here in the preparation of the nanocomposites is optimum for high electrochemical performance, deviation from this value and the presence of  $\text{SrCO}_3$  should have a negative impact on the electrochemical performance. On the other hand, larger amounts of oxygen vacancies in the case of LSM64-SDC in comparison to that of the Sr-free composite should favor the former in terms of performance.

### 3.3. Electrochemical Analysis

Electrochemical impedance spectroscopy (EIS) analysis is crucial to determine the electrochemical performance and mechanisms through which oxygen reduction/evolution reactions take place. Here, EIS measurements were performed on symmetrical half-cells in the electrode/electrolyte/electrode configuration at 500-700 °C and intermittently at 700 °C for 100 hours.

Nyquist plots revealed single semi-circles in both single phase and composite electrodes (**Figure 3.9**), corresponding to a single dominant electrochemical process. The size of the semi-circle is the resistance associated with the inverse of the rate of oxygen reduction/evolution reactions occurring at two symmetrical electrodes. Therefore, to determine the area specific resistance per one electrode ( $\text{ASR}_{\text{electrode}}$ ) the distance between the high and low frequency interceptions must be divided by two. The high frequency interception of the semi-circle corresponds to the resistance to the ionic transport through the YSZ electrolyte along with any additional current collection resistances.

In all samples, the ohmic resistance varied between 6.4 and 7.2  $\Omega \cdot \text{cm}^2$ , which roughly corresponds to the resistance of the dense YSZ electrolyte with the given thickness of  $\sim 1\text{mm}$  at 700 °C. From the summit frequencies and the sizes of the arcs, it was determined through **Equation 3.2** that the area specific capacitances (ASC) of all electrodes were in the  $10^{-4} \text{ F/cm}^2$  range, consistent with the charge transfer reaction at the triple phase boundary [54], [55], [56], [57].

$$f_{summit} = \frac{1}{2\pi \cdot ASR \cdot ASC} \quad (3.2)$$

In general, single-phase electrodes had higher ASR values of 2.34  $\Omega \cdot \text{cm}^2$ , 0.83  $\Omega \cdot \text{cm}^2$  and 1.04  $\Omega \cdot \text{cm}^2$  for LMO, LSM82 and LSM64, respectively. This is expected since Sr enhances electronic conductivity and hinders grain growth. Composites however surpasses single phases due to the addition of SDC phase increases the TPB length by halting grain growth and enhances ionic conductivity. It should be noted that LMO-SDC outperformed LSM64-SDC, as hypothesized, while LSM82-SDC exhibited similar electrochemical performances. Electrode polarization of 0.20  $\Omega \cdot \text{cm}^2$  is achieved with LMO-SDC at 0h, which is quite comparable to literature. For example, Huang Y. et al. obtained 0.5  $\Omega \cdot \text{cm}^2$  at 700 °C with symmetric-cell tests of LSM infiltrated YSZ electrode [58]. In another work, LSF-SDC electrode with performer addition has 0.3  $\Omega \cdot \text{cm}^2$  at 650 °C [59]. Addition of precious metal such as Pt increased electrode performance up to 0.022  $\Omega \cdot \text{cm}^2$  at 800 °C initially for LSM infiltrated study [60]. Yang Y. et al. studied the electrode performance of LSM/YSZ composite cathodes and the lowest electrode polarization resistance they achieved is 0.49  $\Omega \cdot \text{cm}^2$  at 750 °C [61].

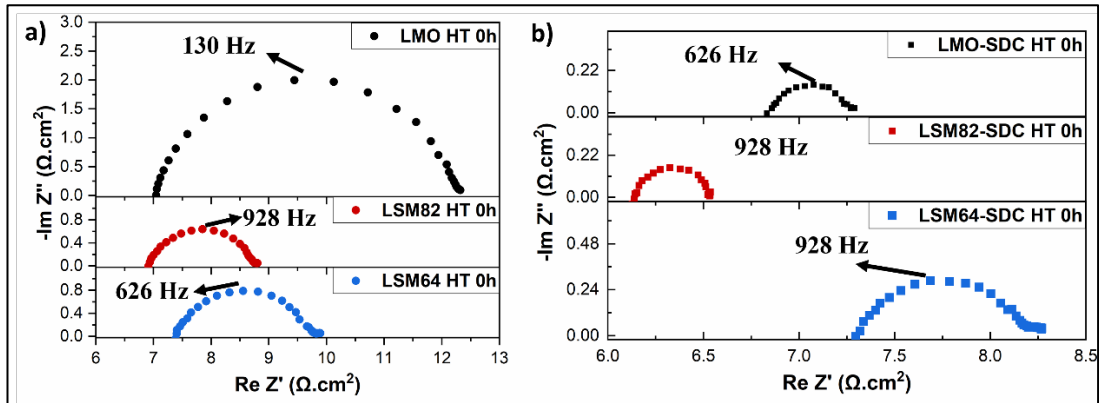


**Figure 3.9:** Nyquist plots for a) single phase and b) composite symmetrical cells at 700 °C in stagnant air as initial state 0 hour.

### 3.3.1. Temperature Dependence of the ASR

Testing of the first performances of the cells is made as short-term working test with increasing the temperature up to 700 °C from 400 °C by 50 °C intervals at the rate of

5 °C per minute vice versa for decreasing temperature before long-term test of the same cells. At different temperatures, polarization resistance changes thus calculation of activation energy through Arrhenius type equation is possible. If we make a linear fit of the data collected at different temperatures, it gives us a slope and using **Equation 3.3** gives activation energy ( $E_a$ ) in eV.  $E_a$  represents how easy or hard reactions on the electrodes are going to be.

$$k = Ae^{\frac{-E_a}{RT}} \quad (3.3)$$

$k$  is reaction rate,  $A$  is pre-exponential factor,  $R$  is gas constant and temperature in Kelvin. If we take  $\ln$  of both sides;

$$\ln k = \frac{E_a}{RT} + \ln A \quad (3.4)$$

Equation becomes linear equation with neglecting constants where we can calculate  $E_a$  using graph of up-down test by simply obtaining slope from it.

$$E_a = \frac{m}{R} \quad (3.5)$$

Note that in **Figure 3.10**, x-axis is reciprocal of temperature in kelvin to match equation and calculate more easily. The activation energy is directly related to the catalytic activity of the electrode materials towards ORR kinetics. Composite samples have greater activation energies compared to single phase counterparts, this behavior can be related to presence of ionic conduction phase thus electrocatalyst phase decreased in volume. Temperature strongly influences ionic conductivity and it can be said that composites are more susceptible to temperature increase (greater activation energy) in result performance is increasing rapidly. It can be seen that mixing SDC with LMO brings down the activation energy of electrode compared within sample groups. For example, LMO has the highest activation energy of 1.11 eV compared to other SPs. LMO-SDC on the other hand has the lowest activation energy of 1.19 eV compared to composites. Values are relevant compared to study of Ekşioğlu et al. [62], which she had 0.97 eV and 1.22 eV for LSM and LSM-SDC samples respectively. Fabrication method is quite similar to this work.

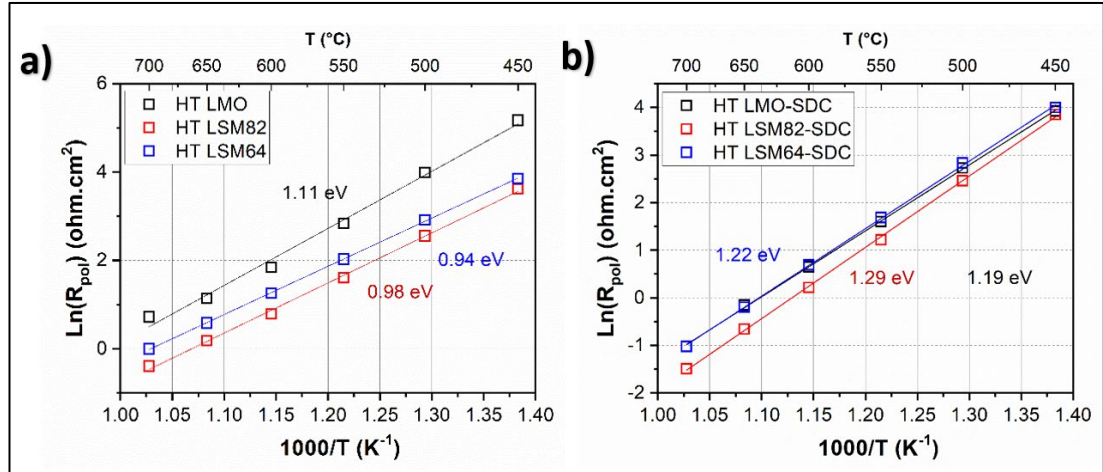


**Figure 3.10:** ASR vs temperature plots of a) single phase and b) composite samples with activation energies calculated.

### 3.3.2. Long-term Stability of the ASR

It is important to determine and understand SOC cell performance in longer operations. In this context, long-term (LT) tests have been carried out. After the temperature dependence measurements, the same cells were evaluated for LT stability.

In **Figure 3.11**, changes in ASR electrode with time at 700 °C are given. In the case of single-phase electrodes, LSM82 exhibited the most stable electrochemical performance, while LMO exhibited the highest initial ASR electrode, which increased even further rapidly with time. In the case of composite electrodes, LMO-SDC and LSM82-SDC exhibited comparable electrochemical performances during long-term operation, while LSM64-SDC performed poorly both initially and upon long-term exposure to 700 °C. These findings suggest that Sr-free perovskite electrodes could replace Sr-doped ones, as hypothesized.

Poor performance of LSM64-SDC initially and after 100 hours is related to excessive  $\text{SrCO}_3$  phase formation on the perovskite surface that hinders electrochemical activity.

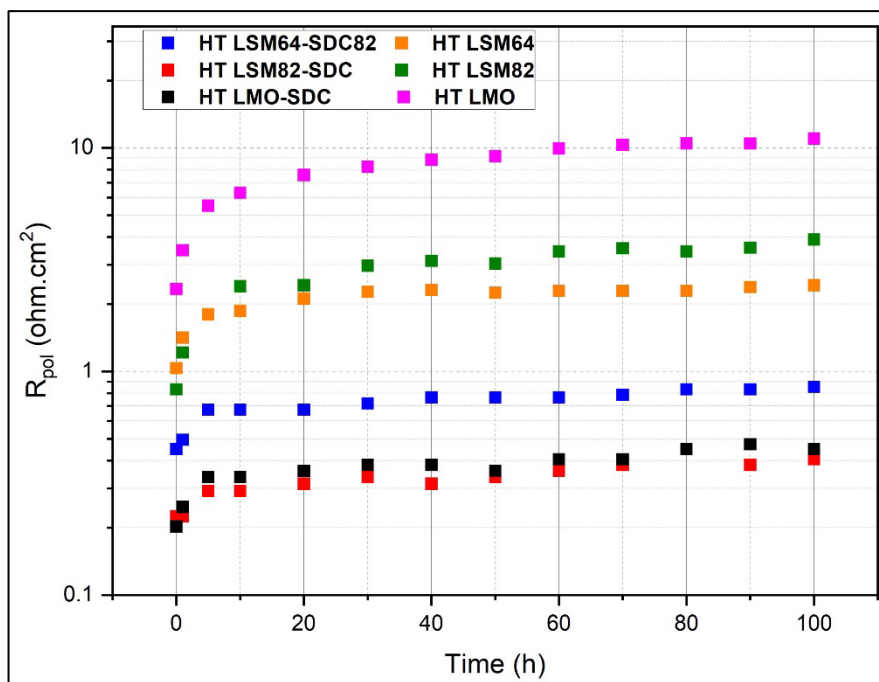


**Figure 3.11:** Electrode polarization of all samples with increasing operation time at 700 °C.

### 3.4. Correlation of Microstructure, Phase and Surface Chemistry Evolution to the Electrochemical Performance

The initial hypothesis of this thesis was that the Sr-dopant in the LaMO<sub>3</sub>-type SOC oxygen electrocatalysts and the consequent performance loss is usually severe and inevitable, hence, Sr-free electrocatalysts may outperform them as they will provide higher uncovered perovskite surface area, especially if they are nanostructured.

Microstructural analyses of electrodes via SEM revealed that Sr addition induced finer particle size, which could enhance TPB length. Addition of SDC further reduced the overall particle size and thus enhanced TPB length. SDC addition also provided microstructural stability by constraining the movement of the perovskite phase.

The polymeric precursor-derived single-phase samples had 214 Ruddlesden Popper and SrCO<sub>3</sub> impurity phases, in addition to the expected 113 rhombohedral phase. While a mixture of 113-214 phases in optimal ratios has been reported to induce fast oxygen reduction [50], [63], excessive amounts of 214 formation could hinder the electrochemical performance. The presence of SrCO<sub>3</sub> is unequivocally undesirable. A

similar trend in phase evolution was observed in composite samples as well. 100 hours of exposure to 700 °C did not affect phase content.

XPS revealed that Sr-containing samples had a significant amount of Sr-containing impurities ( $\text{SrCO}_3$ ) at their surface after 100 h of exposure to 700 °C. Meanwhile, Sr-containing samples had slightly larger amount of surface oxygen vacancies in comparison to undoped ones. In the case of composites LSM64-SDC had a surface with a higher number of perovskite-cations in comparison to the ionic conductor phase cations, Sm and Ce. LMO-SDC had a LMO:SDC ratio close to the expected value.

In the light of these results, the higher performance of LSM64 than LMO after long-term operation is expected, due to the higher amount of oxygen vacancies and the finer microstructure of the former in comparison to the latter. Meanwhile, higher electrochemical performance of LMO-SDC in comparison to that obtained from LSM64-SDC was likely due to larger LSM64: SDC ratio than the initially prepared 60:40 volume ratio, which reduced the effective TPB length. The dominant LSM64 surface was also associated with a significant amount of  $\text{SrCO}_3$ , which partially blocked effective surface exchange at the surface.

## 4. CONCLUSION

Developing nanocomposite La-based electrodes without Sr doping for solid oxide cell applications is studied within scope of this work. LMO-SDC composition showed promising performance in both short-term and long-term test with lowered activation energy of 1.19 eV and  $0.45 \Omega \cdot \text{cm}^2$  ASR after 100 hours. Since LSM82-SDC has lower ASR value after 100 hours but not significantly.

Sr containing samples showed  $\text{SrCO}_3$  formation on the surface both found in XRD and XPS results also Ruddlesden-popper 214 phase was present in Sr doped samples. However, there is no clear indication that 214 reduces catalytic activity or not but it may affect indirectly to other microstructural changes hence electrochemical performance changes also it is not found in our study.

SOCs are promising clean and efficient energy solutions to the world where demand is increasing day by day. Fossil fuels are limited by facts and oil reservoirs would reach peak amounts from 2030 to 2050 from predictions and estimations by energy agencies. Thus, stable and powerful SOC's can be the future of energy production. This work concluded that without need of Sr doping, it is possible to achieve stable air electrodes for SOC's.

## REFERENCES

- [1] European Bureau for Research on Industrial Transformation and Emissions (EU-BRITE), (2021), “Reference Document on Best Available Techniques (BREF) for Energy Efficiency,” European Commission.
- [2] W. H. J. Graus, M. Voogt, and E. Worrell, “International comparison of energy efficiency of fossil power generation,” *Energy Policy*, 2007, vol. 35, no. 7, pp. 3936–3951.
- [3] G. M. Masters, (2004), *Renewable and Efficient Electric Power Systems*, John Wiley & Sons Inc.
- [4] International Energy Agency, (2024) “Oil 2024,” *Int. Energy Agency*.
- [5] M. Steen, (2001), “Greenhouse Gas Emissions from Fossil Fuel Fired Power Generation Systems.. EUR 19754 EN. 2001. JRC21207,”.
- [6] K. L. Ebi *et al.*, “Extreme Weather and Climate Change: Population Health and Health System Implications.,” *Annu. Rev. Public Health*, Apr. 2021, vol. 42, pp. 293–315.
- [7] S. C. Singhal and K. Kendall, (2003.), *High-temperature Solid Oxide Fuel Cells: Fundamentals, Design and Applications.*, Elsevier Ltd.
- [8] Ritchie H., Rosado P., Roser M., (2024), “Statistical Review of World Energy with major processing by Our World in Data,”, Energy Institute - Statistical Review of World Energy, Acces date: 05.03.2025
- [9] F. B. P. Ryan O’Hayre, Suk-Won Cha, Whitney Colella, (2016), *Fuell Cell Fundamentals*, 3rd edition. Hoboken, New Jersey, Canada: John Wiley.
- [10] B. Sørensen, (2005), *Hydrogen and Fuel Cells: Emerging technologies and applications*, Elsevier Academic Press , vol. 0-12–65528, no. 1.
- [11] R. Bove and S. Ubertini, (2013), *Modelling of Solix Oxide Fuel Cells*, Springer Science, vol. 53, no. 9.
- [12] H. S. Song, S. Lee, S. H. Hyun, J. Kim, and J. Moon, “Compositional influence of LSM-YSZ composite cathodes on improved performance and durability of solid oxide fuel cells,” *J. Power Sources*, 2009, vol. 187, no. 1, pp. 25–31.
- [13] S. U. Rehman, R. H. Song, J. W. Lee, T. H. Lim, S. J. Park, and S. B. Lee, “Effect of GDC addition method on the properties of LSM–YSZ composite cathode support for solid oxide fuel cells,” *Ceram. Int.*, 2016, vol. 42, no. 10, pp. 11772–11779.

- [14] V. A. C. Haanappel *et al.*, “Optimisation of processing and microstructural parameters of LSM cathodes to improve the electrochemical performance of anode-supported SOFCs,” *J. Power Sources*, 2005, vol. 141, no. 2, pp. 216–226.
- [15] M. Lo Faro and A. S. Aricò, (2014), “Ceramic membranes for intermediate temperature solid oxide fuel cells (SOFCs): state of the art and perspectives,” A. Gugliuzza and A. B. T.-M. for C. and R. P. A. Basile, Eds., Woodhead Publishing, pp. 237–265.
- [16] J. Fergus, R. Hui, L. Xianguo, D. Wilkinson, and J. Zhang, (2008), *Solid Oxide Fuel Cells: Materials Properties and Performance*, CRC Press.
- [17] V. V. Kharton, F. M. B. Marques, and A. Atkinson, “Transport properties of solid oxide electrolyte ceramics: a brief review,” *Solid State Ionics*, 2004, vol. 174, no. 1, pp. 135–149.
- [18] B. Bilbey, M. Sezen, C. W. Ow-Yang, B. T. Camic, and A. Buyukaksoy, “Formation, Performance, and Long-Term Stability of Nanostructured Ni-YSZ Thin Film Electrodes,” *ACS Appl. Energy Mater.*, 2021, vol. 4, no. 9, pp. 9046–9056.
- [19] J. W. Fergus, “Oxide anode materials for solid oxide fuel cells,” *Solid State Ionics*, 2006, vol. 177, no. 17–18, pp. 1529–1541.
- [20] T. Li and J. Parbey, (2019) “Cermets as anode materials,” *Intermed. Temp. Solid Oxide Fuel Cells Electrolytes, Electrodes Interconnects*, pp. 165–194.
- [21] B. Holówko, J. Karczewski, S. Molin, and P. Jasiński, “Preparation of hydrogen electrodes of solid oxide cells by infiltration: Effects of the preparation procedure on the resulting microstructure,” *Materials (Basel)*, 2020, vol. 13, no. 1.
- [22] M. P. Pechini, (1967) “Method of Preparing Lead and Alkaline Earth Titanates and Niobates and Coating Method Using the Same to Form a Capacitor,” 3,330,697.
- [23] Y. Li, Z. Xu, Y. Wan, S. Zhang, and C. Xia, (2019), Ch. 7. *Progress in perovskite anodes for intermediate-temperature solid oxide fuel cells*. Elsevier Inc., Electrolytes, Electrodes and Interconnects
- [24] Y. A. Mastrikov, D. Gryaznov, G. Zvejnieks, M. N. Sokolov, M. Putniņa, and E. A. Kotomin, “Sr Doping and Oxygen Vacancy Formation in  $\text{La}_{1-x}\text{Sr}_x\text{ScO}_{3-\delta}$  Solid Solutions: Computational Modelling,” *Crystals*, 2022, vol. 12, no. 9.
- [25] M. Á. Cauqui, “Performance of a Direct Methane Solid Oxide Fuel Cell Using Nickel-Ceria-Yttria Stabilized Zirconia as the Anode,” *Materials (Basel)*, 2020, vol. 13(3), no 599.
- [26] D. Papurello, A. Lanzini, S. Fiorilli, F. Smeacetto, R. Singh, and M. Santarelli, “Sulfur poisoning in Ni-anode solid oxide fuel cells (SOFCs): Deactivation in single cells and a stack,” *Chem. Eng. J.*, 2016, vol. 283, pp. 1224–1233,

- [27] N. Mahato, A. Banerjee, A. Gupta, S. Omar, and K. Balani, "Progress in material selection for solid oxide fuel cell technology: A review," *Prog. Mater. Sci.*, , 2015, vol. 72, pp. 141–337.
- [28] S. Onbilgin, B. Timurkutluk, C. Timurkutluk, and S. Celik, "Comparison of electrolyte fabrication techniques on the performance of anode supported solid oxide fuel cells," *Int. J. Hydrogen Energy*, 2020, vol. 45, no. 60, pp. 35162–35170.
- [29] M. B. Mogensen *et al.*, "Reversible solid-oxide cells for clean and sustainable energy," *Clean Energy*, 2019, vol. 3, no. 3, pp. 175–201, Nov.
- [30] E. Demirkal, O. Ozdemir, L. Colakerol Arslan, and A. Buyukaksoy, "Sources of performance degradation in thin film  $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$  air electrodes," *Solid State Ionics*, , 2020, vol. 355, no. February, p. 115420.
- [31] Y. Liu *et al.*, "Recent advances in the heteroatom doping of perovskite oxides for efficient electrocatalytic reactions," *Nanoscale*, 2021, vol. 13, no. 47, pp. 19840–19856.
- [32] C. Mendonça, A. Ferreira, and D. M. F. Santos, "Towards the Commercialization of Solid Oxide Fuel Cells: Recent Advances in Materials and Integration Strategies" *Fuels*, 2021, vol. 2, no. 4, pp. 393–419.
- [33] W. Lee, J. W. Han, Y. Chen, Z. Cai, and B. Yildiz, "Cation size mismatch and charge interactions drive dopant segregation at the surfaces of manganite perovskites," *J. Am. Chem. Soc.*, 2013, vol. 135, no. 21, pp. 7909–7925.
- [34] M. S. Gocmen, A. Eksioglu, and A. Buyukaksoy, "Effect Of Sr Content On The Microstructure Development And Electrochemical Performance of  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  Films", 2024, vol. 12, no. 4, pp. 653–662.
- [35] K. C. Chang *et al.*, "In situ synchrotron x-ray studies of dense thin-film strontium-doped lanthanum manganite solid oxide fuel cell cathodes," *Mater. Res. Soc. Symp. Proc.*, 2009, vol. 1126, no. January, pp. 27–32.
- [36] S. P. Jiang, "Development of lanthanum strontium cobalt ferrite perovskite electrodes of solid oxide fuel cells – A review," *Int. J. Hydrogen Energy*, 2019, vol. 44, no. 14, pp. 7448–7493.
- [37] T. Jin and K. Lu, "Surface and interface behaviors of  $(\text{La}_{0.8}\text{Sr}_{0.2})_x\text{MnO}_3$  air electrode for solid oxide cells," *J. Power Sources*, 2011, vol. 196, no. 20, pp. 8331–8339.
- [38] C. Cai *et al.*, "Enhanced electrochemical performance of  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  cathode via Ba-doping for intermediate-temperature solid oxide fuel cells," *Nano Res.*, 2022, vol. 15, 4, pp. 3264–3272.

- [39] X. Han *et al.*, “New approach to enhance Sr-free cathode performance by high-entropy multi-component transition metal coupling,” *Ceram. Int.*, 2021, vol. 47, no. 12, pp. 17383–17390.
- [40] E. J. Crumlin *et al.*, “Surface strontium enrichment on highly active perovskites for oxygen electrocatalysis in solid oxide fuel cells,” *Energy Environ. Sci.*, 2012, vol. 5, no. 3, pp. 6081–6088.
- [41] C. Tian *et al.*, “Evaluating the electronic structure and stability of epitaxially grown Sr-doped LaFeO<sub>3</sub> perovskite alkaline O<sub>2</sub> evolution model electrocatalysts,” *RSC Appl. Interfaces*, 2025, vol. 2, no. 1, pp. 122–129.
- [42] M. Sezer, H. Sezer, A. Ş. Ahsen, and A. Büyükaksoy, “Surface Chemistry and Phase Evolution in Dense Sr- or Ca-Doped LaCoO<sub>3</sub> Ceramics and Their Correlation to Surface Exchange and Chemical Diffusion Coefficients,” *J. Phys. Chem. C*, 2023, vol. 127, no. 24, pp. 11506–11516.
- [43] M. Sezer, İ. Öztoprak, A. Ş. Ahsen, A. Y. Oral, and A. Büyükaksoy, “Correlation of Phase, Microstructure and Surface Chemistry Evolution to the Long-Term Performance Stability of (La, Ca)CoO<sub>3</sub> SOFC Electrodes,” *J. Electrochem. Soc.*, 2020, vol. 167, no. 12, p. 124508.
- [44] V. Celorrio *et al.*, “Relationship between Mn Oxidation State Changes and Oxygen Reduction Activity in (La,Ca)MnO<sub>3</sub> as Probed by in Situ XAS and XES,” *ACS Catal.*, 2021, vol. 11, pp. 6431–6439.
- [45] A. Samreen *et al.*, “Advancements in Perovskite-Based Cathode Materials for Solid Oxide Fuel Cells: A Comprehensive Review,” *Chem. Rec.*, 2024, vol. 24, no. 1.
- [46] K. L. Briggman and D. D. Bock, “Volume electron microscopy for neuronal circuit reconstruction,” *Curr. Opin. Neurobiol.*, 2012, vol. 22-1, pp. 154–161.
- [47] S. A. Soumia, Z. Messali, A. Ouahabi, S. Trepout, C. Messaoudi, and S. Marco, “Nonparametric Denoising Methods Based on Contourlet Transform with Sharp Frequency Localization: Application to Low Exposure Time Electron Microscopy Images,” *Entropy*, May 2015, vol. 17, pp. 3461–3478.
- [48] E. J. Crumlin *et al.*, “In situ ambient pressure X-ray photoelectron spectroscopy of cobalt perovskite surfaces under cathodic polarization at high temperatures,” *J. Phys. Chem. C*, 2013, vol. 117, no. 31, pp. 16087–16094.
- [49] J. Hayd, L. Dieterle, U. Guntow, D. Gerthsen, and E. Ivers-Tiffée, “Nanoscaled La<sub>0.6</sub>Sr<sub>0.4</sub>CoO<sub>3-δ</sub> as intermediate temperature solid oxide fuel cell cathode: Microstructure and electrochemical performance,” *J. Power Sources*, 2011, vol. 196, no. 17, pp. 7263–7270.
- [50] M. Sase *et al.*, “Enhancement of oxygen exchange at the hetero interface of (La,Sr)CoO<sub>3</sub>/(La,Sr)<sub>2</sub>CoO<sub>4</sub> in composite ceramics,” *Solid State Ionics*, 2008, vol. 178, no. 35–36, pp. 1843–1852.

- [51] A. Eksioğlu, L. Colakerol Arslan, M. Sezen, C. Ow-Yang, and A. Buyukaksoy, "Formation of Nanocomposite Solid Oxide Fuel Cell Cathodes by Preferential Clustering of Cations from a Single Polymeric Precursor," *ACS Appl. Mater. Interfaces*, 2019, vol. 11, no. 51, pp. 47904–47916.
- [52] L. Goral, M. Sezen, C. W. Ow-Yang, B. Günhan, and A. Buyukaksoy, "Evolution of elemental distribution in single liquid precursor-derived nanocomposite solid oxide cell electrodes at nanoscale and its impact on electrochemical performance stability," *J. Solid State Electrochem.*, 2023, vol. 27, no. 3, pp. 655–666.
- [53] M. Zhi *et al.*, "Single crystalline  $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  microcubes as cathode of solid oxide fuel cell," *Energy Environ. Sci.*, 2011, vol. 4, no. 1, pp. 139–144.
- [54] A. Mitterdorfer and L. J. Gauckler, " $\text{La}_2\text{Zr}_2\text{O}_7$  formation and oxygen reduction kinetics of the  $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ ,  $\text{O}_2(\text{g})|\text{YSZ}$  system," *Solid State Ionics*, 1998, vol. 111, no. 3–4, pp. 185–218.
- [55] R. Antunes, J. Jewulski, and T. Golec, "Full parametric characterization of LSM/LSM-YSZ cathodes by electrochemical impedance spectroscopy," *J. Fuel Cell Sci. Technol.*, 2014 vol. 11, no. 1, pp. 1–7.
- [56] B. Molero Sánchez, P. Addo, A. Buyukaksoy, S. Paulson, and V. Birss, "Electrochemistry of  $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$  as an oxygen and fuel electrode for RSOFCs," *Faraday Discuss.*, 2015, vol 182, no 159.
- [57] S. B. Adler, J. A. Lane, and B. C. H. Steele, "Electrode Kinetics of Porous Mixed-Conducting Oxygen Electrodes," *J. Electrochem. Soc.*, , 1996, vol. 143, no. 11, pp. 3554–3564.
- [58] Y. Huang, J. M. Vohs, and R. J. Gorte, "Characterization of LSM-YSZ Composites Prepared by Impregnation Methods," *J. Electrochem. Soc.*, 2005, vol. 152, no. 7, p. A1347.
- [59] A. Eksioğlu, I. A. Sakir, and A. Buyukaksoy, "Formation mechanism of large porosity in solid oxide cell electrode coatings fabricated using ethylene glycol-based precursor solutions and its impact on the electrochemical performance," *Ceram. Int.*, 2023, vol. 49, no. 1, pp. 956–963.
- [60] A. Buyukaksoy, V. Petrovsky, and F. Dogan, "Efficient Cathodes for Solid Oxide Fuel Cells Prepared by Polymeric Precursor Infiltration," *J. Electrochem. Soc.*, 2011, vol. 159, no. 1, pp. B67–B71.
- [61] M. Shah and S. A. Barnett, "Solid oxide fuel cell cathodes by infiltration of  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  into Gd-Doped Ceria," *Solid State Ionics*, Oct. 2008, vol. 179, no. 35–36, pp. 2059–2064.
- [62] A. Ekşioğlu, (2019) "Katı Oksit Yakıt Hücreleri İçin Nanokompozit Katotların Geliştirilmesi," *Gebze Tek. Üniversitesi*, Yüksek Lisans Tezi.

- [63] J. Hayd, H. Yokokawa, and E. Ivers-Tiffée, “Hetero-Interfaces at Nanoscaled (La,Sr)CoO<sub>3-δ</sub> Thin-Film Cathodes Enhancing Oxygen Surface-Exchange Properties ,” *J. Electrochem. Soc.*, 2013, vol. 160, no. 4, pp. F351–F359.
- [64] A. J. Samson, (2012) “Cathodes for Solid Oxide Fuel Cells Operating at Low Temperatures”, *Denmark Technical University*, Ph.D. Thesis, p. 177.
- [65] B. Molero-Sánchez, P. Addo, A. Buyukaksoy, and V. Birss, “ Performance Enhancement of La<sub>0.3</sub> Ca<sub>0.7</sub> Fe<sub>0.7</sub> Cr<sub>0.3</sub> O<sub>3-δ</sub> Air Electrodes by Infiltration Methods ,” *J. Electrochem. Soc.*, 2017, vol. 164, no. 10, pp. F3123–F3130.
- [66] Ishfaq H. A. *et al.*, “Boosting performance of the solid oxide fuel cell by facile nano-tailoring of La<sub>0.6</sub>Sr<sub>0.4</sub>CoO<sub>3-d</sub> cathode” vol. 7, pp. 0–11, 2021.
- [67] S. M. Bartłomiej Lemieszek, Mindaugas Ilickas, Jan Jamroz, Asta Tamulevičienė, Jakub Karczewski, Patryk Błaszczak, Alexey Maximenko, Brigita Abakevičienė, Marcin Małys, Sigitas Tamulevičius, Piotr Jasiński, “Enhanced electrochemical performance of partially amorphous La<sub>0.6</sub>Sr<sub>0.4</sub>CoO<sub>3-δ</sub> oxygen electrode materials for low-temperature solid oxide cells operating at 400 °C.”, *Applied Surface Science*, 2024, vol. 670, no. 160620.

## **BIOGRAPHY**

Ömer Faruk AKSOY, He graduated from Gebze Technical University, Department of Materials Science and Engineering in 2022. He enrolled in the Materials Science and Engineering Master of Science program at Gebze Technical University in 2022. He took part in various projects such as ADEP, TUBITAK 2210-C and Erasmus+ internship program in Gdansk/Poland. These projects are related to SOC's.

## APPENDICES

### APPENDIX A: Presentation from the Thesis

Aksoy Ö. F., Büyükaksoy A., (2024), “Katı Oksit Hücreler İçin A-Pozisyonu Katkısı İçermeyen ABO<sub>3</sub> – Tipi Lantanyum Bazlı Perovskit Hava Elektrotlarının Üretilmesi ve Geliştirilmesi”, Poster presentation at 8<sup>th</sup> Post Graduate Research Symposium in Gebze Technical University

## APPENDIX B: Developing SDC Interlayered LSC Based Symmetrical Cells for Solid Oxide Cells

SDC ( $\text{Sm}_{0.8}\text{Ce}_{0.2}\text{O}_2$ ) is responsible for ionic conduction. In addition to mixing with electrocatalysis to obtain composite MIEC material purposes, presence of SDC layer between electrolyte and electrode also creates buffer layer to prevent unwanted phases such as  $\text{La}_2\text{Zr}_2\text{O}_7$  in YSZ-based electrolytes [40], [64], [65]. SDC also enhances further enhances ionic conductivity and prevents thermal expansion mismatches. Pros and cons of Sr doping are discussed in the main dissertation. Cobalt addition makes electrode more active towards ORR reactions via more electronically conductive compared to Mn.

In this premature study, several  $\text{LaSrCoO}_3$  compositions with and without SDC mixing are assessed. Electrolyte pellets are pressed with linear press from YSZ commercial powders (TOSOH, Japan) and sintered at  $1400^\circ\text{C}$ . Metal nitrate salts are dissolved in distilled water, ethylene glycol added in ratio of specific mole ratios to cations, butoxy ethanol used to enhance wetting performance of the solution precursor. Spin-on coating carried out with 2000rpm for 5 times for SDC interlayer on YSZ electrolyte followed by LSC-SDC coating for 15 times. Heating at  $350^\circ\text{C}$  applied to dry out samples and calcination at  $700^\circ\text{C}$  for 3 hours is done. Symmetrical cell configuration is Ag/LSC-SDC/SDC/YSZ. EIS measurements carried out with Biologic-SP150 potentiostat with frequency range and excitation voltage are set to 0.05Hz to 0.5MHz and  $\pm 10\text{ mV}$  respectively. Both short-term and long-term tests are done to calculate activation energies and stability of the cells.

In **Figure B1**, short-term performance can be seen for all the four samples. At first sight, composite samples are more likely to have lower  $R_{\text{pol}}$  values than single phase samples. However, composites have higher activation energy probably due to introducing of ionic conductive phase.

Long-term operation showed that LCO-SDC composition has best  $R_{\text{pol}}$  of  $0.089\ \Omega\cdot\text{cm}^2$  after 100 hours of working amongst other samples. This performance is very promising compared to literature where  $0.3\ \Omega\cdot\text{cm}^2$   $R_{\text{pol}}$ , at  $650^\circ\text{C}$ ,  $0.109\ \Omega\cdot\text{cm}^2$   $R_{\text{pol}}$  at  $700^\circ\text{C}$  and barrier layer with GDC showed  $0.106\ \Omega\cdot\text{cm}^2$  at  $800^\circ\text{C}$  [59], [66], [67]. All of the samples showed good stability and a decrease in  $R_{\text{pol}}$  is observed even after 70 hours.

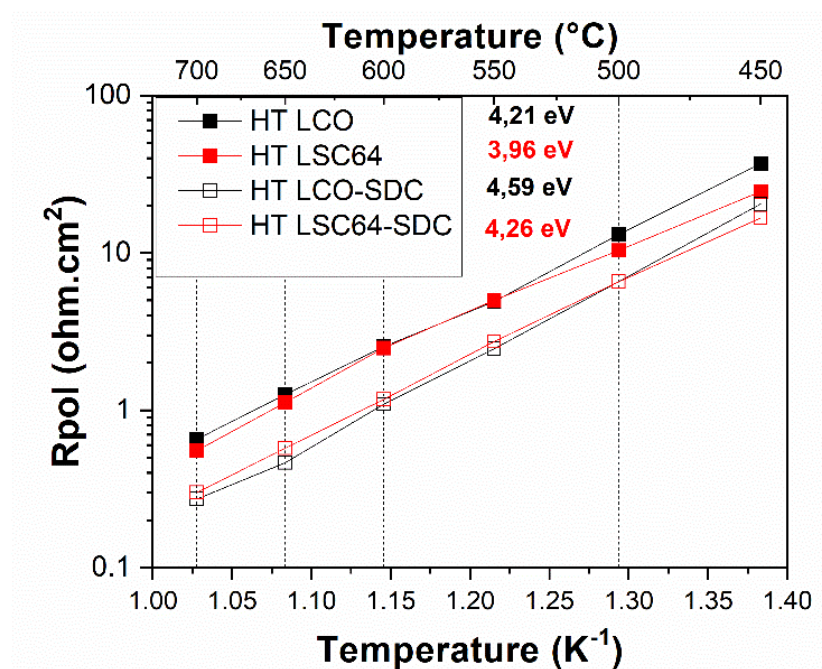


**Figure B1:** ASR vs Temperature data of various LSC-SDC samples with SDC interlayer.

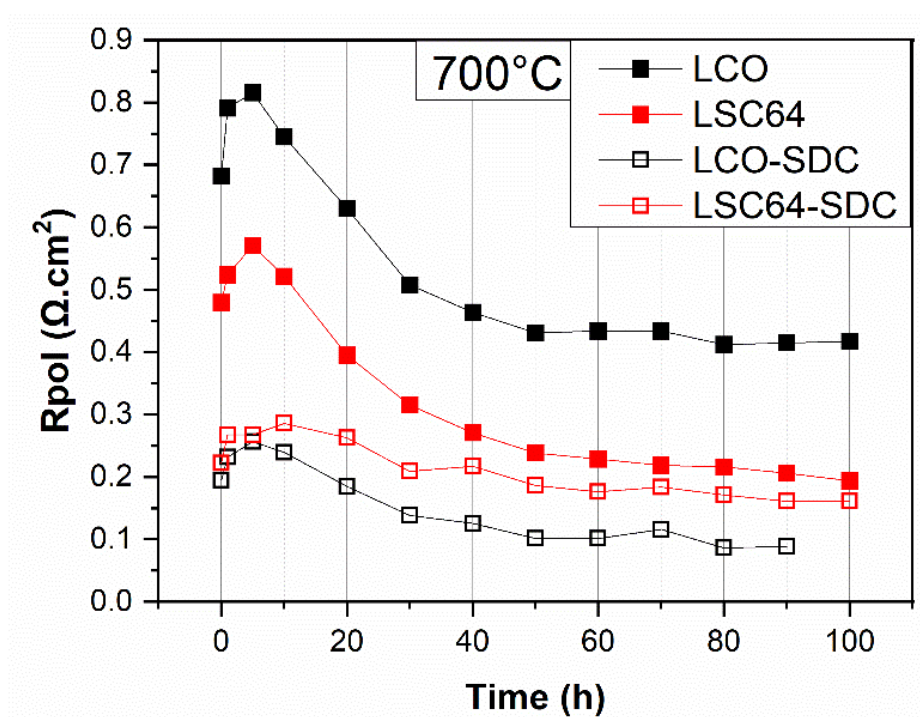


**Figure B2:** Long-term data of samples for 100 hours at 700 °C.