

COMBINATORIAL DEVELOPMENT OF LSF-BASED CATHODE
MATERIALS FOR INTERMEDIATE TEMPERATURE SOLID OXIDE FUEL
CELLS

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**COMBINATORIAL DEVELOPMENT OF LSF-BASED CATHODE
MATERIALS FOR INTERMEDIATE TEMPERATURE SOLID OXIDE
FUEL CELLS**

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ABSTRACT

COMBINATORIAL DEVELOPMENT OF LSF-BASED CATHODE MATERIALS FOR INTERMEDIATE TEMPERATURE SOLID OXIDE FUEL CELLS

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This thesis focuses on the synthesis, characterization, and processing of LSF based composite cathode for solid oxide fuel cells. The cathode comprises three oxides; LSM, LSF and ScSZ which are synthesized by co-sputtering using combinatorial approach. The electrolyte was Scandia doped Zirconia(ScSZ), as it has attractive ionic conductivity at lower temperatures. Having chosen the electrolyte ScSZ as electrolyte. After detailed analysis with regard to conductivity and thermal expansion for each oxide, the compositions selected were $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$, $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_{3-\delta}$ and $\text{Sc}_{0.15}\text{Zr}_{0.85}\text{O}_{2-\delta}$ LSF, LSM, ScSZ respectively.

Electrolyte powder was fabricated by Pechini method using nitrates as precursors, calcined at 900 °C. Electrolyte disc of typically 2mm thick were obtained by pressing

and sintering at 1500 °C. This has yielded an electrolyte with ionic conductivity of $3.5 \times 10^{-4} \text{ S.cm}^{-1}$ at 600 °C.

A total of 21 composite cathodes were deposited on electrolytes, each with a different composition. The performance of cathodes was characterized via EIS measurements on symmetric cells. A temperature ranges from 600 °C up to 800 °C was covered at 50 °C interval. LSM.LSF.ScSZ ternary diagram was mapped in terms of area specific resistance (ASR). The ASR values at 600 °C varied from 29 to 676 ohm.cm^2 . At 800 °C the values were significantly better which ranged from 0.33 to 5.55 ohm.cm^2 . The mapping of ASR values yielded a region close to $\text{LSM}_{0.750}\text{LSF}_{0.125}\text{ScSZ}_{0.125}$ where ASR was minimum. The value obtained was 0.33 ohm.cm^2 implying that the cathode is suitable for use at temperatures slightly above 800 °C.

It was anticipated that in order to reduce operating temperature of SOFC to lower temperature LSM may be replaced by ruddlesden-popper type oxide. It was proposed that $\text{LaSr}_3\text{Fe}_3\text{O}_{10}$ (rp-LSF) may be used in place of LSM with a potential to achieve this reduction.

Keywords: SOFC cathodes, Combinatorial deposition, Magnetron sputtering, Electrochemical impedance spectroscopy, Symmetric cell.

ÖZ

KOMBİNATORİYAL YAKLAŞIMLA LSF ESASLI KOMPOZİT KATOTLARIN ORTA SICAKLIK KATI OKSİT YAKIT PİLLERİ İÇİN GELİŞTİRİLMESİ

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Bu tez, katı oksit yakıt pilleri (KOYP) için LSF bazlı kompozit katotların geliştirilmesini konu almaktadır.

Katot, LSM, LSF ve ScSZ' den oluşacak tarzda kombinatoriyal yaklaşımla sıçratma-çöktürme yöntemi ile sentezlenmiştir. Elektrolit olarak, skandiyum oksit katkılı zirkonyum oksit kullanılmıştır. Her oksit için iletkenlik ve termal genleşme ile ilgili detaylı taramalardan sonra seçilen stokiyometrilere LSF, LSM ve ScSZ için sırasıyla $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$, $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_{3-\delta}$ ve $\text{Sc}_{0.15}\text{Zr}_{0.85}\text{O}_{2-\delta}$ olmuştur.

ScSZ elektrolit tozu, nitratlarından Pechini yöntemi ile 900 °C de kalsinlenerek üretilmiştir. Tipik olarak 2mm kalınlığındaki elektrolit diskler presleme ve 1500

$^{\circ}\text{C}$ 'de sinterleme yöntemiyle üretilmiştir. Bu yöntemle üretilen elektrolitlerde iyonik iletkenlik $600\ ^{\circ}\text{C}$ 'de $3.5 \times 10^{-4}\ \text{S.cm}^{-1}$ olarak tespit edilmiştir.

Katot sentezi her üç üreticinin LSM, LSF ve ScSZ eşzamanlı sıçratılması ile sentezlenmiştir. Üçgen geometrideki üç üretici üzerinde, yine üçgen geometride toplam 21 elektrolit altlık üzerine katot kaplanmıştır. Bu geometride elde edilen katotlar LSM-LSF-SCSZ üçlü diyagramında geniş bir alanda dağılım göstermişlerdir.

Katotların performansı simetrik hücreler üzerinde elektrokimyasal empedans spektroskopisi kullanılarak $600\text{-}800\ ^{\circ}\text{C}$ arasında $50\ ^{\circ}\text{C}$ aralıklarla ölçülmüştür. Alan spesifik direnç (ASR) değerleri $600\ ^{\circ}\text{C}$ 'de katot kompozisyonuna bağlı olarak 29 ila $676\ \text{ohm.cm}^2$ arasında bulunmuştur. $800\ ^{\circ}\text{C}$ 'de bu değerler 0.33 ile $5.55\ \text{ohm.cm}^2$ aralığındadır. ASR değerleri açısından en iyi katot kompozisyonu $\text{LSM}_{0.750}\text{LSF}_{0.125}\text{ScSZ}_{0.125}$ ve yakın kompozisyonlar olarak tespit edilmiştir. Bu kompozisyonda elde edilen $0.33\ \text{ohm.cm}^2$ değeri, katodun $800\ ^{\circ}\text{C}$ ye yakın sıcaklıklarda kullanılabileceğini göstermektedir.

Çalışma sıcaklığını daha düşük sıcaklıklara düşürmek için LSM'nin yerine hem iyonik hem elektronik iletkenlik özelliği bulunan ruddlesden-popper tipi bir oksit ile değiştirilmesinin uygun olacağı düşünülmüştür. Çalışma sıcaklığında böyle bir düşüşü sağlama potansiyeli olan $\text{LaSr}_3\text{Fe}_3\text{O}_{10-\delta}$ (rp-LSF) katot malzemesinin LSM yerine kullanılması önerilmiştir.

Anahtar Kelimeler: SOFC katodu, Kombinatorial yaklaşım, Sıçratma-çöktürme, Elektrokimyasal empedans spektroskopisi, Simetrik hücre



Dedicated to my family

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CHAPTER 1

INTRODUCTION

Globally, the need for energy is continually growing as a result of population increase, industrialization, and technological advancements. Today, fossil fuels provide for the vast majority of the world's energy requirements. Environmental issues such as global warming, climate change, and the greenhouse effect are caused by the release of gases into the environment such as carbon dioxide, carbon monoxide, nitrogen oxides, and sulfur dioxide as a result of the usage of fossil fuels. The most significant consequence is global warming. Natural disasters induced by global warming are mostly caused by the usage of fossil fuels. In addition to rising energy consumption, fossil energy reserves are depleting at an alarming rate. Because it is expected that these fossil fuels will be depleted soon, the hunt for alternative energy sources has gained prominence in scientific circles.

Fuel cell is an energy conversion device that directly transforms the chemical energy of a fuel to electrical energy and heat without the requirement for direct combustion as an intermediary step. It achieves significantly better conversion efficiency than traditional thermomechanical processes. The operational principles of fuel cells, like batteries, are an electrochemical combination of reactants to generate electricity. A variety of gaseous fuels (e.g., hydrocarbon or hydrogen) and an oxidant gas (e.g., oxygen in the air) pass through electrodes in a fuel cell, and a half-cell reaction occurs on the anode and cathode, with charge carriers passing through an ion-conducting electrolyte. Electrons are therefore discharged into an external circuit to generate electricity. A fuel cell, unlike a battery, does not need to be recharged. A

fuel cell is environmentally benign and has a low impact on the natural environment as long as both fuel and oxidant are delivered to the electrodes.

The chemical properties of the electrolyte utilized as the cell's ionic conductor are used to classify fuel cells in general. By far the most substantial research attention has been concentrated on Proton Exchange Membrane fuel cells (PEMFC) and Solid Oxide fuel cells (SOFC).

SOFC is a fuel cell technology that operates at high temperatures. They are useful in large, high-power applications such as industrial stations and large-scale power plants. The electrolyte in a SOFC system is typically solid ceramic, and the system run at high temperatures (600-1000 °C). This high working temperature facilitates quick electro-catalytic reactions with non-precious materials and generates heat as byproduct for cogeneration. The efficiency of this type of fuel cell can be as high as 70%.

SOFCs are made entirely of solid-state materials. Furthermore, the solid-state nature of all SOFC components imposes no basic constraints on cell construction. Cells come in a variety of shapes and sizes, including flat-plate cells, planar button cells, and tubular cells.

A SOFC is made up of electrolyte sandwiched between two electrodes. Fuel gas, such as hydrogen, is injected into the anode of the fuel cell, while oxygen, which is normally delivered by air, enters the cell through the cathode. The anode evenly distributes hydrogen gas across its whole surface and carries the electrons liberated from the hydrogen molecule to be utilized as power in the external circuit. The oxygen delivered to the cathode is distributed onto its surface by the cathode. The cathode carries electrons back from the external circuit, where they can combine with oxygen ions, transported through the electrolyte and reacting with hydrogen to generate water. The electrolyte controls the operating temperature of the fuel cell and prevents the two electrodes from making electrical contact by blocking electrons. It

also permits charged ions to move from one electrode to the other in order to keep the overall charge balance.

Because of its relatively large activation energy for the oxygen reduction process, the cathode electrode is the primary contributor to the overall resistance of a SOFC, especially at intermediate and low operating temperatures. One of the most significant methods for improving cell performance in SOFCs is to reduce the polarization resistance of the cathode electrode. As a result, substantial research has been conducted on the modification and improvement of SOFC cathodes to lower oxygen reduction reaction (ORR) activation energy and resistance of the electrode. For the cathode in SOFCs, the state-of-the-art material has been LSM. At a relatively high temperature, it exhibits strong stability with zirconia-based electrolyte, relatively high electrical conductivity, and enhanced catalytic activity towards ORR. However, due to its limited electrochemical activity at temperatures ranging from 800 to 600 °C, LSM cannot be used for intermediate temperature solid oxide fuel cells (IT-SOFC). Introducing composites cathodes making use of LSM is one of the most often utilized approach in developing cathodes suitable for IT-SOFCs.

LSF is another oxide often used in composite cathodes. LSF has a perovskite type structure, and because it has good oxygen ion conductivity and does not react with a zirconia-based electrolyte, it has been employed as the cathode electrode for SOFCs by numerous studies. Furthermore, because of its oxygen nonstoichiometry at high temperatures, Ruddlesden-Popper type layered perovskite, $\text{LaSr}_3\text{Fe}_3\text{O}_{10}$, has been described as a viable cathode material for solid oxide fuel cells. $\text{LaSr}_3\text{Fe}_3\text{O}_{10}$ has been found to have nearly no overpotential at the air electrode when used as an electrocatalyst for rechargeable metal-air batteries.

In this study, it is aimed to fabricate composite cathodes in LSM/LSF/ScSZ ternary system and to obtain the best composition using combinatorial approach. For this

purpose, thick films of composite cathodes were deposited using magnetron sputtering and were characterized using symmetric cells.



CHAPTER 2

LITERATURE REVIEW

2.1 Intermediate Temperature Solid Oxide Fuel Cells

Solid oxide fuel cell (SOFC) is one of the fuel cell types that often used in large power generation systems. The working mechanism of the solid oxide fuel cell is as follows: The anode is fed with hydrogen or hydrocarbon fuel where an oxidation reaction takes place. Electrons formed as a result of the reaction are transferred to the outer circuit. The cathode is fed with oxidant, accepts electrons from the external circuit, and the reduction reaction takes place. Electric current occurs as a result of external circuit electron flow from anode to cathode.

SOFCs' are more efficient than other fuel cell systems. Efficiency of another commonly used fuel cell type, PEM, is 45-55%, while for SOFC, efficiency can be as high as 70%. Some other outstanding aspects of SOFC systems are, clean energy, silent, efficient for especially stationary power systems.

The first application in solid oxide fuel cells was initiated by the Westinghouse company[1]. At the end of the 80's, solid oxide fuel cells based on tubular geometry were implemented[2]. This application is based on zirconia (YSZ) stabilized with yttria as the electrolyte, lanthanum strontium manganate (LSM) as the cathode and nickel as the anode. In this system operating at 900-1000 °C, the connections are made entirely with lanthanum magnesium chromite. This application brought realization to solid oxide fuel cells, which was a research activity until that time, and produced electricity with 47% efficiency from natural gas with a power of 100kW. This practice was followed by new designs in the mid 90's. An important

development in this context are applications using lanthanum strontium gallium magnesium oxide (LSGM) as electrolyte.

It is stated in the literature that, there are many different applications for low temperature solid oxide fuel cells at the W and MW levels[3]. Almost all large capacity applications are based on high temperature solid oxide fuel cells in the current situation, and there have been significant developments in intermediate and low temperature solid oxide fuel cells especially in the recent period[3]. In this context, an important development is the introduction of a low temperature SOFC with bismuth oxide/ceria two-layer electrolyte[4]. Another application is SOFC developed by a Danish Company with 1-1.5 kW operating at 750 °C[5]. In addition, SOFC systems of 1kW have been put into use recently. The most remarkable system produced in the kW family is the unit produced by Ceres Power (England), and the operating temperature in this application is 500-610 °C[6].

As it is clear from the short summary above, lowering the operating temperature in the SOFCs constitutes the main theme of the studies that have been carried out since 80's. Indeed, the high operating temperature is troublesome due to the longer time required to commissioning the unit and the rapid wear of the components. The biggest challenge caused by the high temperature at the beginning was for the sealants. And also, at high temperatures such as 1000 °C, the electrical connections were necessarily made using ceramic elements. Reducing the operating temperature of SOFC so that the use of metals as contact materials was an important step in the development of IT- SOFCs.

In the classical approach, since both anode and cathode are porous, the decisive factor in temperature reduction is the electrolyte. The ionic conductivity of the electrolyte has been the main determining factor in the SOFC structure, Figure 2.1. In this respect, there are two methods that can be used to reduce the temperature. One of them is to use an oxide with higher ionic conductivity by changing the

electrolyte, and the other is to decrease the electrolyte resistance by decreasing the thickness. In this respect, as can be seen in Figure 2.1, using ScSZ, LSGM or GDC instead of YSZ provides a considerable advantage. The figure shows that the ionic conductivities of bismuth oxide based ESB and DWSB are remarkably superior.

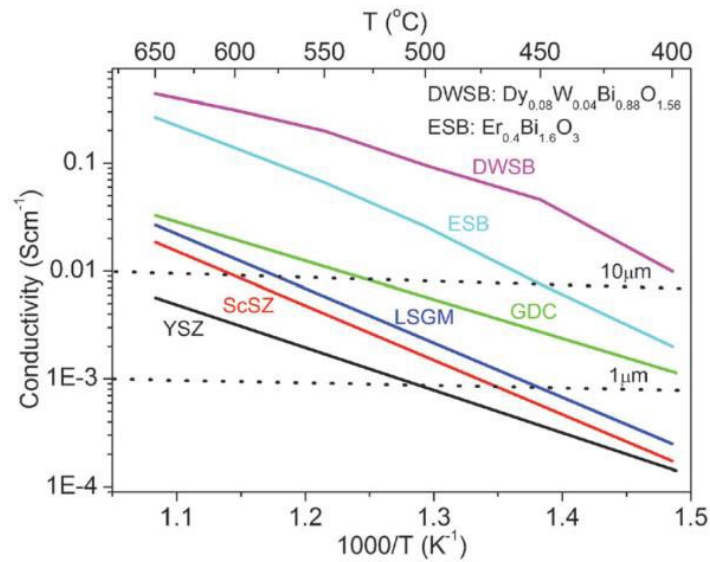


Figure 2.1. Change of ionic conductivity with temperature in different electrolyte material[7].

Fig. 2.1 also provides information about the temperature and electrolyte thickness that must be achieved in order to obtain reasonable resistance values. Of course, the thickness of the electrolyte that can be obtained depends on the method used during production. While thin film techniques allow very low thicknesses, screen printing method, which is more common in mass production, the thinnest film can be 10 micron thick. For 10 micron electrolyte thickness, the operating temperature is 750-800 °C in the case of YSZ, while this value decreases to 600 °C in ScSZ. Fig. 2.1 further shows that temperatures below 400 °C are possible when DWSB is used as electrolyte.

Of course, the choice of electrolyte is not independent from the choice of anode and cathode. It is of great importance that these components be stable at operating temperature and do not react with each other. An additional and just as important aspect is that the components have similar expansion coefficients. Otherwise, the components will crack due to different expansion and after a few cycles, SOFC will not be able to maintain its integrity. Indeed, the harmony in thermal expansion coefficients, possible inter-component reactions and material stability under reducing/oxidizing conditions are important factors that need to be considered.

2.1.1 Cathode

It is known that perovskite-based materials are used intensively as cathode electrodes in the production of solid oxide fuel cells due to their ease of production, microstructure properties, catalytic activity, and stability. There are a great number of perovskite type materials in the literature, and it is known that they show high ionic conductivity and high electronic conductivity, as well as other properties such as high catalytic activity, superconductivity, ferroelectricity and magnetism[8].

Perovskite type oxides are formulated as ABO_3 . In this formula, while A is one of the rare earth elements such as La, Nd, Pr, B is corresponding to one of the transition metals such as Mn, Co, Fe. It has become clear from recent studies that, in order to improve the properties of perovskite type materials, the base oxide remains the same and the B cations are doped as positively charged ions of two different types, and the cathode electrodes produced in this way shows improved power density.

There are manganese, cobalt, and iron based perovskite type materials which are used as cathode materials for SOFCs. $La_xSr_{1-x}MnO_3$ (LSM) is a common example of

this. However pure LSM does not have sufficient catalytic activity at operating temperatures lower than 800 °C, so it is unlikely to be used in IT-SOFCs[9,10].

In LSF and LSC A cation is lanthanum and strontium, and these oxides have gained great importance as cathode materials recently. Undoubtedly, LSC is far superior to LSF and LSM in terms of electronic and ionic conductivity[7]. However, the choice of this material as cathode is not possible for zirconia-based electrolyte systems because it reacts with zirconia. Another problematic aspect of the LSC when used with zirconia based electrolyte is, coefficient of thermal expansion (CTE) of LSC is much higher than CTE of zirconia based oxides[11].

LSF brings many advantages with its high catalytic activity and long-term durability[12]. For example, no deterioration or cracking in the cathode was observed in experiments exceeding 500 hours of operation [13]. In addition, it is confirmed that LSF is compatible with zirconia based electrolytes, unlike LSC which forms $\text{La}_2\text{Zr}_2\text{O}_7$ or a similar insulating phase at the interface[12]. It is concluded that LSF is thermodynamically more stable than cobalt and nickel oxides. In addition, its thermal expansion coefficient is compatible with stabilized zirconia, and can therefore be used successfully as composite cathode [14–17].

It is previously reported that when LaFeO_3 was doped with Sr-, Ba- and Ca, the best ionic conductivity was obtained with LSF, i.e. doping with Sr [18,19]. This result is probably related to the ionic size of Sr^{+2} , which is suitable for ionic movement in the LaFeO_3 lattice. The conductivity and CTE in LSF depend on the amount of Sr doping. With the decrease of Sr content from 0.4 to 0.2, the conductivity increases from 129 Scm^{-1} to a value of 155 Scm^{-1} [13]. The coefficient of thermal expansion has a value of $12.2 \times 10^{-6} \text{ K}^{-1}$, at 0.20 Sr [20]. Unless there is a compelling situation, it seems realistic to keep the Sr content at 0.20 in LSF when used with zirconia-based electrolyte. The ionic conductivity of LSF with 0.2 Sr has a conductivity of

1.2×10^{-5} S/cm at 973K[21]. Patrakeev et al[22]. reports a value of 3.4×10^{-2} S/cm for the same composition at 1023K.

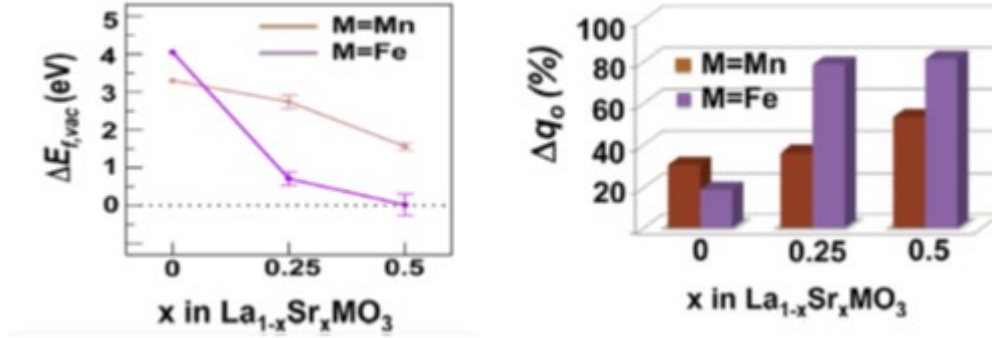


Figure 2.2. a) Energy required for oxygen gap formation in $\text{La}_{1-x}\text{Sr}_x\text{MO}_3$ ($M = \text{Mn}, \text{Fe}$). b) Percentage of electrons that become mobile after oxygen gap formation in LSM[23].

High electronic conductivity of LaMnO_3 is a result of manganese being as Mn^{3+} and Mn^{4+} in the structure. Its electronic conductivity is improved further by adding alkaline earth cations to the structure. The most common one is strontium to form LSM, which show high electronic conductivity[24].

As it is known, LSM is the classical cathode material for SOFCs. The oxygen gap formation is more difficult in LSM, Figure 2.3[23]. This situation is caused by the local reduction of Mn and difficult triggering of the oxygen gap formation. Therefore, LSM's ionic conductivity is lower than LSF. On the other hand, LSM has similar electronic conductivity values with LSF, Figure 2.4. The electronic conductivity to be obtained in the LSM phase depends on the Sr doping. Figure 2.5 shows the temperature variation of electronic conductivity observed at different Sr

contents. For Sr doping from $x=0$ to $x=0.7$, the highest conductivity was observed at $x=0.5$.

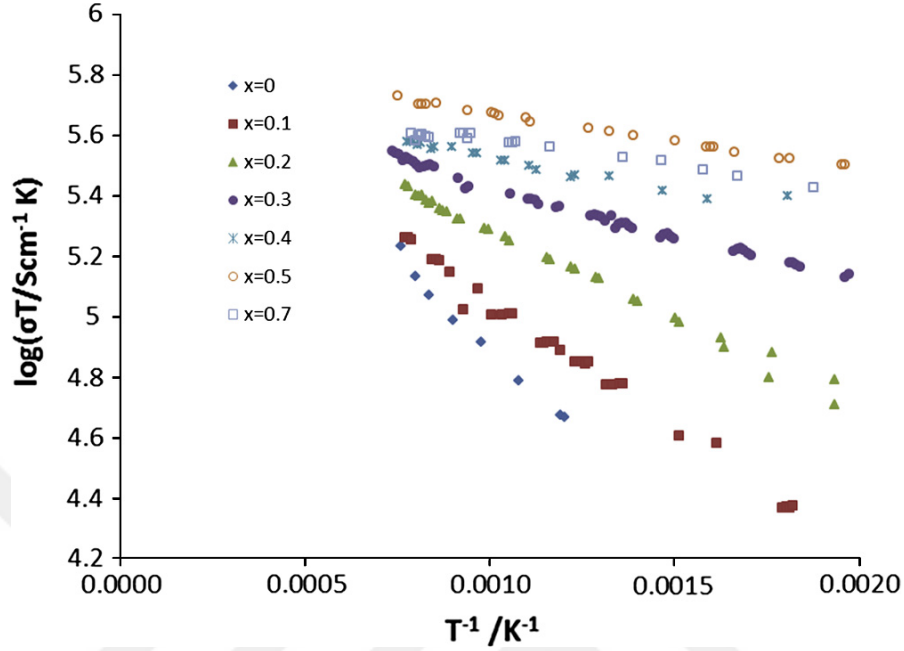


Figure 2.3. Change in electrical conductivity of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ at different temperature at pure oxygen[25].

LaMnO_3 is a p-type intrinsic conductor, and its electronic conductivity can be improved by either doping with Sr or Ca at La sites. Divalent alkaline earth dopants are favored because the resulting perovskites are very stable and have strong p-type conductivity in the oxidative environment on the cathode side of the SOFC. $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSM) records of $x=0.1, 0.2$ exhibit high electronic conductivity while maintaining reasonable mechanical and chemical stability at SOFC operating temperatures[26,27]. Electronic conductivity of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ was measured by Mizusaki et al[25] as a function of temperature up to 1000°C and oxygen partial pressure. They found out that electronic conductivity of LSM is linearly increasing

with x, up to the maximum conductivity at $x=0.5$. Zhang et al.[28] has also reported the same result of x dependency of electronic conductivity of LSM at 1000 °C. An electronic conductivity plot of LSM in pure oxygen is shown in Figure 2.6.

Unlike most other perovskites, lanthanum manganese can be both oxygen deficient as well as oxygen excess[29]. At lower oxygen partial pressure, doped lanthanum manganite becomes oxygen deficient, and the oxygen vacancy defects are compensated by the reduction of Mn^{3+} to Mn^{2+} . In fuel cell operating conditions LSM is oxygen excess. Many defect models have been proposed to describe the defect structure of LSM. Either formation of cation vacancies or oxygen interstitials compensates the oxidation of Mn^{3+} in LSM. However, perovskites have close packed structures, therefore it is unlikely for oxygen ions to be present in the interstitial sites. Therefore, it is likely that cation vacancies provide excess oxygen [30–32].

Production technique also played a role in the electronic conductivity of LSM cathodes. Solid state sintering method provides 40 to 485 S/cm conductivity at 1000 °C, while plasma spraying method exhibits 50-201 S/cm. [26].

There is a general agreement in the literature that the addition of MIEC perovskites, i.e. mixed ionic and electronic conductor either Sr-doped $SmCoO_3$ [33], or Sr-doped $LaCoO_3$ [34] or Sr-doped $LaFe_{0.8}Co_{0.2}O_3$ [35] can decrease ASR of cathode. The problem with these oxides is that they are reacting with zirconia based electrolytes[?]. But adding relatively small amounts seem to solve the problem because they deposit on triple phase boundaries (TPB) in the LSM-YSZ composite cathode. Also, this phenomena describes the improved performance of LSM-YSZ electrodes when mixed with small amounts of Gd-doped ceria[36] or BiO_x [37].

Tao et al[38,39]. shows that $(La_xSr_{1-x})_{1-y}Cr_{0.5}Mn_{0.5}O_3$ with $y \leq 0.1$ is a promising A-site deficient perovskite cathode material with sufficient stability at high temperatures in both reducing and oxidizing environments. This material suffers from low oxide ion conductivity like the titanates.

Lately, there are studies focusing on $\text{Sr}_{1-y}\text{La}_y\text{TiO}_3$ due to its high electronic conductivity in the range of $100\text{--}500\text{ S.cm}^{-1}$ at $700\text{ to }1000\text{ }^\circ\text{C}$ [40–42]. Low oxide ionic conductivity of this material necessitates doping. Ga, Y, Mg, Ce and Sc have doped onto the B-site and was found to increase the ionic conductivity. However, such doping onto the B-site reduces the electronic conductivity of the given material[42–44]. Also, there are studies focusing on the A-site deficient versions of this material which was found to show increased ionic conductivity[45].

$(\text{La}_{0.6}\text{Sr}_{0.4})_{0.9}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ (LS09CF) and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ (BSCF) were synthesized by Baumann et al. by pechini method. They used pulsed laser deposition to prepare thin film cathodes. They found out that substitution of La by Sm improves surface exchange kinetics. Little or no effect was observed while changing Co/Fe ratio between 0 and 1 at $750\text{ }^\circ\text{C}$ [46].

There are also cathodes which has limited ionic conductivity such as pyrochlores. Of these Pyrochlores such as R_2MnRuO_7 ($\text{R} = \text{Tb, Dy, Ho, Tm, Y, Lu and Er}$) were also studied since they have good catalytic activity toward oxygen reduction reaction[47]. These materials are relevant as anodes also. For example, $\text{Gd}_2\text{Ti}_{1.4}\text{Mo}_{0.6}\text{O}_7$ is a sulfur tolerant anode that can operate with $\text{H}_2\text{--}10\%\text{ H}_2\text{O}$ without degradation[48]. The problem with these materials is that they contain rare earth elements with high costs.

Another example is tetragonal $\text{NdBa}_{1-x}\text{Co}_2\text{O}_5$ ($x=0\text{--}0.06$) were synthesized as a cathodic material for SOFC. O_2 vacancy in NBCO seems to increase with increasing Ba concentration, while the CTE is decreasing with Ba concentration. Among these, $\text{NB}_{0.96}\text{CO}$ has appropriate grain size and enough porosity which makes it a cathodic material for IT-SOFCs[49].

2.1.2 Anode

Considering the working principle of the anode in SOFC, the electrode must have electronic conductivity in addition to ionic conductivity. The most important point that causes restrictions in the selection of fuel cell components is the compatibility of the selected materials to the entire system. The stability of the selected material should be quite high depending on both temperature and time.

It is known that high purity Ni, Ag, Pt, Fe, Co, or material consisting of solid electrolyte and metal mixture (cermet) are used as anodes. Cermet systems are electrodes produced by adding electrolyte in different concentrations into powder metal.

A typical anode for SOFC must have electrical conductivity on the order of 10^2 S/cm at minimum at the operating temperature of the SOFC[50–52]. The Ni has electrical conductivity of 2×10^5 S/cm, while the electrical conductivity of porous Ni-YSZ changes from 10^2 to 10^4 S/cm at 1000 °C. The YSZ phase in the Ni-YSZ cermet provides the ionic path for conducting oxygen ions and also lowers the CTE of the anode to match it with the other components of the fuel cell. It also prevents the coarsening of nickel.

The problems with the cermet materials as anode in SOFC are as follows; the performance of the cell changes with a fuel type and Ni/YSZ is not stable when hydrocarbons are used as a fuel. This is due to the re-oxidation of Ni to NiO resulting in the lattice expansion [53] which causes mechanical stress on the electrolyte-anode interface[50,54].

The problem of re-oxidation of Ni to NiO can be solved by controlling the microstructure[51,52]. Itoh et al.[55] used a mixture of two types of YSZ powder as coarse and fine. They concluded that electrochemical properties and stability of such prepared anode is higher than the conventionally prepared Ni-YSZ anode. They also

concluded that the increase in performance and stability of Ni-YSZ anode is due to the microstructural improvements. Due to the existing problems in the conventional mixed oxide route[56], many groups have changed the synthesis method to a different solution chemistry routes like gel precipitation[57], pyrolysis[58], co-precipitation[59], electroless coating[60] and combustion synthesis[61] etc.

Besides these, Ni-YSZ cermet anode suffers from carbon deposition[62] and sulfur poisoning[63] as well as the coarsening of Ni with prolonged use at elevated temperatures[64]. Sulfur poisoning and carbon deposition can be reduced by doping Ni with other transition metals [63,64], but this results in some reduction of anode efficiency[65,66].

Cu based cermets was found to be a good alternative to Ni since Cu does not suffer from coking while reforming hydrocarbon fuels like syngas and CH₄[67]. The problem with Cu is that it has low melting point (1083 °C). This limits the synthesis of Cu based cermets since they cannot be sintered at high temperatures. This constraint made it necessary to develop other synthesis methods that do not involve high temperatures. Lu et. al.[68] produced anodes based on Au-SDC and Cu-SDC with wet impregnation method. The results show that there was no significant performance difference between Au-SDC and Cu-SDC. They found that Cu and Au do not play a role in transporting ions. This makes them stable in the hydrocarbon fuel environment because they are inactive in breaking C-C and C-H bonds. Tsipis et al.[69] compared Cu-CGO and Ni-CGO as anodes. They found that Ni-CGO has higher performance since Cu had a lower catalytic activity.

Costa-Nunes et al.[67] studied the performance of two solid oxide fuel cells one with Cu-CeO₂-YSZ anode and the other with Ni-YSZ anode. The results showed both cells have similar performances. They also studied the effect of Co addition in Cu-CeO₂-YSZ which significantly increased the catalytic activity when CO is used as

fuel. Additional studies on other Cu based anodes may be found in references [67,68,70–72].

Carbon affinity is an important factor in solid oxide fuel cell anodes since the carbon deposition onto anode can dramatically reduce the performance of SOFCs. Carbon affinity on the Nickel is reduced in Ni-ScSZ anodes by the strong interaction of Ni with ScSZ. This is not the case with Ni-YSZ anodes [73,74]. A recent study by Sumi et al. [75] showed that the Ni-ScSZ gives lower overpotentials than that of the Ni-YSZ which was attributed to the formation of amorphous graphite formed on Ni-YSZ. In Ni-ScSZ the graphite whiskers are formed rather than amorphous carbon. In addition, a recent study[76] showed that the Ni-ScSZ has improved tolerance against Sulphur poisoning.

There are also new potential anode materials, such as ceramic composites[77], perovskite [42,78–80], fluorites[81–84] and titanates [85–87].

2.1.3 Electrolyte

The heart of a SOFC unit is the electrolyte, which carries oxide ions from the cathode to the anode, where they react with hydrocarbons to generate H_2O and CO_2 , completing the electrochemical cycle. The oxygen vacancy mechanism, which is activated thermally, is responsible for the conduction of oxide ions. To achieve high ionic conductivity in the electrolyte, its crystal structure must have enough interionic free space made possible by high amount of defect structure and a low migration enthalpy. In such metal oxides, the oxide ion is often bigger in size than the metal cation. As a result, it can be expected that smaller-sized cations would have increased mobility in the lattice. But metal cations have a high valence, preventing this

expected mobility. Some notable examples are, ZrO_2 , Bi_2O_3 , CeO_2 based oxides with the fluorite structure, brownmillerite like phases and LaGaO_3 based perovskites[88].

By far the most common material is Y_2O_3 doped ZrO_2 , also known as yttria-stabilized zirconia. Undoped zirconia does not have enough ionic conductivity by itself. Doping with certain oxides (e.g., CaO , Sc_2O_3 , Y_2O_3 , MgO) stabilizes the cubic fluorite structure at high temperatures and greatly increases the amount of oxygen vacancies by replacing the host Zr^{+4} cations by divalent or trivalent yttrium cations. Although yttria is not the most effective dopant in this aspect, it is commonly used due to its ease of availability and low cost. At 8% molar doping, the ionic conductivity value is optimal. In a wide range of temperatures and oxygen partial pressures, YSZ possesses outstanding mechanical strength, strong shock resistance, and great chemical stability.

Polycrystalline or thin films YSZ at 1000°C , can achieve a practical ionic conductivity of 0.1 S.cm^{-1} , but working at such a high temperature is quite problematic for anode as well as for the cathode[89–91]. As a result, attempts were made to improve conductivity at reduced temperature via grain boundary engineering.

In comparison to zirconia, ceria is another alternative that also has fluorite structure. Ceria was doped with suitable dopants to yield adequate ionic conductivity at low working temperatures with low polarization resistance[92]. Ceria however is associated with a severe problem of electrical conduction at low oxygen partial pressures[93]. Gadolinium doped ceria(CGO), namely $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_2$ and $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2$ suffer from this problem. Dopants such as Sm, Yb, La or Nd were also examined and found to be better as they showed lower conductivity than that of CGO[94].

Mg and Sr doped LaGaO_3 perovskite i.e., LSGM, is another notable electrolyte which has high ionic conductivity at low temperatures. The ionic conductivity of

LSGM is substantially higher than that of YSZ[92] and what is more they have higher stability at low oxygen partial pressures better than CGO. Different doping combinations of La and Sr were examined and the optimum ionic conductivity was obtained $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$ [95].

Fergus et al[92] reviewed zirconia, ceria, and lanthanum gallate based electrolyte materials that can be used at low operating temperatures. After stabilizing the fluorite cubic structure of ceria with suitable dopants YSZ is widely employed as an electrolyte in fuel cells. Sc^{+3} has an ionic radius very similar to that of Zr^{+4} . Therefore, Scandia stabilized zirconia (ScSZ) was found to be a good alternative as electrolyte material. In fact, ScSZ has a more favorable ionic conductivity than YSZ at temperatures above 500 °C. Furthermore, at greater scandia concentrations (>8%), the cubic structure is changed into the rhombohedral structure, resulting in reduction in its ionic conductivity.

Ionic conductivity initially rises with increasing concentration of acceptor dopant cations in ZrO_2 -based systems. However, conductivity peaks as the dopant concentration approaches the bare minimum necessary to properly stabilize the cubic fluorite structure at ambient temperature[96,97]. It is commonly acknowledged that the ionic conductivity of YSZ is maximum when the Y_2O_3 ratio is around 8%. In fact, 8 mol percent Y_2O_3 stabilized ZrO_2 is a well-established electrolyte for high-temperature SOFCs. Further addition of dopant oxide, i.e., above 8 mol percent, causes defect interactions to dominate, obstructing the passage of mobile oxygen vacancy and leading in lower ionic conductivity[92,99]. However, this low stability limit and resulting ionic conductivity are affected by thermomechanical history and microstructural characteristics (including cleanliness of grain boundaries, segregation of dopants, and presence of impurities)[98]. Thus, maxima in conductivity in YSZ and ScSZ varies from dopant concentration from 8 to 11 mol. Percent depending on its processing and precise chemistry.

CHAPTER 3

EXPERIMENTAL

3.1 Synthesis of Active Materials

For the synthesis of active powders, Pechini method was followed. A typical flow sheet for the pechini process is given in Fig.3.1. Precursors used for the synthesis of active powders were nitrates of La, Sr, Fe, Mn, Sc and Zr elements. These are namely $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar, 99.99%), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Alfa Aesar, 99.99%), $\text{Sr}(\text{NO}_3)_2$ (Alfa Aesar, 99%), $\text{Mn}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (98%) for the synthesis of LSM and LSF and $\text{ZrO}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99%), $\text{Sc}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ (Nanografi, 99.9%) for the ScSZ electrolyte.

Nitrates were mixed with deionized water in a large beaker at the intended stoichiometry with the aid of a magnetic stirrer. After the cations were dissolved in water, three times the total number of moles of cations, citric acid was added to the mixture and the solution was mixed for 20 minutes at 100 °C. Subsequently, four times the molar number of citric acid, ethylene glycol was added to the solution and the temperature was gradually increased to 150 °C and then to 200 °C. Mixing was continued at this temperature until foam formation occurred. The gel, which dries after the foam formation, is kept in a 250 °C oven for 12 hours to be purified from organic compounds. As the last process, the dry gel was calcined at the appropriate temperature.

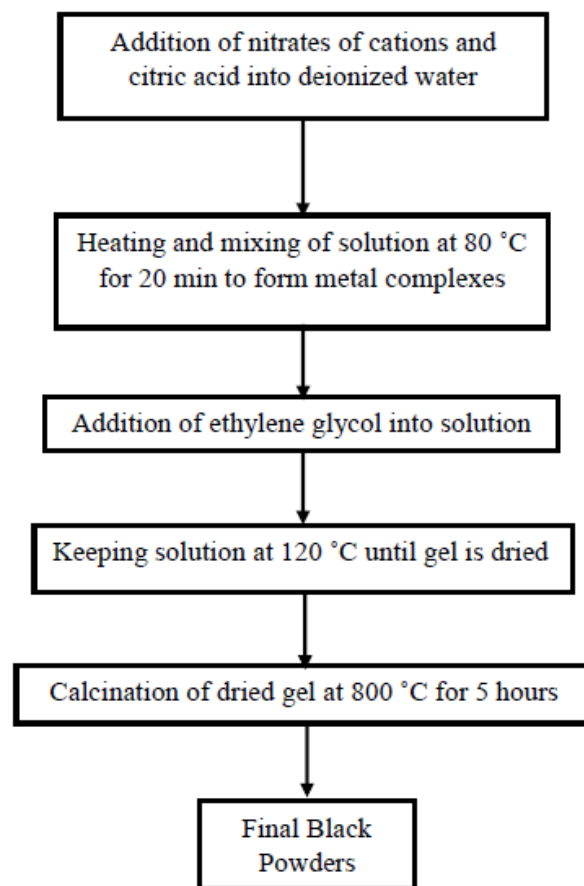


Figure 3.1. Typical flow chart of the Pechini process.

3.2 Fabrication of Sputter Targets

The production of target discs was carried out by pressing followed by sintering. Deformable Teflon dies were used for this purpose, Fig. 3.2. Initially, the powders were compacted to high density using a small die and subsequently sintered at different temperatures.



Figure 3.2. Deformable Teflon dies used in pressing.

Pressing was applied at different pressure values for each material, and the sample that has appropriate density was selected and sintered at different temperatures. The aim here is to determine the suitable sintering temperatures for each material.

LSM was compacted at 6 different pressures, from 80MPa to 160Mpa with 20MPa increments and sintered at three different temperatures 1300, 1400 and 1500 °C for 5 hours. Sintering temperatures were the same for all sputter targets. In the LSF case, 5 different pressures were used. These were from 80 to 160Mpa with 20Mpa increments. For ScSZ, from 100 to 160MPa with 20MPa increments were used.

3.3 Combinatorial Deposition of Cathodes

Thin film cathodes were sputter deposited on electrolytes. For this purpose, a prismatic chamber with dimensions of 500x500x500 mm was used which incorporates one central and three peripheral sputter guns placed in a diameter of 350 mm, Fig. 3.3. In this system, peripheral sputter guns were at the corner of equilateral triangle with center to center distance of 300 mm. The peripheral guns incorporate 2 inch diameter targets. In this study, the substrates are ¾ inch diameter

electrolyte discs and there are total of 21 discs on the substrate holder on triangular distribution, Fig. 3.4. What makes this system special is the ability to produce 21 different composition at the same time.

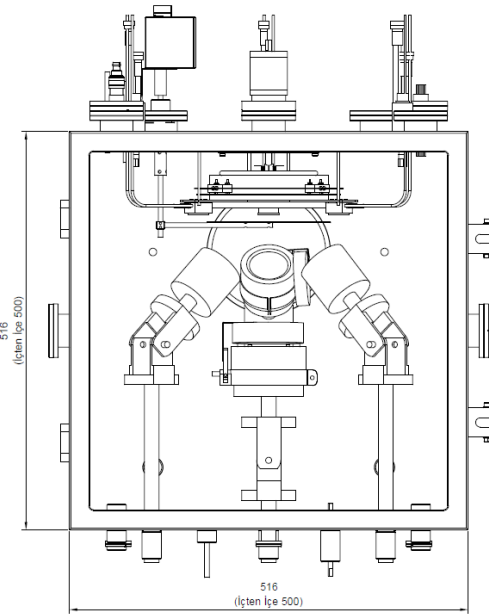


Figure 3.3. 3D view of components in prismatic sputter. Thickness gauges are fixed on a circle in the substrate plane just above the generators.

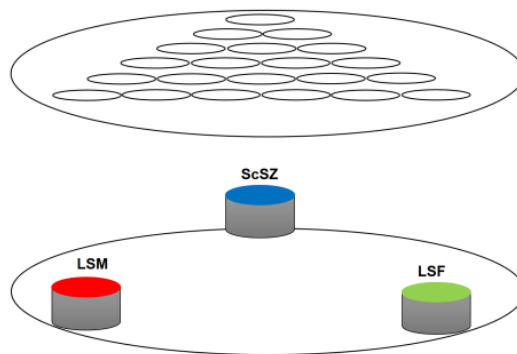


Figure 3.4. Drawing of samples in the substrate holder with guns.

In this study, the central gun was adjusted first and fixed at the distance shown in Figure 3.5(a). In this position, the distance of the central gun to the substrate plane is 92.5mm. Subsequently, the surrounding guns were adjusted. Here, the adjustment was in the form of alignment of the bottom of the gun and the central gun as shown in Figure 3.5(b). This positioning fixes the angular position of the surrounding guns.

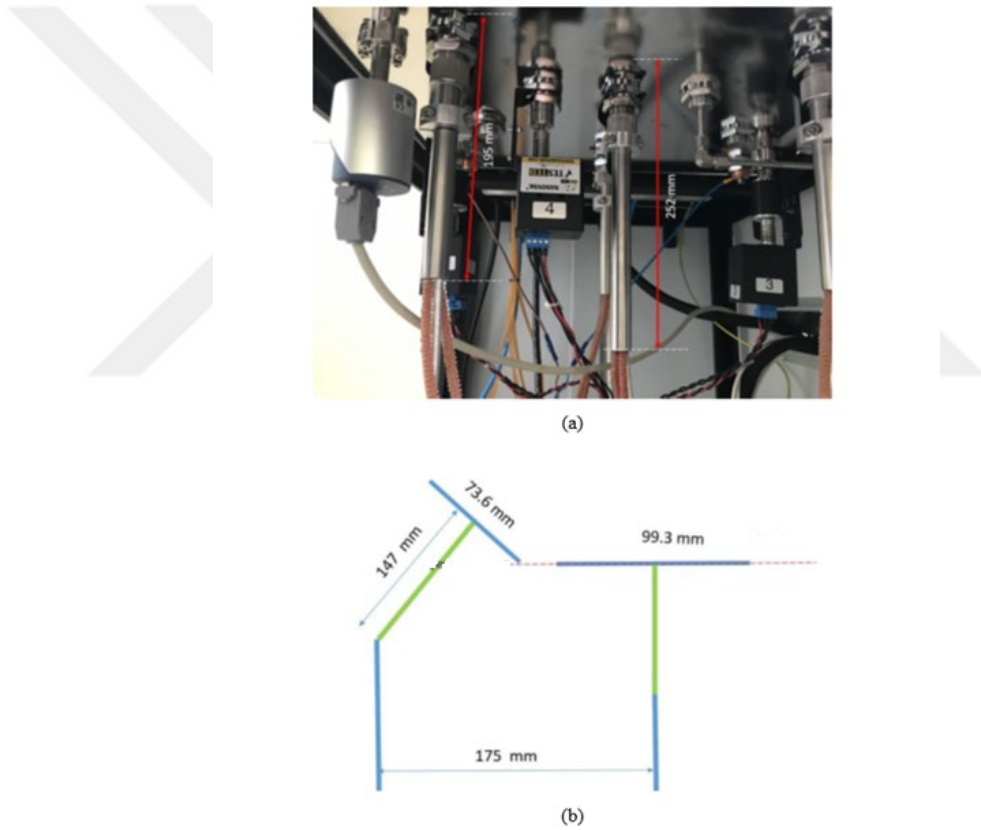


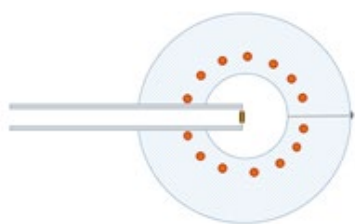
Figure 3.5. a) Positions of the guns outside the chamber. The central gun is set at $Z_{\text{stem-out}}=252\text{mm}$, peripheral gun $Z_{\text{stem-out}}=195\text{mm}$. b) Setting position of the peripheral guns with respect to the central gun.

3.4 Material Characterization

All of the fabricated materials in this thesis were characterized by X-ray diffractometer (XRD). The D/MAX-2200 Rigaku X-ray Diffractometer with Cu-K α radiation with 2°/min scan rate was used. Rietveld analysis were applied to refine the X-ray patterns using Maud software. Fabricated samples were characterized using SEM. For this purpose, FEI Nova NanoSEM 430 were used. Where necessary, the use was also made of EDX attachment in SEM for elemental analysis of the synthesized powders.

3.5 Electrochemical Characterization via Symmetric Cell

Electrochemical characterization of cathodes produced with combinatorial approach was performed by symmetrical cell measurements. The symmetrical cell prepared for electrochemical characterization was placed at the end of an alumina tube with an inner diameter of 14mm and an outer diameter of 24mm, and sealing was provided with AREMCO ceramic adhesive. The setup created is shown in Figure 3.6 as placed in a split oven. The produced symmetrical cells were subjected to EIS measurements at different temperatures.



(a)



(b)

Figure 3.6. Setup used for EIS measurements a) Schematic representation (b) photograph of the setup.

EIS measurements made with Gamry ref. 3000 Potentiostat/Galvanostat. Here, 10mV is used as perturbation voltage and 0.1Hz-0.3Mhz as frequency range. The measurements were carried out between 600-800 °C with 50 °C intervals at atmospheric oxygen pressure.



CHAPTER 4

RESULTS and DISCUSSION

4.1 Synthesis of LSM, LSF, ScSZ Powders

Synthesis of LSF Powder: LSF powders was synthesized using the Pechini route. Related route is given in the experimental section. The amount of precursor nitrates used for LSF113 synthesis are given in Table 4.1 on the basis of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 5gr. As can be seen, the purpose here is to provide $(\text{La}_{0.8}\text{Sr}_{0.2})\text{FeO}_{3-\delta}$ stoichiometry. The dry gel obtained at the end of the Pechini process was calcined at different temperatures.

Table 4.1 Calculation of precursor amounts used for $(\text{La}_{0.8}\text{Sr}_{0.2})\text{FeO}_{3-\delta}$ (LSF) synthesis.

$(\text{La}_{0.8}\text{Sr}_{0.2})\text{FeO}_{3-\delta}$ ($M_A=232.5$ gr)	M_A (gr/mole)	Amount (gr)	Mole
$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	433.10	5.00	0.0115
$\text{Sr}(\text{NO}_3)_2$	211.63	7.33	0.0346
$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	404.00	13.99	0.0346
Citric acid monohydrate	192.12	50.95	0.2424
Ethylene Glycol	62.07	60.00	0.9699

The calcined LSF powder was subjected to detailed EDS analysis to the elemental distribution. The average of EDS analysis results of LSF, calcined at 800°C -5h, performed at 5 different points are given in Table 4.2. As can be seen, the values determined here, and the expected values are close to each other.

Table 4.2 Average EDS results for LSF powder calcined at 800 °C for 5 hours.

LSF	Theoretical (at %)	Measured(at %)
La	40	41.0
Sr	10	10.4
Fe	50	48.6

XRD patterns of LSF calcined at 800 and 900°C are given in Figure 4.1. As can be seen, both temperatures are sufficient for the crystallization of LSF. Rietveld refinement of XRD patterns of the LSF powder calcined at 800 °C for 5 hours is given in Figure 4.2. Lattice constants for LSF determined as a result of the Rietveld refinement are given in Table 4.3. 800 °C 5h was therefore chosen for as calcination temperature for LSF .

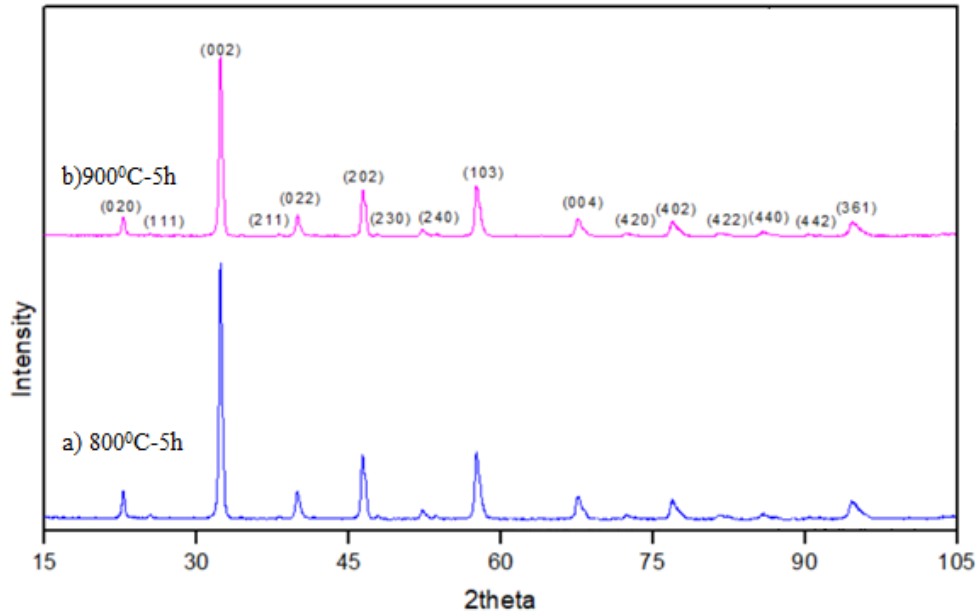


Figure 4.1. XRD patterns of LSF calcined at a)800°C, b)900°C for 5 hours.

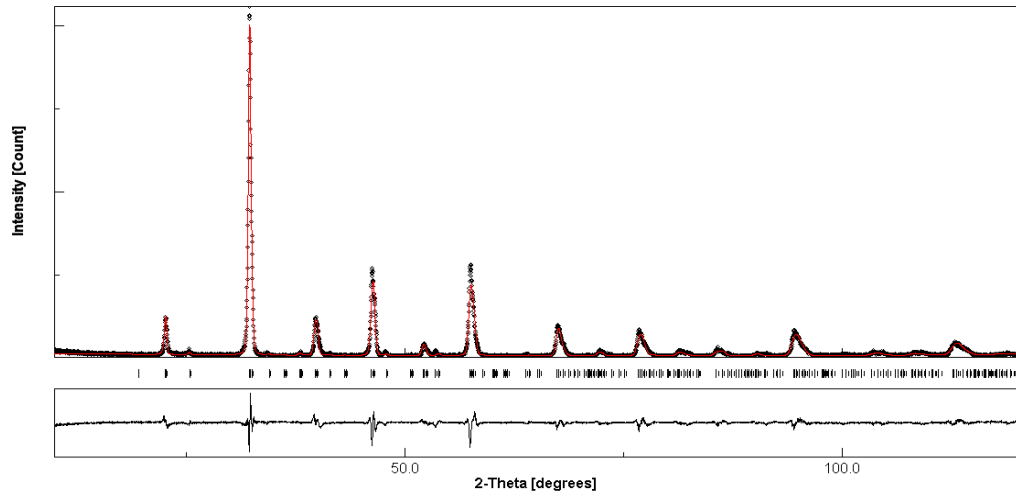


Figure 4.2. Rietveld analysis of the XRD pattern of LSF calcined at 800 °C.

Table 4.3 Lattice constants of LSF, LSM and ScSZ powders produced with pechini after calcination at 800 °C, 800 °C and 900 °C for 5 hours, respectively.

Lattice Constants (Å)			
	<u>a</u>	<u>b</u>	<u>c</u>
LSM	5.445	5.445	7.759
LSF	5.536	7.836	5.550
ScSZ	5.098	5.098	5.098

Synthesis of LSM Powder: The amount of precursor nitrates used for LSM113 synthesis are given in Table 4.4 on the basis of $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 5gr. As can be seen, the purpose here is to provide $(\text{La}_{0.5}\text{Sr}_{0.5})\text{MnO}_{3-\delta}$ stoichiometry.

Table 4.4 Calculation of precursor amounts used for $(\text{La}_{0.5}\text{Sr}_{0.5})\text{MnO}_{3-\delta}$ (LSM) synthesis.

$(\text{La}_{0.5}\text{Sr}_{0.5})\text{MnO}_{3-\delta}$ ($M_A=216.2$ gr)	M_A (gr/mole)	Amount (gr)	Mole
$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	433.10	3.77	0.0087
$\text{Sr}(\text{NO}_3)_2$	211.63	1.84	0.0087
$\text{Mn}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	286.95	5.00	0.0174
Citric acid monohydrate	192.12	20.08	0.1045
Ethylene Glycol	62.07	25.95	0.4181

The calcined LSM powder was subjected to detailed EDS analysis to the elemental distribution. The average of EDS analysis results of LSM, calcined at 800°C -5h, performed at 5 different points are given in Table 4.5. As can be seen, the values determined here, and the expected values are close to each other.

Table 4.5 Average EDS results for LSM powder calcined at 800°C for 5 hours.

LSM	Theoretical (at %)	Measured(at %)
La	25	26.3
Sr	25	26.3
Mn	50	46.9

XRD patterns of LSM calcined at 700 and 800°C are given in Figure 4.3. As can be seen, both temperatures are sufficient for the crystallization of LSM. Rietveld refinement of XRD patterns of the LSM powder calcined at 800°C for 5 hours is given in Figure 4.4. Lattice constants for LSM determined as a result of the Rietveld

refinement are included in Table 4.3. 800 °C 5h was therefore chosen for as calcination temperature for LSF.

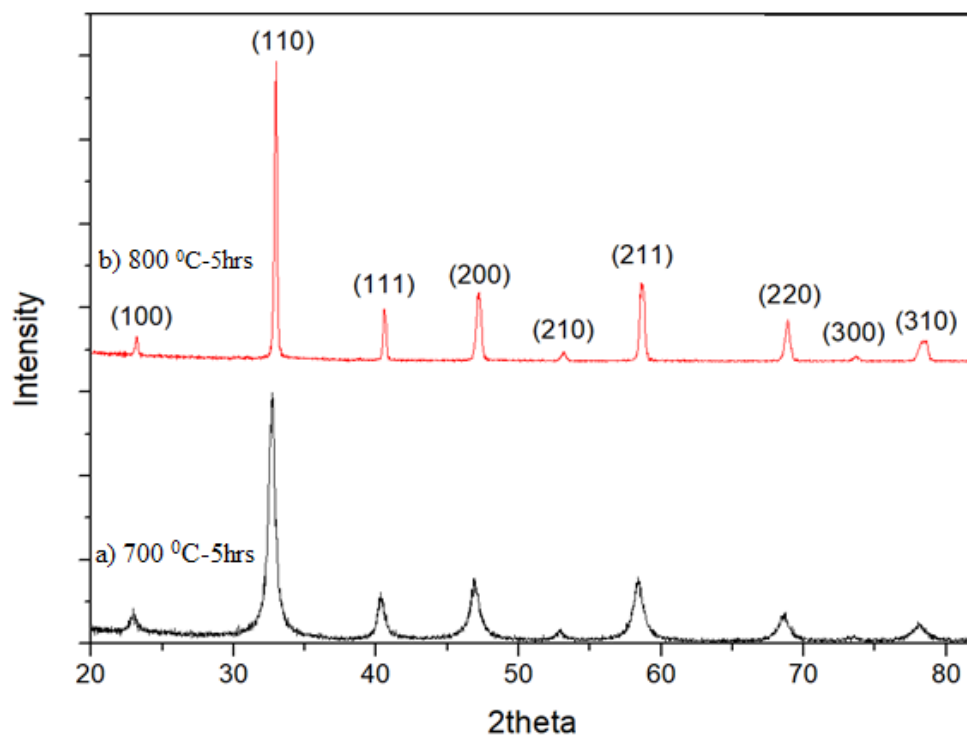


Figure 4.3. XRD patterns of LSM calcined at a) 700 °C-5h, b)800 °C-5h.

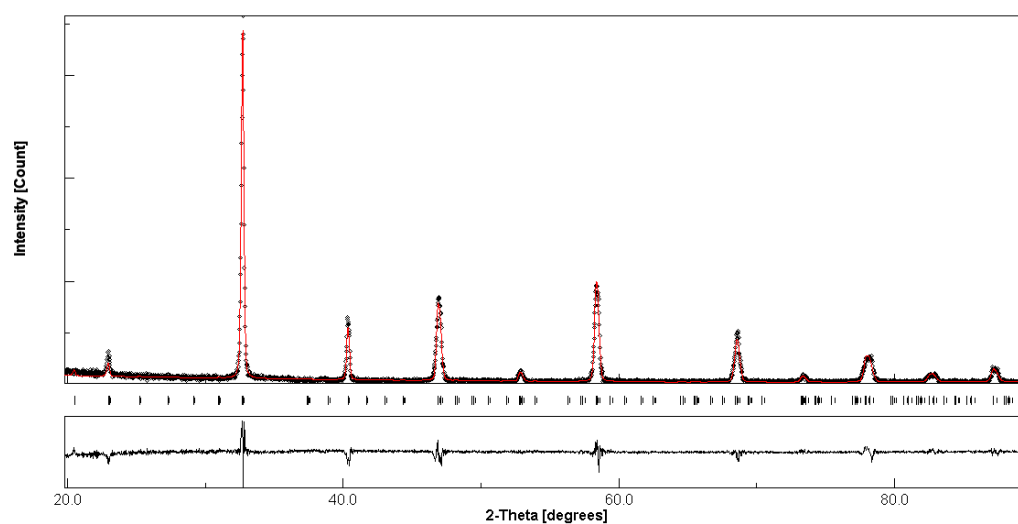


Figure 4.4. Rietveld analysis of LSM calcined at 800 °C for 5 hours.

Synthesis of ScSZ Powder: The amount of precursor nitrates used for ScSZ synthesis are given in Table 4.6 on the basis of $\text{Sc}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ 1gr. As can be seen, the purpose here is to provide $(\text{Zr}_{0.85}\text{Sc}_{0.15})\text{O}_{2-\delta}$ stoichiometry.

Table 4.6 Calculation of precursor amounts used for $(\text{Zr}_{0.85}\text{Sc}_{0.15})\text{O}_{2-\delta}$ (ScSZ) synthesis.

$\text{Sc}_{0.15}\text{Zr}_{0.85}\text{O}_{2-\delta}$ ($M_A=112.5$ gr)	M_A (gr/mole)	Amount (gr)	Mole
$\text{Sc}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$	302.97	1.00	0.0030
$\text{ZrO}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	339.23	6.34	0.0180
Citric acid monohydrate	192.12	12.68	0.0660
Ethylene Glycol	62.07	16.38	0.2640

The calcined LSM powder was subjected to detailed EDS analysis to the elemental distribution. The average of EDS analysis results of LSM, calcined at 800°C -5h, performed at 5 different points are given in Table 4.7. As can be seen, the values determined here, and the expected values are close to each other.

Table 4.7 Average EDS results for ScSZ powder calcined at 900°C for 5 hours.

ScSZ	Theoretical (at %)	Measured(at %)
Sc	15	15.8
Zr	85	84.6

XRD patterns of ScSZ calcined at 850 and 950°C are given in Figure 4.5. As can be seen, both temperatures are sufficient for the crystallization of ScSZ. Rietveld refinement of XRD patterns of the ScSZ powder calcined at 900°C for 5 hours is

given in Figure 4.6. Lattice constants for ScSZ determined as a result of the Rietveld refinement are included in Table 4.3. 900 °C 5h was therefore chosen for as calcination temperature for ScSZ.

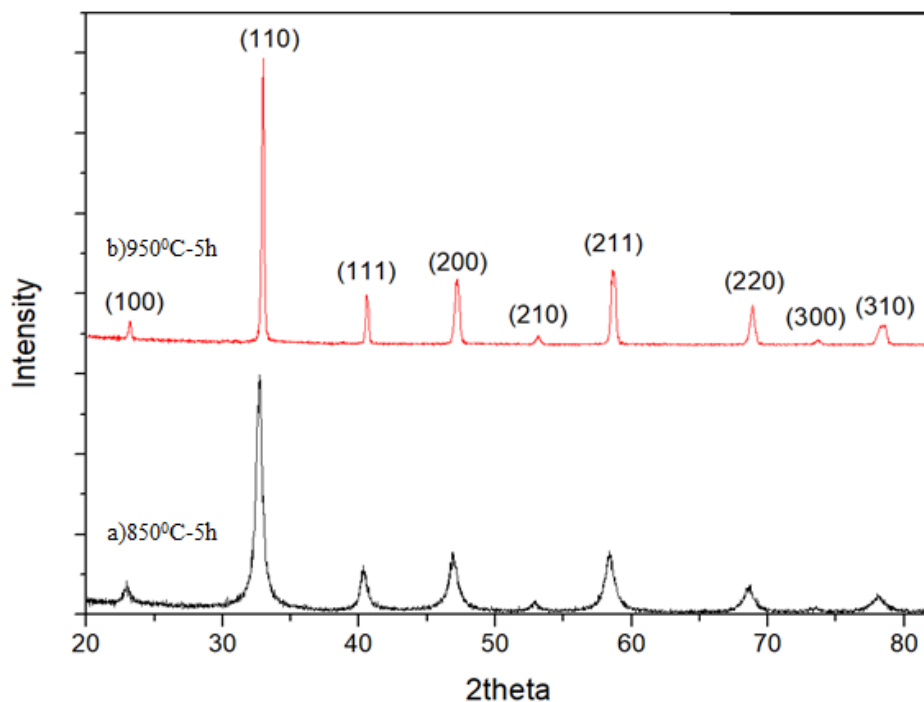


Figure 4.5. XRD pattern of ScSZ calcined at a) 850 °C, b) 950 °C for 5 hours.

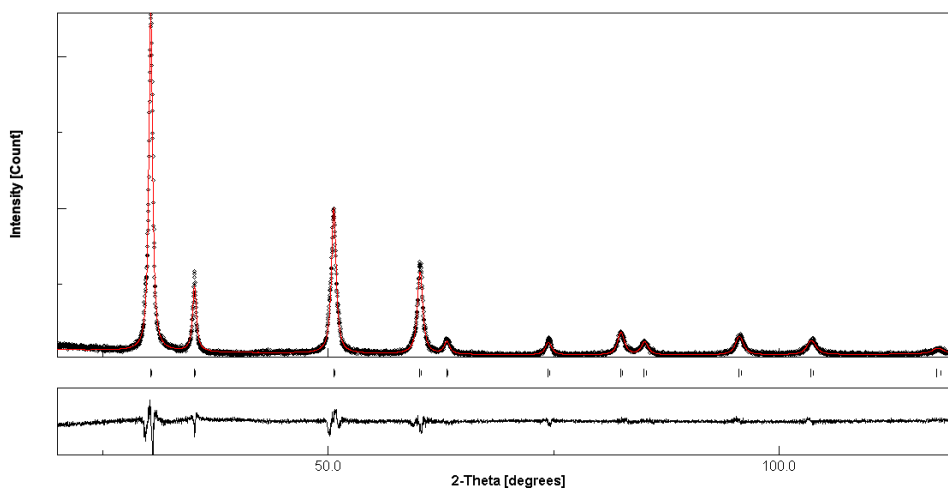


Figure 4.6. Rietveld analysis of XRD pattern of ScSZ calcined at 900°C for 5 hours.

4.2 Preparation of Sputter Targets for LSM, LSF, ScSZ

LSM: For 2-inch the target production, LSM was compacted with 6 different pressures. Relative density vs pressure graph is given in Figure 4.7. As can be seen in the figure, the relative density is above 0.38 at 140MPa and above pressures. For this reason, 140MPa has been chosen as the suitable pressure for LSM. Samples are pressed at 140MPa and sintered at 1300, 1400 and 1500 °C. SEM images after sintering are given in Figure 4.8.

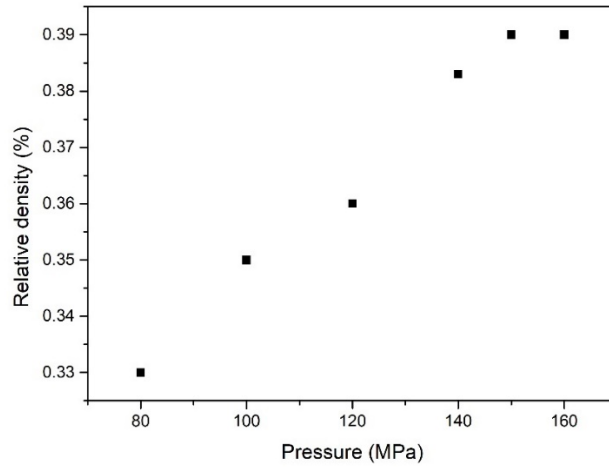


Figure 4.7. Relative density of LSM compacted at different pressures.

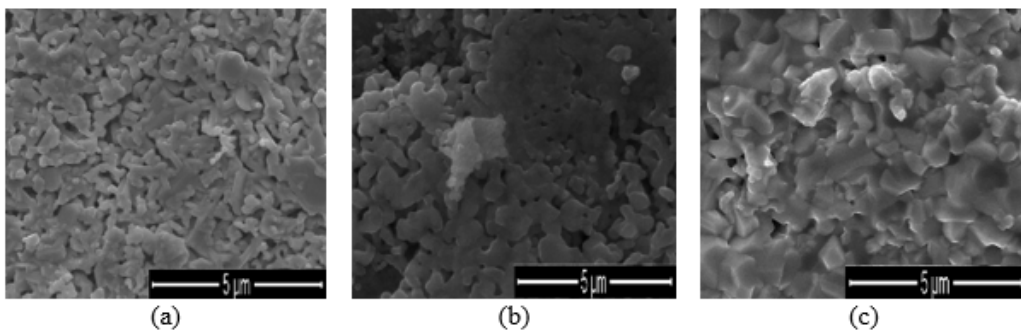


Figure 4.8. SEM images of LSM compacted at 140Mpa sintered at a)1300 °C , b)1400 °C , c)1500 °C for 5 hours.

As can be seen from the SEM images, the number of pores is quite high in LSM sintered at 1300 °C for 5 hours. The sample sintered at 1400 °C is relatively dense. The structure is sintered better at 1500 °C, therefore 1500 °C has been chosen as the suitable sintering temperature for LSM.

The radial shrinkage amounts in LSM sintered at different temperatures are given in Figure 4.9. As seen in the figure, LSM sintered at 1500 °C showed a radial shrinkage of approximately 10%. Based on this result, 55.5mm diameter compact should be produced for 50mm target material. Considering the deformations that may occur on the edges of the pressed material, 60mm Teflon rings were used for pressing, and the diametral excess after sintering was reduced by grinding. 50mm diameter target material sintered at 1500 °C for 5 hours is given in Figure 4.10.

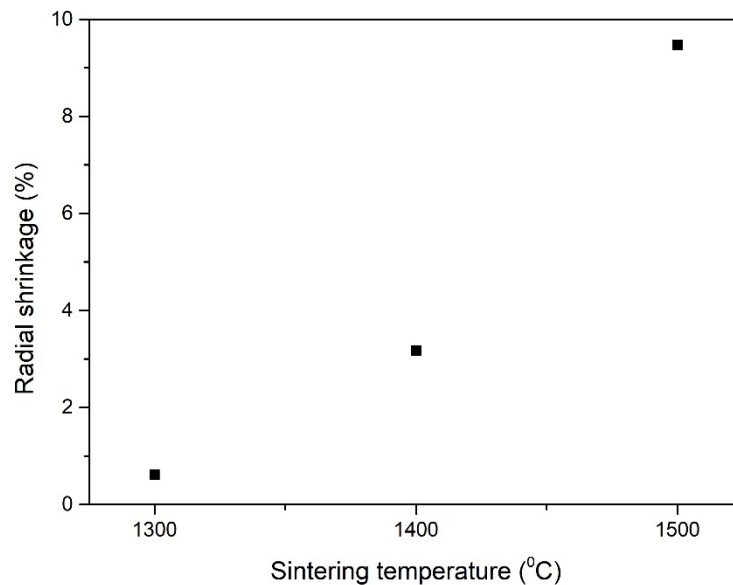


Figure 4.9. Radial shrinkages of LSM sintered at different temperatures.

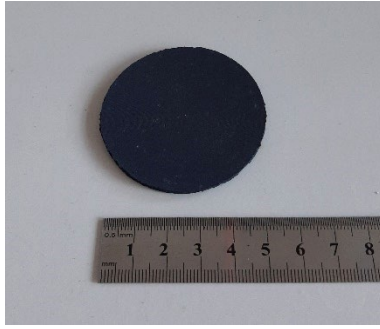


Figure 4.10. LSM target material to be used in sputter system.

LSF: For 2-inch the target production, LSF was compacted with 5 different pressures. Relative density vs pressure graph is given in Figure 4.11. As can be seen in the figure, the relative density values are somewhat lower than LSM. Considering the press capacity used, 140MPa was chosen as a suitable value for pressing. Samples are pressed at 140MPa and sintered at 1300, 1400 and 1500 °C. SEM images after sintering are given in Figure 4.12.

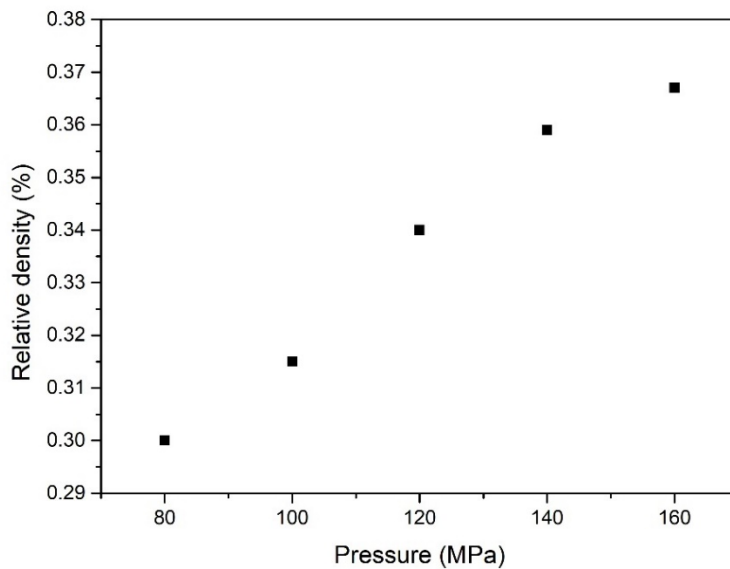


Figure 4.11. Relative density of LSF compacted at different pressures.

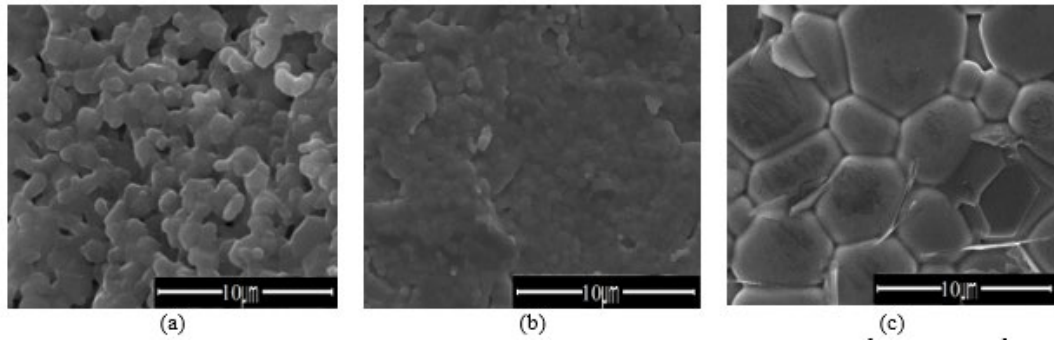


Figure 4.12. SEM images of LSF compacted at 140Mpa sintered at a)1300 °C ,
b)1400 °C , c)1500 °C for 5 hours.

As seen in the figure, the number of pores in LSF sintered at 1300 °C for 5 hours is quite high. On the other hand, sintering at 1400 °C gives a satisfactory small-grained structure. The grain structure is much more evident in the sample sintered at 1500 °C. This structure of 2-7 micron size was found satisfactory and 1500 °C was chosen for sintering.

The sintering temperature – radial shrinkage for LSF is given in Figure 4.13. The radial shrinkage amount for the chosen 1500 °C sintering temperature is 27%. Based on this result, 68.5mm compact is required for the production of 50mm diameter LSF target. LSF was pressed at 140MPa using 68.5mm Teflon mold and sintered at 1500 °C for 5 hours. The image of the 50mm diameter target material is given in Figure 4.14.

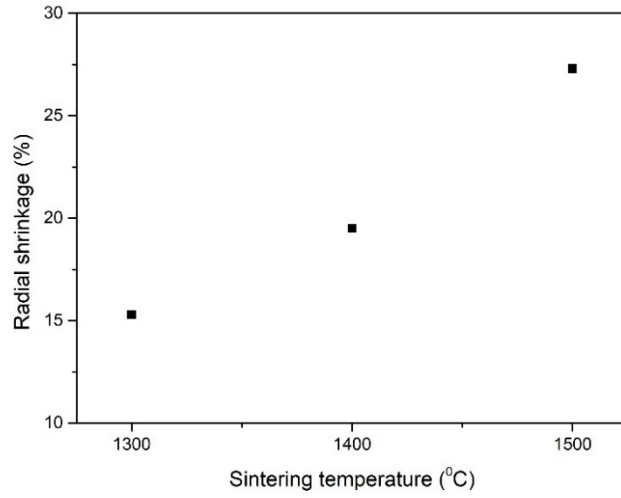


Figure 4.13. Radial shrinkages of LSF sintered at different temperatures.

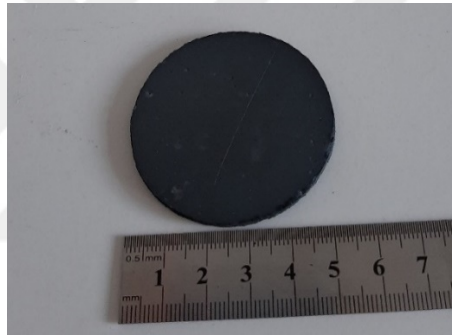


Figure 4.14. LSF target material to be used in sputter system.

ScSZ: For 2-inch the target production, ScSZ was compacted with 4 different pressures. Relative density vs pressure graph is given in Figure 4.15. As can be seen in the figure, the relative density is above 0.53 at 140MPa and above pressures. For this reason, 140MPa has been chosen as the suitable pressure for ScSZ. Samples are pressed at 140MPa and sintered at 1300, 1400 and 1500 °C. SEM images after sintering are given in Figure 4.16.

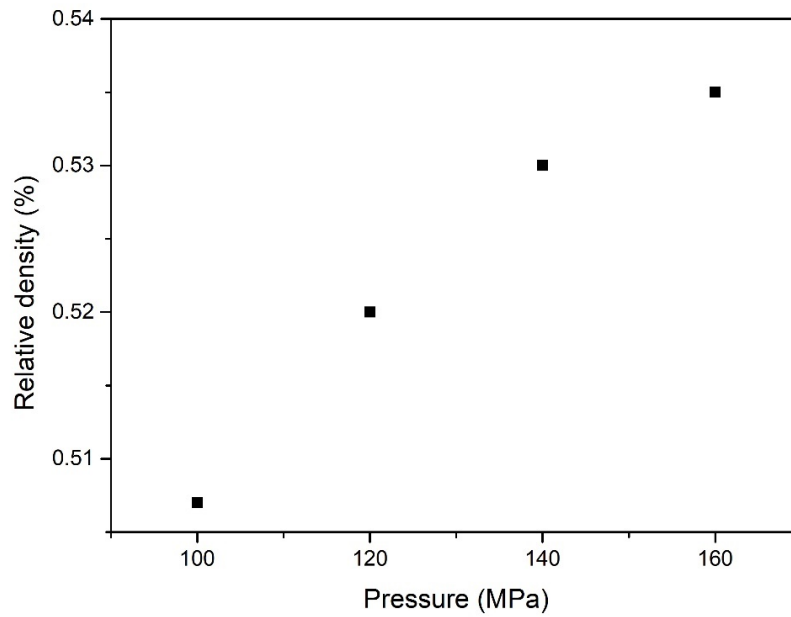


Figure 4.15. Relative density of ScSZ compacted at different pressures.

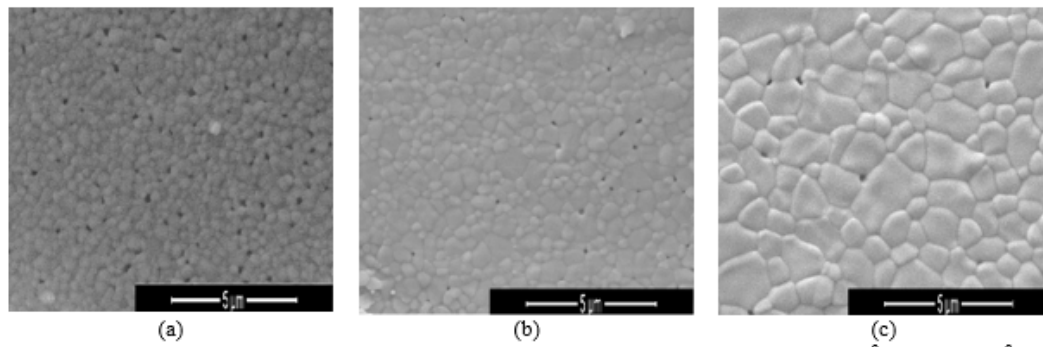


Figure 4.16. SEM images of ScSZ compacted at 140Mpa sintered at a)1300 °C , b)1400 °C , c)1500 °C for 5 hours.

The sintering temperature – radial shrinkage for ScSZ is given in Figure 4.17. The radial shrinkage amount for the chosen 1500 °C sintering temperature is 9.5%. Based on this result, 55.2mm compact is required for the production of 50mm diameter ScSZ target. Considering the deformations that may occur on the edges after being pressed, it has been found appropriate to use 60mm Teflon mold for this purpose.

After sintering, excess piece more than 50mm were grinded. The 50mm ScSZ target sintered at 1500 °C for 5 hours is given in Figure 4.18.

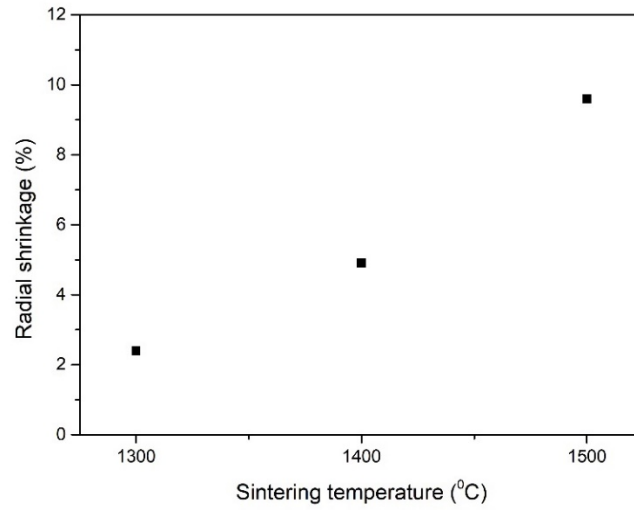


Figure 4.17. Radial shrinkages of ScSZ sintered at different temperatures.

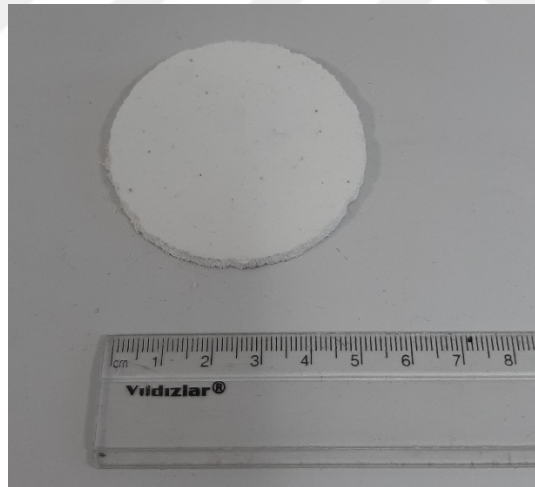


Figure 4.18. ScSZ target material to be used in sputter system.

4.3 Electrolyte Fabrication

For the production of electrolyte disc, 2gr ScSZ powder was used. These powders were pressed into a 19 mm mold with 140MPa and sintered at 1500 °C for 5 hours. Detailed parameters are given in section 4.2. The discs obtained as a result of this process are approximately 2mm thick and 18.5mm in diameter. Microstructure as a result of sintering is given in Figure 4.19. As can be seen from the SEM image, the structure is very dense with little, tiny pores. To determine the phase of the sintered disc, XRD analysis was made, Fig. 4.20. XRD pattern matches perfectly with ScSZ, and no second phases was observed.

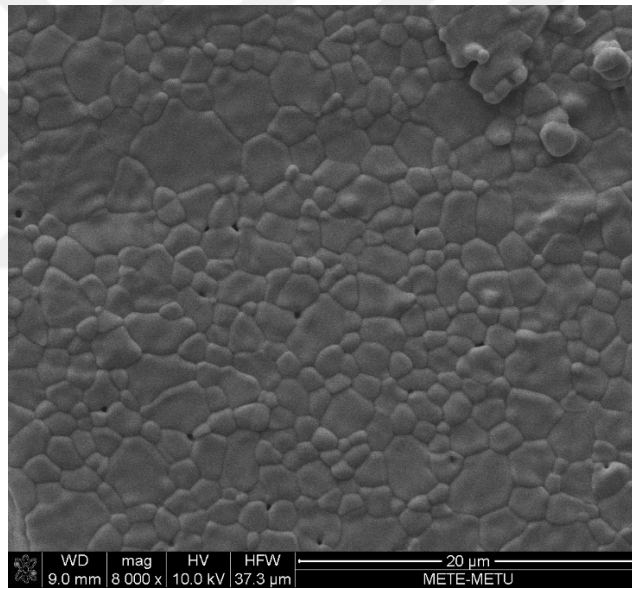


Figure 4.19. SEM image of ScSZ disc sintered at 1500 °C for 5 hours.

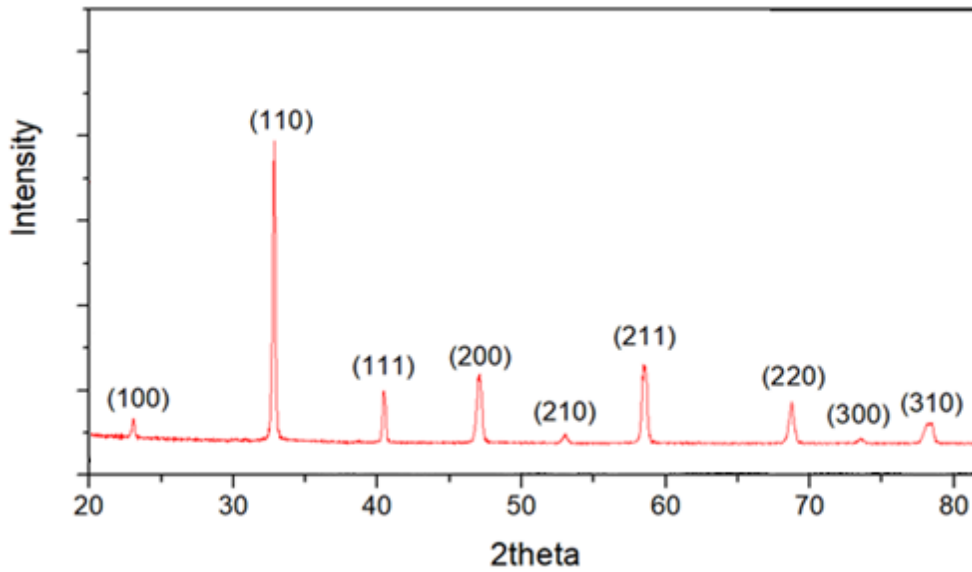


Figure 4.20. XRD pattern of ScSZ sintered at 1450 °C for 5 hours.

As a result of the Rietveld analysis applied to ScSZ powders earlier in this chapter, it is found that the lattice parameter of ScSZ used to fabricate the sputter target is 5.098 Å. Figure 4.21 shows the temperature vs ionic conductivity for ScSZ. Results indicate that ScSZ electrolyte fabricated in this chapter has better conductivity among the ones from the literature[101].

Figure 4.22 shows the lattice parameter of ScSZ as a function of scandia content[102]. Lattice parameter found is corresponding to the scandium content of somewhere close to 0.14 according to this data. This is close to the aimed scandium content which is 0.15 (8ScSZ). Considering the fact that the highest conductivity of ScSZ was found as 0.3 S/cm at 1000 °C in the composition range 8 to 12 mol % Sc₂O₃[103], ScSZ with scandium content of 0.14 can be expected to have conductivity close to 0.3 S/cm at 1000 °C. This result indicates that the ScSZ target produced in this chapter have favorable conductivity.

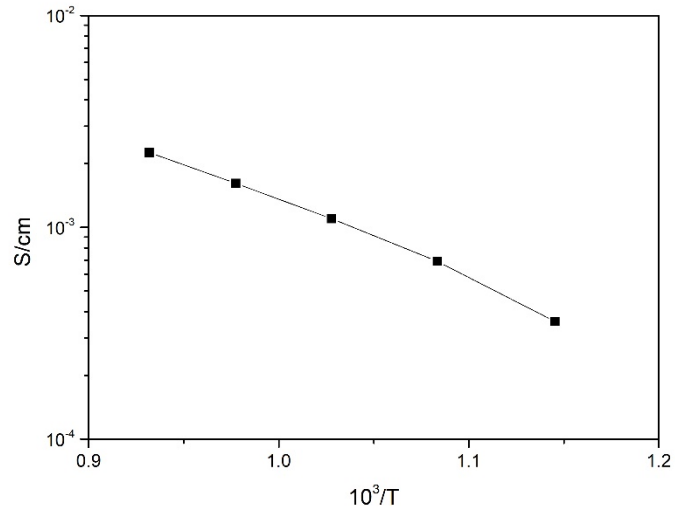


Figure 4.21. Ionic conductivity of 8ScSZ w.r.t temperature.

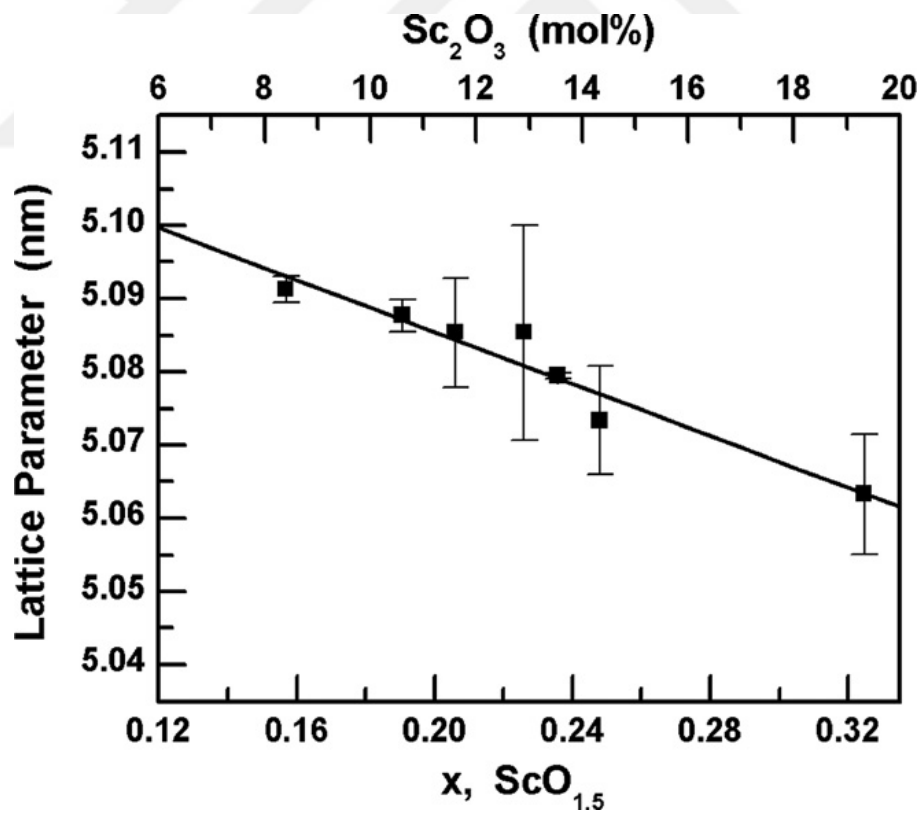


Figure 4.222. Lattice parameter of cubic ScSZ solid solution as a function of scandia content[102].

4.4 Combinatorial Deposition of Cathodes

Geometry of combinatorial cathode deposition was described in chapter 3.3. Sputter targets prepared were loaded on the gun and the system was aligned as described in chapter 3.3. Electrolyte discs were loaded on the sample tray.

The tooling factor was determined separately for each target material. For this purpose, ScSZ target was attached to gun-1, LSM to gun-2 and LSF to gun-3. Substrates were borosilicate glass. Power loading values for each target are given in Table 4.8. For each of the target materials, the initial tooling factor was set to 100, density and the Z factor were entered in the corresponding channel part of the indicator. The initial experiment was continued for 2 hours for each target.

Glass substrate was then broken in two and were examined across its thickness in SEM. The film thicknesses obtained are given in Figure 4.23. As can be seen, a uniform film has been obtained as a result of the coating. The samples with SEM image here are the samples closest to the thickness sensors, that is, at the corner of the triangle. Tooling factor determined for each target are included in Table 4.8.

Table 4.8 Sputter parameters used in determining tooling factors.

Target	Plasma gas, Pressure(mTorr), Flow Rate (sccm)	RF power (Watt)	Time (Min)	Rate (Å/s)	Tooling factor
LSM	Ar, 5, 20	30	120	0,2	83
LSF	Ar, 5, 20	60	120	0,6	30
ScSZ	Ar, 5, 20	60	120	0,1	222

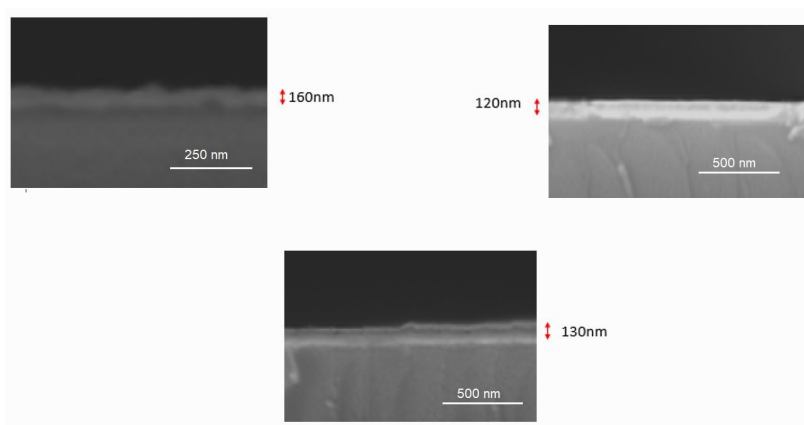


Figure 4.233. Film thicknesses obtained as a result of coating while determining tooling factors a) ScSZ, b) LSM, c) LSF.

Following the determination of the tooling factor, compositional field in the sputtering were checked using aluminum substrates. A total 21 aluminum substrates were placed in the sample tray. In the experiment, sputter deposition was continued for 10 hours. The sputtering parameters used during this coating are given in Table 4.9. EDS analysis was taken from each of the 21 substrates. In this analysis, three elements were chosen to check the chemistry of the cathodes. These were Mn Fe and Zr representing LSM, LSF and ScSZ respectively. Mn, Fe and Zr contents and the amount of corresponding LSM, LSF and ScSZ are given in Table 4.10.

Table 4.9 Sputter parameters of the coating made on aluminum substrate.

Gun	Plasma gas, Pressure(mTorr), Flow Rate (sccm)	RF power (Watt)	Time (Min)	Rate (Å/s)
LSM	Ar, 5, 20	60	600	0.9
LSF	Ar, 5, 20	30	600	1.1
ScSZ	Ar, 5, 20	100	600	0.4

The results are shown plotted in LSM, LSF and ScSZ ternary diagram. The compositional distribution is almost widespread on the ternary composition diagram being slightly more samples located in the middle part of the ternary diagram. Therefore, power loading as well as the alignment of the gun were adequate to investigate the potential of LSM-LSF-ScSZ composites in terms of their suitability as cathode for IT-SOFCs. The obtained distribution is also shown in the ternary diagram in Figure 4.24. The samples obtained by the combinatorial approach were structurally characterized by X-ray diffraction.

XRD pattern of sample No 1 is given in Fig 4.25. Here the major peaks are those of aluminum coming from the substrate. There is however a broad peak centered at $2\theta=30$ which originates from the cathode layer. Since the peak is very broad, this implies that thin film cathode deposited on Aluminum is amorphous. All of the peaks seen here are caused by aluminum used as substrate.

XRD patterns were measured for all 21 samples. These are given in Fig 4.26. Since the first peak of aluminum starts at $2\theta = 39$ degrees, the patterns are shown plotted $20 < 2\theta < 37.5$. Samples close to LSM side have small peaks. This may indicate that the samples whose compositions are rich in LSM are nanocrystalline. However, there is no sign of crystallinity on the rest of the samples. Therefore, the resulting cathodes are not crystalline, but all amorphous.

Table 4.10 Mn, Fe, Zr content of cathodes deposited on Al substrate and the corresponding composition of composite cathodes in terms of LSM, LSF, ScSZ.

	Mn	Fe	Zr	LSM	LSF	ScSZ
1	82.7	8.4	8.9	81.4	8.3	10.3
2	77.9	11.3	10.8	76.5	11.1	12.4
3	73.7	16	10.3	72.4	15.7	11.9
4	64.1	15.4	20.5	61.9	14.8	23.3
5	61.2	20.1	18.7	59.2	19.4	21.4
6	56.8	27.4	15.8	55.3	26.7	18
7	46.6	17.9	35.5	43.8	16.8	39.4
8	52.6	24.7	22.7	50.5	23.7	25.8
9	50.1	31.7	18.2	48.5	30.7	20.8
10	27.6	56.3	16.1	26.9	54.7	18.4
11	31	16.2	52.8	28.4	14.8	56.8
12	37	25.3	37.7	34.7	23.7	41.6
13	33	39.9	27.1	31.5	38.1	30.4
14	30.7	43.8	25.5	29.4	42	28.6
15	14.8	60	25.2	14.2	57.4	28.4
16	16.2	11.9	71.9	14.4	10.6	75
17	25.9	21.3	52.8	23.7	19.4	56.9
18	27.5	36.2	36.3	25.9	34	40.1
19	23.2	47.6	29.2	22	45.3	32.7
20	11.9	66.4	21.7	11.5	63.9	24.6
21	9.1	67.6	23.3	8.7	64.9	26.4

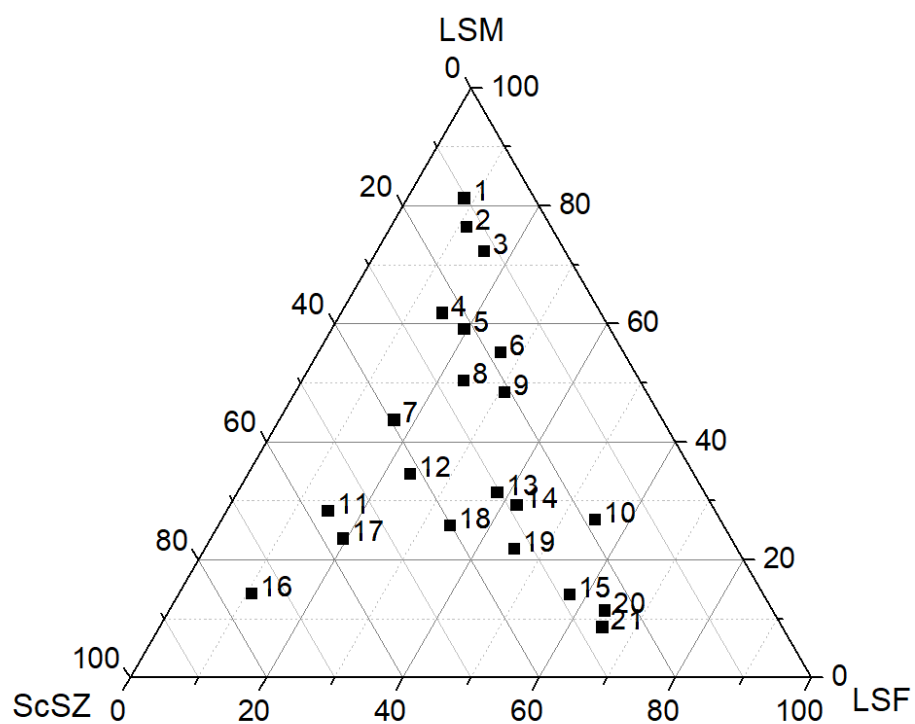


Figure 4.244. Distribution of samples produced by combinatorial approach in ternary diagram.

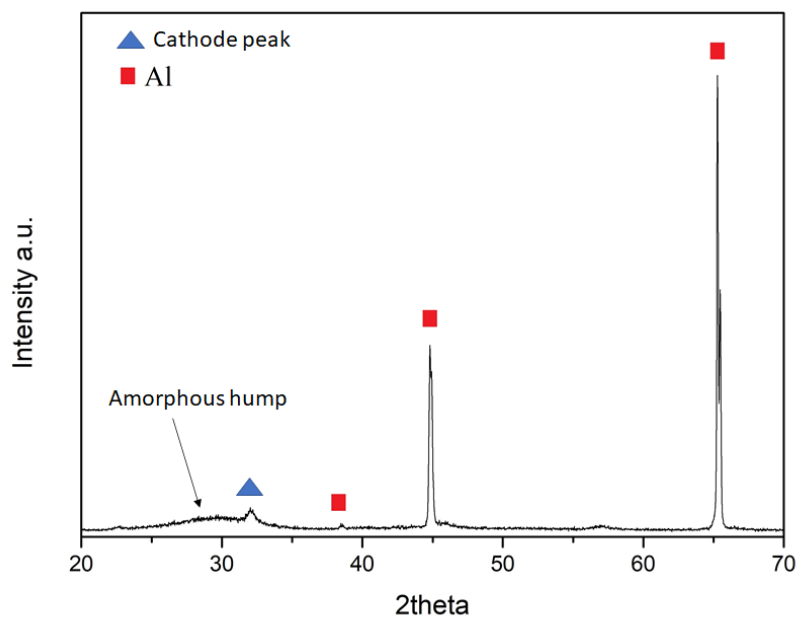


Figure 4.255. XRD pattern of aluminum substrate coating sample number 1.

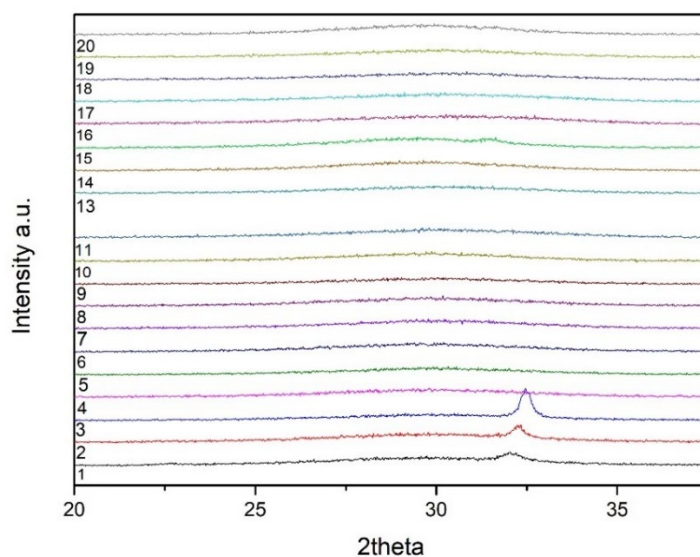


Figure 4.266. XRD diffraction patterns in cathodes deposited on aluminum substrate.

4.5 Electrochemical Characterization via Symmetric Cell

Electrochemical characterization of cathodes produced with combinatorial approach was performed by symmetrical cell measurements. For this purpose, ScSZ electrolyte discs coated on both sides with the same cathode composition were produced. The symmetrical cell is given schematically in Figure 4.27. The symmetrical cell consists of electrolyte production, coating both electrolyte surfaces in masked style and gold plating of the cathode in a masked manner.

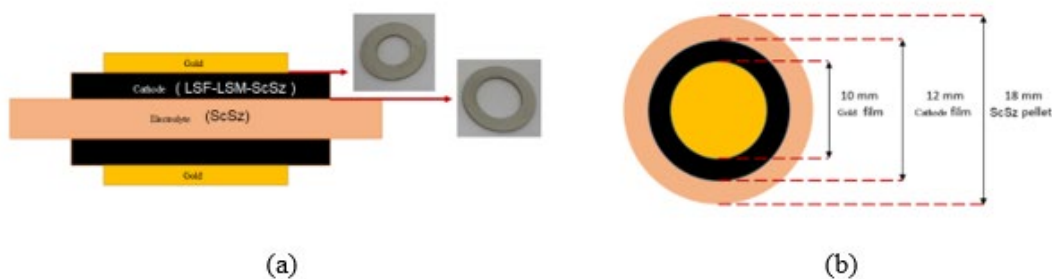


Figure 4.277. Schematic representation of symmetrical cell used in electrochemical characterization a) Symmetrical cell section b) View of the cell in the disc plane.

Prepared 21 electrolyte discs were placed on 12 mm inner diameter and 19 mm outer diameter stainless steel discs and placed in the substrate holder. Subsequently, ScSZ target materials were placed in the first gun, LSM in second and LSF in the third gun. After the substrate holder was placed on the sample plane in the vacuum chamber, the chamber was taken to a vacuum of 1×10^{-6} torr, and subsequently the Ar input was adjusted to 10 sccm and the gate valve was adjusted to keep the vacuum level at 5 mtorr. The substrates were kept at 400 °C using a substrate heater inside the chamber.

All three target materials were operated at the parameter values given in Table 4.9 and the coating was continued for a total of 6 hours. Subsequently, the stainless steel rings were removed, and the electrolyte discs were reversed, and the rings were placed back in place. In this manner, the other sides of the discs were coated with the same sputter parameters for 6 hours. Figure 4.28 shows samples coated in this manner. The coating thickness obtained as a result of this process is approximately 600 nm.



Figure 4.288. Symmetrical cells in a substrate holder after cathode coating.

Gold plating of symmetric cell was achieved via stainless steel rings (outer diameter: 19mm, inner diameter: 10mm). The cathode coated electrolyte discs were placed in a substrate holder on top of stainless steel masks and the holder was rotated at 8 rpm during coating. This coating was applied on both sides of the symmetric cells. The coating thickness obtained as a result of this process was typically 150nm.

EIS measurements were carried out between 600-800 °C with 50 °C intervals. A typical examples of the Nyquist plots are given in Figure 4.29. Note that all measurements are done in atmospheric conditions.

Results are expressed as area specific resistance (ASR). This value is expressed in ohm.cm² by multiplying R_{cathode} by the expose cathode area into the air. The area exposed to air is $(\pi \cdot 0.6^2 - \pi \cdot 0.5^2)$ 0.34 cm² in the given coating geometry in the experimental section. Since both surfaces were coated, it has been calculated as $\text{ASR} = R_{\text{cathode}} \cdot 0.34/2$.

The found ASR values are given in Table 4.11 and mapped in contour ternary graphs, Fig. 4.30 a), b), c), d) and e) for 800, 750, 700, 650 and 600 °C respectively. ASR values decrease with increasing temperature. ASR values in the measured region are quite high. Lowest value is seen in cathode compositions close to the LSM corner with 0.33 ohm.cm² in both sample 2 and 3 at 800 °C.

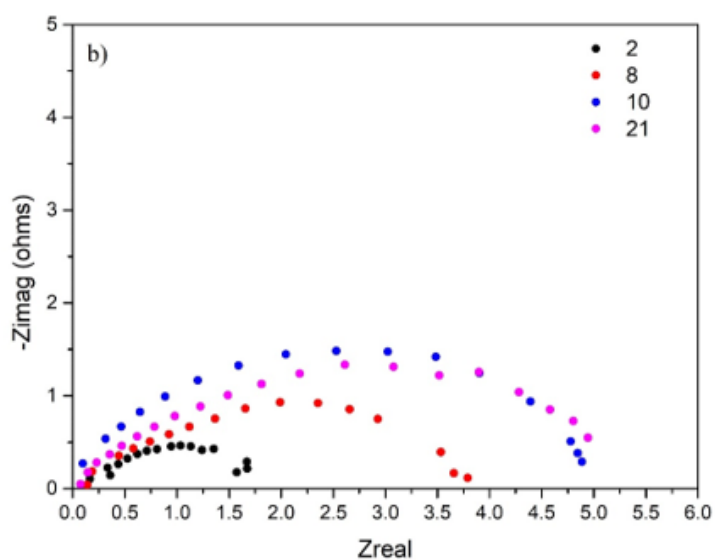
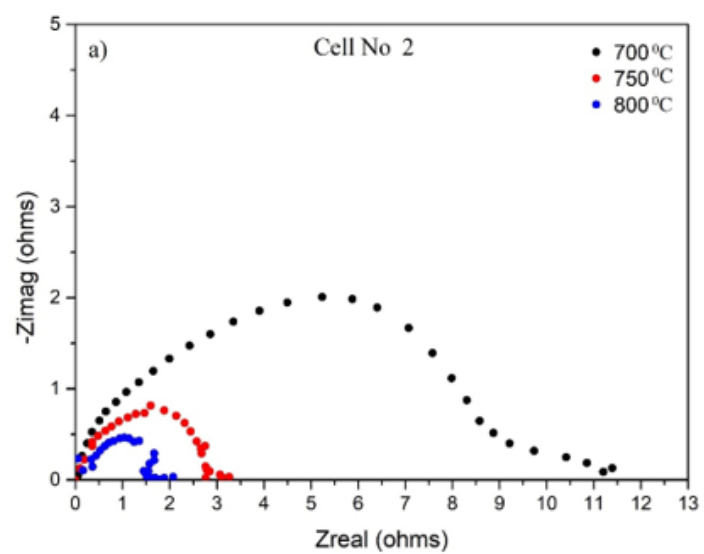
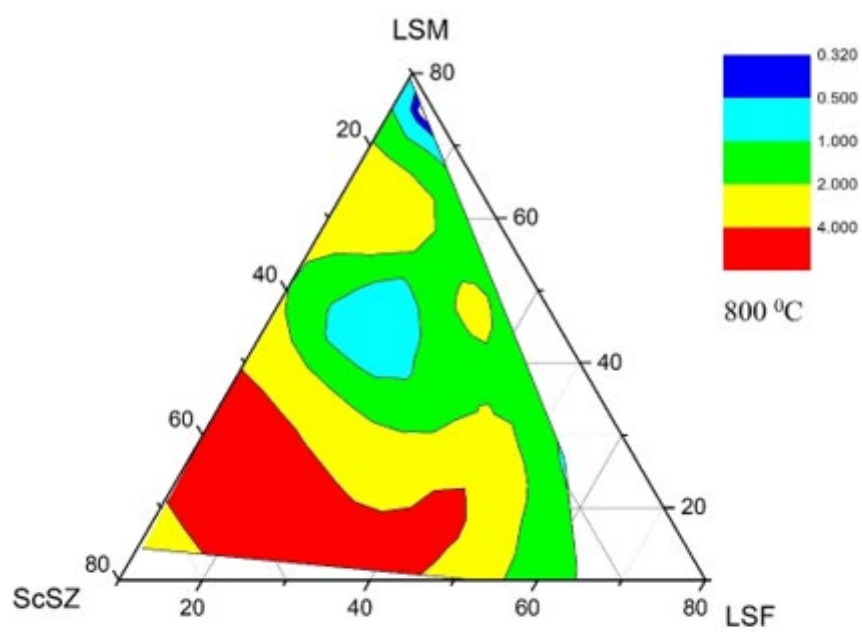


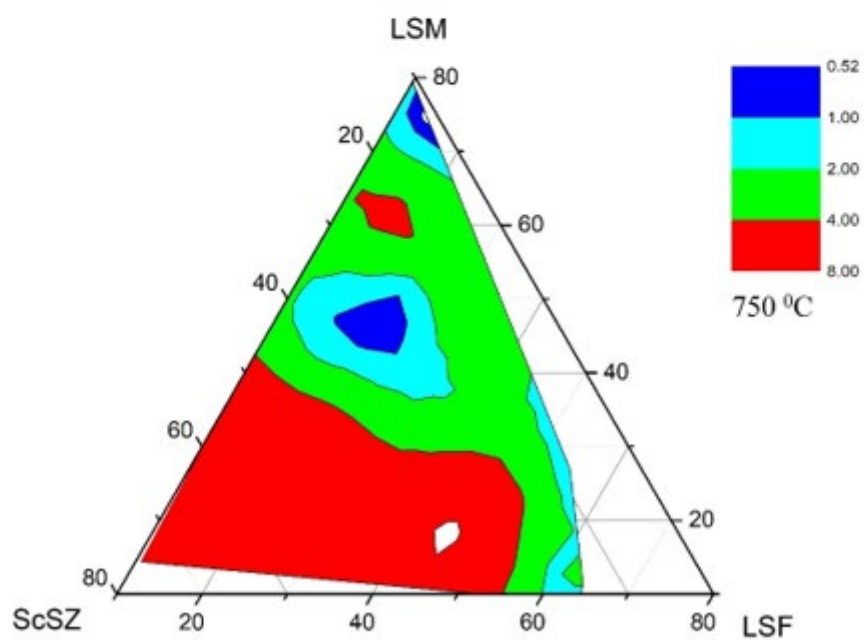
Figure 4.299. a) Nyquist plots of cell number 2 at 800, 750 and 700 °C, b) Nyquist plots of cells number 2, 8, 10 and 21 at 800 °C.

Table 4.11 ASR values of the cathodes deposited via sputter, given in $\Omega\cdot\text{cm}^2$.

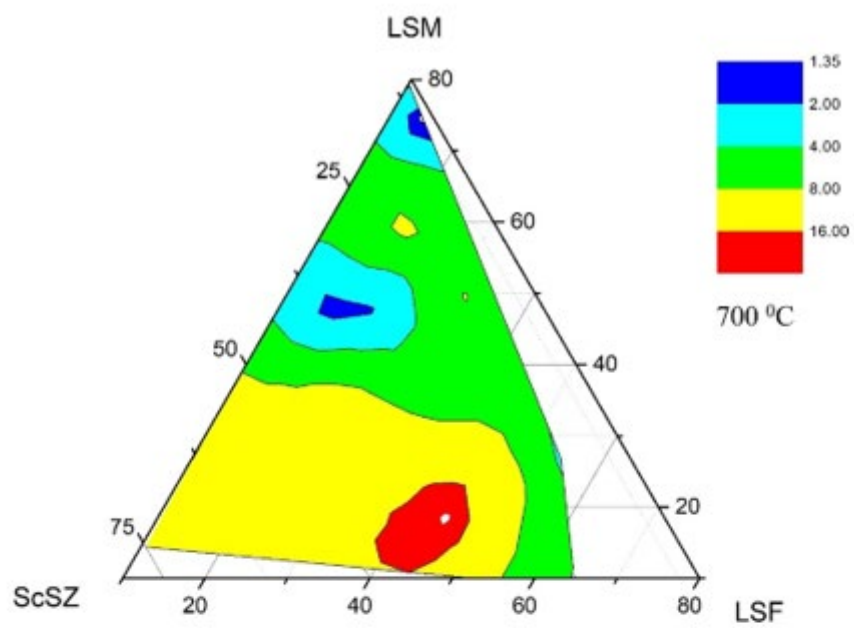
Sample No	600 °C	650 °C	700 °C	750 °C	800 °C	LSM	LSF	SeSZ
1	197	28.8	7.18	2.21	1.36	81.4	8.3	10.3
2	55.6	5.55	1.59	0.53	0.33	76.5	11.1	12.4
3	29.8	5.33	1.35	0.56	0.33	72.4	15.7	11.9
4	194	40.6	7.44	4.41	3.17	61.9	14.8	23.3
5	495	66.46	8.88	4.34	3.08	59.2	19.4	21.4
6	270	55.93	6.93	2.97	1.58	55.3	26.7	18
7	244	32.54	2.56	1.33	1.08	43.8	16.8	39.4
8	116	18.09	2.53	0.92	0.68	50.5	23.7	25.8
9	310	55.33	7.99	3.24	2.23	48.5	30.7	20.8
10	82	11.91	3.47	1.32	0.86	26.9	54.7	18.4
11	676	69.7	11.75	7.5	5.69	28.4	14.8	56.8
12	795	123	10.51	4.28	2.17	34.7	23.7	41.6
13	543	85.54	7.91	2.82	1.78	31.5	38.1	30.4
14	126	53.99	9.84	3.93	2.67	29.4	42	28.6
15	63.9	22.58	5.4	2.11	1.23	14.2	57.4	28.4
16	5726	121	13.6	3.99	2.59	14.4	10.6	75
17	575	44.16	12.06	7.49	5.55	23.7	19.4	56.9
18	489	98.03	12.73	5.23	2.95	25.9	34	40.1
19	277	125	17.8	8.16	4.34	22	45.3	32.7
20	95	31.5	5.64	2.21	1.38	11.5	63.9	24.6
21	60	14.28	2.88	1.21	0.91	8.7	64.9	26.4



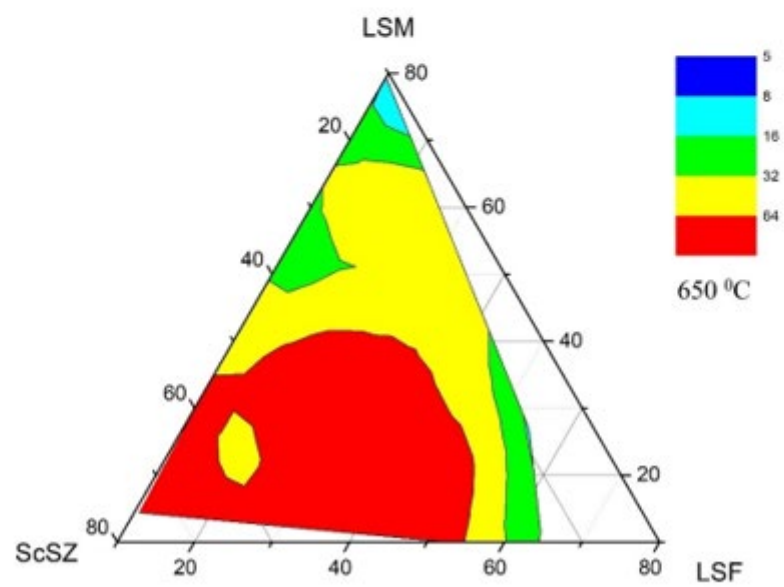
(a)



(b)



(c)



(d)

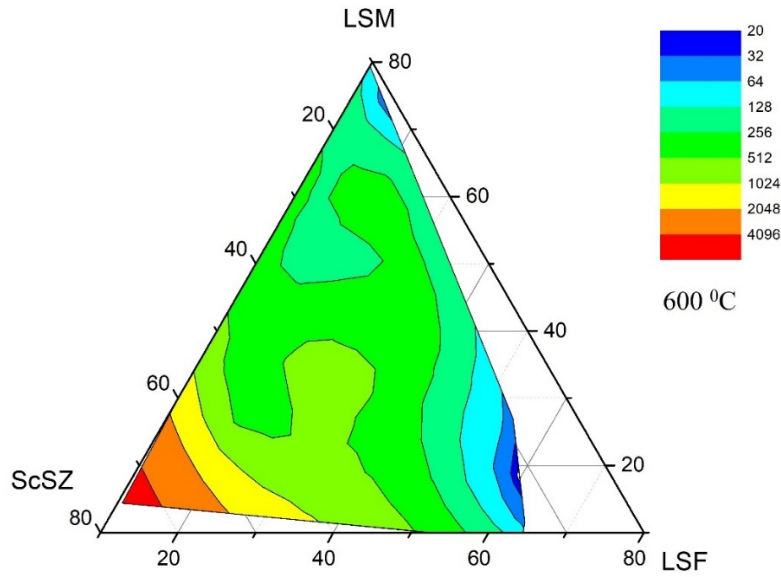


Figure 4.300. The ASR values (ohm.cm^2) determined for cathode compositions in ternary diagram a) 800 $^{\circ}\text{C}$, b) 750 $^{\circ}\text{C}$, c) 700 $^{\circ}\text{C}$, d) 650 $^{\circ}\text{C}$, e) 600 $^{\circ}\text{C}$.

Three regions of favorable ASR value were observed in the ternary diagram. These are the middle region of the diagram, the region close to the LSM and the region close to the LSF. The lowest values in the diagram were observed in cells 2 and 3 with $0.33 \text{ } \Omega.\text{cm}^2$ being **Cell 2**: $\text{LSM}_{77}\text{LSF}_{11}\text{ScSZ}_{12}$ and **Cell 3**: $\text{LSM}_{72}\text{LSF}_{16}\text{ScSZ}_{12}$.

These values in the region close to the LSM corner are relatively better than those seen in the literature. Seyed et al.[104] infiltrated the LSM with LSF and found $2.1 \text{ } \Omega.\text{cm}^2$ at 800 $^{\circ}\text{C}$. In addition, they have found a value of $6.5 \text{ } \Omega.\text{cm}^2$ at 800 $^{\circ}\text{C}$ with pure LSM as cathode. Cebollero et al.[105] studied laser patterned LSM-YSZ composite cathodes and achieved $0.59 \text{ } \Omega.\text{cm}^2$ at 800 $^{\circ}\text{C}$. In another study by Xia et al.[106] showed that a value of $0.3 \text{ } \Omega.\text{cm}^2$ is possible with LSM-GDC composite cathodes. All these values are to be compared with the current cathode which had an ASR value of $0.33 \text{ } \Omega.\text{cm}^2$

Log(ASR) vs 1000/T diagram is shown plotted given Fig. 4.31. The plot covers only the samples with best performance. A horizontal line was drawn in the plot where ASR had a value of $0.15 \Omega \cdot \text{cm}^2$. It should be pointed out that $\text{ASR}=0.15 \Omega \cdot \text{cm}^2$ is a benchmark value that need to be satisfied for SOFC cathode. The intersection of this line with a linear plot yields temperatures of 810°C and 815°C for cathode $\text{LSM}_{77}\text{LSF}_{11}\text{ScSZ}_{12}$ and, $\text{LSM}_{72}\text{LSF}_{16}\text{ScSZ}_{12}$, respectively. For cathodes with compositions of $\text{LSM}_{51}\text{LSF}_{24}\text{ScSZ}_{25}$ and $\text{LSM}_9\text{LSF}_{65}\text{ScSZ}_{26}$, the temperatures are slightly higher and had values of 840°C and 860°C in the respective order.

4.6 Structural Characterization

As reported above, all sputter deposited cathode had amorphous structure. This was except for compositions close to LSM corner where very broad individual peaks could be identified implying an amorphous/ nanocrystalline structure. In this study the aim was to identify temperatures where the composite cathode could have acceptable performance, i.e., $\text{ASR}=0.15 \Omega \cdot \text{cm}^2$. This value could be reached at cathode compositions $\text{LSM}_{77}\text{LSF}_{11}\text{ScSZ}_{12}$ and, $\text{LSM}_{72}\text{LSF}_{16}\text{ScSZ}_{12}$ at temperatures close to 800°C . Since this temperature is rather high, the as-deposited amorphous structure is probably not stable, and the cathode would be expected to crystallize.

This was checked by taking xrd pattern after electrochemical characterization. Fig. 4.32 shows the diffractogram recorded in Bragg-Brentano geometry. It should be noted that XRD contain peaks from ScSZ LSM and LSF. ScSZ peak is strongest since electrolyte also contributes to diffraction.

Table 4.12 shows ASR values in the first cycles(i.e., upon heating) and in the second cycles (i.e., upon cooling). Note that ASR values are quite similar to each other at a given temperature above 700°C . Below the give temperature second cycle values are significantly better than the first cycle. It may be thought that cathode as far the current compositions are concerned probably crystallized at temperature of 700°C .

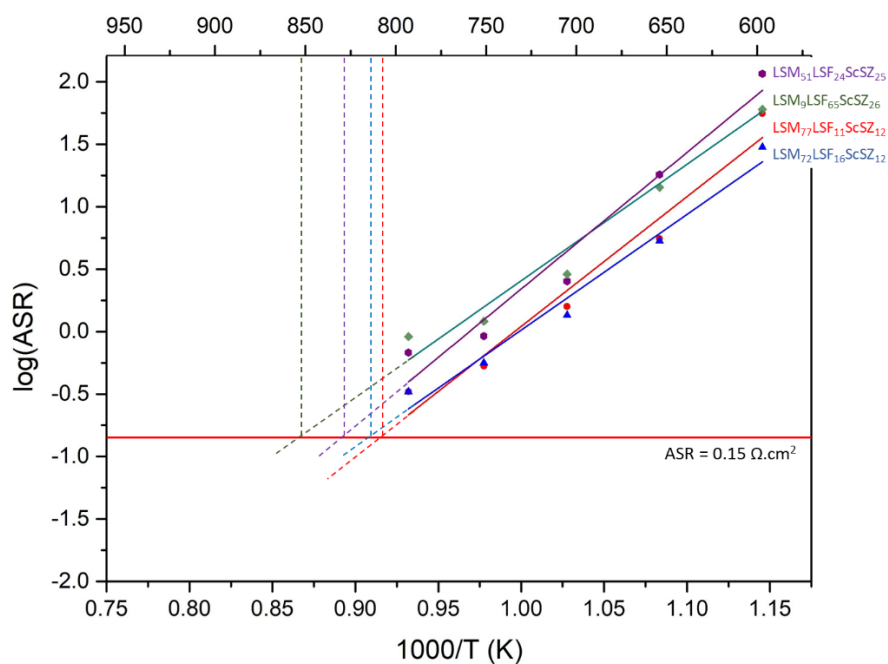


Figure 4.311. $\log(\text{ASR})$ vs $1000/T$ determined for cathodes 2,3,8 and 21.

Table 4.122 ASR values of the cathodes 2,3,8 and 21 in the first cycle (i.e., upon heating) and in the second cycle (i.e., upon cooling), given in $\Omega.\text{cm}^2$.

	2		3		8		21	
	1 st cycle	2 nd cycle	1 st cycle	2 nd cycle	1 st cycle	2 nd cycle	1 st cycle	2 nd cycle
800 °C	0.33	0.33	0.33	0.35	0.68	0.70	0.91	0.91
750 °C	0.53	0.55	0.56	0.58	0.92	0.92	1.21	1.22
700 °C	1.59	1.60	1.35	1.40	2.53	2.55	2.88	2.85
650 °C	5.55	5.10	5.33	5.12	18.09	17.85	14.28	14.14
600 °C	55.6	51.1	29.8	28.2	116	108	60	57.8

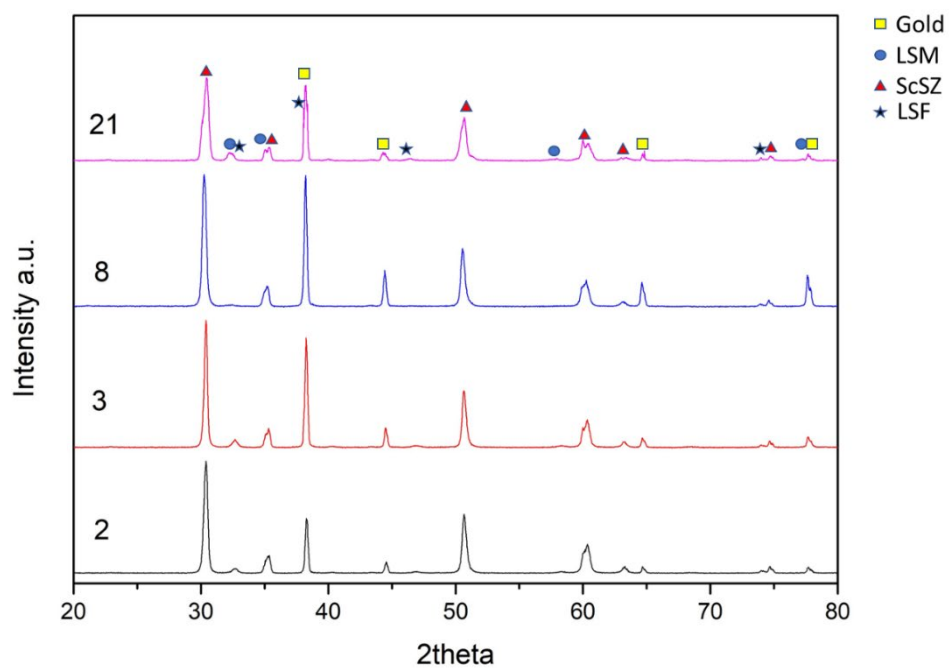


Figure 4.322. XRD patterns of cathodes 2, 3, 8 and 21 after EIS measurements up to 800 °C.

CHAPTER 5

CONCLUSIONS

In this study, a combinatorial study was carried out to develop new cathode materials based on for LSM-LSF-ScSZ ternary system. A total of 21 cathode compositions were sputter deposited each with different compositions and were screened using symmetric cell via electrochemical impedance spectroscopy as a measure of their ORR performance.

The following conclusions can be drawn from this study:

- i.) Combinatorial approach is very useful for determining the optimum composition in the composite cathode system. This approach enables to scan the whole compositional area with a single test.
- ii.) Based on EIS results, the mapping of ASR values yielded a region close to LSM:LSF:ScSZ=75:12.5:12.5 where ASR was minimum. Besides these compositions, the presence of compositions with low ASR was observed where the oxides had nearly equal proportions.
- iii.) The LSM/LSF/ScSZ composite cathodes, when suitably selected, have sufficient catalytic activity towards ORR for operating temperatures can be as low as 800 °C.

It was anticipated that in order to reduce operating temperature of SOFC to still lower temperature LSM may be replaced by Ruddlesden-Popper type oxide. It was proposed that MIEC $\text{LaSr}_3\text{Fe}_3\text{O}_{10}$ (rp-LSF) may be used in place of LSM with a potential to achieve this reduction.



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APPENDICES

A. LSF-LSF(rp)-ScSZ Cathodes for IT-SOFCs

A.1 Preparation of Sputter Target of Ruddlesden-Popper LSF

LSF powders was synthesized using the Pechini route. Related route is explained in the experimental section. The amount of precursor nitrates used for rp-LSF synthesis are given in Table A.1 on the basis of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 5gr. As can be seen, the purpose here is to provide $\text{LaSr}_3\text{Fe}_3\text{O}_{10-\delta}$ stoichiometry. The dry gel obtained at the end of the Pechini process was calcined at different temperatures.

Table A.1. Calculation of precursor amounts used for $\text{LaSr}_3\text{Fe}_3\text{O}_{10-\delta}$ (rp-LSF) synthesis.

$\text{LaSr}_3\text{Fe}_3\text{O}_{10-\delta}$ ($M_A=728.3$ gr)	M_A (gr/mole)	Amount (gr)	Mole
$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	433.10	5.00	0.0115
$\text{Sr}(\text{NO}_3)_2$	211.63	7.33	0.0346
$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	404.00	13.99	0.0346
Citric acid monohydrate	192.12	50.95	0.2424
Ethylene Glycol	62.07	60.00	0.9699

The calcined rp-LSF powder was subjected to detailed EDS analysis to the elemental distribution. The average of EDS analysis results of rp-LSF, calcined at 1200⁰C-5h, performed at 5 different points are given in Table A.2. As can be seen, the values determined here, and the expected values are close to each other.

Table A.2 Average EDS results for LSF powder calcined at 1200 ⁰C for 5 hours.

LSF	Theoretical (at %)	Measured(at %)
La	14	12.4
Sr	43	45.5
Fe	43	42.1

XRD patterns of rp-LSF calcined at 1100 and 1200⁰C are given in Figure A.1. As can be seen, both temperatures are sufficient for the crystallization of LSF. The pattern confirms the formation of rp-LSF, and the observed peaks can be indexed from the standard pattern of LaSr₃Fe₃O₁₀ (JCPDF No. 1-081-1234). Velinov et. al. has studied the formation of different LSF phases and their relationship with the calcination temperature[107]. They found out that at least 1100 ⁰C is needed for the synthesis of LaSr₃Fe₃O₁₀ phase. Below 1100 ⁰C, they observed the formation of perovskite LSF and double layered LSF. Based on this result, 1200 ⁰C 5h was chosen for as calcination temperature for LSF.

Sem image of the calcined powder is given in Figure A.2. Sem micrograph shows that the microstructure consists of agglomerates of very fine powders. These agglomerates have sphere like shape and roughly 30 µm in diameter.

For the fabrication of the 50mm sputter target of rp-LSF, a preliminary experiment is conducted to find the % shrinkage. For this reason, 20mm Teflon ring was used. After compacting with 140MPa and sintering 1500 °C for 5 hours, it is found that the rp-LSF powder shrinks %30 radially. Therefore, 80mm Teflon ring was used for the compaction for the fabrication of the 50mm target and the excess parts were grinded after sintering. Target photo is given included in Figure A.2.

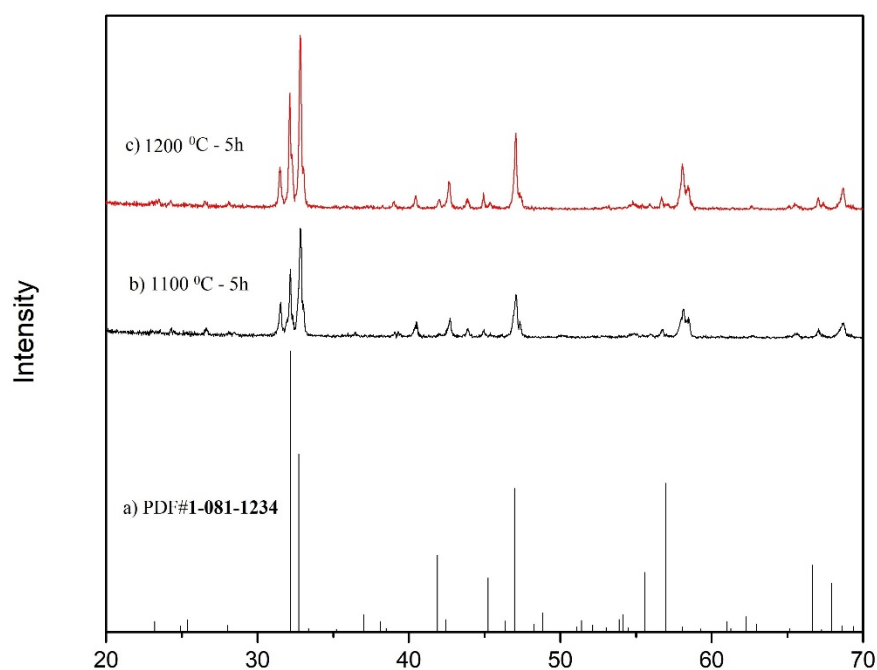


Figure A.1. a) JCPDF No. 1-081-1234, XRD patterns of LSF calcined at b) 1100 °C for 5 hours, c) 1200 °C for 5 hours.

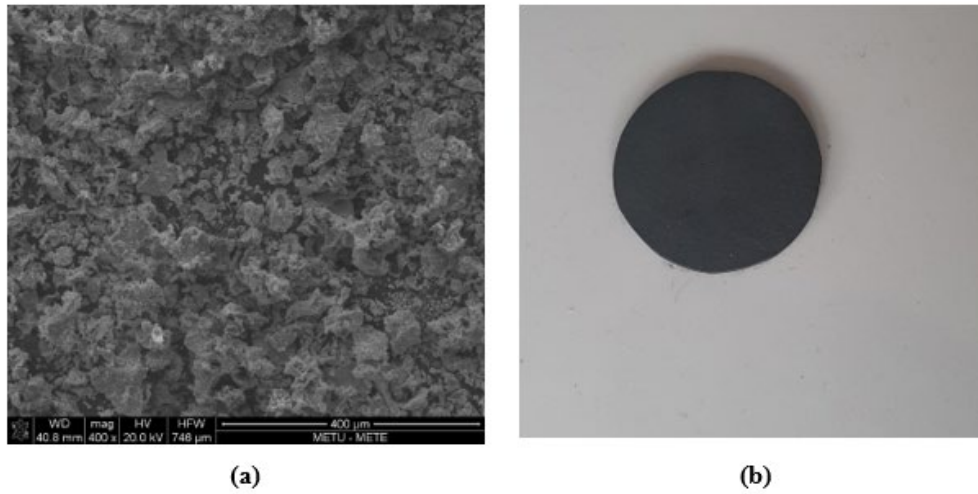


Figure A.2. a) SEM micrograph of rp-LSF powders calcined at 1200 °C for 5 hours, b) sintered and grinded 50mm target of rp-LSF to be used in sputter.

A.2 Electrolyte-Anode Bilayer Fabrication

For the production of anode supported electrolyte substrate (NiO-ScSZ/ScSZ, 50-50%), tape casting method is the most efficient one. Therefore, tape casting was chosen to fabricate the anode-electrolyte bilayers. The thickness aimed was 500 μm for the anode and the electrolyte should be as thin as possible to decrease the ohmic resistance of the electrolyte.

For the fabrication of NiO-ScSZ/ScSZ bilayer water based slurries[108] as well as alcohol based slurries were used[109,110] in the literature. Initial experiments using water based slurries were less successful therefore alcohol based slurry systems were used in this work. First electrolyte was cast. Ingredients used for the preparation electrolyte slurry is given in Table A.3. Slurry was prepared in two steps. First step involves mixing the active material, solvent, and the dispersant. After mixing, ball

milling was applied for 2 hours at 100rpm with 10mm zirconia balls. Second step involves the addition of binder and plasticizer onto the ball mill vial. This way, ball mill was continued for another 2 hours. The slurry was then cast onto mylar film (Polinas, Turkey). The film used for this purpose had a silicone coating for easy removal of the casting. The blade gap was adjusted to 350 μ m, and the slurry was cast at a speed of 7mm/sec.

Following the production of the electrolyte, anode was cast using similar method. Ingredients for the anode slurry is given in Table A.4. Rice starch was added to the composition as a pore former. The slurry was then cast on silicone coated mylar film. After casting, the tape was left for drying for an hour and successfully removed from the mylar film. After drying, the tape thickness was typically 100 μ m.

Table A.3 Amount of ingredients used in preparing electrolyte slurry.

<u>Active Material</u>	<u>Solvent</u>		<u>Dispersant</u>	<u>Binder</u>	<u>Plasticizer</u>
ScSZ	MEK	EtOH	Triethanolamine	Polyvinyl Butyral	Polyethylene glycol
4.24	2.60ml	2.60ml	0.17gr	0.44gr	0.44gr

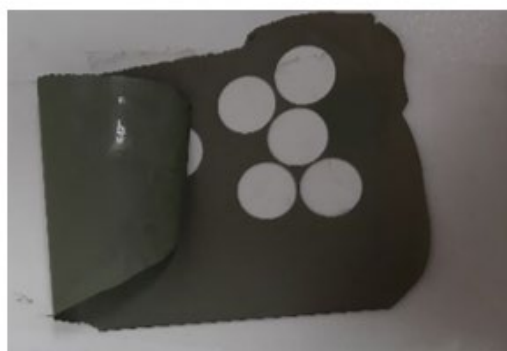
Table A.4 Amount of ingredients used in preparing anode slurry.

<u>Active Material</u>		<u>Solvent</u>		<u>Dispersant</u>	<u>Binder</u>	<u>Plasticizer</u>	<u>Pore Former</u>
ScSZ	NiO	MEK	EtOH	Triethanol amine	Polyvinyl Butyral	Polyethylene glycol	Rice Starch
2.12gr	2.12gr	2.60ml	2.64ml	0.17gr	0.44gr	0.44gr	0.473gr

Subsequently, 20mm diameter discs were cut from the electrolyte and anode tape, Figure A.3. These discs were typically 100 μm thick. For the bilayer, 6 anode discs and 1 electrolyte disc were placed on top of each other and were pressed at a pressure of 5MPa. An image of pressed bilayer is given in Figure A.4.



(a)



(b)

Figure A.3. Tapes stripped of silicone coated mylar a) electrolyte, b) anode. Disc cut to be pressed.



Figure A.4. Pressed anode-electrolyte half-cell a) anode surface, b) electrolyte surface.

In order to determine the sintering regime TGA measurement was taken up to 800 °C, Fig. A.5. This showed that a decrease in mass starts from 50 °C and accelerates after 200 °C. The mass loss is almost complete by 475 °C. Based on this measurement, bilayer was heated with a rate of 0.5 °C/min up to 250 °C where it was kept for an hour. Then it was continued heating with the same rate (0.5 °C/min) up to 700 °C and the heating rate was then increased to 1.5 °C/min and continued up to the sintering temperature and maintained there for 2.5 hours. The bilayer was then cooled to room temperature at a rate of 1.5 °C/min.

Sintering temperature for similar bilayer in literature varies between 1350-1450 °C[111,112]. Therefore, 3 different temperatures (1350 °C, 1450 °C, 1550 °C) were chosen for the initial sintering experiments. SEM images of the bilayers sintered at these temperatures are given in Figure A.6. It is seen clearly that; the density of the electrolyte increases with increase in sintering temperature. Since the electrolyte of the SOFC should be fully dense, 1550 °C seem to be the best sintering temperature for the electrolyte.

A common problem in sintering of bilayers were cracking of the electrolyte layer, as seen in , Fig A.7. This problem was quite severe at high sintering temperatures and could not be solved despite many efforts. Thus, it was not possible to use 1550

$^{\circ}\text{C}$ or 1450°C for sintering. The problem was less severe at 1350°C . Since the electrolyte appear to be quite dense at this temperature, Fig. A.6(a) 1350°C was chosen as sintering temperature for the bi-layers. A photograph of sintered bilayer is given in Fig. A.8.

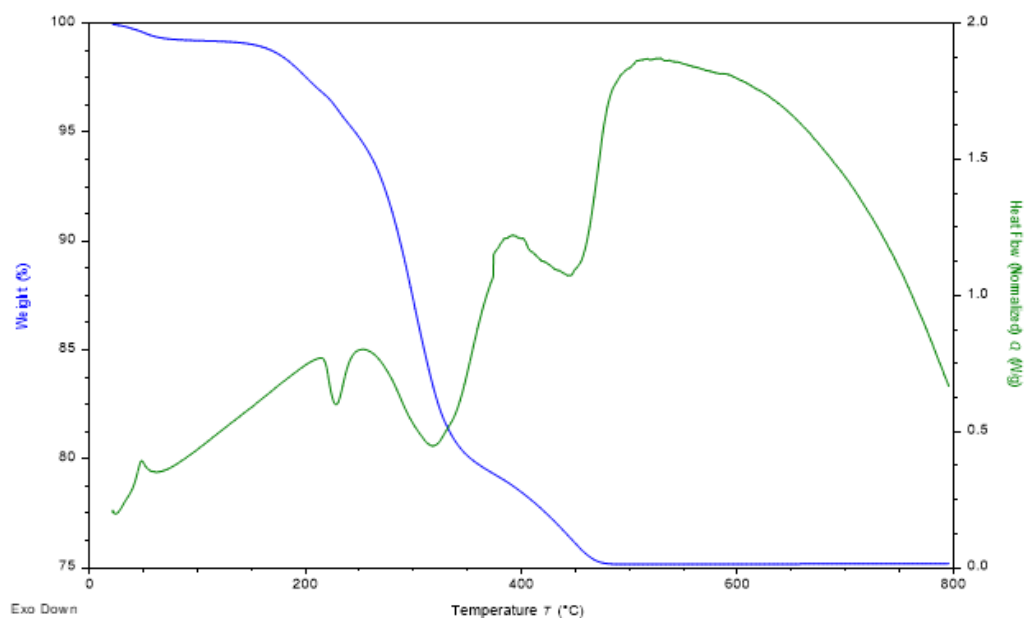


Figure A.5. TGA of ScSZ/ NiO-ScSZ half-cell.

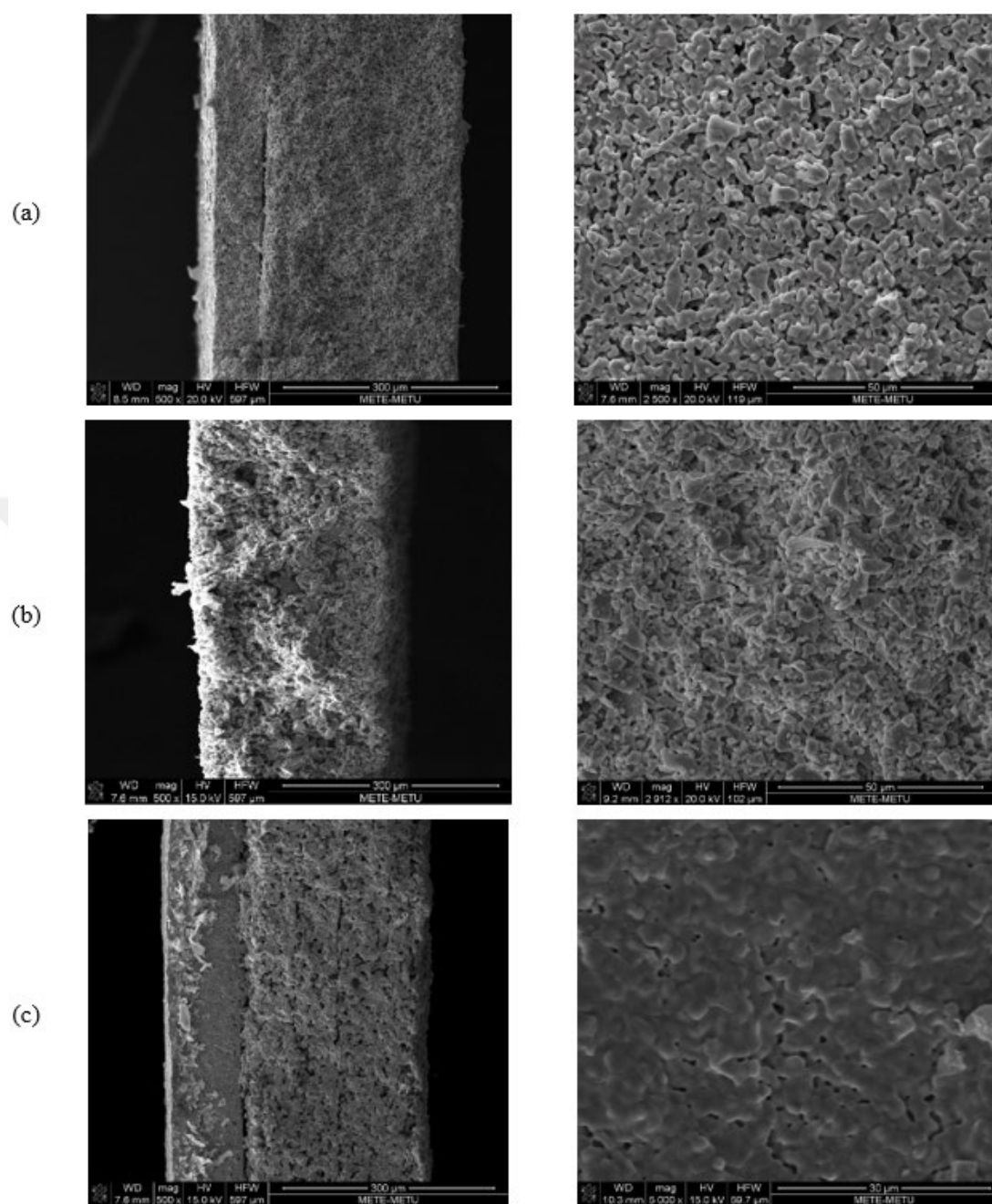


Figure A.6. SEM images of cross sections and electrolyte surfaces of bilayers sintered at **a)**1350 °C, **b)**1450 °C, **c)** 1550 °C.

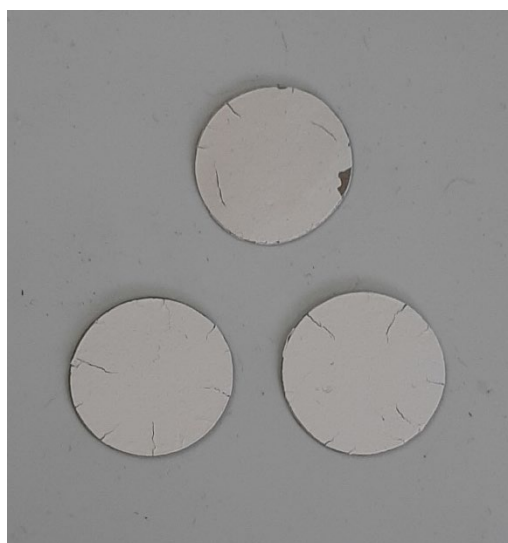
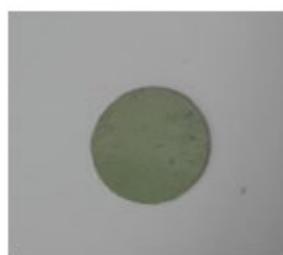


Figure A.7. Cracks in the electrolyte surfaces of bilayers sintered at 1550 °C.



(a)



(b)

Figure A.8. Sintered anode-electrolyte half-cell a) anode surface, b) electrolyte surface.

A.3 Combinatorial Deposition of Cathodes

Geometry of combinatorial cathode deposition was described in Chapter 3.3. Sputter targets prepared were loaded on the guns and the system was aligned as described in Chapter 3.3. Anode-electrolyte bilayer discs were loaded on the sample tray.

Since the tooling factor of for LSF and ScSZ were already determined in Chapter 4, only rp-LSF target was evaluated with respect to the tooling factor. For this

purpose, rp-LSF was placed to gun-3 and the deposition was continued for 2 hours onto borosilicate glass substrate. Power loading and the additional parameters for rp-LSF is given in Table A.5. For the rp-LSF target material, the initial tooling factor was set to 100, density and the Z factor were entered in the corresponding channel part of the indicator. After deposition, borosilicate glass substrate was then broken in two and were examined in SEM. An example is given in Figure A.9 which refer to the sample closest to the rp-LSF target, that is, at the corner of the triangle. Tooling factor determined for rp-LSF target is included in Table A.5.

Table A.5 Sputter deposition parameters used in determining the tooling factors.

Target	Plasma gas, Pressure(mTorr), Flow Rate (sccm)	RF power (Watt)	Time (Min)	Rate (Å/s)	Tooling factor
LSF	Ar-O ₂ , 5, 20-13	60	120	0,6	83
Rp-LSF	Ar-O ₂ , 5, 20-13	60	120	0,7	55
ScSZ	Ar-O ₂ , 5, 20-13	60	120	0,1	222

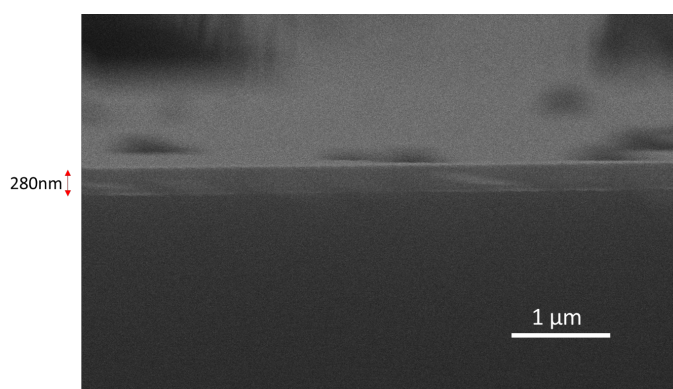


Figure A.9. Film thickness obtained as a result of coating while determining the tooling factor of rp-LSF.

Following the determination of the tooling factor, an experiment was carried out using aluminum substrates. A total 21 aluminum substrates were placed in the sample tray. In the experiment, sputter deposition was continued for 10 hours. The sputtering parameters used during this coating are given in Table A.6. EDS analysis was taken from each of the 21 substrates. In this analysis, three elements were chosen to check the chemistry of the cathodes. These were La Fe and Zr. Since there were two LSF targets with different stoichiometries, La/Fe ratio was taken as the basis when calculating LSF/rp-LSF ratio. Because of the atomic ratio, La/Fe, in each of the two LSF phases are different, this ratio can be used to determine the relative fraction of each phase. La, Fe and Zr contents and the corresponding molar fraction of LSF, rp-LSF and ScSZ are given in Table A.7.

The results are shown plotted in LSF, rp-LSF and ScSZ ternary diagram, Figure A.10. It is seen that the cathodes are distributed relatively homogenously in the ternary compositional field , though there is a slight shift of compositions towards ScSZ corner. The samples obtained by the combinatorial approach were structurally characterized by X-ray diffraction, Fig A.11. Here as in previous chapter, parts of the diffractogram from $10 < 2\theta < 38$ are given so as to exclude Al peaks. It is seen that all samples are amorphous with a very broad peak at $2\theta = 30^\circ$

Table A.6 Sputter parameters of the coating made on aluminum substrate.

Gun	Plasma gas, Pressure(mTorr), Flow Rate (sccm)	RF power (Watt)	Time (Min)	Rate (Å/s)
LSF	Ar-O ₂ , 5, 20-13	60	600	0.9
Rp-LSF	Ar-O ₂ , 5, 20-13	60	600	1.1
ScSZ	Ar-O ₂ , 5, 20-13	100	600	0.4

Table A.7 La, Fe, Zr content of cathodes deposited on Al substrate and the corresponding composition of composite cathodes in terms of LSF, rp-LSF, ScSZ.

	La	Fe	Zr	LSF	Rp-LSF	ScSZ
1	35.0	41.9	10.0	86.3	1.5	12.2
2	24.2	44.5	10.6	47.7	10.4	41.9
3	22.6	44.8	10.2	49.5	15.4	35.1
4	20.5	41.4	13.1	30.2	11.3	58.5
5	19.6	42.5	11.4	31.3	16	52.7
6	19.0	43.8	8.8	35.1	24.2	40.7
7	15.7	37.1	19.9	16.4	9.2	74.2
8	17.4	38.6	14.8	20.7	14.6	64.7
9	18.5	44.1	10.4	31.1	19.3	49.4
10	18.6	45.5	6.3	33.1	26.7	40.1
11	14.4	30.3	27.9	11.1	5.1	83.8
12	14.8	36.0	19.1	11.3	18.7	69.9
13	18.3	41.4	12.7	31.4	12.9	55.6
14	22.0	42.9	10.3	39.8	14.8	45.4
15	22.5	37.4	7.6	40.7	27.7	31.6
16	13.5	26.4	35.9	24.8	5.3	69.9
17	13.3	26.5	24.4	14.6	19.4	66
18	13.1	30.2	14.2	2.2	21.2	76.6
19	17.3	30.8	11.9	14	28.4	57.6
20	27.5	36.2	13.5	5.9	37.2	56.9
21	28.7	43.2	6.54	16.1	42.7	41.1

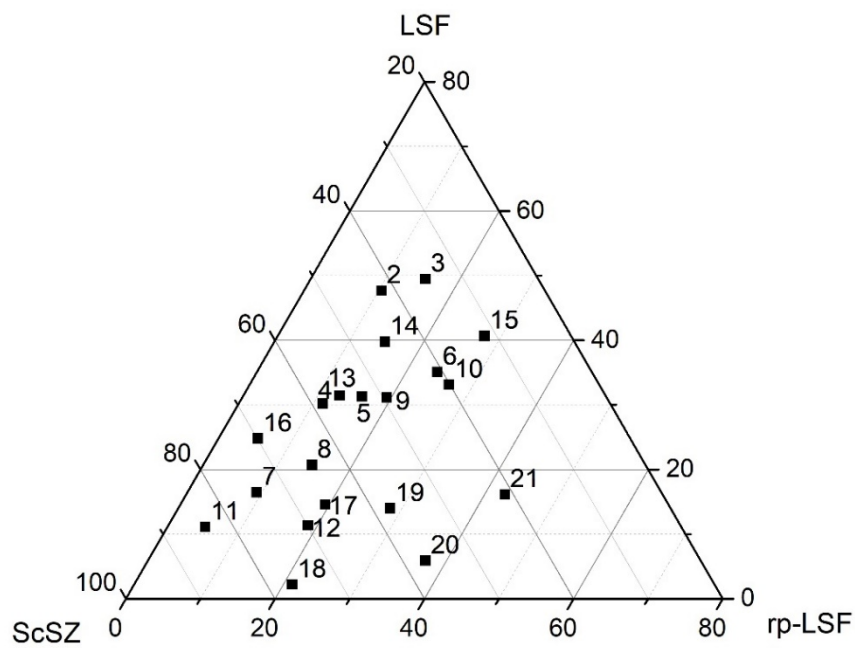


Figure A.10. Distribution of samples produced by combinatorial approach in ternary diagram.

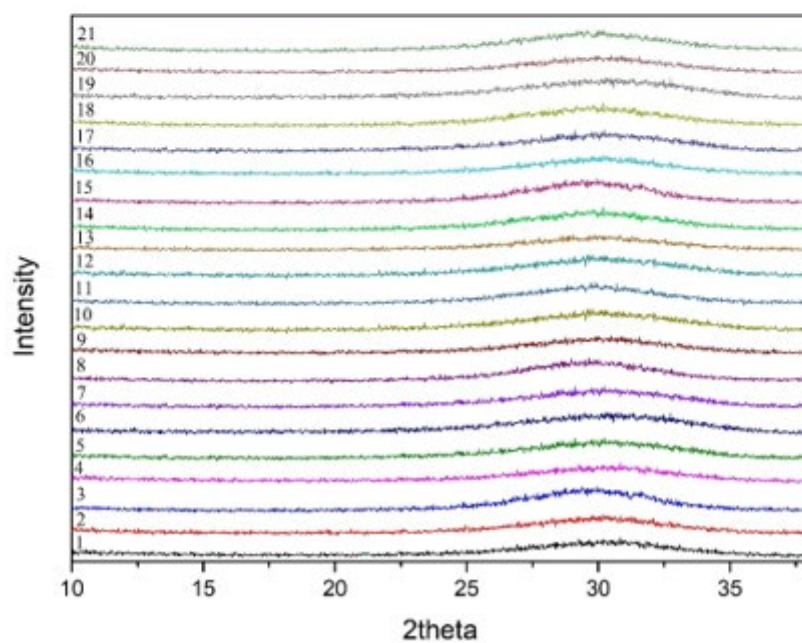
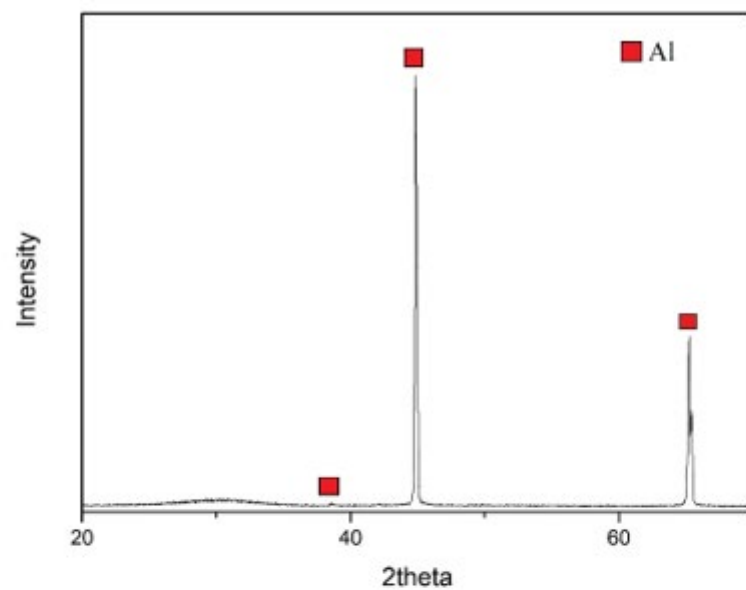


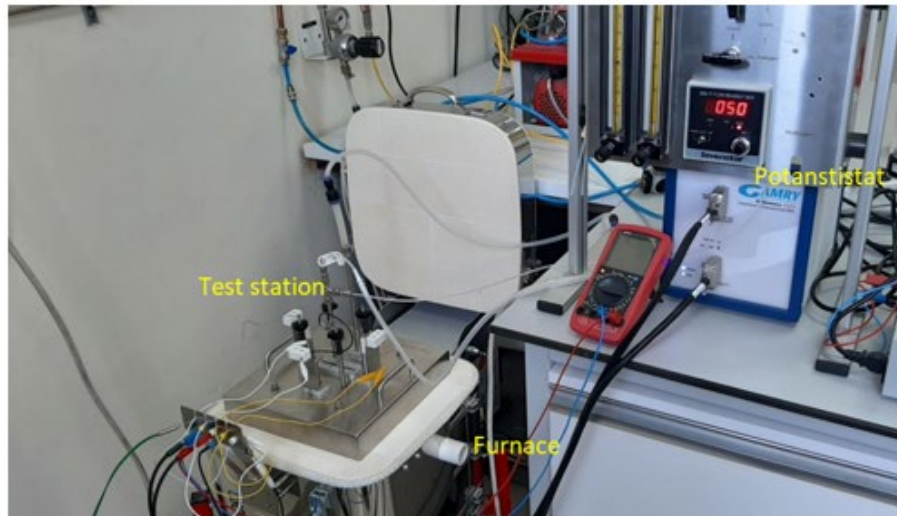
Figure A.11. XRD diffraction pattern of **a)** Cathode number 1, **b)** Al-excluded patterns of all cathodes deposited on aluminum substrate.

A.4 Full Cell Electrochemical Characterization

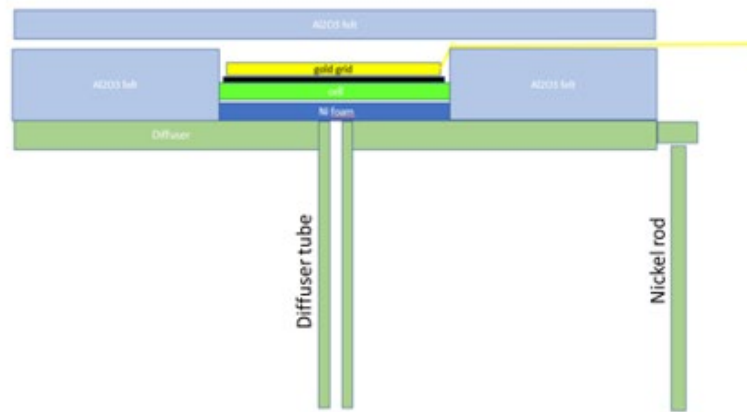
A.4.1 Method

Electrochemical characterization of the full cells was performed using open flange test setup from Fiaxell SOFC Technologies. The system consists of a furnace, test station and the Potentiostat, Figure A.12(a). Schematic representation of test station is given in Fig A.12(b). Here the full cell is centered onto the test station on top of a diffuser plate with a central tube connected to the gas line. The vertical nickel rod at the side is used for anode electrical connection. The cells were squeezed between soft alumina felts so as to prevent any damage to it. Cathode connection was made with a gold grid with a connection wire made of gold also.

Four external springs were used to ensure a controlled and constant pressure on the cell during the whole measurements. The gas channels in the setup were Inconel 600&601. Whole setup was placed on a furnace (Kittec, Germany) and tested on different elevated temperatures. The designed setup can be used for different cell sizes. The detailed usage of the setup is given below.



(a)



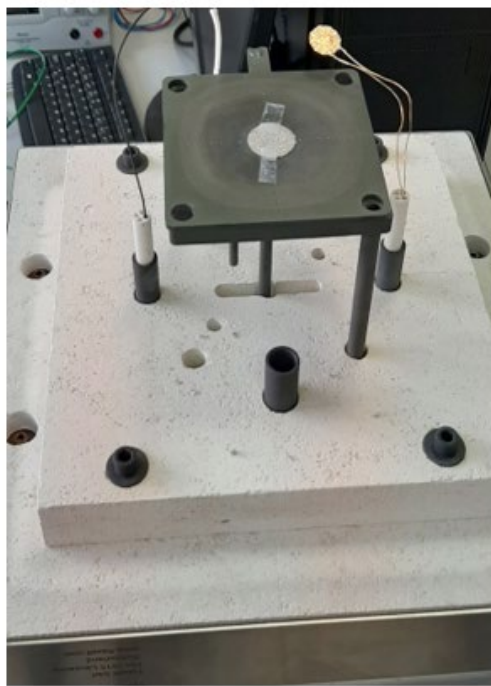
(b)

Figure A.122. a) Photograph of open-flange set-up b) Schematic drawing of test station.

The experiment involved the following steps. Test station was placed upside down. Then, a piece of nickel foam with the dimension of the cell or slightly smaller is cut. Nickel foam was placed on the center of the setup and fixed with the fast glue or a small piece of scotch tape. Then the cell is placed on the nickel foam anode side down and secured with a small piece of scotch tape, Fig A.13. The purpose of nickel

foam underneath is to spread the fuel(hydrogen) over the whole anode surface. (Scotch tape is burned off during the test and does not affect the experiment).

Then alumino-silica felt with a size slightly larger than the furnace cross-section was cut and placed on top of the cell. The center of the felt was punched out with a size slightly larger than the cathode, but smaller than the cell. Then the gold current collector was placed on top of cathode surface. The previously punched out disc felt is placed on top of the gold grid, and the second felt with a size close to the first one was placed on top to ensure the electrical insulation, Fig A.14.



(a)



(b)

Figure A.133. Back side of the test station. a) Nickel foam in the center of the setup, b) Cell on top of nickel foam.

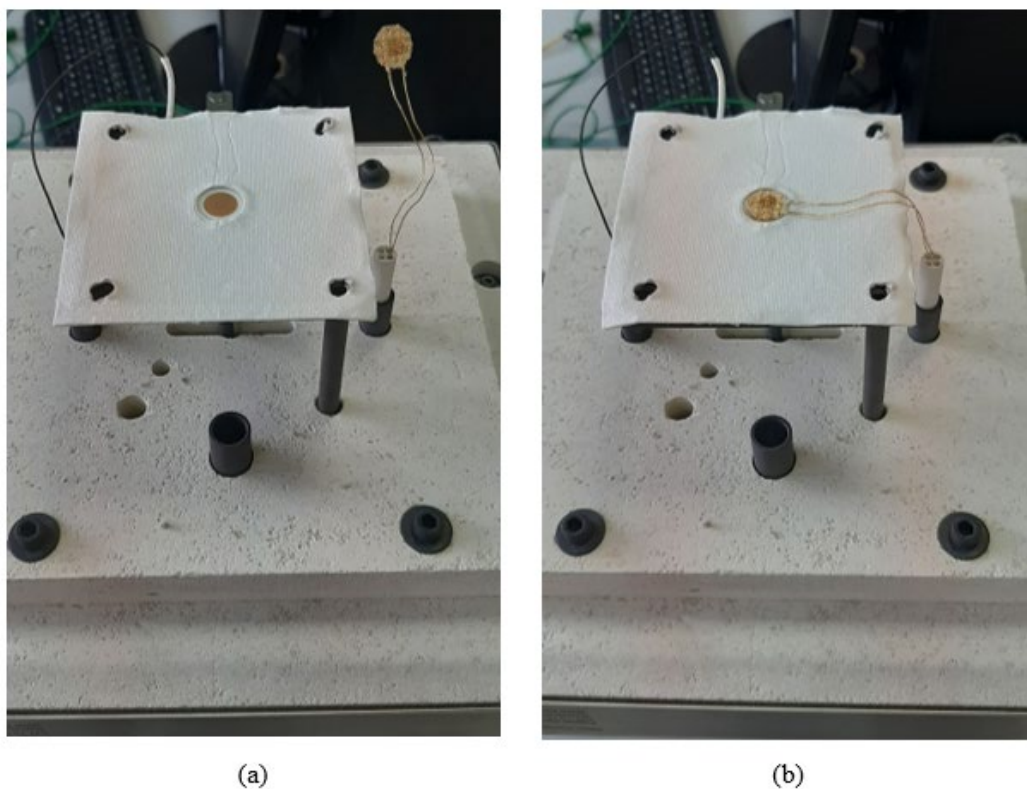


Figure A.144. a) Alumino-silica felt on top of the cell, b) Gold current collector placed on the cathode.

The setup as prepared was closed by placing a flange, Fig. A.15. Threaded rods were inserted through the supporting tubes two of which was stationary and the other two were inserted in place. Threaded rods were secured in place by tightening wing nuts on opposite side of the set-up while maintaining the set-up upside down. During tightening, the first metallic washer, the spring, the second metallic washer and the wing nut was placed in sequence, Fig. A.16.

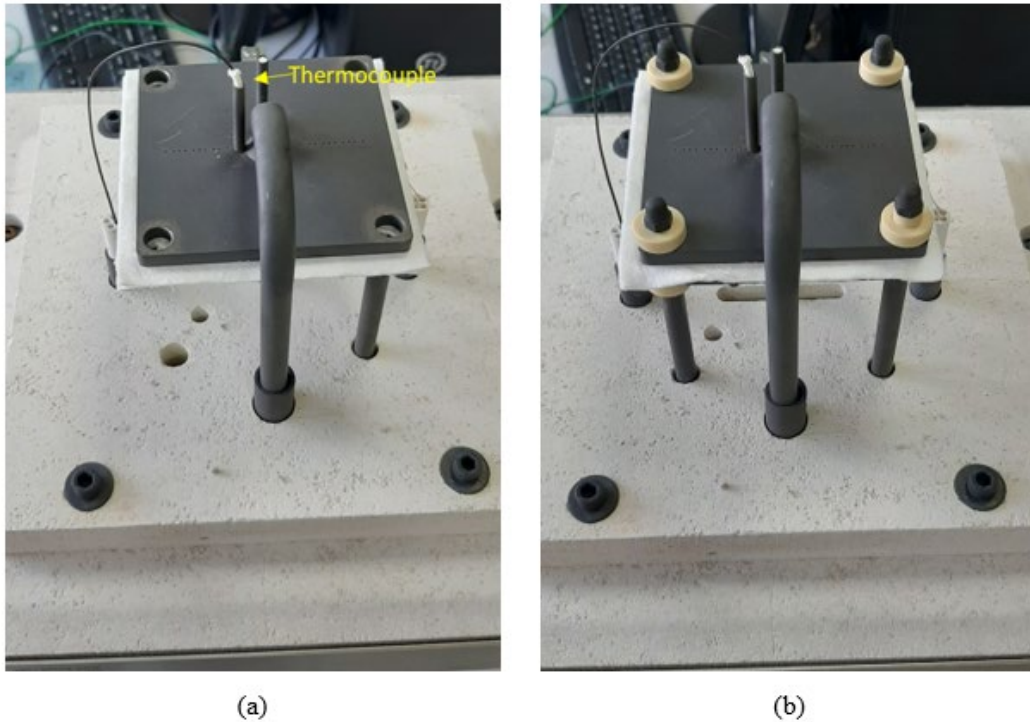


Figure A.155. a) Upper flange , b) Threaded rods that was inserted through the corner holes.

The setup was turned around for spring tightening. Springs are tightened maximum of 2 mm and controlled with a caliper(initial spring length = 29.5mm, spring constant = 2.8kg/mm). After that thermocouple is placed on either one of two holes shown in Fig. A.15(a).

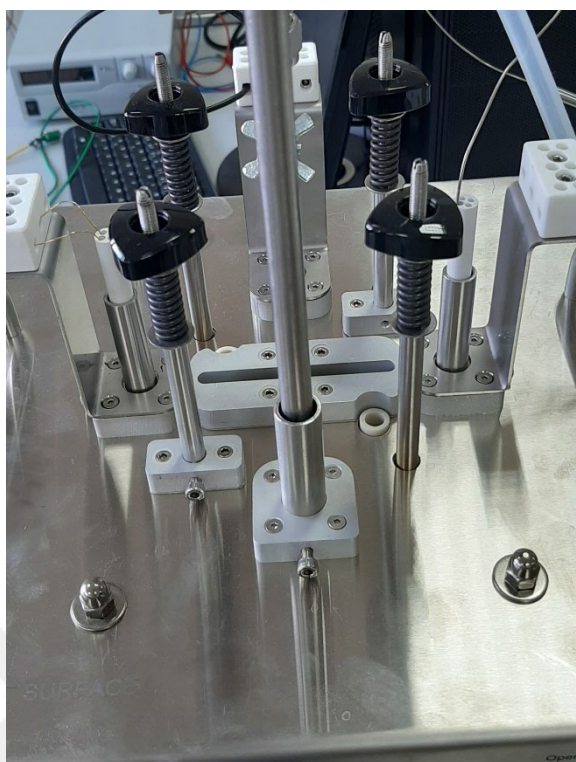


Figure A.166. Front side of the set-up showing the tightening nuts securing the flange in place.

Setup was placed carefully in the furnace supported from the edges. Gas connections, one for the fuel (hydrogen), the other for air were made carefully using silicon tubes ensuring that there would be no leak, Fig A.17.

The test was initiated by heating the furnace to the selected temperature while feeding air (400sccm) to both inlets of the setup. This allows burning of the scotch tape and glue used during the mounting of the cell. After the furnace has reached the programmed temperature, springs were adjusted once again (to 27.5 mm) because during the heating of the setup, the alumina felts shrink due to organic burning. Then, the anode feeding tube is flushed with 200 sccm argon (or nitrogen) for at least 5 minutes to ensure a safe use. Then the hydrogen is gently added to the fuel gas line

and increased slowly till reaching the desired flow rate. At the same time, inert gas(argon/nitrogen) is slowly decreased and finally stopped.

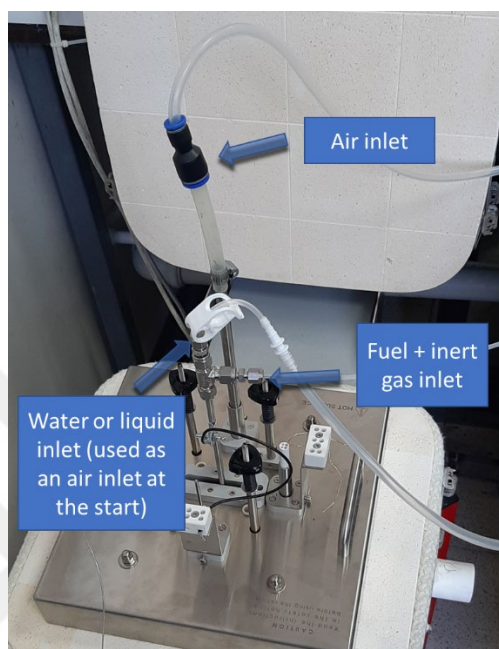


Figure A.177. Air and fuel inlets on the setup.

Two connections were made both for anode and cathode. For anode one connection was made at the middle fuel tube connected to the diffuser, the other via 3 mm nickel rod at the side. Similarly, two connections were made from the cathode using two gold wires connected to the same grid, Fig A.18.

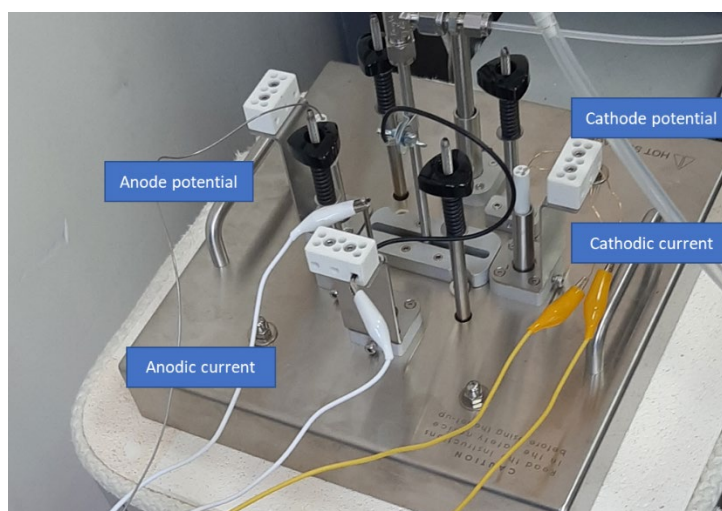


Figure A.188. Current and potential control points on the setup.

The measurements were made via I-V curves using Gamry ref. 3000 Potentiostat/Galvanostat. For this purpose, I-V curves were measured by scanning the potential from the 0.2V to the OCV with a scan rate of 10mV/s and data taken from intervals of 10mV.

A.4.2 Results

Electrochemical characterization of cathodes produced with combinatorial approach was performed by full cell measurements. A schematic representation of the full cell is given in Figure A.19. Here anode-electrolyte bilayer used as a substrate was masked with 12 mm diameter stainless steel ring. This was for the purpose of handling the full cell without the risk of short circuit between anode and cathode.

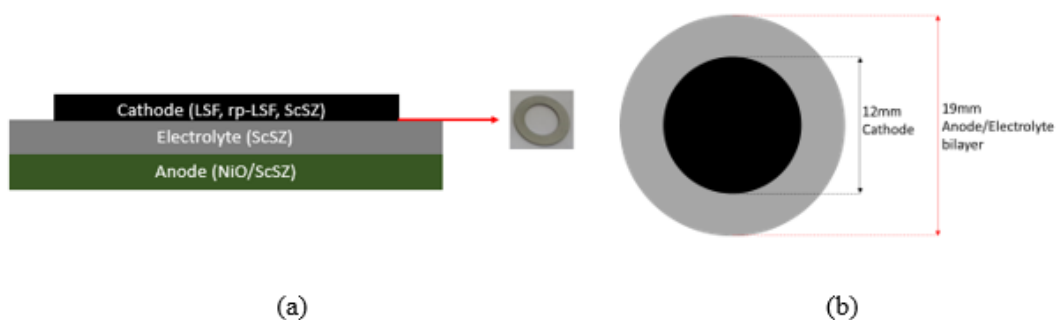


Figure A.199. Schematic representation of full cell used in electrochemical characterization a) Full cell section view, b) View of the cell in the disc plane.

For fabricating the full cell in the geometry given in Fig. A.19 bilayer substrates were placed in the substrate holder. Stainless steel rings of 12 mm inner diameter and 19 mm outer diameter were placed on these substrates for masking purposes. Then the respective targets, ScSZ LSF rp-LSF were secured in place in sputter guns. The chamber was then taken to a vacuum of 1×10^{-6} torr, and subsequently the Ar input was adjusted to 20sccm and O_2 input was adjusted to 13sccm, and the gate valve was adjusted to keep the vacuum level at 5mtorr.

All three target materials were operated at the parameters given in Table A.6 and the coating was continued for a total of 6 hours. The coating thickness obtained as a result of this process was typically 600 nm.

Before the cells were characterized in the open-flange, a sacrificial cell was used for running-in. This was for the purpose of possible chromium deposition at high temperatures which might take place from the Inconel rods used in the set-up. For this purpose, the sacrificial cell was mounted on the setup and was run feeding air through both inlets at $800^\circ C$ for 24 hours. This was for the purpose of oxidizing the inner surface of the Inconel rods.

Before testing the current cells, two well-known samples were tested so as to check the performance of the open flange system. The cells tested composed of LSCF cathode, GDC electrolyte and Ni-GDC anode. Following running-in, the cell was tested by recording I-V curves between 500-700 °C with 50 °C intervals.

For this purpose, hydrogen was maintained at a flow rate of 80sccm, and air was supplied at a rate of 400sccm. Open circuit voltage (OCV) measured is given in Figure A.20. Here it is seen that OCV has a value of 0.97V. (Here OCV value of sacrificial cell was also included where the value was significantly less indicating that the cell performance was affected by running-in test)

Theoretical OCV, U_n , as calculated with

$$U_n = U_g - \frac{R \cdot T}{n \cdot F} \ln (Kp)$$

where Kp is the equilibrium constant of the $H_2 + \frac{1}{2}O_2 = H_2O$ reaction, T is the temperature, R is the gas constant yields a value of 1.01 V which is close to the measured value of 0.97V.

After determination of the OCV and the power density of the cell was evaluated via I-V curves. I-V curve at 600 °C is shown in Fig. A.21. It should be noted that V at zero current has a value of 0.97V which agrees with the OCV curves. Power calculated based on this data is included in the curve. It is seen that power reaches a maximum at 0.55V and 0.45A/cm². Since the current cells has a cathode area of 1.53 cm² (14 mm diameter), the cell has a power density of 0.248W/cm². This value is comparable to that found by Leng et al[113] whose cell was quite similar to the current cell except for the fact that the cathode was a composite of LSCF/GDC rather than a single oxide LSCF. They have achieved the maximum power density of 262 mWcm⁻² at 600 °C with a cathode composition of LSCF/GDC as 40/60%.

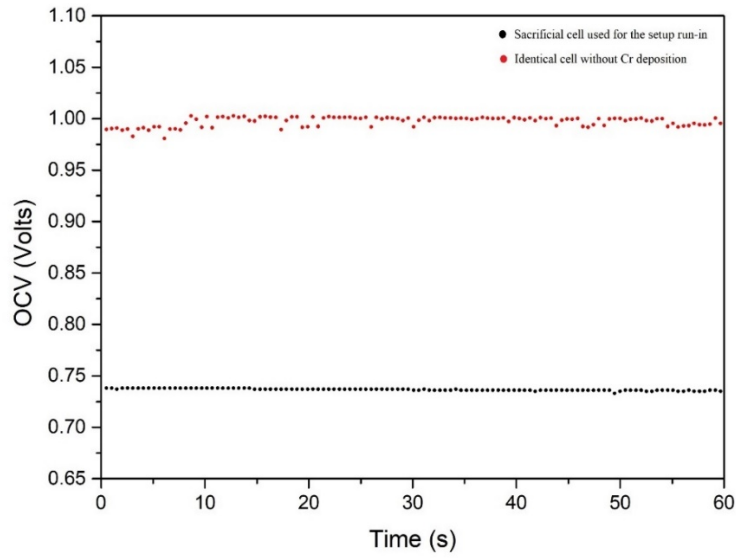


Figure A.200. OCV curves of two identical cells at 600 °C, one used for the setup run-in (sacrificed) and other one used to compare how chromium deposition effects the cell. Cells were composed of GDC electrolyte, NiO/GDC anode and the LSCF cathode.

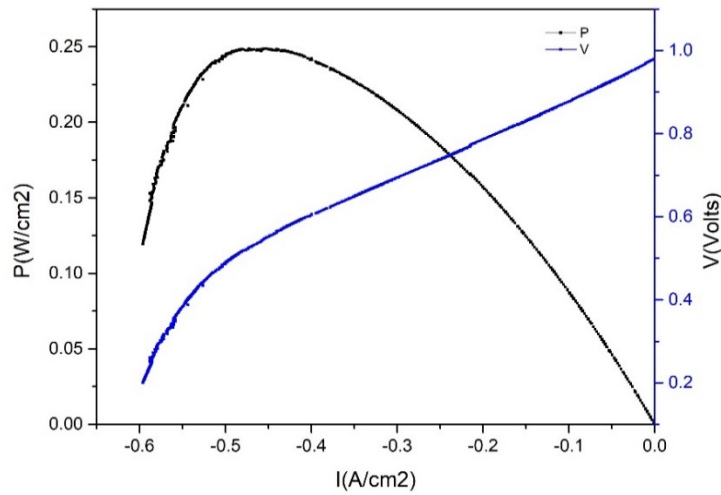


Figure A.211. I-V curve of the non-contaminated cell at 600 °C.

Having checked that the measurement yields a reliable result, the full cells developed via combinatorial approach was evaluated at 600 °C under 400sccm air/ 80sccm H₂ flow. First OCV were determined for a cell close to rp-LSF corner of the triangle, Fig. A.22 Surprisingly OCV which had a value of 0.53 V was very much less than the expected value. Then the other cells were evaluated in terms of OCV, and the results were in the range of 0.35-0.55V.

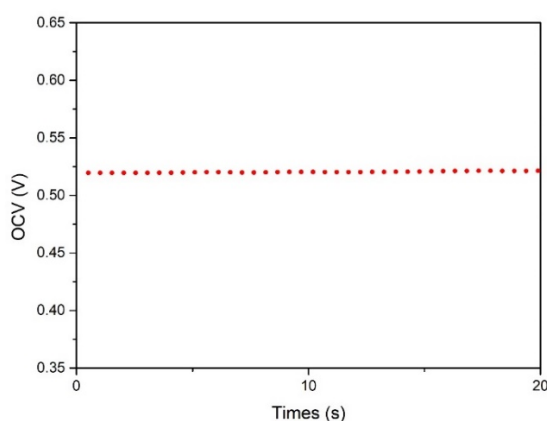


Figure A.222. OCV curve of the cell no: 21 fabricated via combinatorial approach.

Generally, the low OCV of the SOFCs can be attributed to three fundamental problems. One is the low fuel passage from the anode. This is caused by the very low number of pores in the anode. However, this is not the case in this system since the SEM image of the Ni-ScSZ anode given in Fig. A.23(a) shows highly porous structure. The second possible problem is the low performance of the cathode layer. This is basically a materials problem where cathode layer is reducing the O₂ poorly. Since LSF and rp-LSF are mixed ionic and electronic conductors, there is a low chance that cathodes of the full cells in this thesis have low performance towards ORR.

Third possible issue that can cause low OCV is the electrolyte porosity. Porous electrolyte of SOFCs can cause short circuiting and the poor fuel and oxidant

efficiency. This is likely the case in this system. From this point of view, when we look at the cross-sectional view of the half-cell, it is seen that the electrolyte is not at full density, Fig. A.23(b).

To further investigate this problem, OCV values were observed at different hydrogen flows, Fig. A.24. OCV curve showed that OCV decreases at hydrogen flow of more than 80 sccm. The decrease in OCV with increasing hydrogen flow addresses a structural problem. This problem also suggests that low OCV can be caused by pores in the electrolyte. As such, it is not possible to create a logical I-V curves from these cells since the OCVs are very low.

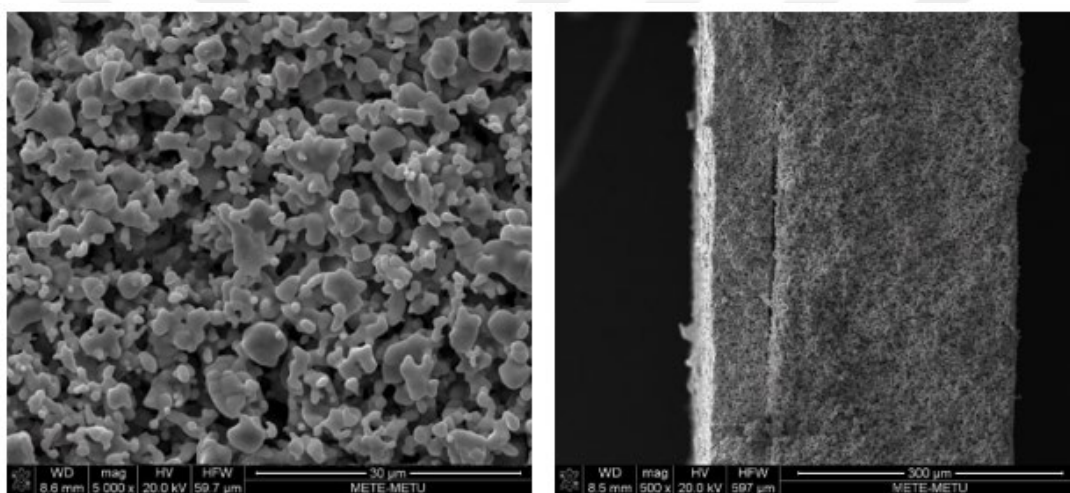


Figure A.233. SEM image of the **a)** NiO/SCSZ anode structure, **b)** Bilayer cross section in a half cell sintered at 1350 °C for 2.5 hours.

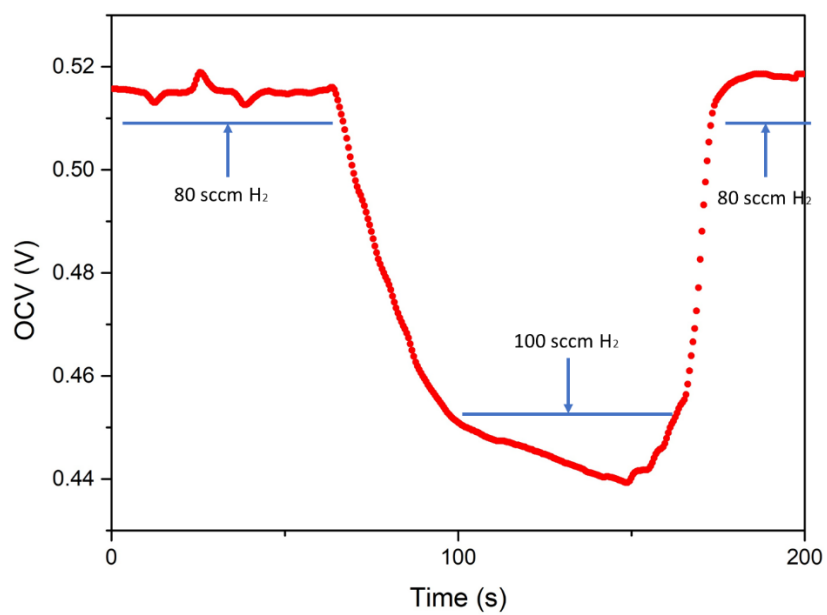


Figure A.244. Change in OCV with time for cell no: 21. Note that, OCV decreases when hydrogen flow increases above 80 sccm.