

Fabrication of Proton Conducting Electrochemical Half-cell Based on Perovskite Structure Material

by

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A thesis

presented to the University Of Waterloo

in fulfillment of the

thesis requirement for the degree of

Master of Applied Science

in

Mechanical and Mechatronics Engineering

Waterloo, Ontario, Canada, 2024

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Author's Declaration

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Abstract

The rising concerns about CO_2 emissions from industrial processes and fossil fuel combustion are driving the development of clean energy sources. Among these, hydrogen energy stands out as an efficient carrier with high storage capacity and minimal environmental impact. This thesis focuses on the fabrication of a solid oxide electrochemical half-cell (SOC) based on proton-conducting materials in a perovskite structure, which can be used for hydrogen generation or utilization. The primary material used is Barium Zirconium Cerium Yttrium Oxide (BZCY) due to its proton conductivity, chemical stability, and mechanical strength under varying conditions.

In this work, several nanomaterials synthesis methods were utilized, including sol-gel and combustion processes, to achieve high-purity BZCY172 material with the desired particle size and composition. A variety of membrane fabrication techniques, such as screen printing, dry pressing, and manual blade coating were employed to construct the bi-layer electrolyte membranes, aiming for uniformity and high-density. Through extensive experimentation, the optimal sintering temperature for the bi-layer membrane was determined, which successfully produced a dense electrolyte layer with a thickness of $20\text{-}30\mu\text{m}$. Furthermore, the maximal diffusion coefficient (D_o) and activation energy for diffusion (E_a) values for barium ion diffusion within the BZCY172 material were determined using Fick's second law model based on experimental data, offering new insights into material performance under high-temperature conditions.

This thesis also tackled key challenges in proton-conducting SOC fabrication, such as optimizing the sintering process to enhance densification, controlling barium evaporation during high-temperature sintering, and incorporating suitable additives to promote grain growth and reduce porosity. Characterization techniques, including X-ray diffraction (XRD) and scanning electron microscopy (SEM), were employed to analyze the microstructure and chemical composition of the synthesized materials and fabricated membranes, further advancing the understanding of their performance in electrochemical applications.

Overall, this research contributed to the field of hydrogen energy and proton-conducting SOC by providing a detailed investigation into the fabrication and optimization of BZCY-based electrochemical systems.

Acknowledgements

First and foremost, I want to express my sincerest gratitude to my supervisors, Professor Xiaoyu Wu, in the Department of Mechanical and Mechatronics Engineering. His insightful feedback, patience, and expertise have been invaluable in shaping this work. I am profoundly grateful for his mentorship, which has greatly contributed to both my academic and personal growth. Thank you for believing in me and for your constant dedication to my success.

Additionally, I want to acknowledge Professor Eric Croiset of the Department of Chemical Engineering for his invaluable assistance in this research and his generosity in allowing me to work in his lab, and Professor Peng Peng in the Mechanical and Mechatronics Engineering department for being a valuable committee member. Thank you all for providing me the chance to conduct this research and offering me valuable suggestions during my study.

Next, I would like to thank the entire team at Greener Production Group led by Professor Xiaoyu Wu at the University of Waterloo for their contributions to the field and their valuable insights. Thank everyone for consistently supporting me, my research, and providing such a positive collaborative environment.

Meanwhile, I would like to recognize the financial support of the Government of Canada, New Frontiers in Research Fund for their contribution was essential to the project.

Last but not least, I would like to thank my wife, parents, and friends, who have been always the strongest support in my life and my study. Their kind words and encouragements have helped me go through challenges and obstacles.

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Chapter 1

Literature Review

1.1 Chapter Introduction

This chapter provides an in-depth introduction to Solid Oxide Electrochemical Cells (SOCs), detailing their definition, advantages, and disadvantages. It examines suitable proton-conducting materials for optimal SOC performance and discusses various powder synthesis methods, emphasizing the importance of selecting the appropriate method for specific applications. The chapter also covers membrane production techniques, highlighting the need for advanced equipment and approaches to ensure high-quality membranes. Additionally, it summarizes the challenges in membrane fabrication, emphasizing the complexities and hurdles in developing efficient and reliable SOC membranes.

1.2 Solid Oxide Electrochemical Cell (SOC)

A solid oxide electrochemical cell is a high temperature device that can efficiently convert chemical energy into electricity and vice versa. It operates using solid electrolytes and electrodes at temperatures ranging from 500°C to 1000°C [1]. This fuel cell system has two operating modes, using fuels like hydrogen to generate electricity is called solid oxide fuel cells (SOFCs), or an external direct current power is applied to produce hydrogen from water splitting which is named solid oxide electrolysis cells (SOECs) [2]. The key components like electrodes and electrolytes play crucial roles in the overall performance. Research has focused on optimizing materials and fabrication techniques to enhance the efficiency and stability of solid oxide electrochemical cells [3]. Long-term stability tests have been conducted to understand the degradation mechanisms in solid oxide electrochemical cells, aiming to overcome performance loss issues during extended operation [4]. Overall, SOCs hold great promise for sustainable energy storage and conversion.

1.2.1 Solid Oxide Fuel Cell (SOFC)

The SOFC is an efficient device converting chemical to electrical energy, consisting of a solid electrolyte, cathode, and anode. The oxygen reduction reaction (ORR) happens at the cathode side, the oxide ions are produced and migrated through the dense electrolyte layer to the anode side. Hydrogen (H_2) gas as the fuel reacts with oxygen ions to produce electrons at the anode side. The generated electrons are transported through an external circuit and back to the cathode keeping the process going, as shown in Figure 1-1.

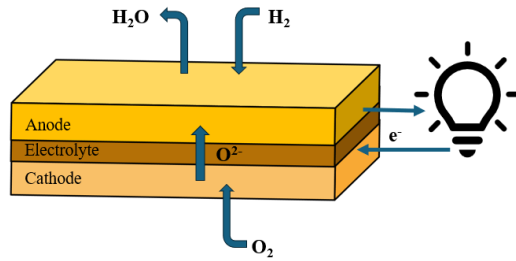
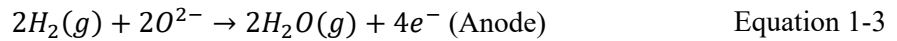
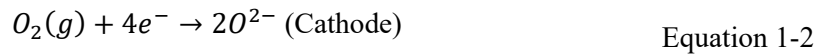
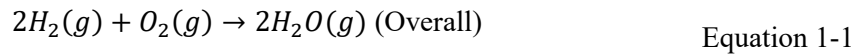


Figure 1-1. Scheme of a solid oxide fuel cell

The overall reaction of solid oxide fuel cell, and the reaction in the cathode and anode sides are:



1.2.2 Solid Oxide Electrolysis Cell (SOEC)

A SOEC can convert electrical energy into chemical energy by electrolyzing water to produce hydrogen and oxygen. While the water (H_2O) splits into hydrogen (H_2) and oxygen (O_2) at the cathode, oxygen ions and electrons are generated and migrated to the anode through the electrolyte layer, and electrons are transported again via an external circuit to the cathode side. Then, hydrogen is produced on the cathode side, as shown in Figure 1-2.

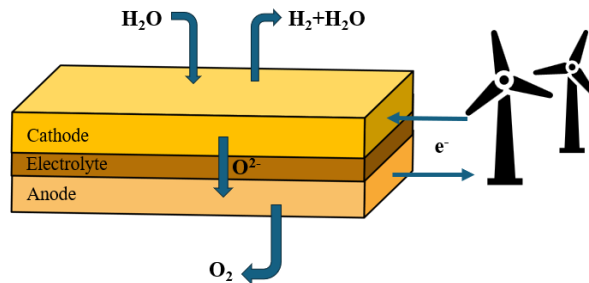
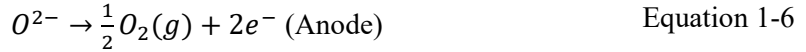
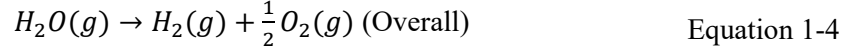


Figure 1-2. Scheme of a solid oxide electrolysis cell

Also, as temperature increases, the amount of electrical energy is reduced to decompose water [5]. The overall reaction of water electrolysis, and the reaction in the cathode and anode sides are:



1.2.3 Advantages of Solid Oxide Fuel Cell System

For this fuel cell system, it employs various materials. The electrolyte is typically made of a dense ceramic material that allows oxide ions to migrate from one electrode to another based on its mode [6]. There are two types of electrolyte materials, ion conducting materials and proton conducting materials. For example, yttria-stabilized zirconia (YSZ) is used for electrolytes and nickel-YSZ for fuel electrodes; the cell operates at high temperature from 800°C to 1000°C for high ionic conductivity and chemical stability [5]. For the proton conducting electrolyte, for example, yttrium doped-barium zirconate (BZY) and the cerate–zirconate (BZCY), it operates between 500°C to 700°C, in electrolysis mode, only hydrogen is generated in the hydrogen electrode and there is no need for gas separator to separate water steam and hydrogen [5]. Moreover, for either oxygen or proton conducting electrolyte, the electrolyte material should not exist electronic conductivity to prevent short-circuiting of the cell [6].

Solid oxide fuel cell system is a high temperature device range from 500°C to 1000°C [1]. It aims to achieve electrochemical reaction at elevated temperatures. This is advantageous for applications that require high-temperature reactions. For example, the ammonia decomposition happens at quite high temperature without presence of catalyst because of strong hydrogen bonds within ammonia molecules [7], usually temperature range between 800°C and 1000°C, and pressure range between 5000 Kpa and 20000 Kpa [8]. So, this high temperature capability is particularly beneficial for processes like ammonia decomposition.

High temperature fuel cell systems avoid using precious metal material. For instance, ruthenium (Ru) is the most active single-metal catalyst for the ammonia decomposition, most of the literature cited about Ru-based catalysts [9], [10], which accelerate the decomposition of ammonia at lower temperature. However, the high cost of Ru necessitates the exploration of alternative catalyst

materials for commercial applications [8]. Elevating the operating temperature obviates the need for employing costly catalysts in this case.

Entirely solid state of SOC can allow more complex designs. Tubular design and planar design show the flexibility of SOFC/SOEC, see Figure 1-3.

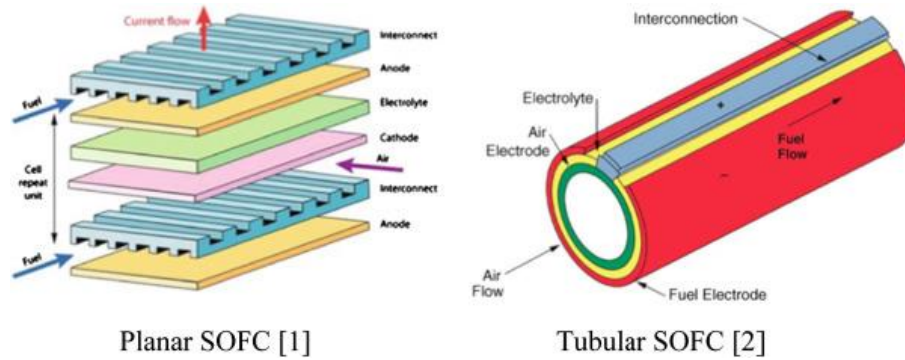


Figure 1-3. Solid oxide fuel cell of planar configuration and tubular configuration (Reprinted from [11] with permission from Elsevier)

Tubular design can enhance mass transport and power density performance [12]. Extrusion-based methods allow for large-scale production of tubular solid oxide fuel cells. Its geometry provides higher mechanical strength compared to planar design of same wall thickness [13]. This section means to demonstrate the potential designs for solid oxide fuel. Different designs are enabled by solid state depending on practical requirements.

1.2.4 Disadvantages of SOC System

SOCs provide numerous advantages, such as high energy conversion efficiencies, low pollution exhaust, and fuel flexibility, making them promising alternatives to traditional electrical generators [14]. However, there are several disadvantages associated with SOC systems. A primary limitation is the elevated operational temperatures necessary, typically falling within the range of 800 to 1000°C. Although the high operating temperature of SOC offer advantages, such as avoiding using precious metal as catalysts, it also presents notable disadvantages. It limits their widespread industrial application due to issues like long start-up periods and material degradation concerns [15]. Additionally, the long-term stability of SOC electrodes in different gas environments poses a challenge, particularly with Nickel-cermet anodes experiencing volume changes during redox cycles that can lead to cell failure [16]. Furthermore, the use of producer gas (carbon monoxide, H_2) as a fuel source for

SOCs presents challenges due to contaminants like tar, particulate matter, and hydrogen sulfide (H_2S), which can impact anode materials and require further research for identifying maximum tolerance limits [17]. The technology of SOC are ongoing research and development within the scientific community and commercialization.

1.3 Proton conducting Material in Perovskite Structure

1.3.1 Perovskite Structure Material for SOC

The perovskite structure material has the standard formula ABX_3 . These materials have a crystal structure where the B cations are located within octahedra formed by X anions, with the A cations occupying the interstitial spaces [18]. They are applied in solar cells, fuel cells, batteries, and electrocatalysts due to their exceptional performance and stability. Perovskite oxides are being explored as cost-effective electrocatalysts for oxygen evolution reactions, offering a promising alternative to noble metal-based catalysts [19]. Moreover, perovskite-based solar cells can be integrated into self-charging power packs and photo-electrochemical devices for solar water splitting and CO_2 reduction, enhancing energy diversity and utilization [20].

Perovskite materials have the potential to change SOC technology by serving as efficient components such as electrodes, electrolytes, and anodes. Perovskites like strontium-iron-niobate double perovskite (SFN) and lanthanum-strontium-titanate (LST) exhibit high chemical stability, conductivity, and low reactivity with electrolytes, making them ideal fuel electrode materials for SOC [21]. Additionally, perovskite-structured ceramics offer flexibility in dopant control, influencing ionic conductivity and electrical properties crucial for SOC components [22].

1.3.2 Proton Conducting Material

The development of proton conducting materials has a profound impact on the field of energy storage by enhancing the performance and efficiency of various energy devices. Proton conductors play a vital role in applications such as SOFCs and metal-organic frameworks (MOFs) for fuel cells and batteries [23], [24]. These materials are multifunctional perovskite possessing electrical, structural, and chemical compatibilities that function as key elements in proton conducting SOFC [24]. Moreover, the integration of proton-conducting membranes in electrolysis technology contributes to advancing energy conversion and storage technologies [25]. Overall, the continuous development of proton conducting materials is essential for the advancement of effective and sustainable energy storage solutions.

Separator materials in SOFCs have traditionally been oxide ion conductors such as ZrO₂, and CeO₂, and LaGaO₃ or diverse pyrochlores. These materials have high activation enthalpies for conductivity, necessitating high operating temperatures (usually above 800°C for YSZ) and the use of methane (natural gas) as a fuel for internal reforming in relatively wet conditions. The high conductivity of zirconia-based ceramics in SOFC applications is mainly due to oxide ions. Protons are discovered in some oxides as minority charge carriers in the 1960s [26]. Acceptor-doped oxides like LaAlO₃, LaYO₃, and SrZrO₃ show potential as proton conductors, SrCeO₃ and BaCeO₃ compounds demonstrate high proton conductivities in electrochemical cells at relatively high temperature and humidified hydrogen environment [26], [27]. Proton-conducting oxides can lower SOFCs' operating temperature, but low stability of creates pose a challenge. Experimental tests reveal SrCeO₃ and BaCeO₃ are not stable and react to carbonates and form hydroxides, so using hydrocarbons as fuels is not feasible due to the production of CO₂ and H₂O. The crystallographic structure of oxides such as SrCeO₃ and BaCeO₃ based materials is perovskite type. Especially, BaCeO₃-based materials, show the highest proton conductivities, and it has the highest molar volume among perovskites and a smaller deviation from the ideal cubic perovskite structure than SrCeO₃ [26].

Proton conduction relies on the presence of proton defects at an intermediate temperature and the dissociative absorption of water. These protonic defects are created when water breaks down into a proton and a hydroxide ion; the proton then bonds covalently with the lattice oxygen while the hydroxyl ion occupies the oxygen vacancy [27]. The process can be represented by Kroger-Vink notation as:



It is commonly agreed upon that the movement of protons in perovskite-type oxides occurs through two main stages. In the first step, shown in the Figure 1-4, the O-H group is reoriented towards the nearby oxygen ion, reducing the bond length and making it easier for protons to transfer through the cleaving and creating of hydrogen bonds. In the second step of proton transfer, the proton moves between neighboring oxide ions through proton hopping, facilitated by the presence of protonic defects. This involves the breaking of fragile O-H bonds and the creation of novel O-H bonds with adjacent oxygen ions as the proton moves from one oxygen ion to another [27].

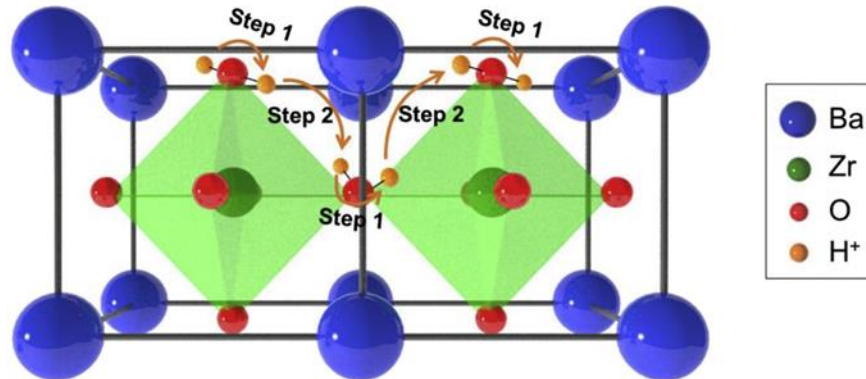


Figure 1-4. Schematic illustration of the reorientation (Step 1) and proton transfer (Step 2) pathways. The small orange balls represent the minimum energy position of the proton, and they are equivalent due to the symmetry of the crystal (Reprinted from [27] with permission from Elsevier).

1.3.3 Barium Zirconium Cerium Yttrium Oxide (BZCY)

The studies of BZCY began with strontium cerate (SrCeO_3) and barium cerate (BaCeO_3), BaCeO_3 and SrCeO_3 perovskite-type oxides exhibit the most superior proton conductivity compared to other high-temperature proton conductors [26]. Nevertheless, they tend to react with water vapor and acidic gases such as CO_2 and SO_2 , leading to the formation of hydroxides and carbonates, which impacts their stability [7], [27], [28]. Potential long-range pathways for proton conduction can be influenced by distortions in the perovskite structure, chemical disruptions due to cation doping, and associations between protons and dopants [27]. Any alteration in crystal symmetry away from the perfect cubic structure hinders proton conduction. One of the most frequently seen examples involves Y-doped BaCeO_3 and Y-doped SrCeO_3 . When Y is added to SrCeO_3 , it enhances orthorhombicity, making proton migration in Y-doped BaCeO_3 easier [27].

Due to the harsh operating conditions of protonic ceramics solid oxide fuel cells (PC-SOFCs), the degradation of barium-based electrolyte is observed, thereby restricting its utility in PCFCs [27]. The introduction of dopants has been proposed as a solution to enhance the chemical stability of BaCeO_3 without compromising its high proton conductivity. On the other hand, BaZrO_3 exhibits notable chemical stability when exposed to water vapor and a CO_2 atmosphere [26]. However, this stability comes at a cost, as the sintering process for BaZrO_3 -based proton conductors can be complex and difficult to control. One drawback associated with proton conductors based on BaZrO_3 is the challenging sintering process required to produce dense membranes, as well as the elevated resistance

encountered for proton conduction along the grain boundaries [26]. Y-doped BaZrO₃ combines high bulk proton conductivity with high stability. The creation of this material involves minimal compromise, a fact explained by its characteristics of high bulk proton conductivity, high stability, and a broad ionic domain, making Y-doped BaZrO₃ a compelling base material for the advancement of proton-conducting electrolytes for SOFC applications [26], [27].

Several studies have concentrated on creating chemically stable and highly conductive electrolytes through the fabrication of solid solutions involving BaZrO₃ and BaCeO₃. By adjusting the Zr fraction in BaZrO₃ with Ce, it is feasible to produce a stable electrolyte with targeted proton conductivity since both BaZrO₃ and BaCeO₃ can be mixed. Enhancing the content of Ce in BaZrO₃ typically enhances the overall conductivity, sinter ability, while reducing the chemical stability in CO₂ and water vapor. Additionally, the incorporation of BaCeO₃ into Y doped BaZrO₃ could potentially alleviate issues by minimizing chemical expansion and enhancing ceramic toughness [26], [27]. In conclusion, research efforts have focused on developing chemically stable and highly conductive electrolytes through the fabrication of solid solutions involving BaCeO₃ and Y doped BaZrO₃, creating a new proton conducting material- Barium Zirconium Cerium Yttrium Oxide.

1.4 Powder Material Synthesis Methods

1.4.1 Solid State Reaction Method

Solid-state synthesis is a most conventionally method for preparing complex oxides [29]. It typically starts with commercially available single oxides of the desired elements. However, for some elements like alkaline, alkaline earth elements, and rare earths, stable oxides are not readily available due to reactions with ambient CO₂ or humidity. In these cases, carbonates and hydroxides can be used as precursors since they decompose into oxides at high temperatures during synthesis. Precursors need to be mixed homogeneously, often by grinding with a mortar or ball mill machine. The mixture is then annealed to high temperatures to promote diffusion and crystallize the new complex oxide phase. The success of the reaction depends on the diffusion pathways, influenced by the morphology and homogeneity of the starting powders [30]. The diffusion step in solid-state reactions is limited by the resultant product from reactant particles, which leads to an increase in particle sizes at high temperatures, so multiple calcining and ball-milling steps are necessary to achieve the desired products [29].

Figure 1-5 illustrates three scenarios. Coarse grains necessitate extended heat treatment for the reactants to combine and produce the product due to the long diffusion distance. Fine agglomerated grains, despite being finer than coarse grains, result in unfavorable reactions because of the lack of homogeneity leading to long diffusion distances. In the case of fine grains, where fine powders are well mixed, short diffusion distances and a favored reaction occurs. Furthermore, fine powders with higher specific areas enhance the driving force for diffusion, resulting in faster reaction kinetics due to both shorter diffusion distances and faster diffusion [30].

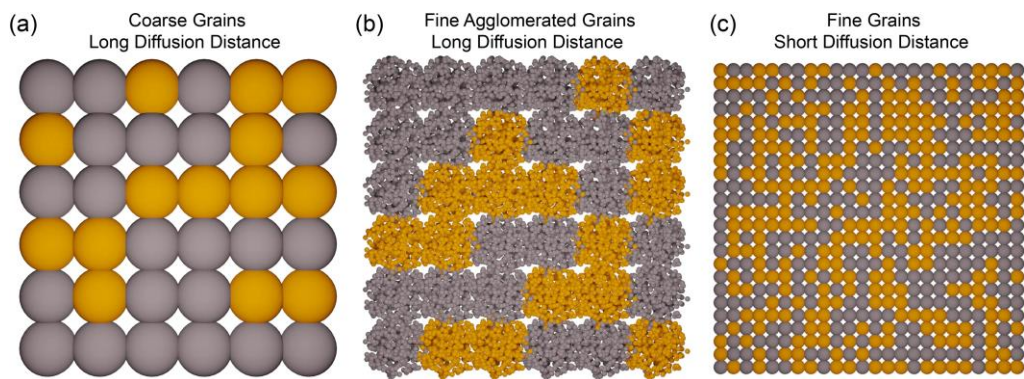


Figure 1-5. Illustration of three cases for solid state synthesis: (a) coarse grains, (b) agglomerated fine grains, and (c) fine grains. The diffusion distance corresponds to the length that cations need to diffuse for the reaction to take place (Reprinted from [30] with permission from Springer Nature)

Figure 1-6 shows the steps of solid-state reaction synthesis. This method faces two main challenges: contamination between materials and leftover precursors. Extended mixing and grinding can cause contamination from the grinding tools, which can be minimized by cleaning with dilute nitric acid. Inadequate mixing may result in powders with unreacted starting materials after heating. An extra grinding step before a next heating phase can help by redistributing unreacted materials and potentially reducing grain size [30].

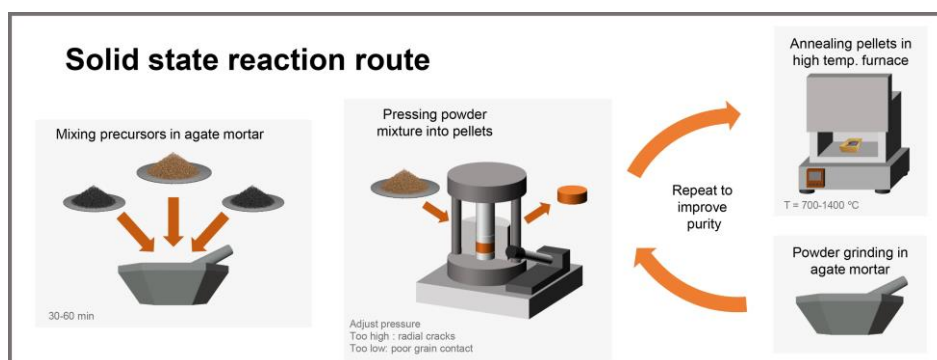


Figure 1-6. Illustration of the steps involved in the solid-state reaction route (Reprinted from [30] with permission from Springer Nature)

1.4.2 Sol-gel Method

The Pechini route (sol-gel) is an alternative to solid-state synthesis, using a sol-gel method that involves polymerizing an organic acid (usually citric acid) and an alcohol (usually ethylene glycol) to trap cations in solution and preserve their distribution [29]. This method works with various soluble cation precursors, like nitrates and acetates, though chlorides can be problematic due to substitution of oxygen in the final oxide. It is versatile and applicable to many complex oxides, the sol-gel method produces nanometric scale powders (10–100 nm) after calcination, which need annealing to crystallize. These powders often agglomerate into micrometric clusters and can sinter during annealing, forming larger particles. Drawbacks include the need for annealing, potential agglomeration, and low atom efficiency, making large-scale production expensive [30].

Figure 1-7 illustrates the detailed process of sol-gel approach. Enhancing the uniformity of oxides and modifying solid structural characteristics, such as porosity and specific surface area, is achieved through this technique. It is essential to carefully regulate the pH of the aqueous solution to avoid the precipitation of cation precursors during the process at elevated pH levels, which would hinder their integration into the polymeric matrix. Furthermore, strict safety measures must be adhered to, and the synthesis process should be carried out in a fume hood due to the emission of hazardous gases like NO_x [29], [30].



Figure 1-7. Illustration of the steps involved in the Pechini route (Reprinted from [30] with permission from Springer Nature)

1.4.3 Combustion Method

If maintaining nanoscale grain size is crucial, the sol-gel method may not be appropriate for synthesizing nanoscale powders of complex oxides. Instead, combustion synthesis is a better choice to produce 10-20nm particle size [31]. While it uses similar chemicals (like nitrates and citric acid) and steps (gel formation and calcination) as the sol-gel route, combustion synthesis involves a highly exothermic reaction that directly crystallizes the complex oxide. This method, inspired by propellant chemistry, typically uses redox reactions between a strong oxidizer (such as nitrates) and a reducing agent (fuel) like urea, glycine, or citric acid [30].

In combustion synthesis, the precursor solution is evaporated to form a dry mixture, which is essential for an efficient reaction. The rapid combustion reaction provides sufficient energy for crystallization without allowing time for significant grain growth or sintering, making it ideal for producing nanoscale powders with high surface areas. The drying process plays a crucial role as any remaining water can lower the flame temperature during combustion, impacting the purity and morphology of the material. Consistent drying, preferably at 110°C overnight, is essential for achieving consistent results. It is important to avoid higher temperatures to prevent the fuel and nitrate ions from decomposing partially, which can disrupt the balance between fuel and oxidizer [30].

As shown in Figure 1-8, using a cover that allows gas to pass through helps prevent strong reactions that could blow away the powder. After powder is gathered, it is crushed to remove any foam-like formations. Calcination should be carried out at a temperature range of 400-600°C to prevent

premature growth of grains, maintaining surface area and enhancing the sintering process for producing dense ceramics [30].

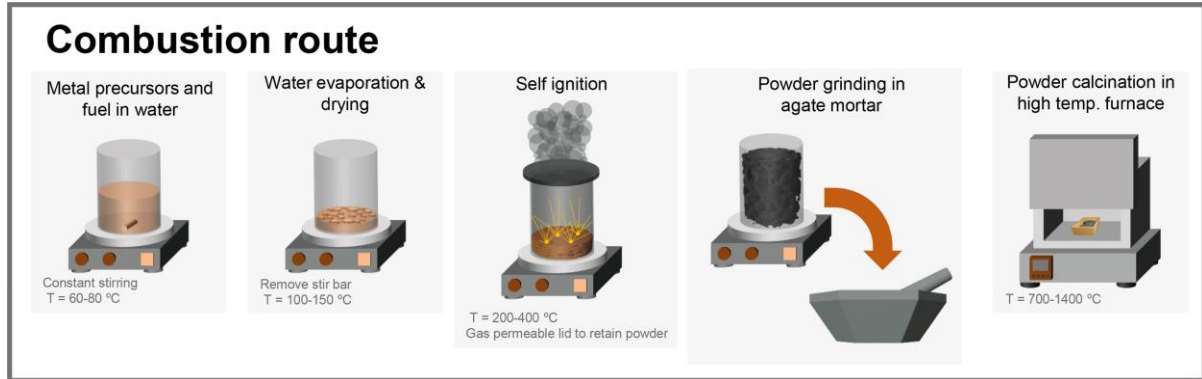


Figure 1-8. Illustration of the steps involved in the combustion route (Reprinted from [30] with permission from Springer Nature)

1.4.4 Precipitation Method

The precipitation technique quickly turns a solution of metal precursors into oxide powder by triggering solid particle formation from soluble precursors. This method exploits the insolubility of most metal hydroxides in water. Metal cations are stable in acidic solutions but precipitate as solid hydroxides when the pH is increased, typically using a strong base like ammonia. The precipitated hydroxides are filtered, washed, dried, and then annealed to form the final oxide. The technique often produces fine powders (10–100 nm), but the annealing step can cause significant grain growth, especially if the powders are agglomerated. To prepare complex oxides, the pH levels for all component cations must be similar to avoid segregation. This method is ideal for phases that include similar cations, such as doped ceria or $\text{Li}(\text{Ni}, \text{Mn}, \text{Co})\text{O}_2$, used in Li-ion batteries [29], [30].

In precipitation, unlike the sol-gel method, precipitation involves several steps (precipitation, filtration, drying). Different laboratory equipment is needed for each step to ensure efficient performance and prevent material loss (see Figure 1-9). The choice of filter is crucial, depending on the size of the precipitate particles, which can be adjusted by choosing the appropriate molar concentrations of precursors and precipitating agents. Achieving uniformity in nanoparticle size distribution and co-precipitation solid solutions requires precise control when adding precipitation agents, usually done drop by drop under constant stirring using a burette or syringe pump, with crucial monitoring of pH levels, especially when co-precipitating oxides of multiple elements with varying

cation precipitation pH values, to prevent phase separation and ensure complete cation precipitation, while aging the solution with continuous stirring post-precipitation can further ensure homogeneity [30].



Figure 1-9. Illustration of the steps involved in the precipitation route (Reprinted from [30] with permission from Springer Nature)

1.5 Proton Conducting SOC's Fabrication Methods

The transition from particle synthesis to SOC fabrication involves several techniques to shape powder materials into functional components. This section covers three key methods: tape casting, dry pressing, and screen printing. Understanding these methods is essential for optimizing SOC fabrication and improving device performance.

1.5.1 Tape Casting Method

Tape-casting technology can convert various powdered materials into thin sheets, with a thickness as low as 5 μm [32]. This technique is widely utilized in the production of membranes, electrodes, fuel cell components, and ceramic substrates. Tape casting allows for the efficient and rapid production of large, thin, flat ceramic or metallic objects, making it a more cost-effective option compared to dry-pressing [33]. The resulting green tapes are flexible and easy to mold, enabling the creation of multilayered ceramics, metallic components, or ceramic-metallic blends. Figure 1-10 illustrates the fundamental concept of the tape-casting procedure as commonly found in contemporary factories and research facilities. In a standard tape-casting device, the primary components consist of the blade, the reservoir, and the motorized carrier with a heating mechanism [29].

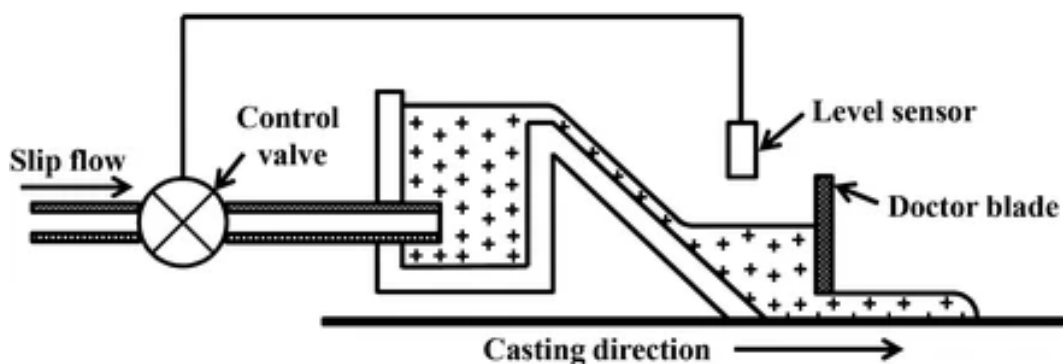


Figure 1-10. Basic principle of the tape-casting process (Reprinted from [29] with permission from Springer Nature)

In order to prepare ceramic powders for shaping, various organic additives such as solvents, plasticizers, binders, dispersants, and other substances are utilized. Solvents help dissolve these additives and disperse ceramic particles to regulate the viscosity of the slurry. Dispersants increase the solids content, reduce the need for solvents, and enhance the density of the green tape, thus lowering costs. Binders play a critical role in creating networks within the material, influencing the strength and flexibility of the green ceramic tape. Plasticizers enhance the flexibility of the dried green tape, counterbalancing the rigidity and brittleness caused by binders [29]. Prior to casting, the slurry must undergo filtration and degassing under vacuum conditions [29], [32]. To achieve a high-quality slurry, it is essential to ensure uniform dispersion, correct viscosity, high solids content, and suitable strength and flexibility once dried.

1.5.2 Dry pressing Method

Dry pressing is a commonly used technique in shaping ceramics because of its simplicity, making it suitable for both laboratory and industrial purposes. This method entails compressing dry powders under high pressure, up to 1000MPa, without any visible liquid phase. Depending on the machine and mold design, dry pressing can create ceramic components ranging from large tiles (1000 mm) to small gears (1 mm). The process consists of four key steps: powder pretreatment, loading the powder into the mold, compacting, and unloading the sample. Powder pretreatment is essential for producing high-density green samples by incorporating organic binders and plasticizers to enhance powder flowability and plasticity. Lubricants may also be utilized to facilitate mold unloading. Adequate pretreatment guarantees plastic deformation and high initial density during the pressing stage [29].

1.5.3 Screen-printing Method

Screen-printing is a cost-effective, simple, and convenient method for fabricating SOC components, including anodes, electrolytes, and cathodes. This technique is beneficial for producing thin ceramic films ranging from 10 to 100 μm . High-quality inks are crucial for fabricating high-quality SOFC films, with ink quality depending on the rheological properties of binders, solvents, and dispersants. The process involves feeding viscous ceramic paste through open screen meshes using a squeegee to form thin films (see Figure 1-11). Sintering and drying processes enhance the quality of the components by removing excess solvents. The technique can produce dense electrolyte layers as thin as 2.5 μm and as large as 33 $\times$ 33 cm^2 , though multiple printing passes and drying times are often needed for gastight electrolytes. Recent advancements have demonstrated the feasibility of achieving less than 5 μm thick dense electrolytes in a single printing cycle, significantly improving performance and reducing production time [32], [33].

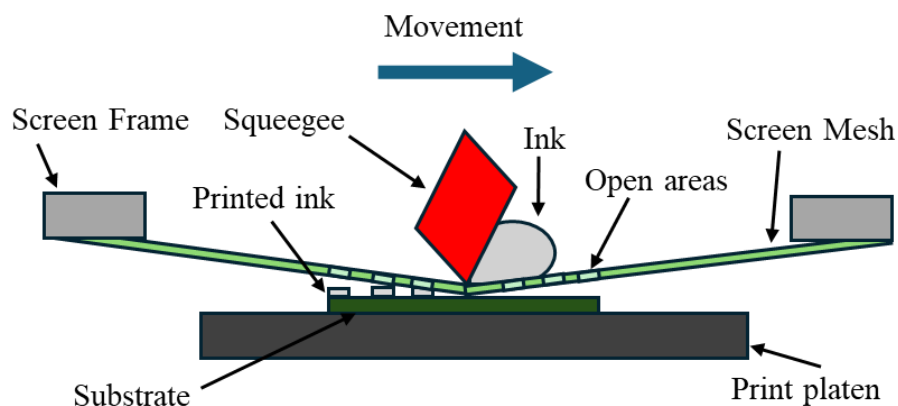


Figure 1-11. The illustration of screen-printing method

1.5.4 Additives Choices for Ink Preparation

For both tape-casting and screen-printing methods, it is crucial to have high-quality ink as it plays a significant role in the final output of the process; therefore, it becomes essential to carefully consider and select various additives that can be incorporated into the ink to enhance its properties and performance.

Table 1-1. Solvents, dispersants, binders, and plasticizers frequently used for ink preparation [29]

Additive type	Additives
Solvents	Water, methyl ethyl ketone (MEK), ethanol, xylenes, toluene, acetone, 1,1,1trichloroethane, methanol, MIBK, cyclohexanone, butanol, isopropanol, nitropropane, etc.
Dispersants	Polyisobutylene, linoleic acid, oleic acid, citric acid, stearic acid, lanolin fatty acids, salts of polyacrylic acids, salts of methacrylic acids, blown menhaden fish oil, corn oil, safflower oil, linseed oil, glycerol trioleate, synthetic waxy esters, etc.
Binders	Polyvinyl alcohol (PVA), polyvinyl butyral (PVB), polyvinyl chloride (PVC), vinyl chloride-acetate, polyacrylate esters, polymethyl methacrylate, polyethyl methacrylate, petroleum resins, polyethylene, ethylene oxide polymer, polypropylene carbonate, polytetrafluoroethylene (PTFE), poly-alpha-methyl styrene, poly isobutylene, atactic poly(propylene)/poly(butene), polyurethane, cellulose acetate-butyrate, nitrocellulose, methyl cellulose, ethyl cellulose, hydroxyethyl cellulose hydroxypropyl methyl cellulose, etc.
Plasticizers	Dibutyl phthalate, dioctyl phthalate, butyl benzyl phthalate, mixed esters phthalate, dimethyl phthalate, ethyltoluene sulfonamides, glycerine (glycerol), tri-nbutyl phosphate, butyl stearate, methyl abietate, tricresyl phosphate, propylene carbonate, water, polyethylene glycols (PEG), polyalkylene glycols, polypropylene glycols, triethylene glycols, dipropylglycol dibenzoate, etc.

1.6 Challenges of Fabrication Proton-conducting Solid Oxide Cell

1.6.1 Optimizing the Material Synthesis

Optimizing the synthesis of proton-conducting powder materials can enhance sinter ability and proton conductivity of membrane [34]. Challenges arise from the necessity to achieve high purity-phase nanoparticles, optimize doping strategies, and ensure uniform doping. Overcoming these challenges is crucial for advancing proton-conducting fuel cell technology by improving sinter ability, conductivity, and overall cell performance. So, the expected particles' topography is shown in Figure 1-12(a).

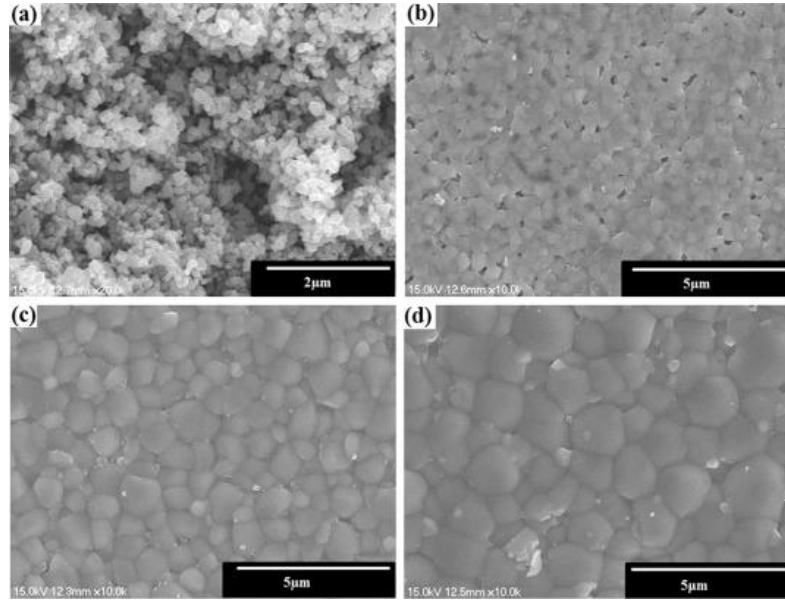


Figure 1-12. Scanning electron microscope (SEM) images of BZCY electrolyte materials: (a) BZCY powder calcined at 1000°C; BZCY pellets sintered at (b) 1300 °C, (c) 1400 °C, and (d) 1500 °C (Reprinted from [35] with permission from Elsevier)

As mentioned in previous sections of this report, various techniques exist for the synthesis of the powder materials. For example, to obtain the pure phase of perovskite structure, for BZCY materials synthesis in wet chemistry routes, the minimum calcination temperature cannot be below 1000°C, the duration may vary depending on specific synthesis method [36], [37], [38], [39]. Furthermore, for all oxides materials, with the combustion method yielding homogenous distribution of elements and smaller particles' size. The combustion technique is categorized within the wet chemistry route. For all wet chemistry routes, it is significant that the precursor materials are dissolved in the reaction medium, as this is crucial for ensuring a uniform distribution of elements and preventing demixing and segregation [40]. When the precursors are dissolved completely dissolve in the solvent, it forms homogenous solution. Moreover, the reduction of particle size in powder synthesis stage facilitates densification and grain growth at sintering process, enabling the attainment of 25nm for BZCY powder using microwave sintering at relatively low temperature (900°C) with a brief dwell time of 1 hour [40]. The desired particles should not agglomerate either. In the case of combustion method, the powder formed after combustion is amorphous on a nanometric scale, but they tend to form agglomerated micrometric clusters, those clusters easily sinter during calcination stage [30].

1.6.2 Electrolyte Layer Requirements

Electrolyte layer presents a challenge for proton-conducting solid oxide cells due to the critical impact it has on cell performance [41], [42], [43]. Challenges include ensuring the deposition of a thin, pinhole-free electrolyte layer for efficient cell operation [42], and achieving a gas-tight electrolyte layer without degrading the support structure [43]. Various conventional deposition methods like spraying, blade coating [41], screen printing [44], spin coating [45], [46], and tape casting [47], [48] have been explored to optimize electrolyte deposition and to address these challenges. These efforts are crucial for enhancing the efficiency and stability of proton-conducting solid oxide cells.

The electrolyte layer in proton-conducting solid oxide cells needs to be very thin to minimize ohmic loss and enhance performance, the electrolyte layer typically 10-20 μm (less 30 μm) thick or thinner, plays a crucial role in minimizing ohmic resistance, the performance is generally compromised by the high ohmic resistance of the relatively thick stability layer [49], [50]. The performance of cells is heavily influenced by the electrolyte's ohmic loss, and the resistance caused by electrode polarization. Therefore, efficient operation at lower temperatures necessitates the utilization of materials with superior electrical properties and the implementation of cost-effective and flexible techniques for creating cell structures with thinner electrolytes and enhanced electrode microstructure [51]. The thin electrolyte layer is essential in proton-conducting fuel cells to optimize performance and efficiency by minimizing ohmic loss and enhancing reaction rates.

The electrolyte layer in proton-conducting fuel cells is gas-tight to prevent gas cross leakage and electron leakage, ensuring efficient cell operation and durability [42]. The electrolyte layer in proton-conducting solid oxide cell means that only allow protons to cross from one electrode to another, see Figure 1-13.

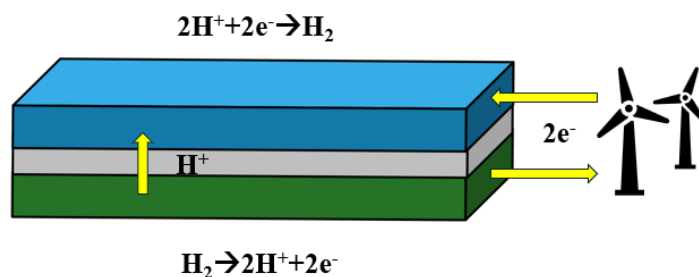


Figure 1-13. Scheme of a proton-conducting solid oxide electrolysis cell

In order to achieve a gas-tight electrolyte layer within the cell, efforts have been directed towards various aspects. The densification of proton-conducting material poses challenges in the sintering process.

Researchers employ the exploration of sintering additives to potentially address pore filling within the electrolyte layer or facilitate the melting of proton conducting material. The investigation demonstrates the impacts of sintering additives of NiO, ZnO, and CuO at varying doping levels (0.5wt%, 1wt%, 2wt%) on proton-conducting electrolyte disks utilizing BZCYYb4411 and BZCY442 sintering at 1650°C and 1600°C respectively. These additives dissolve within the perovskite lattice, influencing acceptor concentration, hydration, and grain growth. Interestingly, the effective acceptor concentration is lower in NiO-inclusive samples compared to those containing ZnO and CuO for both BZCYYb4411 and BZCY442, with differences becoming more pronounced as the sintering additive content increases. Consequently, NiO plays a significant role in enhancing densification and grain growth, with a minimal amount of 0.5 wt%, since a decrease in the effective acceptor concentration can result in an enlargement of the grain size. And NiO or CuO being preferable for optimizing both sintering and hydration processes [39]. A study is performed on two distinct proton-conducting materials, namely BZY82 and BZCY172, which are combined with 2 mol.% NiO electrolyte layers in SOCs. Both materials undergo sintering at 1400°C for a duration of 6 hours to achieve dense electrolytes [52]. Another study utilizes NiO and CuO as additives for sintering in order to facilitate the compaction of the electrolyte layer in the solid oxide cells during sintering processes at temperatures of 1450°C and 1400°C for a duration of 18 hours, employing various techniques for membrane production, and the study revealed that the addition of NiO resulted in a higher peak power density compared to CuO in terms of cell performance [44].

The densification of electrolyte layer may also be influenced by the proportion of specific components present in the material. For instance, variations in the zirconium (Zr) composition within BZCY material can cause tremendous effects during the sintering stage. The SEM image of BZCY pellets subjected to identical pressure and sintered under same circumstances is illustrated in Figure 1-14.

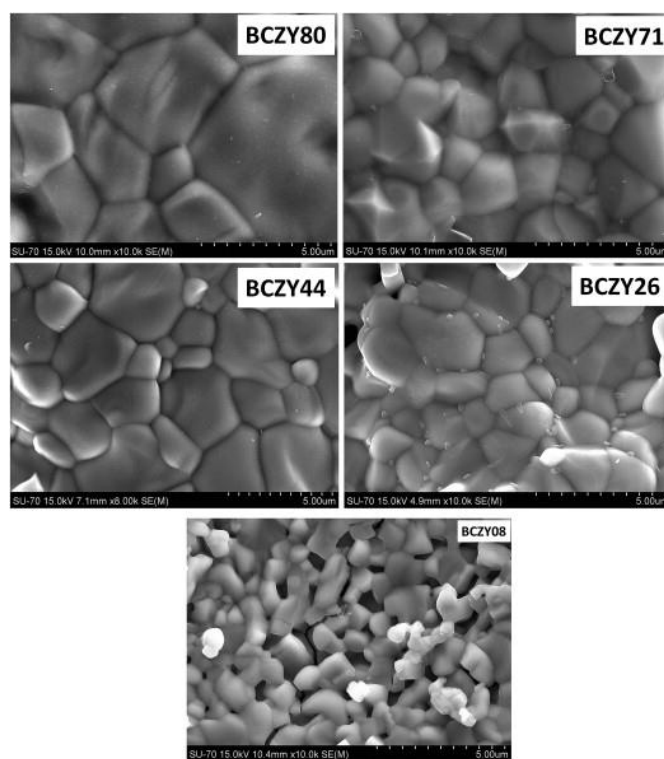


Figure 1-14. SEM of surface of $\text{BaCe}_{0.8-x}\text{Zr}_x\text{Y}_{0.2}\text{O}_{3-\delta}$ pellets sintered at 1500°C for 8 h (Reprinted from [31] with permission from Elsevier)

Under identical conditions, it is observed that an increase in zirconium concentration leads to a reduction in grain size and a decrease in the densification of BZCY pellets. And the table data presents the variations in grain size and relative density corresponding to distinct levels of zirconium content within the BZCY compositions. This suggests that the initiation of powder synthesis should commence with lower zirconium content.

Table 1-2. Grain size and relative density of $\text{BaCe}_{0.8-x}\text{Zr}_x\text{Y}_{0.2}\text{O}_{3-\delta}$ materials synthesized by nitrate free acetate– H_2O_2 combustion method, isostatically pressed at 200 MPa and sintered at 1500°C for 8 hours [31].

x (Zirconium)	Relative Density (%)	Grain Size (μm)
0	98.5	4.73+/-1.65
0.1	98	1.94+/-0.63

0.4	96	2.61+/-0.82
0.6	92	1.75+/-0.51
0.8	82	0.97+/-0.18

To achieve a dense electrolyte layer, one may utilize the two-step sintering technique in the sintering process. Specific insights regarding this approach are available in section 1.6.3, as it pertains primarily to the manner in which sintering temperatures are managed.

1.6.3 Sintering Strategy

Achieving densification of electrolyte materials is challenging and usually requires very high sintering temperatures. For BZCY materials, it has been documented that they are sintered within a temperature range of 1300 to 1650°C [31], [35], [39]. Sintering, a high-temperature process driven by the reduction of surface free energy, involves five mass transport mechanisms: evaporation–condensation, surface diffusion, lattice diffusion from the surface, lattice diffusion from grain boundaries, and grain boundary diffusion. The first three mechanisms cause grain coarsening without significantly affecting density, beneficial for strengthening porous ceramic membranes. The last two mechanisms lead to densification. The sintering outcome is influenced by conditions such as temperature, duration, heating/cooling rate, atmosphere, pressure, grain size, and additives. Additionally, factors like particle size, agglomeration, distribution, specific surface area, shaping method, and green body conditions impact the process and membrane characteristics. Thus, careful selection of sintering programs and preparation methods is essential for producing membranes with desired dense and porous layers [29].

There are three stages in the process of sintering, during the initial stage, sintering necks are formed by evaporation-condensation, surface diffusion, and lattice diffusion, requiring a quick temperature increase to achieve high density. The intermediate stage sees the sintering necks enlarge, grain size increase, and density rise, while in the final stage, relative density surpasses 90% and gas pores diminish, as illustrated in SEM images (see Figure 1-15).

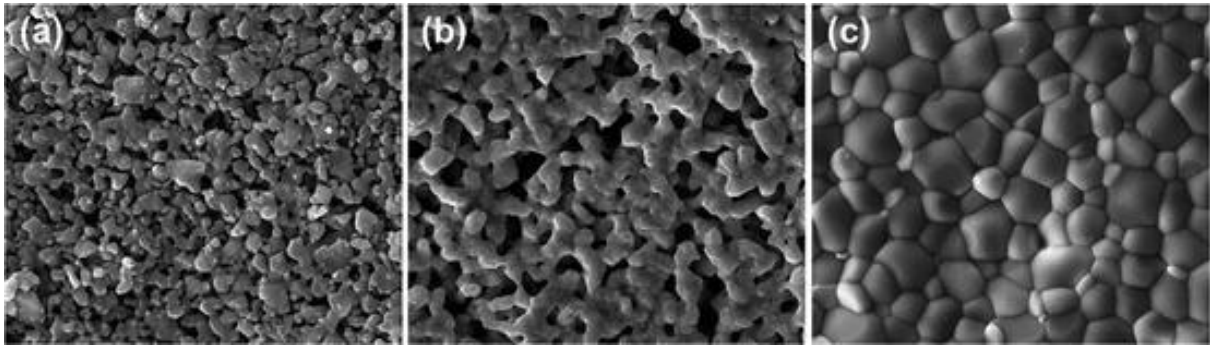


Figure 1-15. Typical SEM pictures of the three stages in sintering: (a) initial stage, (b) intermediate stage, (c) final stage (Reprinted from [29] with permission from Springer Nature)

The researchers utilized a two-step sintering technique in their research to improve the formation of nano-sized bulk materials. Initially, the temperature is raised significantly to achieve a relative density of over 75%, and then it is reduced to complete the densification process. This method tackles the issue of isolated pores commonly seen in traditional sintering by encouraging boundary diffusion for densification while restricting boundary movement to prevent grain growth, which requires higher activation energy. By keeping the temperature lower during the final sintering stage, grain growth is minimized, maintaining a nearly constant grain size. To prevent cracking during heating, it is advised to gradually increase the temperature, especially when using organic additives in the membrane green body. This strategy effectively combines sintering mechanisms with the two-step method for both dense and porous membranes [29].

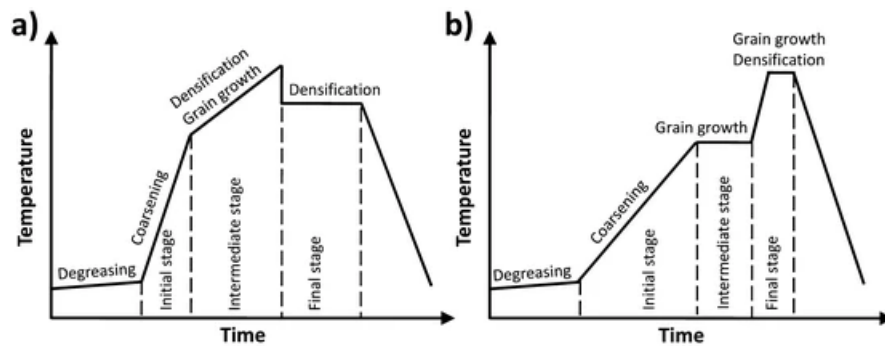


Figure 1-16. Two different sintering procedures, a) for dense ceramic membranes and b) for porous ceramic membranes (Reprinted from [29] with permission from Springer Nature)

1.6.4 Problems Caused by High Sintering Temperature

During the process of sintering thin films containing barium (Ba), a major issue arises due to the loss of Ba at high temperatures caused by evaporation and chemical reactions with the electrode substrate, and the extent of this loss tends to rise with higher sintering temperatures [48]. This volatility of Ba is a common problem in electrolytes based on BaCeO_3 and BaZrO_3 , leading to the redistribution of dopants and a decrease in the crucial oxygen vacancy concentration required for co-ionic transport. As a result, the electrical and mechanical properties deteriorate, secondary phases segregate at grain boundaries, and there is a risk of electrolyte decomposition. Ba loss is particularly troublesome in thin films with a thickness of less than $10\mu\text{m}$ [51].

The presence of Ba in the electrolyte is anticipated to have a negative impact on the performance of electrolytes due to the well-documented fact that the conductivity of BZCY is greatly influenced by the level of Ba content it contains [48]. The higher sintering temperature leads to increased Y_2O_3 secondary phase formation, which can be detrimental due to potential transformation to $\text{Y}(\text{OH})_3$ in humid conditions. The sintering temperature of 1550°C works well for ceramic samples but is too high for a BZCY electrolyte layer. In this case, Y_2O_3 precipitation occurs to maintain cation balance and avoid cation vacancies, leading to the movement of Y from the B-site to the A-site [47], [53].

Methods for addressing Ba depletion include sintering the film with a powder of the same composition, applying a protective layer of BaCeO_3 before sintering, or utilizing $\text{BaZrO}_3/\text{BaCO}_3$ powder nearby to reduce potential barium oxide (BaO) losses through evaporation [47], [51]. Another approach is increasing the thickness of the electrolyte to more than $20\mu\text{m}$ [51]. Reducing the sintering temperature of the BZCY-based half-cell to below 1300°C is another possible solution to avoid the loss of Ba through evaporation during the sintering process [48]. Also, it is essential to control the BaO activity in the atmosphere due to its high volatility at sintering temperatures, a task that can be accomplished by choosing a suitable sintering technique [53]. Because of the information provided in earlier sections 1.6.2 and 1.6.3, it is evident that the incorporation of sintering aids along with an appropriate sintering technique can play a crucial role in decreasing the sintering temperature, thereby minimizing the loss of Ba and preserving the pristine perovskite structure post-sintering.

1.6.5 Shrinkages, Cracks, and Warping During Sintering Stage

An electrochemical cell usually consists of a sandwich-like design comprising of a minimum of three layers: an anode, a cathode, and an electrolyte. These systems function at high temperatures (300–800°C), which poses a challenge due to the thermal differences between the layers. In the process of tape casting, it requires precise management of the shrinkage of each layer to avoid warping and fractures during sintering. The layers that are sintered together are impacted by stress caused by differences in shrinkage at the interfaces, which stem from varying rates of thermal expansion and sintering behavior. Disparities in thermal expansion coefficients can lead to thermal stress, resulting in cracks, separation at the interfaces of the layers, and potentially causing the entire device to fail [48], [54].

Slow heating rates, involving a gradual temperature increase over an extended period, positively impact the process of leveling creep stress in materials under load. This controlled heating allows for a more uniform thermal energy distribution, reducing the risk of stress concentrations and potential structural instability [47]. The shape transformation and flexing behavior of the half-cell during sintering, with the BZCY electrolyte layer facing upwards is described. No noticeable bending occurs until about 900°C, when a slight convex shape appears, curving towards the NiO-BZCY support side due to its faster sintering rate. This curvature remains until around 1280°C, where the direction reverses, bending towards the electrolyte side. The most significant curvature occurs around 1400°C. Further heating to 1450°C begins to compensate for the bending, mainly due to the NiO-BZCY electrode substrate. After holding at 1500°C for 3 hours, the half-cell becomes completely flat and remains so until the end of the sintering process [48].

The thermal expansion coefficients (α) of Y-doped BaZrO₃-BaCeO₃ solid solutions show a specific trend, where α decreases as the Zr-content increases (see Table 1-3). These patterns provide a way to adjust the thermal expansion coefficient of the electrolyte to prevent thermal mismatch with other parts of the electrochemical device. By increasing the amount of Ce in the BaZrO₃-BaCeO₃ solid solution or by adding more yttrium dopant, α can be increased [54].

Table 1-3. Thermal expansion coefficients of barium zirconate and barium cerate based perovskites (in order of increasing Zr-content) [54]

compounds	α ($10^{-6}K^{-1}$)
$BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$	11.3 / 12.1
$BaZr_{0.2}Ce_{0.6}Y_{0.2}O_{3-\delta}$	11.3
$BaZr_{0.3}Ce_{0.5}Y_{0.2}O_{3-\delta}$	10.8
$BaZr_{0.4}Ce_{0.4}Y_{0.2}O_{3-\delta}$	10.9
$BaZr_{0.5}Ce_{0.3}Y_{0.2}O_{3-\delta}$	9.3
$BaZr_{0.6}Ce_{0.2}Y_{0.2}O_{3-\delta}$	9.1
$BaZr_{0.7}Ce_{0.1}Y_{0.2}O_{3-\delta}$	8.4
$BaZr_{0.7}Ce_{0.2}Y_{0.1}O_{3-\delta}$	12.7/10.2/9.3
$BaZr_{0.8075}Ce_{0.0425}Y_{0.15}O_{3-\delta}$	8

1.7 Chapter Summary

This chapter provides a thorough introduction to Solid Oxide Cells (SOCs), detailing their definition, benefits, and limitations to offer a comprehensive understanding of the system. It delves into proton-conducting materials that can be effectively utilized in SOC applications to achieve optimal performance. Additionally, the chapter reviews conventional powder synthesis methods, emphasizing the importance of selecting the most suitable technique based on specific application requirements. It also covers membrane production techniques, stressing the need for advanced equipment and approaches to ensure high-quality manufacturing. Furthermore, the chapter addresses the challenges in membrane fabrication, highlighting the complexities researchers face in developing efficient and reliable SOC membranes. Overall, this chapter serves as an in-depth guide to SOC systems, materials, synthesis methods, membrane fabrication techniques, and the associated challenges.

Chapter 2

Experimental Methods

2.1 Chapter Introduction

This chapter aims to provide an overview of the primary apparatus employed in the proton-conducting material powder synthesis and membrane fabrication. The methodologies of combustion and sol-gel are delineated for the synthesis of powder materials. Screen-printing and manual blade coating techniques are selected for membrane fabrication processes. Sintering methods are also introduced to prevent warpage, Ba loss, and adhesion problems in bi-layer membranes. Characterization techniques such as X-ray diffraction (XRD) and scanning electron microscope (SEM) are applied to analyze the properties of both powder and membrane materials discussed in this section.

2.2 Apparatus for Powder Synthesis

To obtain the precise chemical composition and the desired particle size, it is critical to control the powder synthesis conditions, e.g., chemical precursor weights, gel formation temperature, and uniformity of oxides. The apparatus that used for powder synthesis is shown in Figure 2-1. The analytical balance is utilized for weighing the chemical precursors to obtain the desired stoichiometric and chemical compositions, whereas the temperature probe and thermometer are employed for the measurement of the actual oil bath temperature. The hot plate is equipped with functionalities for both heating and stirring, which help achieve desire gel formation temperature and homogenous solution.

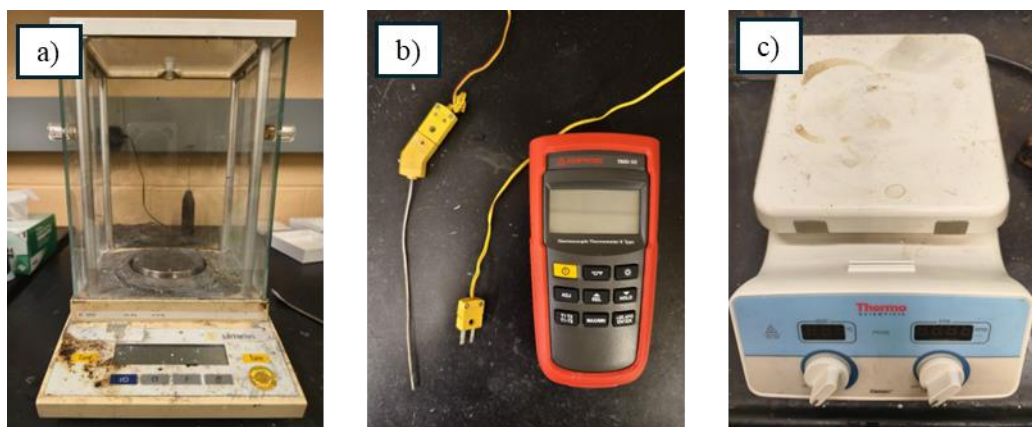


Figure 2-1. a) Sartorius-BL 120S analytical balance, b) Temperature probe and Amprobe TMD-50 thermocouple thermometer K-Type, c) Thermo Scientific-Cimarec+ stirring hotplate

The type 47900 furnace is used for drying and combustion of gel materials, which often require temperatures below 1000°C. The type 47900 furnace is general purpose laboratory and heat-treating furnace (see Figure 2-2 a)). Barnstead International suggests that to ensure the optimal lifespan of the element, it is advisable to adhere to specific temperature ranges. These ranges are recommended as follows: between 1000°C to 1093°C for continuous operation, or between 1093°C to 1200°C for intermittent operation. Continuous operation refers to using the furnace for a period exceeding 3 hours, whereas intermittent operation refers to using the furnace for a period less than 3 hours. The furnace's controller is equipped with the capability of single ramp and dwell programming.

And the high temperature muffle furnace is utilized for powder calcination, typically operating at temperature or above 1000°C. The KSL-1700X-A1 represents a bench-top high-temperature muffle furnace, comprising high-quality alumina fiber insulation and 1800 grade MoSi₂ heating elements (see Figure 2-2 b)). Its operation is overseen by a high precision SCR (Silicon Controlled Rectifier) and temperature controller, ensuring an accuracy of $\pm 1^\circ\text{C}$ and offering 30 programmable segments, reaching up to 1700°C. This equipment stands as an excellent choice for materials annealing and sintering processes. To prolong the element's lifespan, it is advised by Across International to adhere to specific temperature guidelines: 1600°C for continuous use and 1700°C for intermittent use. Continuous use is operating the furnace for more than 3 hours and intermittent use is operating the furnace for less than 3 hours. It is recommended to maintain a heating rate that is less than or equal to $10^\circ\text{C}/\text{min}$.

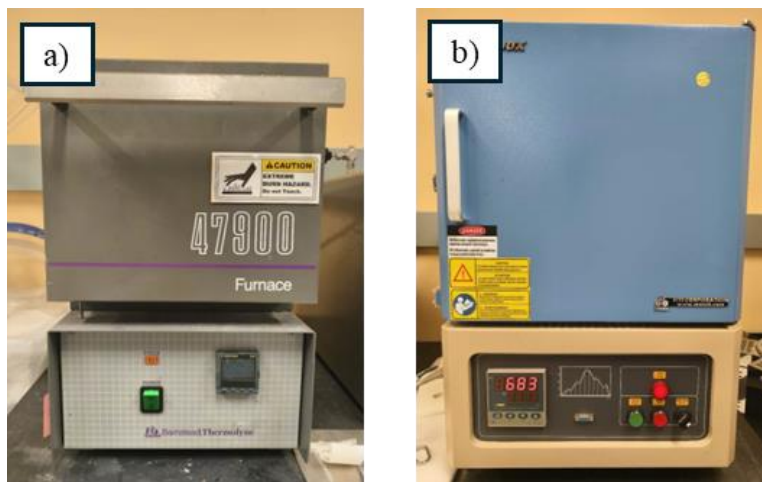


Figure 2-2. a) Barnstead International-type 47900 furnace, b) MTI-KSL-1700X-A1 high temperature muffle furnace

2.3 Methods Chosen for BZCY172 Powder Synthesis

There are different oxide synthesis methods, such as solid state reaction method, sol-gel method, combustion method, and precipitation, which were discussed in section 1.4. In this thesis, wet chemical route is used to synthesize the desired proton conducting oxides. The selection of the wet chemical route for powder synthesis is justified by its ability to achieve a high level of homogenization in comparison to solid-state synthesis. Within the scope of this study, the combustion method and sol-gel method are being explored for their potential to produce small particle sizes and porosity, as well as their impact on the densification of cells during the sintering process. The powder synthesis process is conducted within a fume hood to mitigate the risk of exposure to hazardous chemicals and nanomaterials in the workplace; personal protective equipment such as safety goggles, lab coats, and masks is utilized throughout the operation.

2.4 Apparatus for Membrane Fabrication

Once obtaining the BZCY172 powder material, the manufacturing process of the membrane can be initiated. The first step involves the preparation of a suitable substrate for electrode foundation. The bench top press and die set are employed for the compression of powder materials into substrate pellets. (see Figure 2-3). The press can apply force with a capacity of up to 11 metric tons. The powder substance is inserted into the die set, which can then be positioned on the lower square platen; subsequently, the lever elevates the lower square platen to compress the die set between the two square platens.

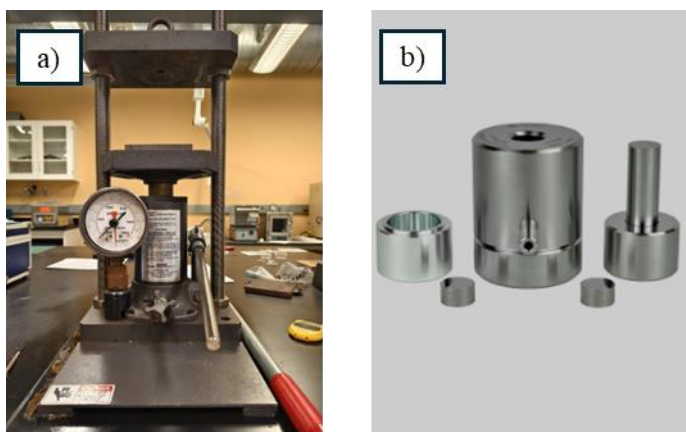


Figure 2-3. a) Carver-bench top manually unheated mini C 3850 model press, b) MSE PRO-0.5" (12.7 mm) diameter dry pellet pressing die set

The 30ml Fisherbrand leakproof HDPE wide-mouth bottles can be placed on rollers with a maximum speed of 100 revolutions per minute (rpm) for slurry mixing. The two stage rotary vane pump is employed for the purpose of extracting air bubbles from the slurry mixture within a leak-proof bottle; the paste mixture will exhibit higher viscosity, thereby there is no necessity to remove bubbles. The planetary ball mill, which is more powerful with a maximum speed of 600 rpm, can be used for mixing more viscous paste mixing. The planetary ball mill has been specifically crafted for the purposes of blending, homogenizing, finely grinding, mechanically alloying, disrupting cells, producing small volumes of high-tech materials, and engaging in colloidal grinding. Positioned eccentrically on the "Sun Wheel" of this planetary ball mill are four integrated grinding stations. As the Sun Wheel executes rotations, the grinding balls within the grinding jars experience overlaid rotational motions known as Coriolis Forces. The disparity in velocities between the grinding balls and the containers generates a combination of frictional and impact forces, thereby unleashing substantial dynamic energies. Ultimately, the final grinded products can achieve a minimal granularity of merely 0.1 micron [55].

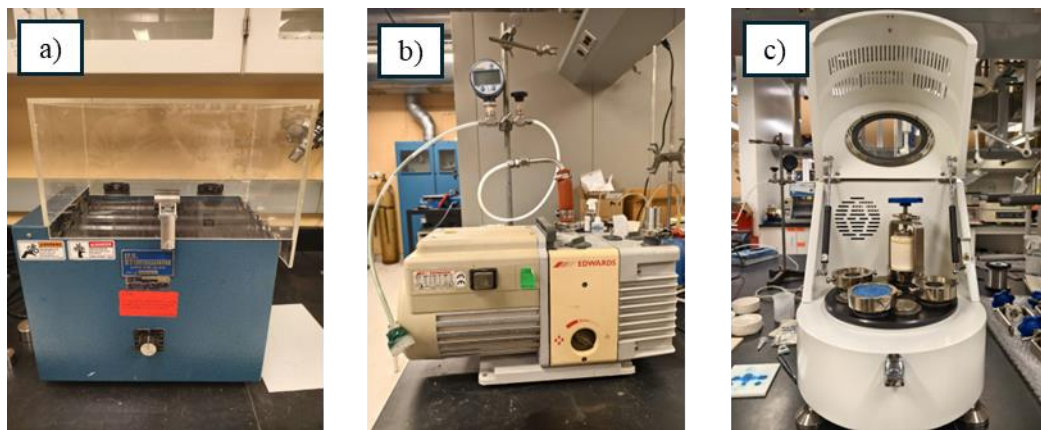


Figure 2-4. a) U.S. Stoneware-roller, b) Edwards Vacuum-RV two stage rotary vane pump, c) Across International-planetary ball mill 4x100ml gear-drive 0.4L

The screen printer is used to print the slurry material on substrate pellets. The platen assembly is a crucial component of a screen-printing machine, serving as a platform for the squeegee drive mechanism and the screen frame. It is driven vertically by a pneumatic cylinder and sits on a high precision die-set. The upstroke is cushioned internally, and the downstroke is slowed by hydraulic shock absorbers. The platen's downward movement is controlled by a micrometer stop, known as a z-stop, which determines the height of the screen above the substrate, or the "snap-off" distance. The Model 3230-BL has one rear z-stop [56] (see Figure 2-5).

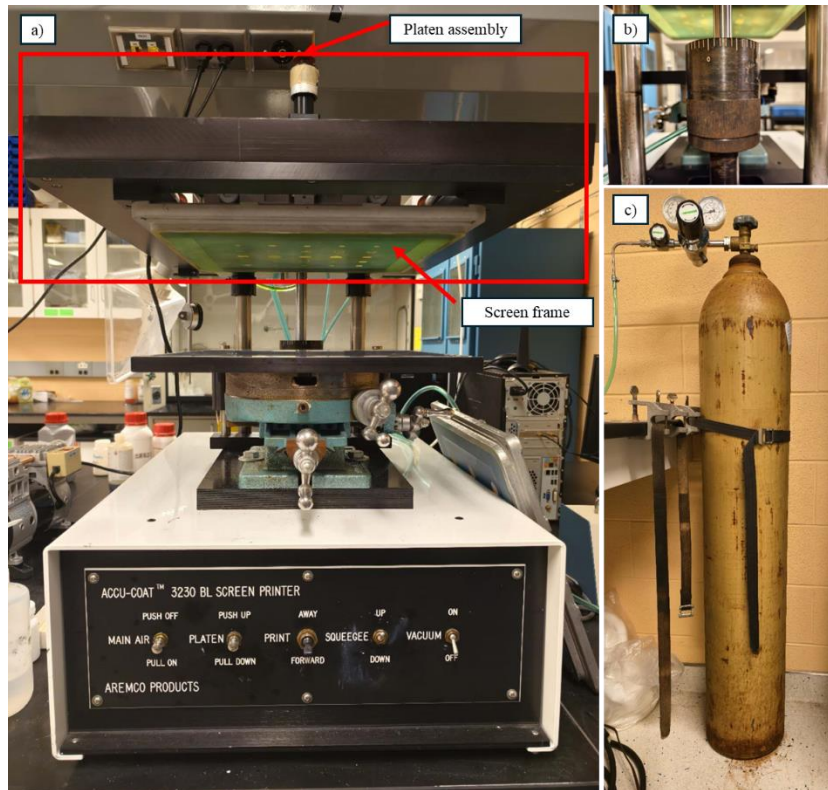


Figure 2-5. ACCU-COAT Model 3230-BL screen printer a) platen assembly, b) z-stop, and c) pneumatic cylinder

The yoke is constructed to move the squeegee horizontally across the screen. It travels on a set of bushings along 3/4-inch diameter stainless steel shafts. A variable speed hydraulic cylinder is responsible for driving the yoke, with speed controls positioned on the rear side of the air-oil tanks. The squeegee mechanism comprises an up/down pneumatic cylinder, a squeegee mounting block, a squeegee clamp, and squeegee rubber. The cylinder moves the squeegee vertically to and from the screen surface, with travel length controlled by a knob. A pressure regulator (0-60 psi) controls the squeegee pressure [56] (see Figure 2-6).

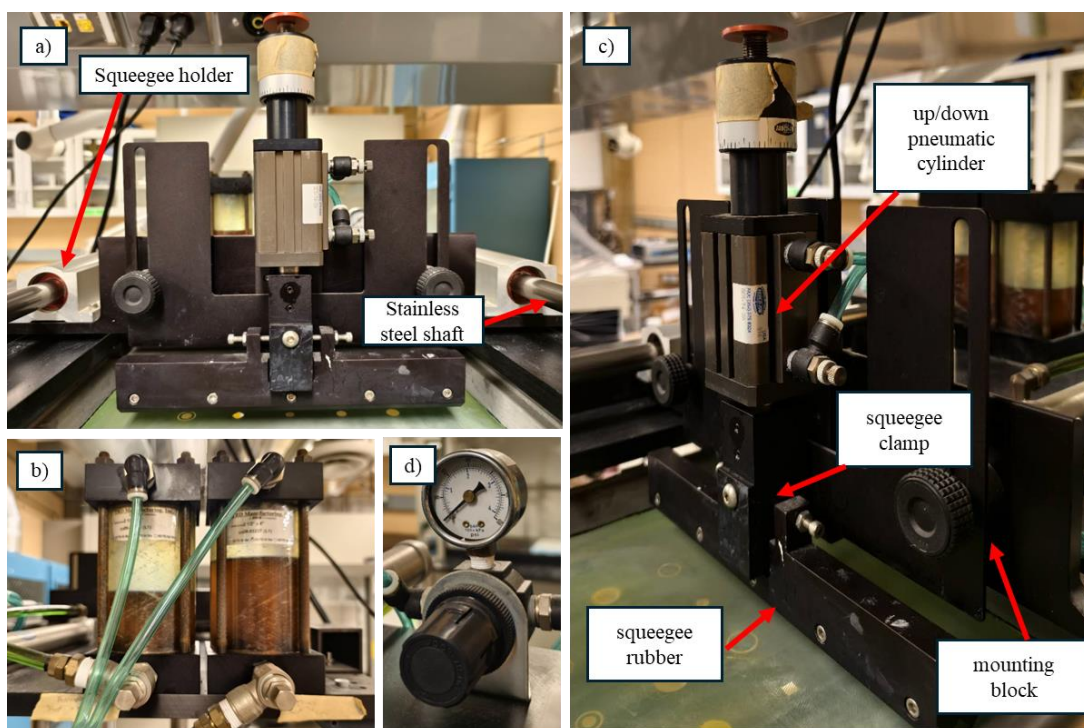


Figure 2-6. Screen printer: a) yoke assembly, b) air-oil tanks, c) squeegee mechanism, and d) squeegee pressure regulator

The manual blade coating process is simpler compared to the screen-printing method. First, clamping the stainless-steel stub securely onto a table clamp and apply double-sided tape to the top of the stub. Then, attaching the pre-sintered substrate to the tape. Finally, using an alumina rod to coat the paste material evenly onto the substrate manually. The equipment used for the manual blade coating method is shown in Figure 2-7.

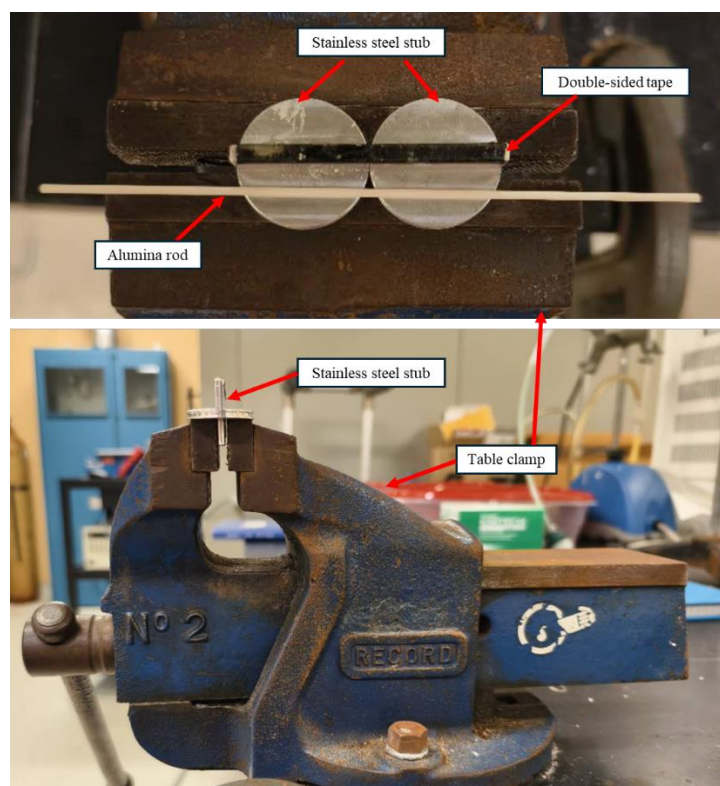


Figure 2-7. The manual blade coating set up on the table clamp

2.5 Methods Chosen for Membrane Fabrication

There are several techniques to manufacture the membrane. Although the tape casting method can fabricate both electrodes and electrolytes, it requires different additives to create flexible green tapes. The slurry recipe for these green tapes often remains a secret in literature. Therefore, finding the best recipe for tape casting slurry requires a lot of experimentation. On the other hand, the slurry or paste for the screen-printing method requires fewer additives, making it easier to develop a suitable recipe. In this thesis, die pressing method is chosen for fabricating the substrate, then screen-printing and manual blade coating approach to apply the electrolyte layer on the substrate.

2.6 Sintering Method

To prevent any potential warpage issues during the sintering process, a bi-layer membrane is strategically positioned between alumina plates, as illustrated in Figure 2-8. The upper alumina plate serves as a weight to compress the bi-layer membrane, preventing warpage.

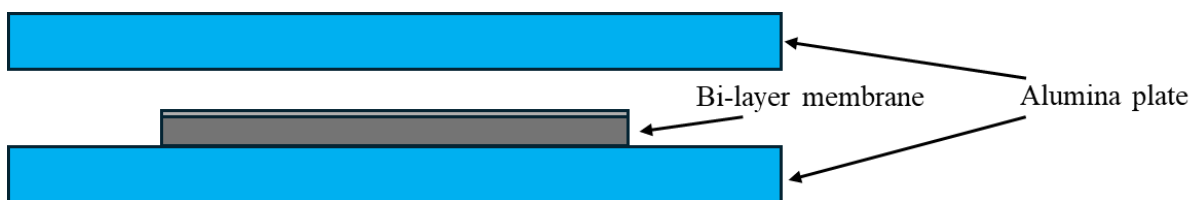


Figure 2-8. Schematic diagram of BZCY172-Starch|BZCY172 sintering in between alumina plates in muffle furnace

We endeavor to address the issue of barium loss by establishing a controlled environment rich in barium content throughout the sintering process. This involves utilizing a layer of BZCY172 powder to cover the electrolyte surface, as shown in Figure 2-9.

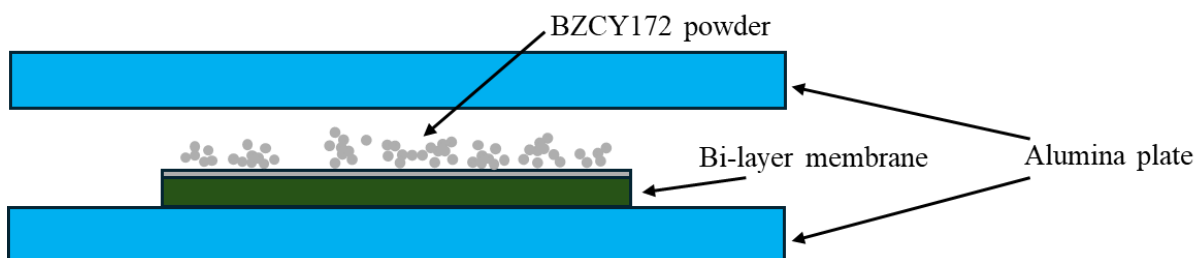


Figure 2-9. Schematic diagram of BZCY172-NiO-Starch|BZCY172 sintering in between alumina plates covered with a layer of BZCY172 powder in muffle furnace

In order to address the uneven dispersion of BZCY172 powder on the bi-layer membrane, a sintered BZCY172 pellet is used to cover the membrane and prevent the loss of barium (see Figure 2-10). Also, the pristine BZCY172 pellet is manually pressed on a bench top press using a die slightly larger in diameter than the bi-layer membrane to ensure complete coverage. Subsequently, this pristine BZCY172 pellet sinters at 1600°C for a duration of 2 hours.

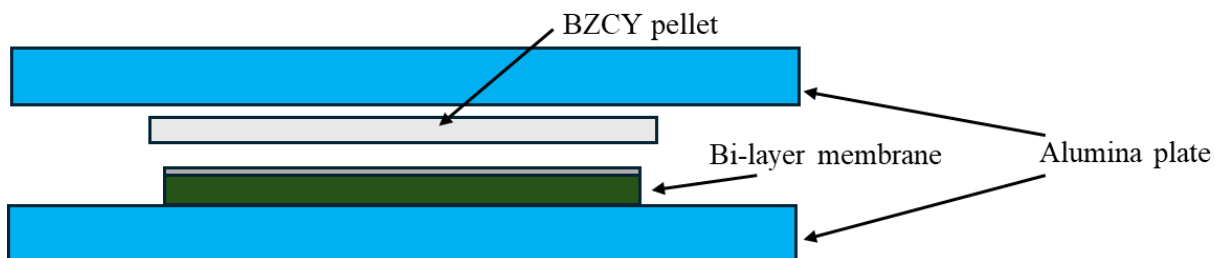


Figure 2-10. Schematic diagram of BZCY172-NiO-Starch|BZCY172 sintering in between alumina plates covered with a pure BZCY172 pellet in muffle furnace

Based on our observations, the BZCY172 powder does not adhere well to the bi-layer membrane, and it exhibits an irregular distribution on the surface of the electrolyte. In contrast, the sintered BZCY172 pellet displays a uniformly even distribution but tends to adhere strongly to the electrolyte layer. A potential solution could involve their combined application to mitigate their shortcomings (see Figure 2-11).

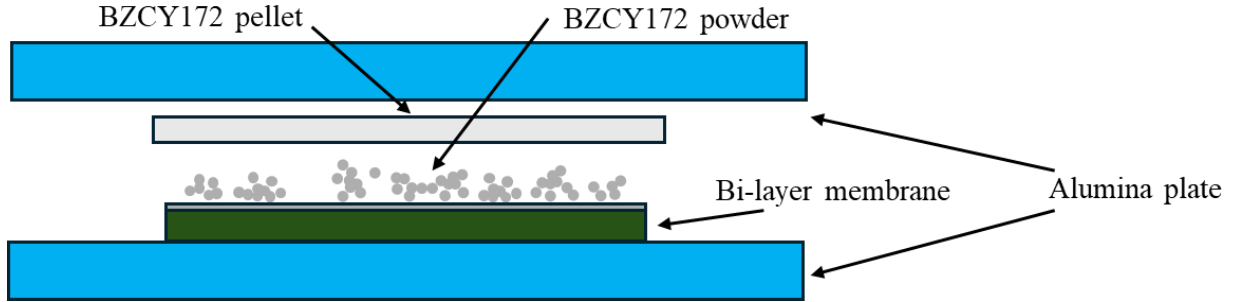


Figure 2-11. Schematic diagram of BZCY172-NiO-Starch|BZCY172 sintering in between alumina plates covered with a pure BZCY172 powder and pellet in muffle furnace

2.7 Characterization Methods

2.7.1 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) is a method employed to analyze material characteristics such as crystal structure, size of crystallites, and strain. This analytical technique is instrumental in confirming the structural composition and integrity of the synthesized materials. The technique is based on Bragg's equation, which encompasses the reflection of a focused X-ray beam from the crystal planes of a sample. XRD depends on broad-angle elastic scattering and is commonly applied to materials with a well-ordered structure (crystalline materials) as opposed to disordered materials. As X-rays pass through a specimen, they are deflected by the atoms, and the resulting interference is examined using Bragg's law along with a detector to ascertain the crystalline arrangement of the material [57], [58]. The principle of Bragg's law as follows:

$$\sin(\theta) = \frac{n\lambda}{2d} \quad \text{Equation 2-1}$$

When X-ray light reflects off a crystal, diffraction patterns are created, unveiling the physico-chemical characteristics of the crystal's structure. These patterns in powder samples mirror the structural

attributes of the material. By comparing these unique diffraction patterns with a reference database like the JCPDS (Joint Committee on Powder Diffraction Standards) library, materials can be identified. Additionally, the diffraction patterns offer insights into the sample's purity or the presence of impurities [59].

2.7.2 Scanning Electron Microscope (SEM)

A scanning electron microscope (SEM) is commonly utilized to observe and analyze micro- and nanoparticles within solid materials because of its exceptional resolution of 10 nm, with more advanced versions achieving as low as 2.5 nm. SEM can be paired with energy-dispersive X-ray microanalysis (EDX, EDS, EDAX) to identify the composition or orientation of individual crystals [57]. EDS is used to conduct elemental analysis of a sample. A high-energy beam, consisting of charged particles such as electrons or protons, or a beam of X-rays, is directed at the specimen to generate characteristic X-rays. This incoming beam can excite an electron in an inner shell, displacing it and creating an electron hole. An electron from an outer shell then fills this gap, emitting an X-ray in the process. The energy dispersive spectrometer measures the quantity and intensity of the emitted X-rays to determine the elemental composition of the specimen [58].

The electron source typically consists of a tungsten filament or field emission gun, with extremely low-pressure conditions. The electron beam is accelerated using a high voltage system (20 kV), controlled by apertures and lenses, and moves across the surface of the specimen. Images are produced from signals resulting from the interaction between the beam and the specimen, with emitted electrons being captured by a detector. High magnification enhances surface topography analysis and spatial resolution [57].

2.8 Chapter Summary

This chapter provides a comprehensive overview of the key apparatus and methods used in the synthesis of proton-conducting material powders and the fabrication of membranes. It highlights combustion and sol-gel techniques as primary synthesis methods, known for their ability to produce materials with high surface area, good porosity, excellent homogenization, and precise particle size control. In membrane fabrication, the chapter discusses techniques such as die pressing, screen printing, and manual blade coating, emphasizing their roles in achieving high-quality membranes. Sintering techniques are also addressed, focusing on their importance in preventing warping, barium depletion,

and adhesion issues in bi-layer membranes. Additionally, the chapter introduces Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD) as essential characterization tools, which provide crucial insights into the structural and morphological properties of the materials studied.

Chapter 3

Optimization of Powder Synthesis

3.1 Chapter Introduction

This chapter aims to present the BZCY172 powder synthesis process utilizing combustion and sol-gel techniques, along with the calcination temperature profiles. The chapter also discusses the characterization results of powder materials calcinated at varying temperatures.

3.2 BZCY172 Powder Synthesis Process

3.2.1 Combustion Method

There are a pair of formulas that are employed for this combustion method. The initial recipe uses both nitric acid (HNO_3) and deionized water as solvents, because yttrium oxide (Y_2O_3) and Zirconium (IV) carbonate basic ($\text{Zr}(\text{OH})_2\text{CO}_3 \cdot \text{ZrO}_2$) cannot dissolve in the deionized water, the HNO_3 is used to dissolve them. The procedure is as follows: first, Y_2O_3 is dissolved in HNO_3 , then $\text{Zr}(\text{OH})_2\text{CO}_3 \cdot \text{ZrO}_2$ is added to the solution. The solution is heated and stirred continuously at $70\text{--}80^\circ\text{C}$ on the hot plate. Once the solution is clear, barium acetate ($\text{Ba}(\text{CH}_3\text{COO})_2$) and cerium nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) are added. The quantity of initial substances is in stoichiometric proportions (see Table 3-1). Subsequently, citric acid as a complexing agent with a molar ratio of metal ions of 1.5:1 is introduced, and the acidity level is calibrated to approximately 7 using ammonium hydroxide solution and verified utilizing pH indicator paper. Keep heating at 100°C until yellow solution transform to yellow gel, the stirring bar is removed from the container at this stage, and then yellow gel dry overnight completely yields white solid [37].

Table 3-1. The amount of chemical compounds to synthesize 5 grams of BZY172 for initial recipe

Chemical compounds	Mass of each chemical compound (g)
$\text{Ba}(\text{CH}_3\text{COO})_2$	4.116
$\text{Zr}(\text{OH})_2\text{CO}_3 \cdot \text{ZrO}_2$	0.249
$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	4.900
Y_2O_3	0.728
Citric acid	9.287

The white solid material is combusted in furnace (47900 furnace) at 200°C for 3 hours with heating speed of 10°C/min, it gives black powder (see Figure 3-1). The black powder is grinded for 5 minutes manually.



Figure 3-1. the white solid material before combustion in the alumina crucible (right), and after combustion at 200°C for 3 hours (left)

The black powder and white solid are then put into furnace (47900 furnace) calcinating at 1000°C for 3 hours [37] with heating speed of 5°C/min to get white powders. After the calcination process, the particles that directly calcinated from white solid are dispersed in the furnace, indicating a high intensity of combustion. It is recommended that the combustion phase be distinct from the calcination phase to prevent loss of materials, and the combustion phase could take place on the hot plate.

The second recipe uses all-nitrates as the precursors, using stoichiometric amount of barium nitrate ($\text{Ba}(\text{NO}_3)_2$), cerium nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), zirconium nitrate ($\text{Zr}(\text{NO}_3)_4$) and yttrium nitrate ($\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) [38] (see Table 3-2).

Table 3-2. The amount of chemical compounds to synthesize 5 grams of BZY172 for second recipe

Chemical compounds	Mass of each chemical compound (g)
$\text{Ba}(\text{NO}_3)_2$	4.211
$\text{Zr}(\text{NO}_3)_4$	0.547
$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	4.900
$\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	1.234
Citric acid	9.287

The chemicals initially dissolve in the deionized water, the mixture inside the container is heated and agitated continuously at 60°C on a hot plate. Citric acid acting as a complexing agent with a molar proportion of metal ions of 1.5:1 is included, and the acidity level is modified to approximately 7 with ammonium hydroxide solution and assessed using pH indicator paper. The oil bath is introduced to achieve homogenous heat distribution (see Figure 3-2), the silicon oil is selected, and a temperature sensor is linked to a thermometer to measure the real temperature of the oil. As the heat dissipates to the surroundings, the hot plate is adjusted to 220 °C to enable the silicon oil to reach 100 °C to vaporize all the solvent while being stirred and turned into a denser form, the stirring bar is removed from the container at this stage, and allowed to air dry overnight to solidify completely [30].

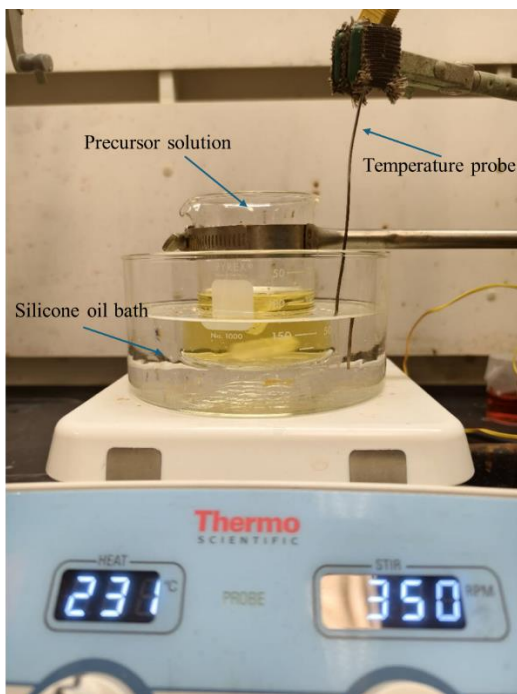


Figure 3-2. Oil bath setup, the hot plate temperature set at 231°C and stirring at 350rpm

The dried gel is combusted directly at hot plate temperature of 300°C. Aluminum foil is placed around the container to prevent heat loss. Unlike the initial recipe, this combustion is less intense and can also be done in the 47900 furnace. Following 25 minutes of manual grinding, the as-prepared powder is gathered and subjected to calcination at 1000°C for 3 hours in the muffle furnace (KSL-1700X-A1).

3.2.2 Sol-gel Method

The sol-gel method is very similar to combustion method, but it does not require the neutralization of precursors solution, using all-nitrates as the precursors, stoichiometric amount of $\text{Ba}(\text{NO}_3)_2$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Zr}(\text{NO}_3)_4$ and $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ as the starting materials [38]. The precursor compounds initially dissolve in the deionized water, then citric acid as a complexing agent with a molar ratio of metal ions of 1.5:1 is added. Stir continuously for 30 minutes to achieve complete complexation. Next, the hot plate temperature is adjusted to 220°C and heat the silicone oil elevated to 100°C . As the solvents evaporate, the gel starts to puff like a yellow bread. Once the puffing stops, the material is transferred into furnace (47900 furnace) for desiccation. We obtained a brownish as-synthesized powder, after 5 minutes and/or 25 minutes of manual grinding, subjected to calcination at 900°C , 1000°C , 1250°C individually.

3.2.3 Calcination Conditions

After obtaining the dried as-prepared powder from the 47900 furnace, manually grind it in a mortar to produce fine powders. Then, calcine the ground powder and transfer it to the muffle furnace (KSL-1700X-A1) for further processing. The fundamental concept entails setting the heating rate at $2^\circ\text{C}/\text{min}$ from ambient temperature up to our desired temperature. To ensure the muffle furnace's integrity, it is imperative to establish a cooling program, the cooling rate of $2^\circ\text{C}/\text{min}$ until 200°C , and then let furnace cool down by itself. In this thesis, four different temperature profiles are used for the powder calcination step to test differences in the powder's crystallinity and morphology. The temperature profiles for powder calcination are shown in Figure 3-3.

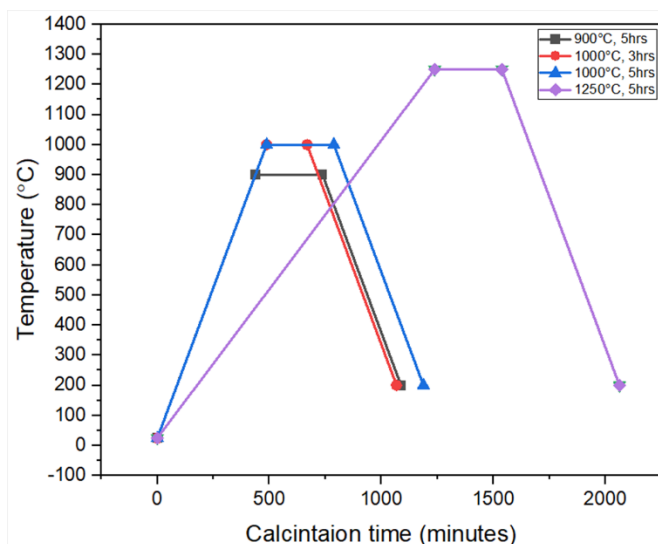


Figure 3-3. The powder calcination temperature profiles: 900°C, 5 hours; 1000°C, 3 hours; 1000°C, 5 hours; 1250°C, 5 hours

3.3 BZCY Powder Characterizations

3.3.1 BZCY172 Powder's Crystallinity

In the initial recipe of the combustion technique, various combustion temperatures were experimented with in order to completely burn the gel form material. The conditions of 300°C, 2 hours and 500°C, 2.5 hours both result in the production of as-prepared yellow powder. It is worth noting that due to the poor heat insulation of the furnace model used (47900 furnace), the actual heating rate may be significantly slower than the predetermined setting, consequently leading to extended heating durations beyond the anticipated time frame. This consequently led to the emergence of secondary phases such as BaCO_3 and CeO_2 , as identified using X-ray diffraction (XRD) analysis via the Rigaku Ultima IV instrument. On the other hand, it has been verified that the minimal temperature for calcination for achieving a pure perovskite structure of BZCY172 is 1000°C for both recipes, since there are no existences of secondary phases. The depiction of the pure perovskite structure of BZCY172 in a muffle furnace (KSL-1700X-A1) can be observed in Figure 3-4 a), where the blue line signifies this structural purity.

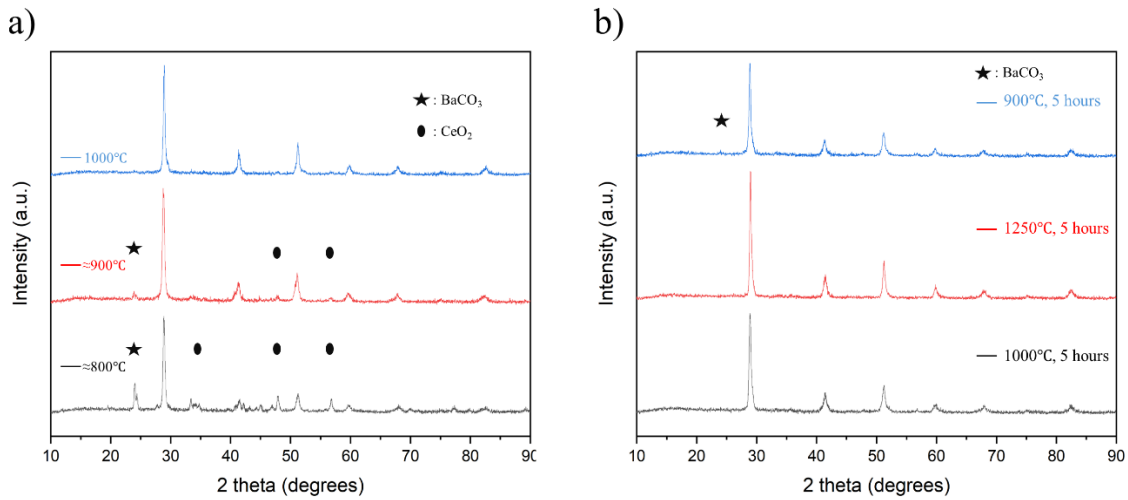


Figure 3-4. XRD results of BZCY172 powder calcinated using a) combustion method in the 47900 furnace, b) sol-gel method in the muffle furnace for 5 hours

In the process of utilizing the sol-gel technique, it is observed that under the calcination conditions set at 900 °C for 5 hours, there is a negligible presence of a BaCO_3 peak. However, as the temperature is increased to 1000°C and beyond, a formation of the pure perovskite structure becomes evident. Therefore, it is important to maintain the calcination temperature at 1000°C for a period of 5 hours to achieve the desired pure BZCY172 perovskite structure [35], [40] (see Figure 3-4 b)).

3.3.2 BZCY172 Powder's Morphology and Atomic Ratio

The scanning electron microscope (SEM) images of the BZCY172 powder are displayed in the visual representations provided below, illustrating the microstructural characteristics and morphology of the powder material in a highly detailed manner.

When comparing two recipes for the combustion method, one can observe that all-nitrates method results in a more porous powder. In the initial recipe, the powder tends to agglomerate, whereas all-nitrates recipe assists in creating a more porous powder (see Figure 3-5 a) and b)). In literature, the manual grinding process for a significant amount of time aids in reducing the formation of agglomerated clusters [24]. Nonetheless, in comparing the powders synthesized outlined in Figure 3-5 b) and c), it is noted that in c), it is observed that in this instance, grinding for a long time does not contribute significantly to reducing agglomeration.

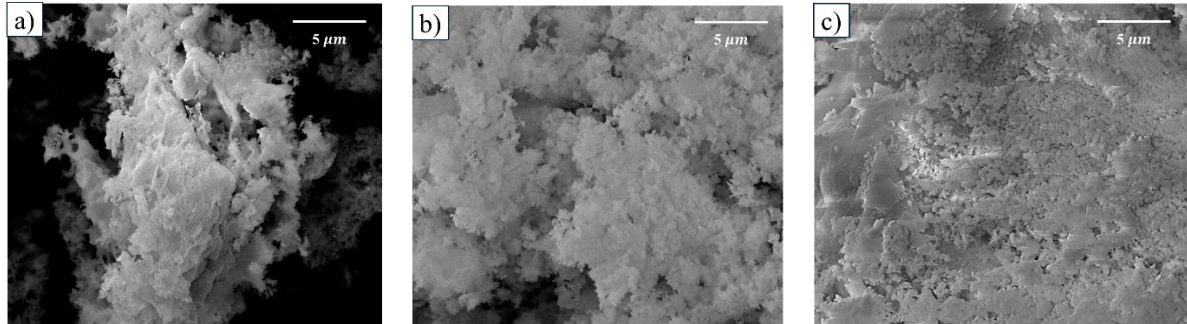


Figure 3-5. SEM images of calcinated BZCY172 powder after manually grinding as-prepared powder using combustion method a) initial recipe sintering at 1000°C, 3 hours, after grinding for 5 minutes, b) all-nitrates recipe sintering at 1000°C, 3 hours after grinding for 5 minutes, c) all-nitrates recipe sintering at 1000°C, 3 hours after grinding for 25 minutes [30]

The increased porosity and smaller particle size resulting from the all-nitrates recipe, so we also apply this recipe to sol-gel method. Figure 3-6 a) and b) show the as-prepared powders subjected to calcination at 1000°C and 1250°C, separately. Both 1000°C and 1250°C calcination temperatures yield a pure perovskite structure, as shown in Figure 3-4 b), with similar SEM results. However, a higher calcination temperature may cause premature sintering [30]. The critical aspect of sol-gel method lies in controlling agglomeration and grain growth during the calcination process [30]. Thus, it is crucial to ensure the material is calcinated at a relatively low temperature while maintaining a good phase quality. Again, grinding for a long time does not contribute significantly to reducing agglomeration (see Figure 3-6 a) and c)).

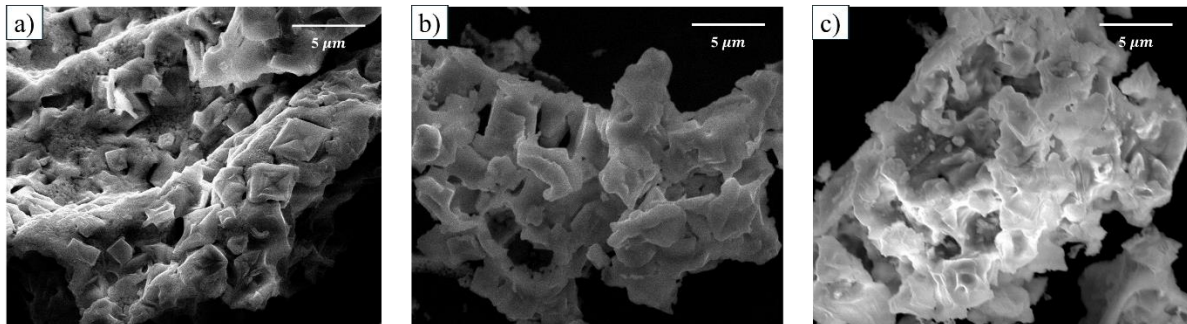


Figure 3-6. SEM images of calcinated BZCY172 powder after manually grinding as-prepared powder using sol-gel method and all-nitrates recipe a) sintering at 1000°C, 5 hours after grinding for 5 minutes,

b) sintering at 1250°C, 5 hours after grinding for 5 minutes [38], c) sintering at 1000°C, 5 hours after grinding prepared powder for 25 minutes

An additional rationale for the decision to disregard the initial recipe is the relatively low Zr content contained in the BZCY172 powder. It has been reported that the BZCY80 material lacks any Zr doping within its perovskite structure, resulting in larger grain sizes and enhanced relative density at high-temperature sintering [31]. And it is crucial to note that Zr plays a vital role in upholding exceptional chemical stability against H₂O and CO₂ environment and ensuring high levels of bulk proton conductivity [26].

As shown in the above Table 3-3, the initial recipe does not follow to the anticipated stoichiometric ratio, resulting in a notably lower Zr content compared to the theoretical value. Conversely, the all-nitrates recipe demonstrates improved suitability for both combustion and sol-gel techniques, exhibiting atomic ratios that align more closely with the theoretical values. This suggests that the all-nitrates approach could be more effective in achieving the desired composition in Zr-doped materials synthesis.

Table 3-3. Energy dispersive X-ray analysis (EDX) shows atomic ratio of each element

BZCY172	Atomic ratio of initial recipe combustion method	Atomic ratio of all-nitrates recipe combustion method	Atomic ratio of all-nitrates recipe sol-gel method	Theoretical values
Barium	0.780±0.246	0.971±0.255	0.954±0.329	1
Zirconium	0.074±0.071	0.118±0.024	0.183±0.162	0.1
Cerium	0.590±0.190	0.665±0.08	0.647±0.243	0.7
Yttrium	0.334±0.154	0.217±0.05	0.169±0.116	0.2

3.4 Chapter summary

This chapter provides a detailed synthesis procedure for BZCY172 powder using combustion and sol-gel methodologies. It demonstrates that by carefully adjusting the calcination profiles, the BZCY172 perovskite material begins to crystallize at 1000°C. The comparison between two recipes reveals that the all-nitrate recipe produces atomic ratios that closely match the theoretical values, while also resulting in less agglomerated powder compared to the initial recipe. Moreover, the combustion

method is shown to produce finer particles. Consequently, by combining the all-nitrate recipe with the combustion method, a more isolated and finer particle size can be achieved, which is particularly beneficial for enhancing the sintering process.

Chapter 4

Optimization of Bi-layer Membrane Fabrication

4.1 Chapter Introduction

This chapter aims to present the bi-layer membrane process utilizing die pressing, screen printing, and manual blade coating methods, along with the sintering temperature profiles. The chapter also discusses the characterization results of bi-layer membrane at different sintering temperatures to get the dense electrolyte layer and porous electrode layer, elucidating the implications of their properties in relation to the challenges outlined in the literature review. The problem of Ba loss has been examined from a thermodynamic standpoint through the utilization of a MATLAB simulation. Furthermore, a gas impermeable experimental setup has been created for the purpose of evaluating the hermeticity of dense double-layer structures.

4.2 Bi-layer Membrane Fabrication Process

4.2.1 Die Pressing the Porous Substrate as Electrode

The acquired BZCY172 powder is mixed with nickel oxide (NiO) and starch using a literature weight ratio 40:60:10 via roller ball milling in ethanol for 3 hours at a speed of 20 rpm [46]. The function of the starch in this process is to serve as a pore former within the electrode. Here are more details about the process. First, the powders are added in a 30ml Fisherbrand leakproof HDPE wide-mouth bottle along with five 10mm diameter zirconia balls. Then, ethanol is poured into the leakproof bottle until it covers all the zirconia balls. With the cap on, the bottle is now placed on rollers. Five zirconia balls can be aligned closely inside the bottle while bottle is rolling, preventing any tilting, and ensuring a more uniform mixture. After 3 hours on the rollers, the bottle is placed in the fume hood with cap removed, allowing the mixture to air dry overnight for complete ethanol evaporation. Finally, the mixed powders are ready to be transferred into a die and pressing them onto a substrate.

The substrate is produced under elevated pressure through the utilization of a bench top press, employing a 12.7 mm diameter dry pellet pressing die. The procedure is as follows. First, a quantity of 0.5 grams of previously prepared mixed powders is placed within the die. Then, it is subjected to compression at 50 Mpa for 2 minutes, resulting in the formation of a 1mm thick green pellet. Following this, the green pellets undergo pre-sintering at 800°C and 1000°C for a duration of 2 hours individually.

The 800°C and 1000°C pre-sintering temperatures are from literatures [45], [46], to enhance their mechanical strength for the subsequent electrolyte deposition process.

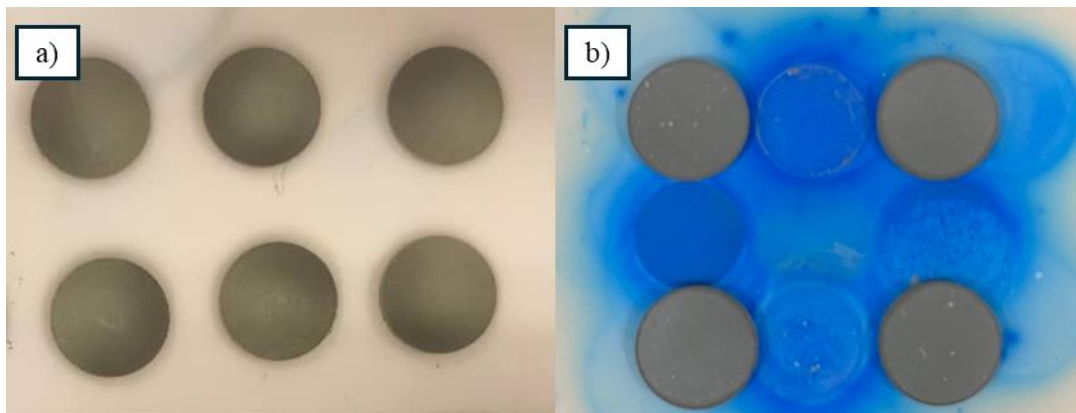


Figure 4-1. NiO+BZCY172+starch substrate pellets a) before pre-sintering (i.e., green pellet), b) after pre-sintering

4.2.2 Screen Printing Electrolyte Layer

To start the process, an electrolyte slurry is formulated through the utilization of a roller ball milling machine. In this step, BZCY172 powders are combined with a laboratory-synthesized organic binder in a weight ratio of 3:5, this organic binder is composed of a mixture of ethyl cellulose and terpinol as suggested in the reference [46]. And the exact composition depends on the printing results and will be discussed later. Then, the BZCY172 and organic binder are introduced to the leakproof bottle with five 10mm zirconia balls. The bottle is then positioned on rollers and undergoes the ball milling at 20 rpm for 48 hours.

The binder composition impacts the printed layer significantly. It is found that the slurry with 3 wt% ethyl cellulose and 97 wt% terpineol is not viscous enough to adhere to the substrate after printing; conversely, the slurry (2) is excessively thick and led to a significant amount of clustering of BZCY172 and ethyl cellulose. Moreover, the slurry (3) exhibits a small amount of ethyl cellulose clustering. Therefore, a modified formulation slurry (4) with 4 wt% ethyl cellulose and 96 wt% terpineol is used to achieve a uniform and stable BZCY172 slurry with better printing results (see Table 4-1).

Table 4-1. The binder composition (ethyl cellulose and terpineol) of BZCY172 slurries for screen-printing, mix using roller with BZCY172 powder and binder weight ratio 3:5

	Ethyl cellulose (wt%)	Terpineol (wt%)	Slurry condition
Slurry (1)	3	97	Not adhesive
Slurry (2)	10	90	Clusters
Slurry (3)	5	95	Clusters
Slurry (4)	4	96	uniform

After the powders and binder are thoroughly mixed into a stable slurry, they can be printed onto the substrate using a screen printer. The mesh screen, main parts of the screen printer, and printing cycle steps are shown in Figure 4-2. First, place the pre-sintered substrate on the print platen. Lower the screen frame until the mesh is in close contact with the print platen. Collect the slurry and place it on one side of the circular 325 mesh screen, which should be slightly larger than the substrate to ensure the gas-tight electrolyte layer fully covers the substrate, preventing gas leaks. Next, compress the squeegee onto the mesh fabric and push the BZCY172 slurry from the left side to the right side of the circular mesh. Then, lift and lower the squeegee to the right edge of the circular mesh and push it back to the left edge. This completes the two printing cycles, resulting in a screen-printed double-layer membrane.

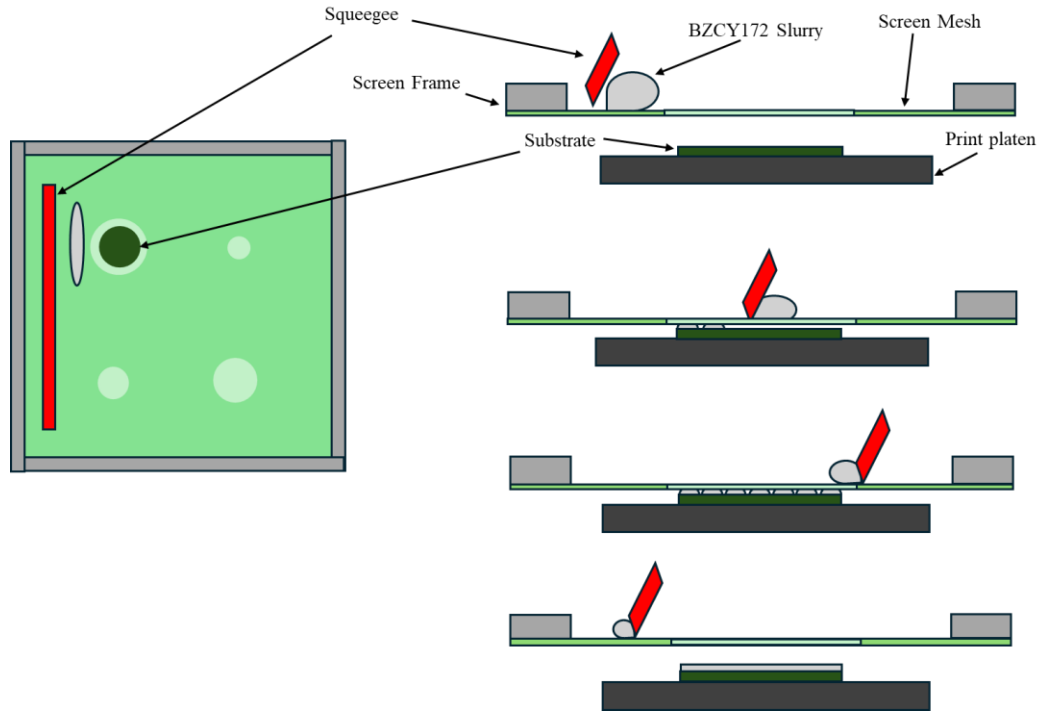


Figure 4-2. Mesh screen, screen-printing cycle steps, main parts of screen-printing machine are detailed along with the process sequence [60]

The homogeneous and stable BZCY172 slurry is screen-printed onto the pre-sintered NiO-BZCY172-starch composite substrate, as shown in Figure 4-3 b). During the printing process, it is observed that pellets pre-sintered at 1000°C existed superior mechanical resilience compared to pre-sintering at 800°C. The substrate that pre-sintered at 800 °C is easier to break under the pressure of squeegee (see Figure 4-3 a)), and 1000°C pre-sintered substrate also exhibited cracks but more complete. Bi-layer membranes are sintered at different temperatures and time using a programming muffle furnace (KSL-1700X-A1) thus the half-cell of NiO-BZCY172-starch|BZCY is obtained.

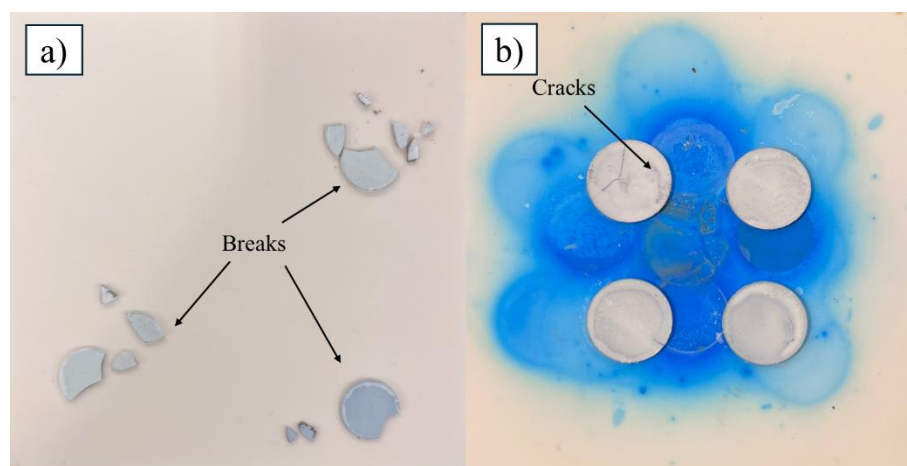


Figure 4-3. Screen printed bi-layer membrane (NiO-BZCY172-starch|BZCY172), a) substrate pre-sintered at 800°C, b) substrate pre-sintered at 1000°C

However, due to the low sinter ability of slurry material, it is hard to get a dense and even electrolyte layer, we need a thicker paste and new electrolyte deposition method. Therefore, to achieve a dense layer on the substrate, a manual blade coating method is developed using a thicker paste, and the thicker paste adheres better to the substrate.

4.2.3 Manual Blade Coating Electrolyte Layer

Due to the uneven distribution and poor sinter ability of slurry printed on the substrate as mentioned above, there is a necessity to augment the proportion of powder and organic binder. Nevertheless, the roller ball milling apparatus operates at a maximum of 100 rpm, leading to prolonged processing duration and causing substantial aggregation when the powder content in the mixture is elevated. It is difficult to get homogenous and stable BZCY172 paste using roller.

To overcome this, the planetary ball milling machine is introduced with maximum 600 rpm. The electrolyte paste is prepared using planetary ball milling machine by mixing BZCY172 powders with an organic binder in a weight ratio of 6:4 [61] (see Table 4-2).

Table 4-2. The binder composition (ethyl cellulose and terpineol) of BZCY172 paste for manual blade coating, mix using ball mill with BZCY172 powder and binder weight ratio 6:4

	Ethyl cellulose (wt%)	Terpineol (wt%)	Paste condition
Paste (1)	4	96	Adhesive and uniform

The powder and organic binder are added into the ball milling jar, the milling balls-to-powder weight ratio is 10:1 [62], [63], the milling balls are mixed with 10mm and 6mm in diameter. The grinding velocity is established at 600 rpm, for each iteration: 5 minutes of grinding, 2 minutes of pausing for forward direction, and identical iteration for backward direction. Iterated for 10 cycles, overall grinding duration is 140 minutes. Planetary ball mill features four grinding stations, when in operation, it is essential to have two containers positioned diagonally to equalize the mass. The BZCY172 suspension following ball grinding is highly adhesive, resembling more of a paste. The BZCY172 paste is unable to penetrate the circular 325 mesh due to its viscosity. Therefore, we choose to manually apply the BZCY172 adhesive onto the substrate.

The substrate is affixed on a stainless stub, then homogenous and stable BZCY172 paste is applied on the substrate using a slender alumina rod. It requires several attempts to evenly spread the paste layer. Following each application, the paste must be dried prior to the subsequent application, the simple procedure is shown in Figure 4-4.

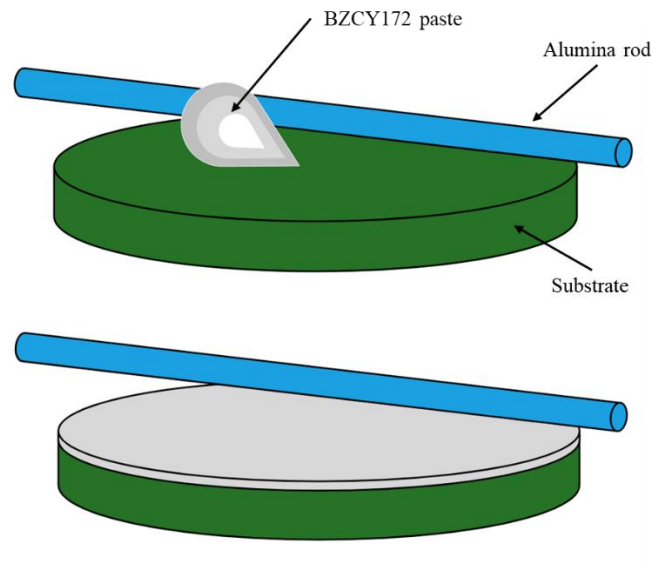


Figure 4-4. Manual blade coating steps

The distribution of the BZCY172 paste on the substrate has a higher level of uniformity in comparison to the distribution of the BZCY172 slurry, as evidenced by the visual observations (see in Figure 4-5). The even distribution of the paste suggests a more controlled and precise application

process, possibly due to its rheological properties and application method, which could have significant implications for the overall performance and efficiency of the coating process.



Figure 4-5. Manually blade coated bi-layer membrane (NiO-BZCY172-starch|BZCY172) stick on stainless stub, the white paste is coated on pre-sintered substrate

Bi-layer membrane is then sintered at different temperatures and durations using a programming muffle furnace (KSL-1700X-A1) to obtain the half-cell of NiO-BZCY172-starch|BZCY172, which will be described later in this chapter.

4.2.4 Sintering Conditions

After obtaining the bi-layer membranes, the subsequent step involves the sintering process which takes place within the muffle furnace (KSL-1700X-A1). It is important to note that there exists a range of sintering temperatures and durations that have been documented in various literature sources, providing guidance on the optimal conditions for sintering the membranes. It is advised that a reduction in the heating rate be implemented when operating at elevated temperatures to be effective in minimizing the occurrence of undesirable outcomes such as cracks and delamination within the membrane sample. The characteristics of the co-sintered electrolyte layer and electrode layer are unavoidably impacted by stresses arising from shrinkage mismatches at the interfaces, these stresses have the potential to induce processing defects such as warpage, micro-cracks, or delamination at the interlayer interfaces [48]. The fundamental concept entails setting the heating rate at 2°C/min from ambient temperature up to 1000°C, then adjusting it to 1°C/min for temperatures exceeding 1000°C. To ensure the muffle furnace's integrity, it is imperative to establish a cooling program, the cooling rate of 1 °C/min until reaching 1000°C, followed by an adjustment to 2 °C/min until 200°C, and then let furnace cool down by itself (see Figure 4-6).

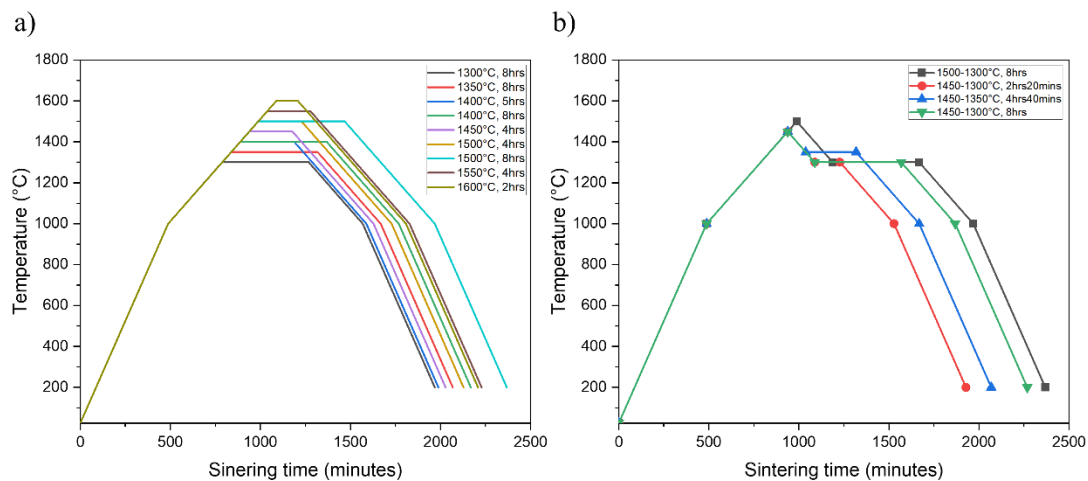


Figure 4-6. The sintering temperature profiles a) conventional sintering method, b) two-step sintering method

As we see, there are a lot of different sintering temperature profiles. For the conventional sintering method, we tested temperatures ranging from the lowest (1300°C) to the highest (1600°C) reported in the literature to achieve a dense electrolyte layer (see Figure 4-6 a)). After obtaining a dense layer at 1500°C, we use a two-step sintering method (see Figure 4-6 b)). The rationale behind employing the two-step sintering method is multifaceted. It aims to address the issue of adhesion between the electrolyte layer and the weighting material. This is crucial because the presence of a weighting material is essential to mitigate the warping of the bi-layer membrane, which is attributed to the distinct thermal expansion coefficients exhibited by the electrolyte and electrode materials. This approach also helps avoid prolonged sintering at very high temperatures, thereby reducing Ba loss potentially.

4.3 Sinter Ability of Screen-printed Bi-layer Membranes

In this section, all BZCY172 powder is synthesized through the combustion method according to a specified initial recipe.

4.3.1 Electrolyte without Sintering Aids

The BZCY172 powders are combined with only starch, serving as a pore-forming agent, in a specific weight ratio of 4:1. This blending process is carried out using a roller-milling apparatus (Stoneware-roller), in an ethanol medium for a duration of 24 hours to ensure homogeneity.

Subsequently, the BZCY172 slurry (4) is applied onto a pre-sintered substrate via a screen-printing technique. Then it is sintered at 1400°C for 5 hours and covered with alumina plates.

As illustrated in Figure 4-7, the membrane comprises a two-layer configuration consisting of an approximately 10µm thick electrolyte layer characterized by its non-dense nature. As enlarge the cross section, the porous layer exhibits a favorable appearance, featuring smaller pores that enhance the surface area for expediting the reaction, while larger pores are created by starch, can facilitate mass transfer and gas diffusion. However, this bi-layer membrane is quite fragile. The subsequent action involves adding NiO into the electrode to enhance its mechanical strength [35], [46].

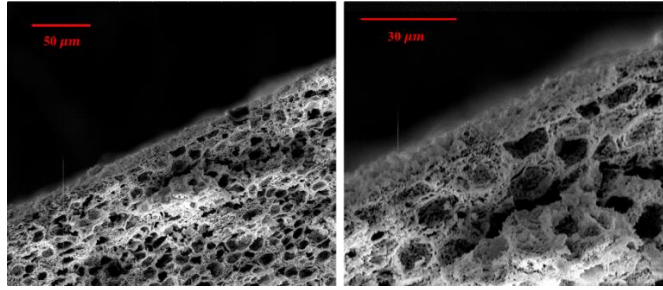


Figure 4-7. SEM cross section images of bi-layer membrane (BZCY172-Starch|BZCY172) sintered at 1400°C for 5 hours and covered with alumina plates

Figure 4-8 shows the bi-layer membrane with NiO in the electrode. NiO is introduced into the electrode and mixed using a Stoneware-roller in a leakproof bottle. Following sintering at 1400°C for 5 hours covering with alumina plates. Upon closer inspection of the electrode surface, distinct nickel grains can be observed, distinguished by their darker hue and larger size. As illustrated in a cross-sectional SEM image, the electrolyte layer measures approximately 15 µm and exhibits a low density. The bi-layer membrane has good mechanical strength with the aid of NiO.

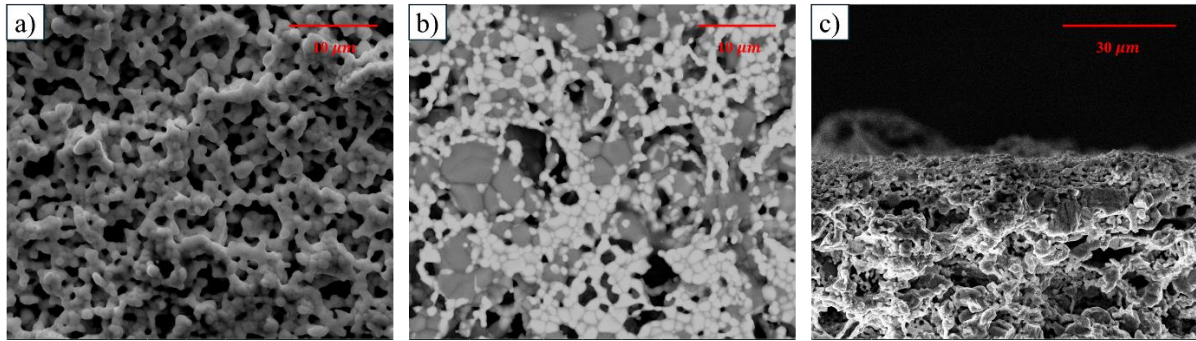


Figure 4-8. SEM images of bi-layer membrane #1 (BZCY172-NiO-Starch|BZCY172) sintered at 1400°C for 5 hours and covered with alumina plates, a) electrolyte surface, b) electrode surface, c) cross section

Since the sintering temperature 1400°C cannot obtain a dense electrolyte layer, experiments are being conducted with 1500°C sintering temperature for bi-layer membrane to determine the resultant outcomes. The observation in Figure 3-8 a), b), and c) appears dense, but it reveals the presence of segregation, with smaller, darker grains, nickel particles emerging from the electrode to aid in the formation of a new oxide, characterized by long, darker grains, and normal BZCY172 grains, represented by white grains. This may indicate that the temperature is excessive to cause the segregation, and the thickness of the electrolyte layer needs to be increased to avoid nickel emerging. The presence of large NiO grains in the Figure 4-9 d) illustrates their role in promoting the sintering of BZCY172 due to their proximity [44], [52], [53].

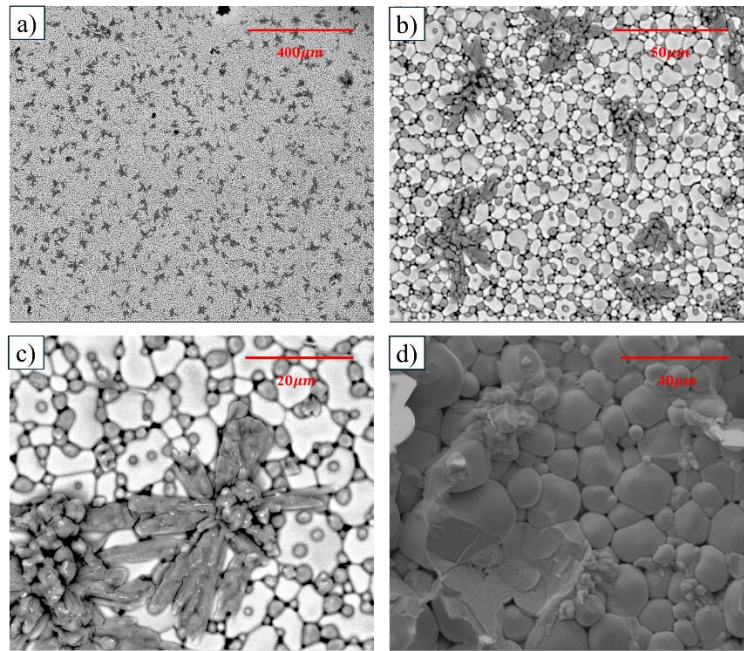


Figure 4-9. SEM images of bi-layer membrane #2 (BZCY172-NiO-Starch|BZCY172) sintered at 1500°C for 8 hours and covered with alumina plates a), b), c) electrolyte surface in different scales, d) electrode surface

Therefore, to mitigate the presence of segregation and the loss of barium, we first try to lower the sintering temperature or sintering duration. This adjustment is crucial in maintaining the integrity and properties of the material being processed.

4.3.2 Segregation Phenomena and Bubbles Appearance in Slurry

To optimize the sintering process, a strategic decision is made to reduce the sintering temperature from its original setting to a lower temperature of 1400°C and maintain this condition for a period of 8 hours. Alternatively, another approach is considered which involves decreasing the sintering duration to 4 hours while maintaining the temperature at 1500°C. Furthermore, an effort is made to enhance the quality of the electrolyte layer by increasing its thickness through screen-printing method repeated 15 times. This process allows for a well-controlled thickness of the electrolyte layer, ensuring it falls within the desired range of 20 to 30µm.

In the illustration presented as Figure 4-10 a), it is evident that there exist oval-shaped bubbles evenly dispersed across the surface of the electrolyte. Upon closer inspection of the region surrounding these bubbles on the electrolyte surface, as depicted in b), it becomes apparent that the density of this area is high. Conversely, after examining the regions encapsulated by the bubbles on the electrolyte surface, it is observed that these areas exhibit a high degree of porosity. An additional observation reveals the occurrence of segregations within the electrolyte layer even though at relative low temperature. For the cross-sectional view of the electrolyte, it is distinguished that the thickness of the electrolyte layer has been increased to approximately 20µm, resulting in a denser appearance but with minimal presence of pores.

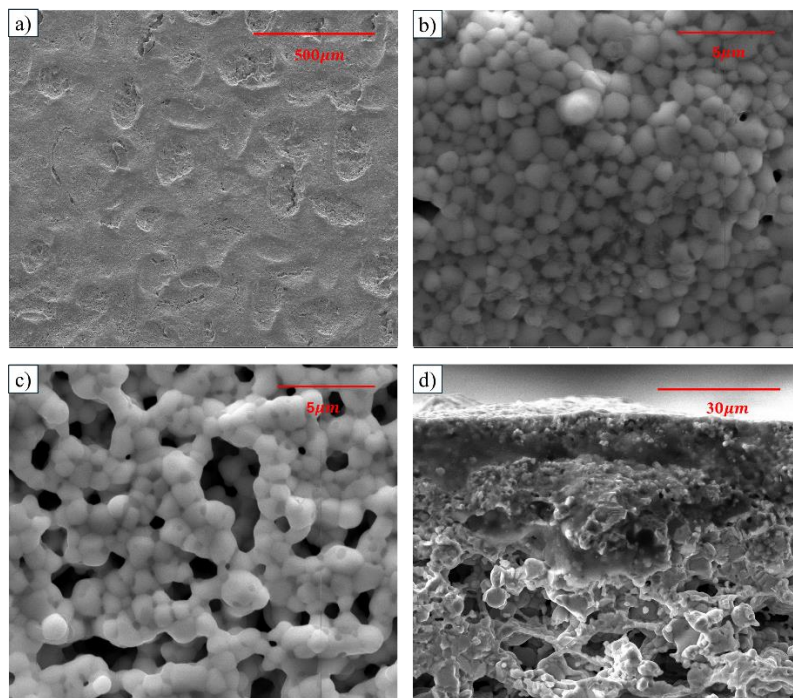


Figure 4-10. SEM images of bi-layer membrane #3 (BZCY172-NiO-Starch|BZCY172) sintered at 1400°C for 8 hours and covered with alumina plates a) electrolyte surface, b) dense part of electrolyte surface, c) porous part of electrolyte surface, d) cross section

In the case of the bi-layer membrane that sintering at a temperature of 1500°C for a duration of 4 hours (Figure 4-11), it can be observed that the bubbles present exhibit a consistent distribution pattern similar to that of the previous sample. Additionally, an analysis of the cross-sectional view of the electrolyte layer reveals the presence of similar segregations within its structure.

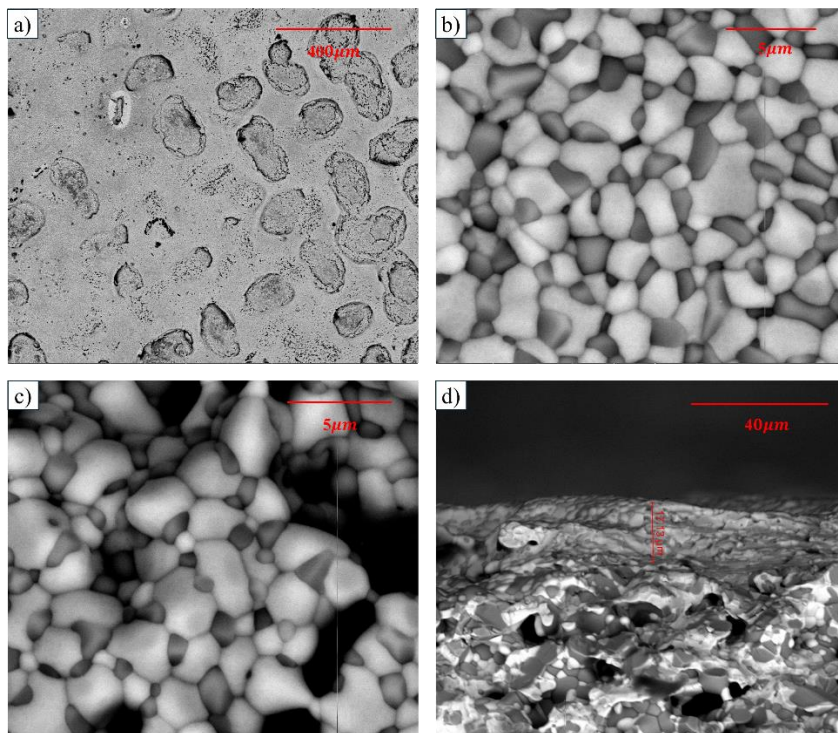


Figure 4-11. SEM images of bi-layer membrane #4 (BZCY172-NiO-Starch|BZCY172) sintered at 1500°C for 4 hours and covered with alumina plates a) electrolyte surface, b) dense part of electrolyte surface, c) porous part of electrolyte surface, d) cross section

Similar segregations are detected in all the above cases, this indicates a recurrence of the same characteristics and features in the membrane, it is a serious problem that needs to be considered.

Through the mapping of SEM (see Figure 4-12), those darker and smaller grains observed can be identified as YSZ. It has been determined that the segregation phenomenon occurs at an early stage during the BZCY172 powder synthesis process (see Figure 3-4 a)), hence necessitating the utilization of a pure perovskite structure for conducting the experimental procedures. Due to the discovery that the powder exhibits segregation as a result of issues with the furnace, it is decided that all calcination processes will be carried out in the muffle furnace (KSL-1700X-A1). In order to address the presence of bubbles in the BZCY172 slurry, a pump (Edwards Vacuum-RV) is employed to effectively remove the bubbles from the slurry.

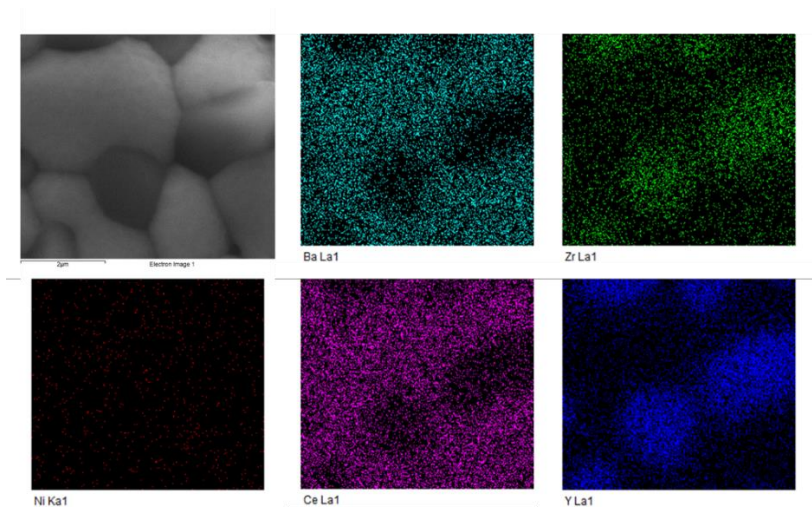


Figure 4-12. SEM and EDX images of electrolyte surface mapping bi-layer membrane (BZCY172-NiO-Starch|BZCY172) sintered at 1500°C for 4 hours

After the removal of bubbles present in the pristine perovskite structure BZCY172 slurry, the bi-layer membranes experience a sintering process at distinct temperatures of 1300°C, 1400°C, and 1500°C separately. SEM results (see Figure 4-13) provide visual representations that indicate a clear correlation between the rise in temperature and the subsequent growth of grains within the membranes, leading to an enhancement in density.

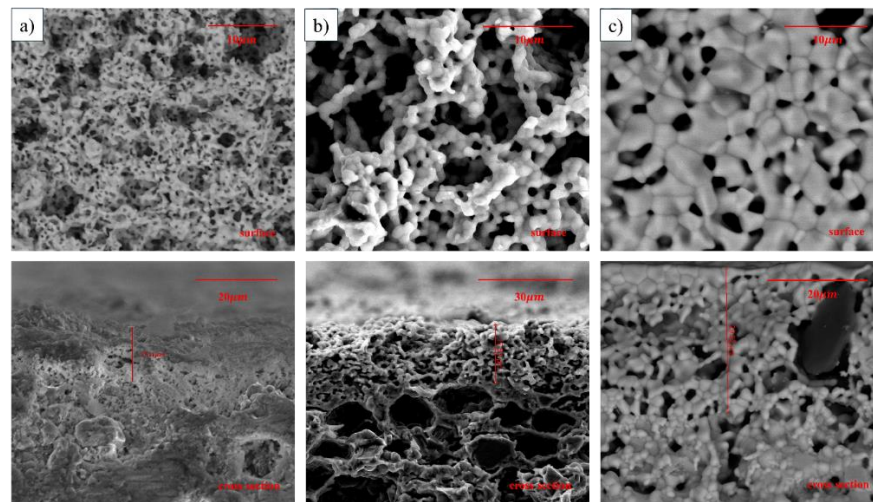


Figure 4-13. SEM images of bi-layer membrane (BZCY172-NiO-Starch|BZCY172) of electrolyte surface sintered and covered with alumina plates at a) #5 1300°C for 8 hours, b) #6 1400°C for 5 hours, c) #7 1500°C for 4 hours

From Table 4-3, the segregation phenomenon occurs due to the presence of secondary phases in the powder materials, and segregated particles help the densification of electrolyte layer. Moreover, it is observed that the concentration of barium decreases with the rise in sintering temperature. The phenomenon of barium loss is almost unavoidable during high-temperature sintering processes, however, at relatively lower temperatures, there appears to be a limitation on grain growth within the material. Reducing the sintering temperature below 1300°C in BZCY-based half-cell is the primary objective in order to limit the evaporation-induced barium loss during the sintering process [48]. The effects of barium loss on the electrolyte performance are essential, given the BZCY conductivity is highly dependent on barium levels [48].

Table 4-3. Summary of screen-printed bi-layer membranes #1 to #7.

Bi-layer membrane #	Sintering condition	Sintering aid	Electrolyte layer surface average atomic ratio	Segregated particles	Densification
1	1400°C, 5 hours	No	$\text{Ba}_{0.80}\text{Zr}_{0.11}\text{Ce}_{0.61}\text{Y}_{0.28}\text{O}_{3-\delta}$	No	No
2	1500°C, 8 hours	No	$\text{Ba}_{0.59}\text{Zr}_{0.051}\text{Ce}_{0.42}\text{Y}_{0.53}\text{O}_{3-\delta}$	Yes	Yes
3	1400°C, 8 hours	No	$\text{Ba}_{0.6}\text{Zr}_{0.058}\text{Ce}_{0.53}\text{Y}_{0.411}\text{O}_{3-\delta}$	Yes	Yes
4	1500°C, 4 hours	No	$\text{Ba}_{0.44}\text{Zr}_{0.28}\text{Ce}_{0.355}\text{Y}_{0.62}\text{O}_{3-\delta}$	Yes	Yes
5	1300°C, 8 hours	No	$\text{Ba}_{0.57}\text{Zr}_{0.051}\text{Ce}_{0.7}\text{Y}_{0.24}\text{O}_{3-\delta}$	No	No
6	1400°C, 5 hours	No	$\text{Ba}_{0.4}\text{Zr}_{0.0038}\text{Ce}_{0.81}\text{Y}_{0.19}\text{O}_{3-\delta}$	No	No
7	1500°C, 4 hours	No	$\text{Ba}_{0.006}\text{Zr}_{0.018}\text{Ce}_{0.7}\text{Y}_{0.28}\text{O}_{3-\delta}$	No	No

4.3.3 Electrolyte with Sintering Aids

Due to the absence of a dense electrolyte layer achieved at high sintering temperatures, sintering aids have been introduced to facilitate the sintering process. Subsequently, all bi-layer membranes are subjected to sintering at a temperature of 1300°C for a duration of 8 hours to minimize the loss of barium during the sintering step.

Our initial approach involves the utilization of sintering aids specifically designed for the synthesis of BZCY172, with the primary objective of addressing the issue of porous structures and potential contamination. The segregated YSZ that is identified in a previous scenario has shown promising potential in facilitating the sintering process, as illustrated in both Figure 4-10 and Figure

4-11. Therefore, at the temperature of 1300°C, it is advisable to incorporate Y_2O_3 , $\text{Zr}(\text{OH})_2\text{CO}_3 \cdot \text{ZrO}_2$, and YSZ powder into the slurry to determine its impact on the sintering process. It is worth noting that both $\text{Zr}(\text{OH})_2\text{CO}_3 \cdot \text{ZrO}_2$ and YSZ have demonstrated the capability to fill pores, but the presence of smaller pores remains observable (see Figure 4-14).

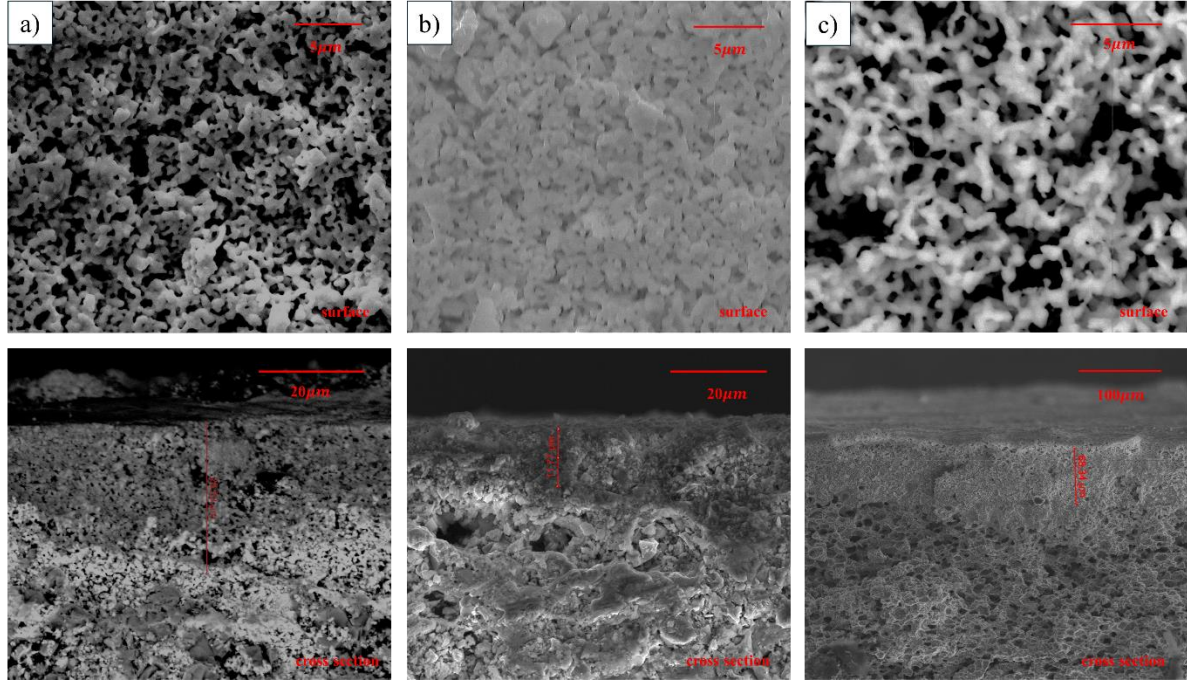


Figure 4-14. SEM images of bi-layer membrane (BZCY172-NiO-Starch|BZCY172 mix with sintering aid) sintered and covered with alumina plates at 1300°C for 8 hours with a) #8 Y_2O_3 , b) #9 $\text{Zr}(\text{OH})_2\text{CO}_3 \cdot \text{ZrO}_2$, c) #10 YSZ

In various literatures, the selection and comparison of sintering aids for BZCY material involved the consideration of ZnO, CuO, and NiO. It is found that among these options, NiO emerges as the most effective sintering aid for BZCY materials with maximum 2wt%, as indicated by previous research [53]. Furthermore, previous studies also identified NiO as the preferred sintering aid for BZCY materials [44], [52]. Consequently, an experimental approach is undertaken to investigate the effects of incorporating NiO in combination with BZCY172 in the electrolyte.

The slurry is prepared by mixing 2wt% of NiO with BZCY172 slurry (4). The outcomes of these experiments are presented in the Figure 4-15, indicating a slight improvement compared to using only BZCY172 in the electrolyte as illustrated in Figure 4-13. However, it is apparent that the

distribution of NiO within the slurry may not be uniform. Therefore, there is a need to explore more efficient methods for integrating nickel into the electrolyte slurry system.

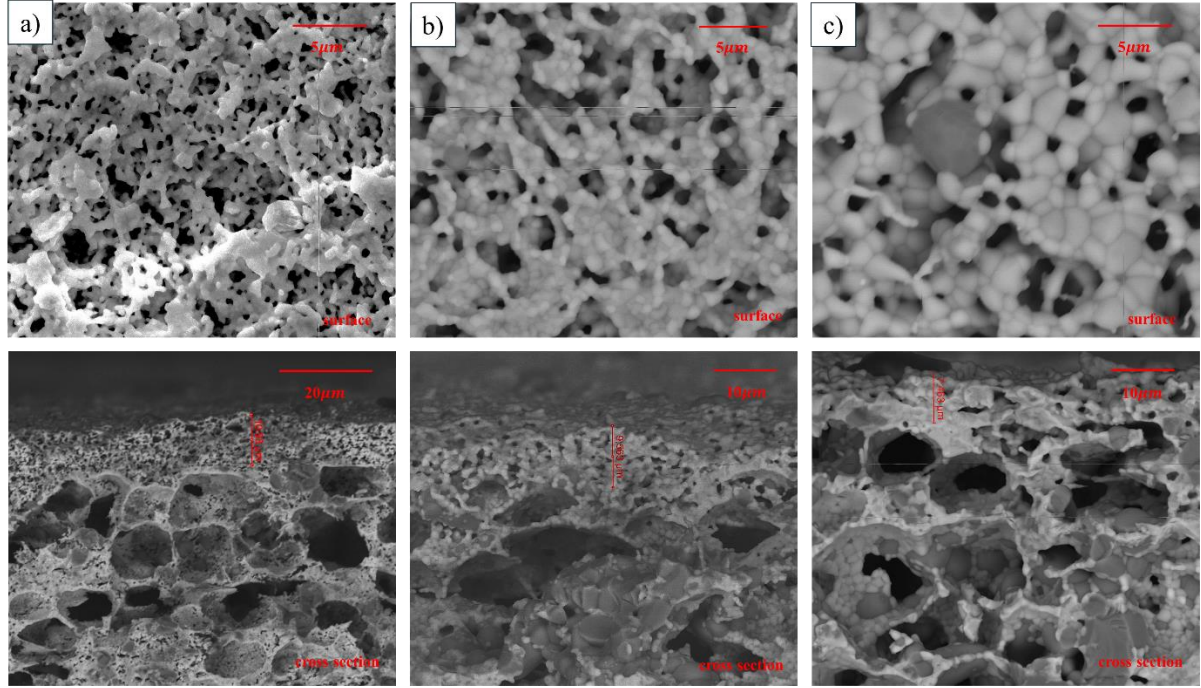


Figure 4-15. SEM images of bi-layer membrane (BZCY172-NiO-Starch|BZCY172+NiO) sintered and covered with alumina plates at a) #11 1300°C for 8 hours, b) #12 1400°C for 8 hours, c) #13 1450°C for 8 hours

Wet impregnation is a widely used technique employed in the synthesis of heterogeneous catalysts. There has been limited focus on the utilization of wet impregnation methodology for the incorporation of nano-scale particles within the electrode architecture of SOFCs [64]. We aim to utilize the modified wet impregnation technique for depositing nickel particles around BZCY172 particles. The procedure involves the dissolution of 3wt% nickel nitrate in deionized water, followed by the addition of BZCY172 powder to the nickel nitrate solution and thorough mixing. Subsequently, the solution is subjected to heat treatment on hot plate to obtain the dry nickel impregnated BZCY172 powder. Part of the impregnated powder is formulated into a slurry, applied on a substrate via screen-printing, and sintered at 1400°C for 8 hours, revealing an improved dense layer compare with other sintering aids (see Figure 4-16).

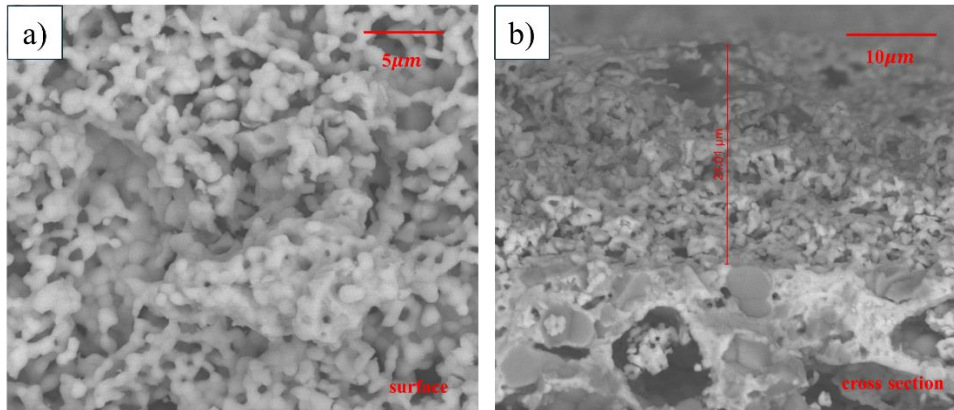


Figure 4-16. SEM images of bi-layer membrane #14 (BZCY172-NiO-Starch|nickel nitrate impregnated BZCY172) sintered and covered with alumina plates at 1400°C for 8 hours a) surface, b) cross section

Sintering aids are not helping the densification in the electrolyte layer at sintering condition 1300°C, 8 hours. We can observe from Table 4-4, the Ba loss is very severe above 1300°C.

Table 4-4. Summary of screen-printed bi-layer membranes #8 to #12.

Bi-layer membrane #	Sintering condition	Sintering aid	Electrolyte layer surface average atomic ratio	Segregated particles	Densification
8	1300°C, 8 hours	Y_2O_3	$Ba_{0.71}Zr_{0.058}Ce_{0.72}Y_{0.22}O_{3-\delta}$	No	No
9		$Zr(OH)_2CO_3 \cdot ZrO_2$	$Ba_{0.88}Zr_{0.14}Ce_{0.56}Y_{0.30}O_{3-\delta}$	No	No
and 10		YSZ	$Ba_{0.80}Zr_{0.1}Ce_{0.55}Y_{0.35}O_{3-\delta}$	No	No
11		NiO (surface area: 0.29m ² /g)	$Ba_{0.81}Zr_{0.14}Ce_{0.60}Y_{0.26}Ni_{0.063}O_{3-\delta}$	No	No
12	1400°C, 8 hours	NiO (surface area: 0.29m ² /g)	$Ba_{0.54}Zr_{0.085}Ce_{0.52}Y_{0.40}O_{3-\delta}$	No	No
13	1450°C, 8 hours	NiO (surface area: 0.29m ² /g)	$Ba_{0.054}Zr_{0.062}Ce_{0.52}Y_{0.40}Ni_{0.063}O_{3-\delta}$	No	No
14	1400°C, 8 hours	Impregnation of nickel nitrate	$Ba_{0.13}Zr_{0.14}Ce_{0.57}Y_{0.29}O_{3-\delta}$	No	No

4.3.4 Die pressing of BZCY172 Pellets

The pure BZCY172 pellets are to investigate whether the elevated pressure will enhance densification at comparable temperatures. The BZCY172 powder is put into the die and pressurized under the top bench press. The Figure 4-17 demonstrates that despite the pressure applies, the pure BZCY172 pellet exhibits inadequate density.

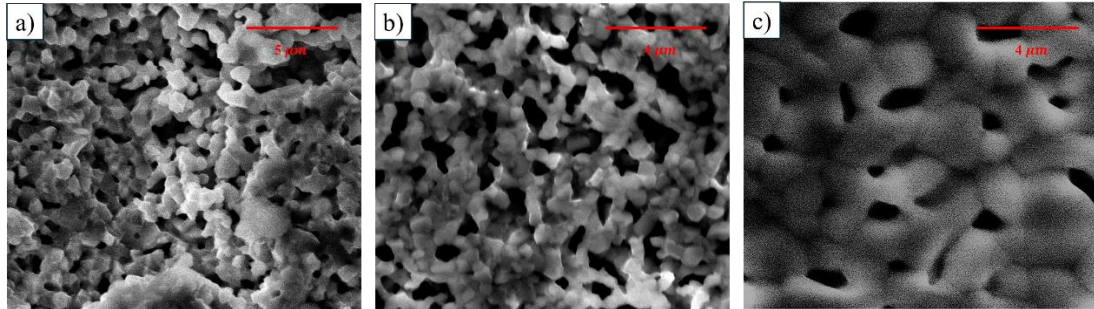


Figure 4-17. SEM images of pure BZCY172 pellets sintered and covered with alumina plates a) #1 at 1400°C for 5 hours showing cross section, b) #2 1500°C for 8 hours showing cross section, c) 1500°C for 8 hours showing surface

A portion of the impregnated BZCY172 powder is then pressed and sintered, specific outcomes denoted as Figure 4-18 a) and b). The impregnated BZCY172 pellet, sintered at 1400°C for 8 hours, exhibits a dense microstructure both on the surface and in the cross section. Additionally, incorporating finer NiO particles into the BZCY172 pellet facilitates densification at a lower temperature of 1350°C, as evidenced by the appearance of melting in the surface and cross-sectional view.

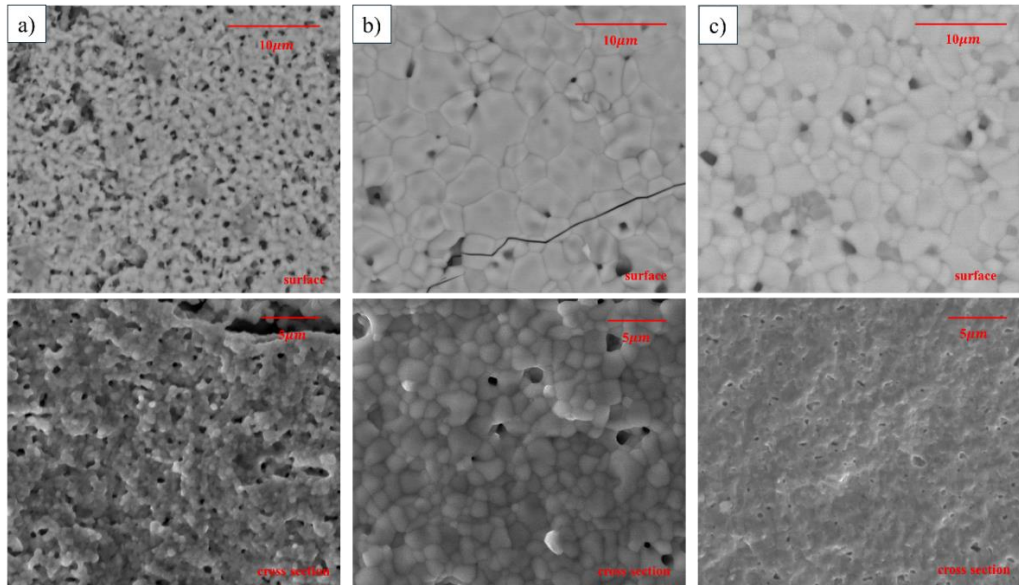


Figure 4-18. SEM images a) #3 nickel nitrate impregnated BZCY172 pellet sintered at 1300°C for 8 hours, b) #4 nickel nitrate impregnated BZCY172 pellet sintered at 1400°C for 8 hours, b) #5 finer NiO particles mixed with BZCY172 pellet sintered at 1350°C for 8 hours (covered with alumina plates)

In this scenario, it appears that BZCY172 undergoes sintering at a temperature exceeding 1300°C, and barium loss is inevitable, particularly at the surface of the sintered pellet. The sinter ability of BZCY172 can be improved by both pressure and impregnated nickel sintering at 1400°C, 8 hours (see Table 4-5). However, by adding sintering aid, it will also introduce the undesirable electronic conduction to electrolyte and potentially decrease the proton conductivity [65]. Consequently, it is significant to try a new powder synthesis recipe and membrane manufacturing approach.

Table 4-5. Summary of BZCY172 pellets #1 to #4

BZCY172 pellet #	Sintering condition	Sintering aid	Electrolyte layer surface average atomic ratio	Segregated particles	Densification
1	1400°C, 8 hours	No	$\text{Ba}_{0.69}\text{Zr}_{0.026}\text{1Ce}_{0.69}\text{Y}_{0.29}\text{O}_{3-\delta}$	No	No
2	1500°C, 8 hours	No	$\text{Ba}_{0.015}\text{Zr}_{0.051}\text{1Ce}_{0.53}\text{Y}_{0.42}\text{O}_{3-\delta}$	No	No
3	1300°C, 8 hours	Impregnation of nickel nitrate	$\text{Ba}_{0.24}\text{Zr}_{0.051}\text{1Ce}_{0.46}\text{Y}_{0.47}\text{Ni}_{0.071}\text{O}_{3-\delta}$	No	No

4	1400°C, 8 hours		$\text{Ba}_{0.016}\text{Zr}_{0.0631}\text{Ce}_{0.50}\text{Y}_{0.502}\text{Ni}_{0.016}\text{O}_{3-\delta}$	No	Yes
5	1350°C, 8 hours	Finer NiO (surface area: 3.4 m ² /g)	$\text{Ba}_{0.041}\text{Zr}_{0.0511}\text{Ce}_{0.476}\text{Y}_{0.474}\text{Ni}_{0.112}\text{O}_{3-\delta}$	No	Yes

4.4 Sinter Ability of Manual Blade Coated Bi-layer Membrane

We commence the utilization of the sol-gel method and all nitrates recipe for the synthesis of BZCY172 powder. Sol-gel BZCY172 powders are combined with a laboratory-synthesized organic binder in a weight ratio of 6:4 to form the BZCY172 paste [61]. This organic binder is composed of 4 wt% ethyl cellulose and 96 wt% terpineol (BZCY172 paste (1)).

4.4.1 Alumina Plates Sintering Method

Due to the high viscosity of the paste, the mixing process with a roller is insufficient, leading to a transition to a ball milling machine (planetary ball mill). Subsequently, the BZCY172 paste is applied twice onto a substrate manually, using a thin alumina rod, to ensure the uniformity of the electrolyte layer. The bi-layer membrane is then subjected to sintering at two distinctive temperatures of 1500°C and 1550°C separately (see Figure 4-19).

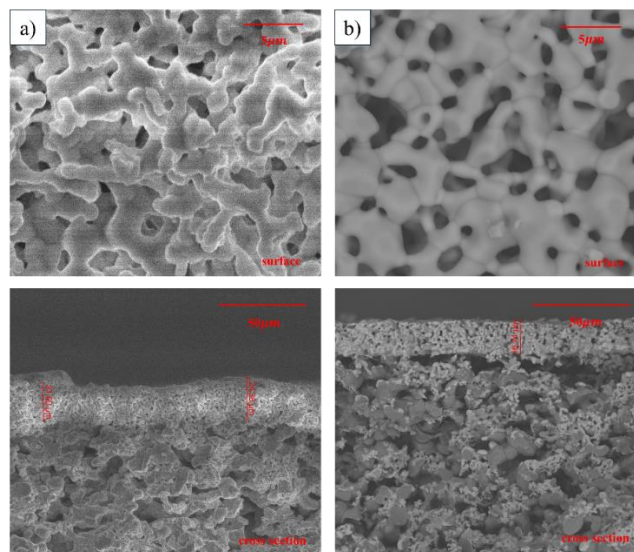


Figure 4-19. SEM images of bi-layer membrane (BZCY172-NiO-Starch|BZCY172) sintered and covered with alumina plates at a) #1 1500°C for 4 hours, b) #2 1550°C for 4 hours

Given the positive impact of pressure on the sinter ability of BZCY172 material, we make the decision to apply pressure on the bi-layer membrane after multiple coating cycles. The pressing occurs after the paste has dried; however, the membrane breaks after pressing. SEM results (see Figure 4-20 a), b)) revealed a dense region at the top and a porous region at the bottom of the electrolyte layer, with a loss of pores in the electrode. This outcome, while highlighting areas for improvement, also serves as a valuable test as it enables the observation of a dense layer in cases of increased thickness. Unfortunately, aluminum contamination was detected due to the high-speed impact occurring between alumina jar and alumina grinding balls.

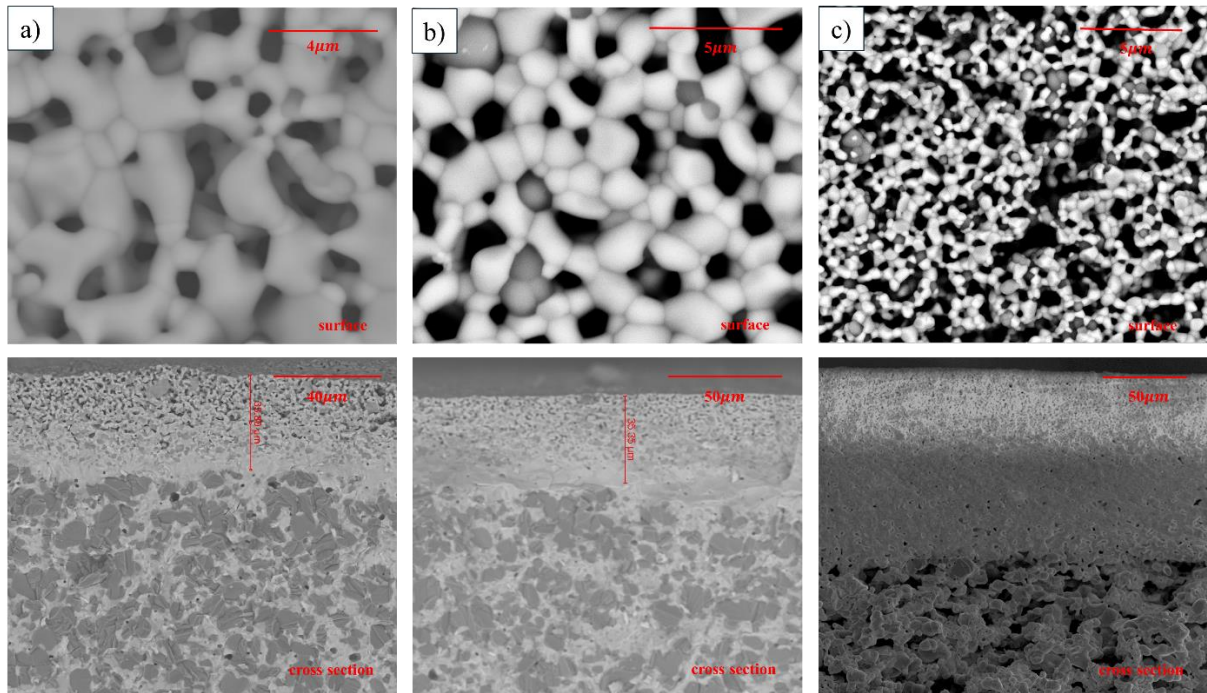


Figure 4-20. SEM images of bi-layer membrane (BZCY172-NiO-Starch|BZCY172) a)/b) #3/4 pressed after coating and then sintered at 1500°C for 4 hours, c) #5 sintered using two-step method 1500°C to 1300°C for 8 hours

By increasing the thickness of the electrolyte layer through multiple coating processes, a decision is made to implement a two-step method in order to limit the loss of barium during high-temperature sintering. Initially, the temperature is elevated to 1500°C to facilitate grain growth, followed by a reduction to 1300°C and maintained for a duration of 8 hours to achieve densification [29]. Analyzing it under SEM, a distinct boundary between non-dense and dense regions in electrolyte

layer becomes apparent, as illustrated in Figure 4-20 c). The feasibility of the two-step sintering approach is confirmed. Most importantly, from surface to the dense part of electrolyte layer, changes in barium content can be observed, thereby indicating the presence of pores resulting from barium depletion (see Table 4-6).

Table 4-6. Summary of manual blade coated bi-layer membranes #1 to #5.

Bi-layer membrane #	Sintering condition	Sintering aid	Electrolyte layer average atomic ratio	Segregated particles	Densification
1	1500°C, 4 hours	No	Surface: $\text{Ba}_{0.082}\text{Zr}_{0.15}\text{Ce}_{0.62}\text{Y}_{0.22}\text{O}_{3-\delta}$	No	No
2	1550°C, 4 hours	No	Surface: $\text{Ba}_{0.03}\text{Zr}_{0.086}\text{Ce}_{0.68}\text{Y}_{0.23}\text{O}_{3-\delta}$	No	No
3/4	1500°C, 4 hours	No	Surface: $\text{Ba}_{0.069}\text{Zr}_{0.069}\text{Ce}_{0.63}\text{Y}_{0.27}\text{O}_{3-\delta}$	No	Yes
5	1500°C->1300°C, 4 hours	No	Surface : $\text{Ba}_{0.182}\text{Zr}_{0.05}\text{Ce}_{0.69}\text{Y}_{0.26}\text{O}_{3-\delta}$ Porous region: $\text{Ba}_{0.49}\text{Zr}_{0.12}\text{Ce}_{0.72}\text{Y}_{0.16}\text{O}_{3-\delta}$ Dense region: $\text{Ba}_{1.1}\text{Zr}_{0.076}\text{Ce}_{0.75}\text{Y}_{0.17}\text{O}_{3-\delta}$	No	Yes

4.4.2 Apply the BZCY172 Powder/Pellet Sintering Method

We endeavor to address the issue of barium loss by establishing a controlled environment rich in barium content throughout the sintering process. This involves utilizing a layer of BZCY172 powder to cover the electrolyte surface, and alumina plate is placed above BZCY172 powder.

As we see in the Figure 4-21 a) and b), two distinct categories of electrolyte layer can be identified in the same sample. In the first scenario, as depicted in figure a), there are two clearly demarcated regions within the electrolyte layer. The second scenario, illustrated in figure b), highlights a very thin area within the electrolyte layer that is not dense, with the majority of the layer exhibiting a

higher density. These observations may suggest the presence of an uneven distribution of BZCY712 powder. It can be inferred that areas where BZCY172 powder is absent tend to be less dense.

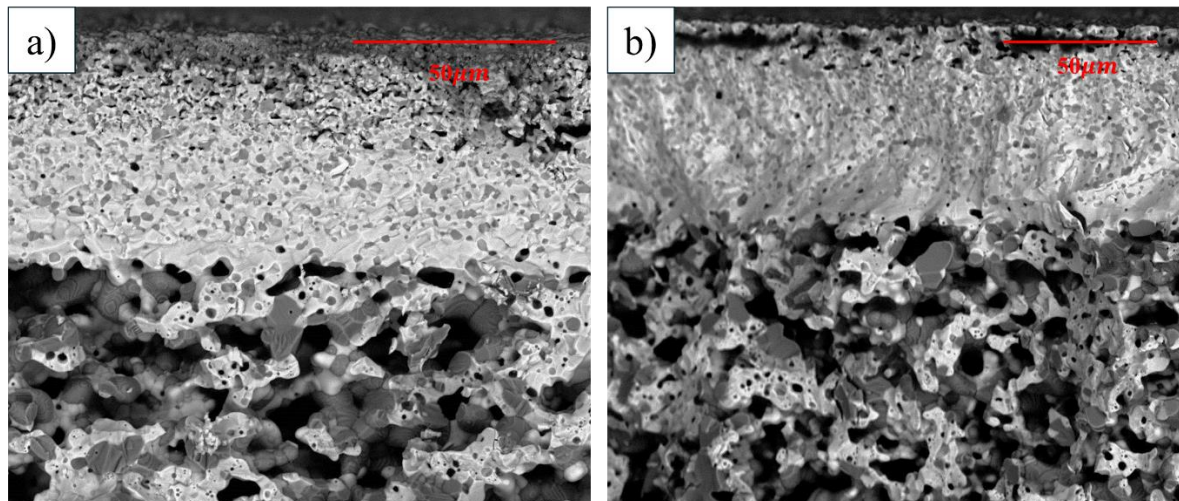


Figure 4-21. SEM images of bi-layer membrane (BZCY172-NiO-Starch|BZCY172) a)/b) #6 BZCY172 powder covered and sintered at 1500°C for 4 hours (covered with BZCY172 powder and alumina plates)

As the Figure 4-22 shown, the analysis of line scanning data from EDX reveals a significant variation in barium concentration as one moves along the distance from the surface of the electrolyte layer to the electrode. Specifically, within the region covered by BZCY172 powder, ranging from 0 to 4µm, there is a dramatic increase in barium concentration followed by a stabilization at a constant level. Moreover, additional data have been gathered from various positions, all exhibiting a similar trend in terms of barium concentration variation along the distance.

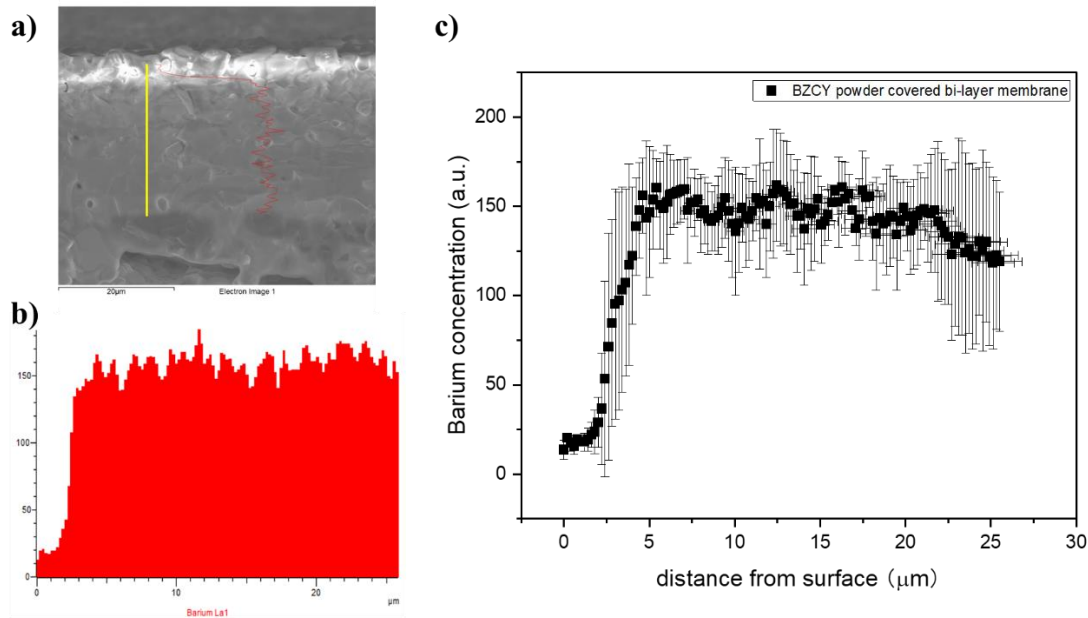


Figure 4-22. SEM images of cross-sectional electrolyte layer line scanning result of bi-layer membrane (BZCY172-NiO-Starch|BZCY172) sintered at 1500 °C for 4 hours a) cross section, b) barium concentration change along the line, c) the average barium concentration changing profile at different locations of electrolyte layer

As many aluminum particles are identified in the previous sample, we decide to substitute alumina balls with zirconia balls during the ball milling process for producing BZCY172 paste. In order to address the uneven dispersion of BZCY172 powder on the bi-layer membrane, a sintered BZCY172 pellet is used to cover the membrane and prevent the loss of barium. Also, the pristine BZCY172 pellet is manually pressed on a bench top press using a die slightly larger in diameter than the bi-layer membrane to ensure complete coverage. Subsequently, this pristine BZCY172 pellet sinters at 1600°C for a duration of 2 hours.

The BZCY172 pellet covered bi-layer membrane sinters at a temperature of 1500°C for a duration of 4 hours. However, the adhesion between the electrolyte layer of the bi-layer membrane and the pure BZCY172 pellet is strong, making it challenging to separate them as a whole membrane. Observation in the Figure 4-23, it is evident that both the surface and cross-section of the electrolyte layer exhibit high density, with the reappearance of YSZ segregation on the surface of the electrolyte layer.

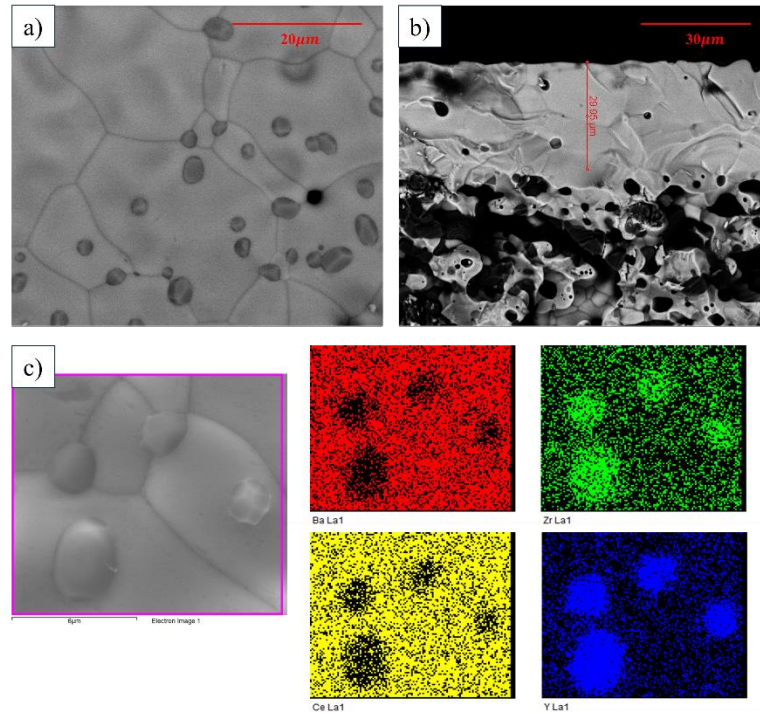


Figure 4-23. SEM images of bi-layer membrane #7 (BZCY172-NiO-Starch|BZCY172) sintered covered with BZCY172 pellet and alumina plates at 1500°C for 4 hours a) electrolyte surface, b) cross section, c) mapping of YSZ segregation on electrolyte surface

Once more, the phenomenon of YSZ segregation is observed; however, in contrast to the previous instance, the pure perovskite structure of BZCY172 powder is employed as the material. Consequently, in order to mitigate the segregation issue and avoid the adhesive complication through a decrease in the sintering temperature, it is understood that a temperature of 1500°C results in stickiness; thus, the desired maximum temperature is set at 1450°C. And since the two-step method has been proved to effectively help the sintering, we also apply it in the experiments. The electrolyte layer, as illustrated in the Figure 4-24, exhibits low sintering density at its peak temperature of 1450°C; however, the bi-layer membrane can be split from the pristine BZCY172 pellet.

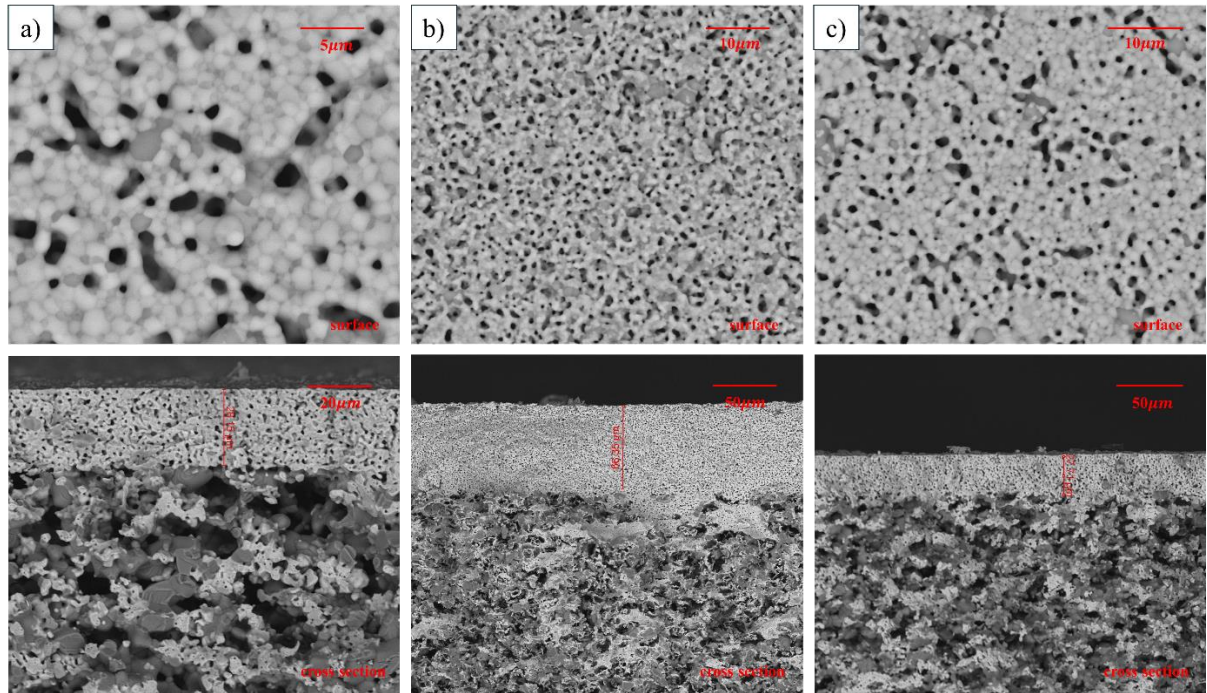


Figure 4-24. SEM images of BZCY172 pellet covered bi-layer membrane (BZCY172-NiO-Starch|BZCY172) a) #8 sintered at 1450°C for 4 hours, b) #9 sintered at 1450°C to 1300°C for 8 hours, c) #10 sintered at 1450°C to 1400°C for 140 minutes (covered with BZCY172 pellet and alumina plates)

From Table 4-7, the temperature of 1500°C is crucial in achieving the dense layer. This specific temperature setting plays a significant role in the structural integrity and properties of the resulting layer. Furthermore, the incorporation of BZCY172 pellet into the system has shown promising potential in mitigating the loss of Ba during the sintering process.

Table 4-7. Summary of manual blade coated bi-layer membranes #6 to #11.

Bi-layer membrane #	Sintering condition	Sintering aid	Electrolyte layer average atomic ratio	Segregated particles	Densification
6	1500°C, 4 hours	No	Surface : $\text{Ba}_{0.029}\text{Zr}_{0.041}\text{Ce}_{0.58}\text{Y}_{0.38}\text{O}_{3-\delta}$	No	Yes
7	1500°C, 4 hours	No	Surface : $\text{Ba}_{0.75}\text{Zr}_{0.11}\text{Ce}_{0.55}\text{Y}_{0.35}\text{O}_{3-\delta}$	Yes	Yes
8	1450°C,	No	Surface :	No	No

	4 hours		$\text{Ba}_{0.90}\text{Zr}_{0.11}\text{Ce}_{0.69}\text{Y}_{0.20}\text{O}_{3-\delta}$		
9	1450°C-> 1300°C, 8 hours	No	Surface : $\text{Ba}_{0.85}\text{Zr}_{0.09}\text{Ce}_{0.61}\text{Y}_{0.30}\text{O}_{3-\delta}$	No	No
10	1450°C-> 1300°C, 140 minutes	No	Surface : $\text{Ba}_{0.98}\text{Zr}_{0.11}\text{Ce}_{0.66}\text{Y}_{0.24}\text{O}_{3-\delta}$	No	No

Based on previous observations, the BZCY172 powder does not adhere well to the bi-layer membrane, and it exhibits an irregular distribution on the surface of the electrolyte. In contrast, the sintered BZCY172 pellet displays a uniformly even distribution but tends to adhere strongly to the electrolyte layer. A potential solution could involve their combined application to mitigate their shortcomings.

For both bi-layer membranes sintered at a temperature of 1500°C, the electrolyte surface and cross-section exhibit high density despite a reduction in sintering duration to 2 hours (see Figure 4-25). In both cases, the bi-layer membranes are easily detachable from the sintered BZCY172 pellet, indicating the effectiveness of our strategy. The presence of sintered irregular shapes of BZCY172 powder on the electrolyte surface for a duration of 4 hours is logically consistent, given the overlay of BZCY172 powder on the electrolyte surface. Additionally, darker grains are observed in the 4-hour scenario, while smaller grains are evident in the 2-hour scenario, a topic that will be discussed later.

For the electrodes, the BZCY172 powder produced by combustion method has a better morphology (Figure 4-25 a)). It features smaller pores that increase the surface area and larger pores that facilitate gas diffusion. The electrode material made from sol-gel BZCY172 powder appears relatively dense (Figure 4-25 b)), suggesting it is well-suited as an electrolyte material. In contrast, the combustion BZCY172 material should be used as the electrode material.

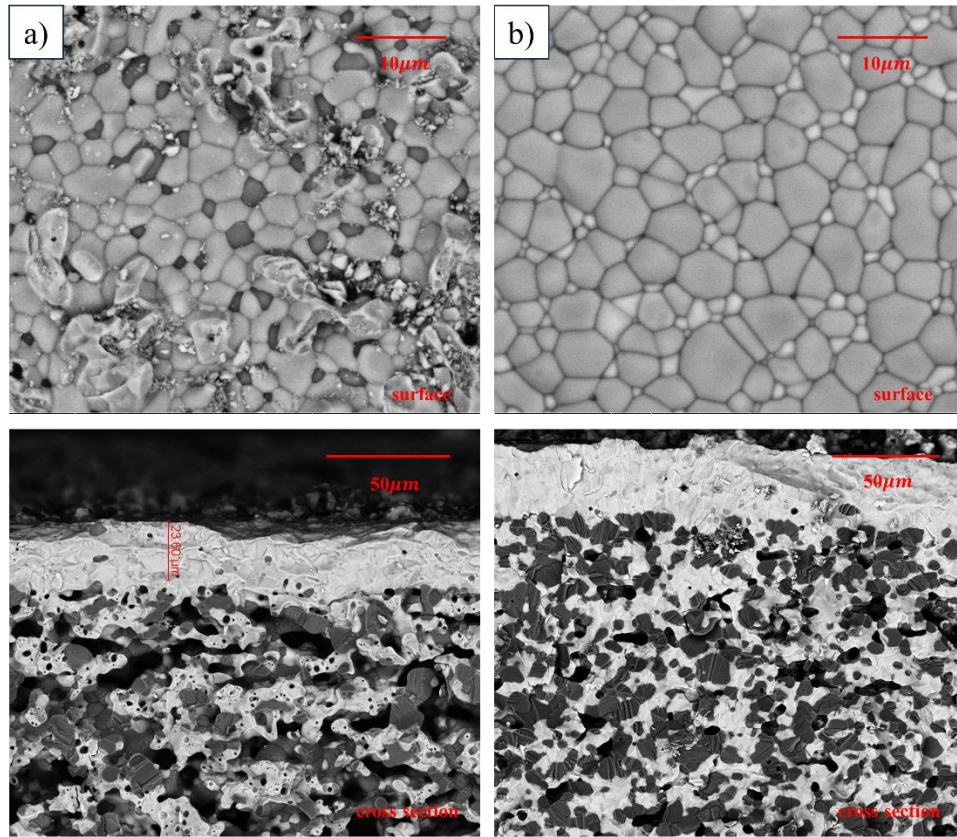


Figure 4-25. SEM images of bi-layer membrane (BZCY172-NiO-Starch|BZCY172) a) #11 sintered at 1500°C for 4 hours, b) #12 sintered at 1500°C 2 hours (covered with BZCY172 powder, BZCY172 pellet, and alumina plates)

The uneven distribution of aluminum contamination results in the formation of a new oxide when aluminum is present in certain parts, as illustrated in see Figure 4-26 a). In these areas, aluminum reacts with the segregated barium to create a distinct chemical compound barium aluminum oxide (BAL). This structural transformation is a direct consequence of the interaction between barium and aluminum in the contaminated areas. Conversely, in regions without aluminum as shown in see Figure 4-26 b), segregated barium particles are observed without any oxide formation. In both scenarios, the presence of barium segregation leads to the development of a novel crystal structure resembling barium cerium oxide (BC) and cerium zirconium yttrium oxide (CZY).

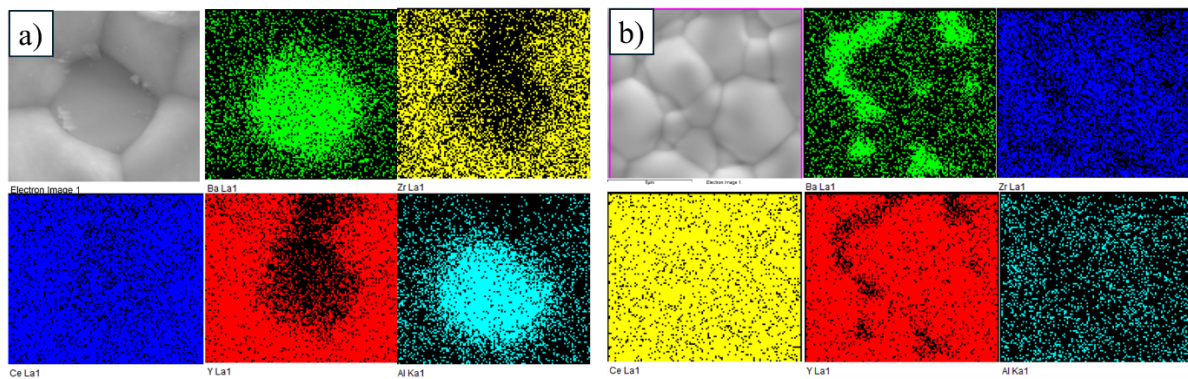


Figure 4-26. SEM images of electrolyte cross section mapping bi-layer membrane (BZCY172-NiO-Starch|BZCY172) sintered at a) 1500°C for 4 hours, b) 1500°C for 2 hours

Base on observation of the line scanning analysis conducted on the cross section of the electrolyte layer, the concentration of barium remains relatively stable from the surface to the bottom of the electrolyte layer. However, there are sudden drops in the barium concentration levels. For example, see Figure 4-27 a), in the scenario where the sintering duration is 4 hours, at approximately 4 μ m into the layer, there is a distinct valley in the barium concentration. Simultaneously, at this same location, there is a slight decrease in cerium concentration while Zr and yttrium concentrations experience a peak, indicating the possible presence of CZY or YSZ segregation phenomena. Furthermore, at positions 16 μ m and 18 μ m, both barium and cerium concentrations exhibit drops, whereas Zr and yttrium concentrations reach peaks, suggesting the occurrence of YSZ segregation in the electrolyte layer. It is noteworthy that at a temperature of 1500°C for a duration of 2 hours (see Figure 4-27 b)), the trends observed for each element remain consistent, implying that the perovskite structure remains unaffected by the high temperature conditions. Any segregations and new crystal structures are predominantly confined to the surface bulk crystals, as evidenced by the analysis results.

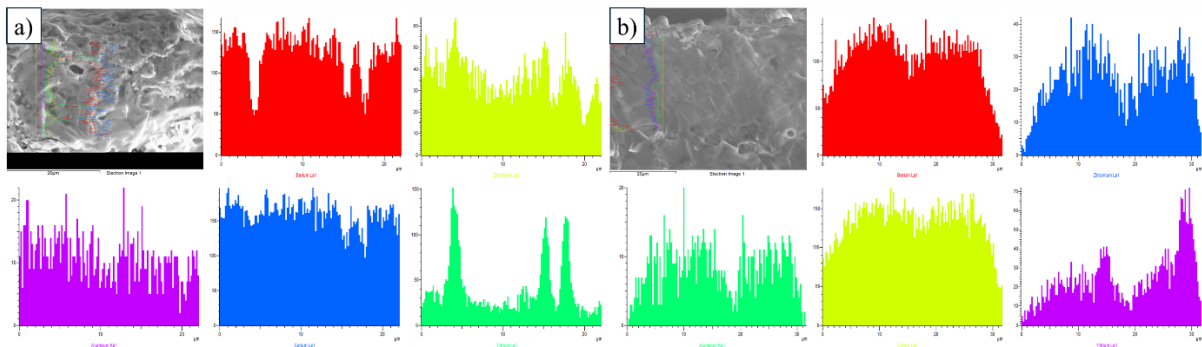


Figure 4-27. SEM images of electrolyte cross section line scanning bi-layer membrane (BZCY172-NiO-Starch|BZCY172) sintered at a) 1500°C for 4 hours, b) 1500°C for 2 hours

From Figure 4-28, the observation of a dark color in the sintered BZCY172 electrolyte layer serves as a clear indication that the sintering process has reached its conclusion for the respective materials [48]. The presence of the "stains" observed on the surface can be attributed to the transformation of the BZCY172 powder into a molten state.

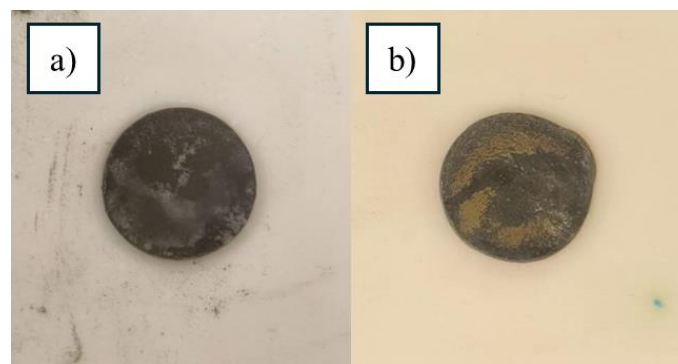


Figure 4-28. Images of bi-layer membrane (BZCY172-NiO-Starch|BZCY172) a) #11 sintered at 1500°C for 4 hours, b) #12 sintered at 1500°C 2 hours (covered with BZCY172 powder, BZCY172 pellet, and alumina plates)

4.5 Dense Bi-layer Membrane Electrolyte Layer Crystallinity

After the discovery of segregations and new crystal structures present on the surface of the electrolyte layer, it is necessary to conduct XRD analyses on both the electrolyte and electrode surfaces to validate the presence of these phenomena (see Figure 4-29). The electrolyte surface exhibits the presence of BZCY [35], [40], YSZ [66], and cerium zirconium oxide (CZ) [67]. In the preceding section, it is mentioned that there might be the presence of CZY [68]; however, upon comparison with

existing literature findings, it appears to align more closely with the characteristics of CZ as indicated by XRD analysis. In addition, the electrode surface displays the presence of BZCY, YSZ, CZ, and NiO [46]. Fewer BZCY172 peaks have been observed on the electrode surface due to the absence of precautions taken on the electrode side.

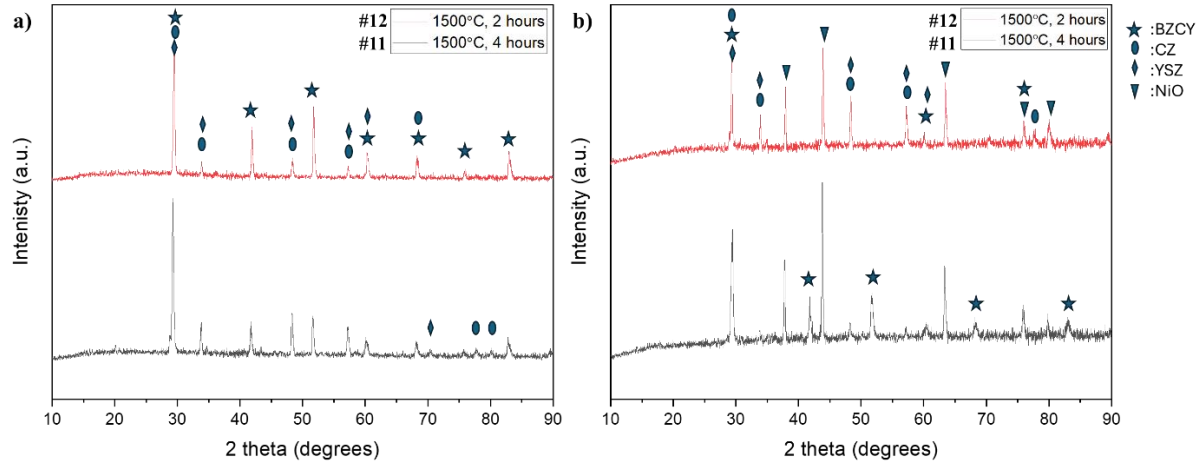


Figure 4-29. XRD results of BZCY172 powder and pellet covered bi-layer membranes #12 and #13 (BZCY172-NiO-Starch|BZCY172) a) electrolyte surface, b) electrode surface

Yttria-stabilized zirconia (YSZ) is characterized by its high ionic conductivity, a critical property for its role in SOFCs, allowing the efficient migration of oxygen ions within the cell. The temperature-dependent nature of YSZ's ionic conductivity, enabling effective operation within the temperature range typically from 700 to 900°C in SOFCs [5], [69]. A low activation energy is noted in the CZ composition, attributed to mobility of oxygen vacancies leading to increased conductivity. The study infers that CZ_{0.4} (Ce_{0.6}Zr_{0.4}O_{1.8}) exhibits improved electrochemical properties, establishing a promising electrolyte for intermediate temperature solid oxide fuel cell (IT-SOFC) applications [67].

As summarized in Table 4-8, in both sintered electrolyte layers, the presence of segregated particles is evident on the surface; however, with a reduction in sintering duration to 2 hours, the integrity of the cross-sectional BZCY perovskite structure remains unchanged. Significantly, the utilization of a BZCY172 paste recipe and manual blade coating technique has enabled the acquisition of a dense layer.

Table 4-8. Summary of manual blade coated bi-layer membranes #11 and #12.

Bi-layer membrane #	Sintering condition	Sintering aid	Electrolyte layer surface average atomic ratio	Segregated particles	Densification
11	1500°C, 4 hours	No	$\text{Ba}_{1.05}\text{Zr}_{0.037}\text{Ce}_{0.49}\text{Y}_{0.47}\text{O}_{3-\delta}$	Surface: yes Cross section: yes	Yes
12	1500°C, 2 hours	No	$\text{Ba}_{0.66}\text{Zr}_{0.089}\text{Ce}_{0.57}\text{Y}_{0.34}\text{O}_{3-\delta}$	Surface: yes Cross section: no	Yes

4.6 Study of Barium Loss in Electrolyte Layer

TBZCY powder is covered above the electrolyte layer to compensate the Ba element loss to reduce the porosity (#6). Based on the SEM images, about 4 μm thickness of top region still experience Ba loss. Through SEM mapping, we can determine how the relative concentration of Ba loss changes with the thickness of the electrolyte layer at a specific point, which is also observed in various locations. Therefore, the average thickness and relative Ba concentration can be calculated and plotted (see Figure 4-22).

Studies have been conducted on the phenomenon of Ba loss from a material science perspective [47], [51], [53], and we are interested in exploring this further from the standpoint of thermodynamics to gain a more comprehensive understanding of the sintering process. As observed in this bi-layer membrane case covered with BZCY172 powder, it is evident that the variation in Ba concentration correlates with the thickness of the electrolyte layer, exhibiting a trend like that of a semi-infinite solid. This similarity in trends suggests a relationship between the two parameters that is worth further exploration.

A semi-infinite solid is a theoretical model that extends infinitely in all directions except one, thus being characterized by a single identifiable surface (see Figure 4-30). When there is a sudden alteration in conditions at this surface, the solid undergoes transient, one-dimensional heat conduction. This model proves to be beneficial for examining numerous practical issues, as it simplifies the mathematics while still yielding precise results for specific time intervals. For example, it can estimate the transient thermal reaction of a thick slab. In this scenario, the semi-infinite solid approximation

remains valid in the initial stages of the transient period, when the internal temperatures of the slab mostly remain unaffected by surface variations.

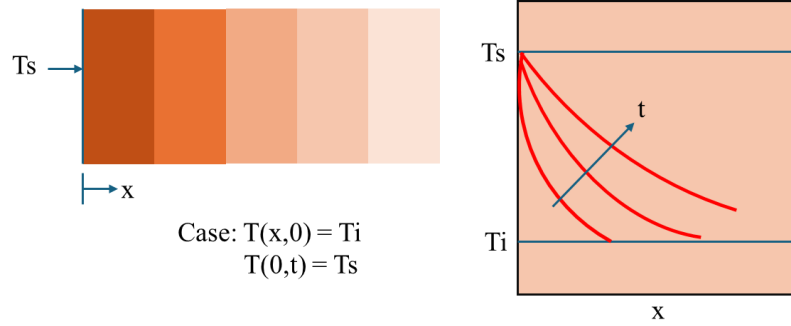


Figure 4-30. Transient temperature distributions in a semi-infinite solid for constant surface temperature surface conditions

To solve the transient concentration distribution in this semi-infinite solid, we need to use Fick's second law (diffusion equation). As illustrate in Figure 4-31, for the electrolyte layer, the concentration of Ba is high at one end and low at another end, the concentration profile can be plotted. Given a specific location x along with a cross-sectional area A and a volume V , concentration gradient j_x exists at that point. Another concentration gradient, $j_{x+\Delta x}$, is present at a different location $x+\Delta x$. At position x , j_x facilitates the transport of material into volume, while $j_{x+\Delta x}$ transports material out of the volume. The objective is to investigate the temporal evolution of the concentration within this volume and quantify the resultant changes in concentration over time (Δt). As a result, Fick's second law can be derived from mass balance equation, the detailed calculations are described below.

The mass entering ΔV at location x in time interval Δt :

$$m_x = j_x \times A \times \Delta t \quad \text{Equation 4-1}$$

The mass leaving ΔV at location $x+\Delta x$ in time interval Δt :

$$m_{x+\Delta x} = j_{x+\Delta x} \times A \times \Delta t \quad \text{Equation 4-2}$$

Mass accumulating in ΔV in Δt :

$$\Delta m = m_x - m_{x+\Delta x}$$

$$\Delta m = j_x \times A \times \Delta t - j_{x+\Delta x} \times A \times \Delta t$$

$$\Delta m = -(j_{x+\Delta x} - j_x) \times A \times \Delta t$$

$$\Delta m = -\Delta j \times A \times \Delta t$$

Equation 4-3

Concentration changes in ΔV in Δt :

$$\Delta C = \frac{\Delta m}{\Delta V}$$

$$\Delta C = \frac{-\Delta j \times A \times \Delta t}{A \times \Delta x}$$

$$\Delta C = -\frac{\Delta j}{\Delta x} \times \Delta t$$

$$\frac{\Delta C}{\Delta t} = -\frac{\Delta j}{\Delta x}$$

Equation 4-4

which means the change of concentration in Δt equal to the negative rate of change of flux with Δx .

By taking limits on both sides:

$$\lim_{\Delta t \rightarrow 0} \left(\frac{\Delta C}{\Delta t} \right) = - \lim_{\Delta x \rightarrow 0} \left(\frac{\Delta j}{\Delta x} \right)$$

$$\frac{\delta C}{\delta t} = -\frac{\delta j}{\delta x}$$

Equation 4-5

and replacing j with Fick's first law:

$$j = -D \frac{\delta^2 C}{\delta x^2}$$

Equation 4-6

which D is independent of x .

The diffusion equation/ Fick's second law can be written as:

$$\frac{\delta C}{\delta t} = -D \frac{\delta^2 C}{\delta x^2}$$

Equation 4-7

and D is temperature dependence of diffusion coefficient in m^2/s , which:

$$D = D_0 \times \exp\left(-\frac{E_a}{RT}\right)$$

Equation 4-8

D_0 is the maximal diffusion coefficient (at infinite temperature; in m^2/s), E_a is the activation energy for diffusion (in J/mol), T is the absolute temperature (in K), $R=8.314 \text{ J}/(\text{mol}\cdot\text{K})$ is the universal gas constant.

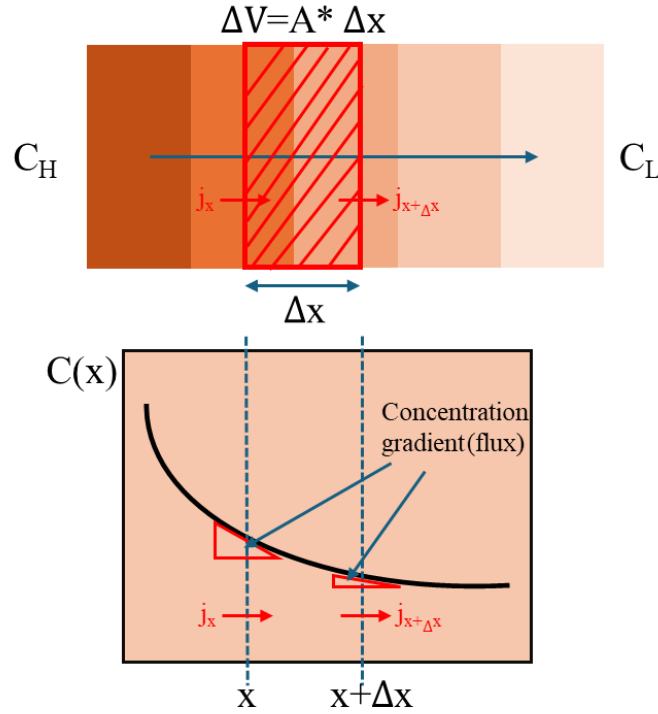


Figure 4-31. The illustration of concentration changes over a finite volume

Upon examination of various membranes sintered at varying high temperatures, it is noted that the loss of Ba starts once temperatures exceeded 1300°C . Furthermore, a temperature-time profile is also available in the analysis, the mass diffusion coefficient is a function of time, so:

$$\frac{1}{D(t)} \frac{\delta C}{\delta t} = \frac{\delta^2 C}{\delta x^2} \quad \text{Equation 4-9}$$

$$D(t) = D_0 \times \exp\left(-\frac{E_a}{RT(t)}\right) \quad \text{Equation 4-10}$$

The temperature profile has five segments, the heating from room temperature (25°C) to 1000°C with heating rate of $2^\circ\text{C}/\text{mins}$, from room temperature 1000°C to 1500°C with heating rate of $1^\circ\text{C}/\text{mins}$, constantly heat at 1500°C for 4 hours, cooling from 1500°C to 1000°C with cooling rate of $1^\circ\text{C}/\text{mins}$,

and cooling from 1000°C to 200°C with cooling rate of 2°C/min. The temperature is in Kelvin in equations.

$$T_1(t) = \frac{1}{30}t + 298.15K, (0 \leq t < 29280s) \quad \text{Equation 4-11}$$

$$T_2(t) = \frac{1}{60}t + 785.15K, (29280 \leq t < 59280s) \quad \text{Equation 4-12}$$

$$T_3(t) = 1773.15K, (59280 \leq t < 73680s) \quad \text{Equation 4-13}$$

$$T_4(t) = -\frac{1}{60}t + 3001.15K, (73680 \leq t < 103680s) \quad \text{Equation 4-14}$$

$$T_5(t) = -\frac{1}{30}t + 4729.15K, (103680 \leq t < 127680s) \quad \text{Equation 4-15}$$

The numerical method is chosen to solve the partial differential equation (Equation 4-9), the unknown parameters in Equation 4-10 are D_0 and E_a , the objective of model is to find the best D_0 and E_a values to fit with the experimental data. There are certain aspects that require careful consideration. The first aspect is to set proper initial values, based on some research, the Ba ion diffusion in BaTiO₃ perovskite material, E_a and D_0 have magnitudes of 10² kJ/mol and 10⁻¹⁰-10⁻¹² cm²/s [70], [71]. The second aspect pertains to the enhancement of experimental data to elevate the precision of the model. In Figure 4-22 c), a notable decline in concentration from 23.52 to 25.53μm is observed, potentially attributed to the diffusion of the base towards the porous electrode, so data points within that particular region have been excluded. Also, the initial condition:

$$C(x, 0) = C_i \quad \text{Equation 4-16}$$

boundary conditions:

$$C(x = 0, t) = C_s \quad \text{Equation 4-17}$$

$$C(x = \infty, t) = C_i \quad \text{Equation 4-18}$$

C_i is initial concentration, and C_s is surface concentration. Moreover, the experimental data provides the relative concentration of Ba; however, the real concentration of Ba in BZCY bulk is required in the model.

The unit cell of BZCY is a cubic structure, and Ba is at the A site of the bulk, which means the one BZCY bulk contains one Ba atom. The structural configuration of BZCY is characterized by a cubic unit cell, with the presence of Ba located specifically at the A site within the bulk (see Figure 1-4), and each individual BZCY unit cell is composed of a one Ba atom. The lattice parameter (α) of a sintered BZCY pellet is $4.263 \cdot 10^{-10} \text{m}$ [47], and volume of BZCY bulk can be calculated:

$$volume = \alpha^3 \quad \text{Equation 4-19}$$

$$volume = (4.263 \times 10^{-10})^3 = 7.747 \times 10^{-29} \text{m}^3$$

The mass of one Ba atom may be determined by considering the molecular weight (MW) of Ba and Avogadro's constant (N_A):

$$mass = \frac{MW}{N_A} \quad \text{Equation 4-20}$$

$$mass = \frac{137.327}{6.022 \times 10^{23}} = 2.280 \times 10^{-22} \text{g}$$

Subsequently, the real Ba concentration (C_{real}) can be calculated:

$$C_{real} = \frac{mass}{volume} \quad \text{Equation 4-21}$$

$$C_{real} = \frac{2.280 \times 10^{-22} \text{g}}{7.747 \times 10^{-29} \text{m}^3} = 2.944 \times 10^6 \frac{\text{g}}{\text{m}^3}$$

The relationship between C_i and C_{real} can be derived to transform relative concentration into real concentration:

$$ratio = \frac{C_i}{C_{real}} \quad \text{Equation 4-22}$$

The best D_0 and E_a values are determined in Table 4-9. The plot displays the profile of both the experimental data and the model (see Figure 4-32). And the MATLAB code can be found in Appendix: MATLAB Code for Barium Concentration Model. This discrepancy of D_0 and E_a values with literature values could be due to constraints in the model's assumptions, simplifications, or parameter estimations, emphasizing the need for additional enhancements and verification of the model to enhance its predictive precision and usefulness in practical scenarios. And further experimentation is required in order to validate the precision and reliability of the model.

Table 4-9. Best model values of barium ions in BZCY172 compared with barium ions in BaTiO₃

	Model values (Ba ²⁺ /BZCY172)	Literature values (Ba ²⁺ /BaTiO ₃) [70]
D_0 (cm ² /s)	7.328×10^{-9}	1.995×10^6
E_a (kJ/mol)	127.80	512.10

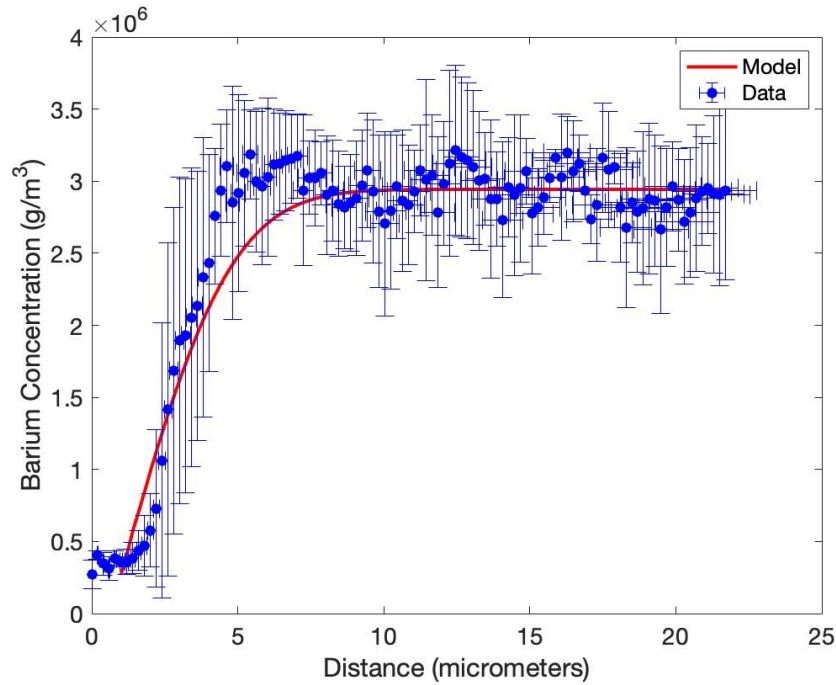


Figure 4-32. The modelled concentration profile of Ba along the depth of the electrolyte layer of BZCY172 powder covered bi-layer membrane.

This Arrhenius plot (see Figure 4-33) illustrates the temperature dependence of diffusion coefficients for various ions in different perovskite structure materials, with each line representing a specific ion-material combination [70]. The slope of each line indicates the activation energy for diffusion, with steeper slopes suggesting higher energy barriers. The position of the lines allows for a comparison of diffusion rates, where higher lines indicate faster ion movement. For example, Ba²⁺ in BZCY172 shows lower activation energy, suggesting potentially higher diffusion rates at elevated temperatures compared to other materials. Overall, this comparison allows us to evaluate how the

diffusion of Ba^{2+} in BZCY172 compares with the diffusion of other ions in similar perovskite structures, particularly in terms of temperature dependence and diffusion rates.

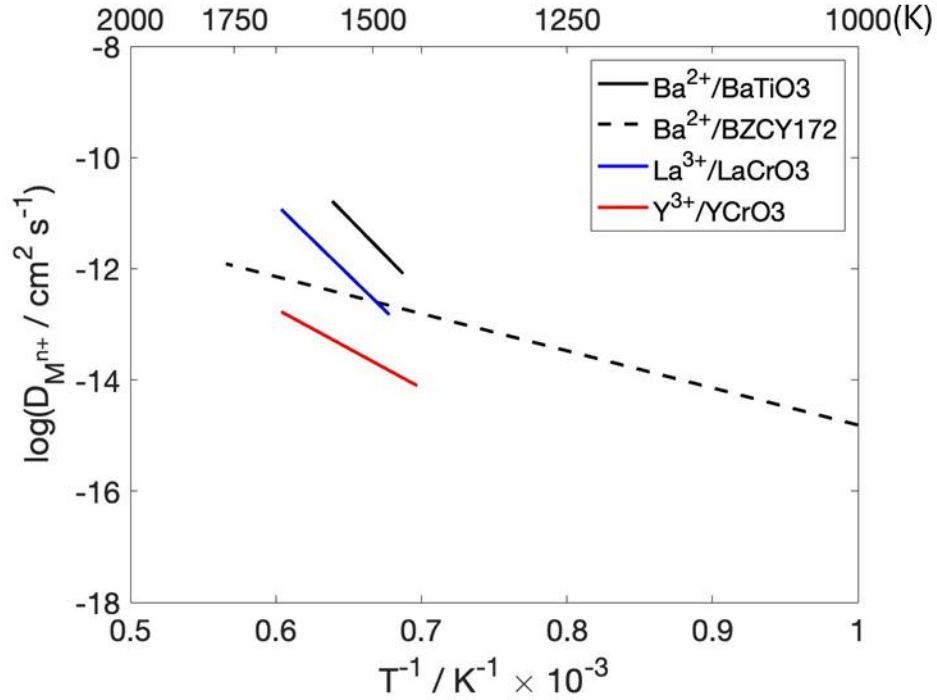


Figure 4-33. The self-diffusion coefficient of barium ions in BZCY172 compared to entries found in the literature [70]

As a result, this model is used to solve a partial differential equation that describes the diffusion of barium ion in a BZCY172 perovskite material over time and space. For materials science and engineering, understanding how materials behave under different conditions is essential. This model helps in understanding how barium diffuses in a medium, which can be important for various applications like battery design, fuel cells, and other chemical processes. Moreover, by understanding the diffusion behavior, one can predict how the material will perform over time. This is critical for designing materials that need to maintain certain properties over their operational lifetime. Additionally, the model can be adapted to different temperature profiles and different materials by changing the input parameters. This makes it a versatile tool for studying diffusion in various contexts.

4.7 Gas-tight Bi-layer Membrane Testing

After we obtain the dense bi-layer membrane, a gas-tight testing is performed using the gas-tight testing device (see Figure 4-34). This device is inspired by the components of vertical tube furnace (from company *Across International*), the components are designed to establish a gas-tight setting within the vertical tube furnace. O-rings are positioned on both sides of the pressing ring, which is then placed between the flanges. Bolts are utilized to connect the two flanges and press the O-ring, creating a gas-tight environment. In our scenario, the pressing ring is substituted with a specially made ring, which has the same dimension as the pressing ring, while Teflon tape is employed to improve the seal between the components. The super glue is utilized for the purpose of affixing an objective to the manufactured ring. The compressed air is linked to the gas inlet to provide pressure.

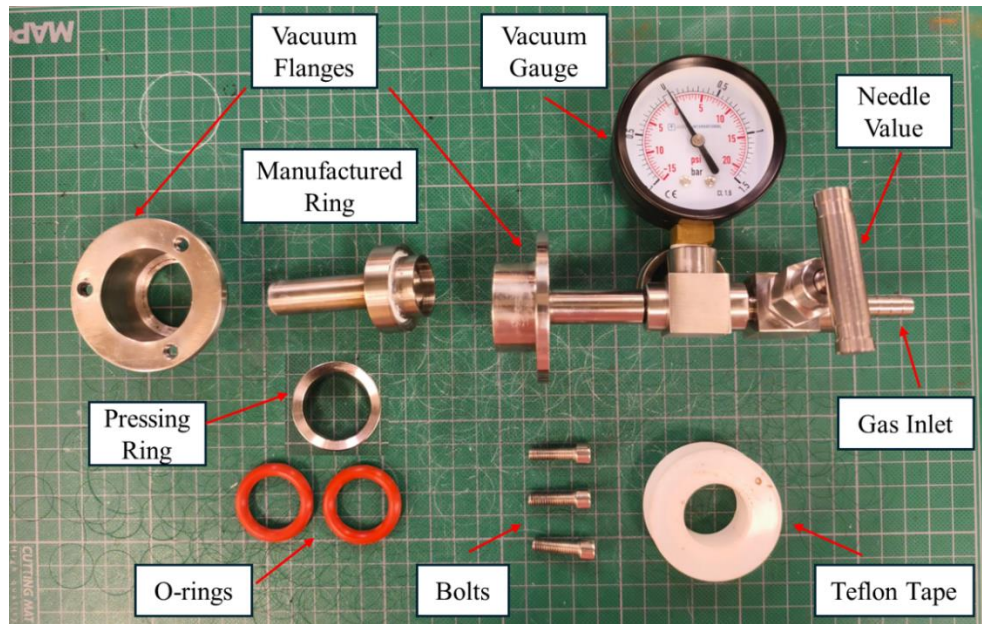


Figure 4-34. The gas-tight testing device is displayed unassembled with various components.

The different views of manufactured ring are shown in Figure 4-35, the inner diameter of the ring is 9mm which is smaller than the diameter of bi-layer membrane intended for the purpose of mounting. The lower sleeve is welded to the ring, serving the function of positioning the O-ring and keeping the ring stable in the flange.

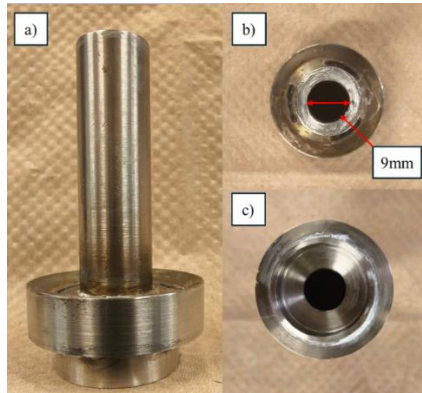


Figure 4-35. The manufactured ring of a) side view, b) top view, c) bottom view

The assembled device is shown in Figure 4-36 a), the first step is to eliminate the possible leakages from the device itself and test the super glue's airtightness. Soap water is employed to identify potential areas of leakage. A glass bottle is mounted on ring using super glue, the slender cylinder of the ring and glass bottle is submerged in soap water to assess the hermetic sealing of the super glue. The outcomes indicate the efficacy of the super glue in preventing leaks between the glass bottle and the ring, while revealing leakages occurrence between the flange and O-rings (see Figure 4-36 b)). Notably, when the vacuum gauge registers 1.5 bar, it requires more than 1 hour decrease to atmospheric pressure, a duration deemed sufficient for testing purposes. Acetone can be utilized for the purpose of eliminating super glue.

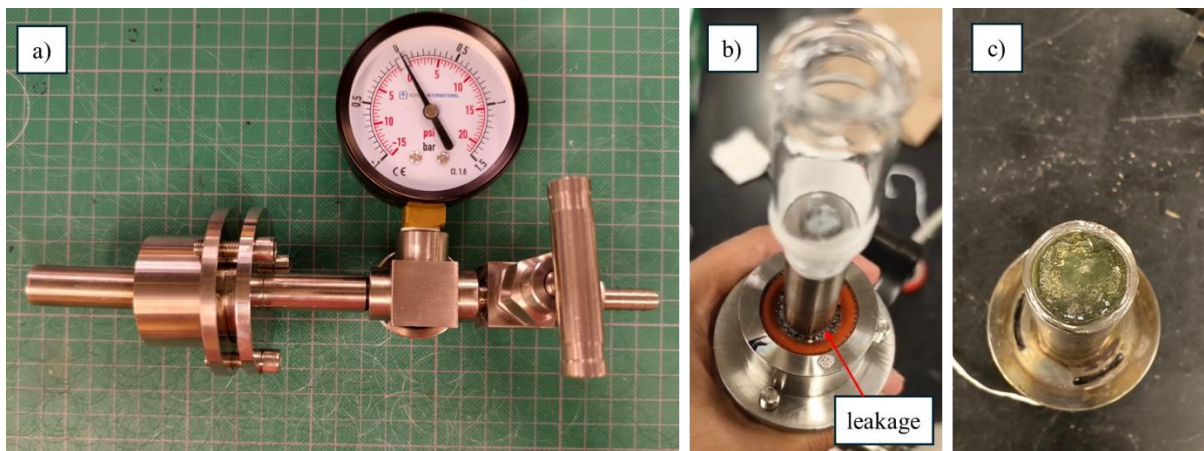


Figure 4-36. The images of a) assembled gas-tight testing device, b) locating the leakage point using a glass bottle, c) mounting bi-layer membrane on ring

The next step involves assessing the airtightness of our bi-layer membrane. As demonstrated in Figure 4-36 c), the pressure rapidly diminishes from 1.5 bar to atmospheric pressure within a few seconds when the bi-layer membrane (the electrolyte layer facing upward with a thickness of approximately 20-30 μ m) is adhered to the ring, the tested bi-layer membranes are from manual blade coated #11 and #12. The application of soap water on the membrane reveals the presence of points of leakage. Subsequently, we increase the thickness of the electrolyte layer to about 100 μ m and subjected it to sintering alongside BZCY powder and pellet covering. The pressure drop is slower upon mounting the membrane on the ring, with fewer leakage points observable on the electrolyte layer using soap water. Finally, the sintered pure BZCY172 pellet #4 is mounted on the ring, resulting in a pressure drop speed like that observed when a glass bottle is mounted on the ring, and there are no bubbles when it soaks in soap water, thereby confirming the airtightness of the sintered BZCY172 pellet (see Table 4-10).

Table 4-10. Gas tightness of dense electrolyte layers

Testing medium	Time spending from 1.5 bar to 0 bar
Glass (reference)	Over 1 hour
Bi-layer membrane with 20-30 μ m electrolyte layer	5 seconds
Bi-layer membrane with 100 μ m electrolyte layer	30 seconds
1mm thick BZCY172 pellet	Over 1 hour

In consequence, it is evident that with the increase in the thickness of the dense layer, there is a corresponding increase in the ability of airtightness. This trend continues until the testing of the pure BZCY172 pellets, where the desired level of airtightness is attained due to the ability to achieve a certain thickness in millimeters. It is evident that the uneven spread of electrolyte pastes on the substrate by using manual blade coating is a significant factor to consider.

4.8 Chapter Summary

This chapter presents a comprehensive exploration of various techniques that have successfully led to the creation of both dense electrolyte layers and porous electrode layers. While the application of screen printing with BZCY172 slurry prove challenging in achieving an evenly distributed electrolyte layer, and sintering aids does not significantly enhance the sintering process, alternative

approaches show promise. Die-pressed BZCY172 powder with finer NiO particles and nickel nitrate-impregnated BZCY172 powder demonstrate improved densification, though barium evaporation is observed at the surface. To mitigate barium loss, a method involving manual blade coating with a BZCY172 paste recipe and a sintering process where the electrolyte layer is covered with BZCY172 powder and a pellet is employed, resulting in minimized barium evaporation. However, when sintering a bi-layer membrane at 1500°C for 2 hours, secondary phases such as barium aluminum oxide, barium cerium oxide, and cerium zirconium yttrium oxide are detected on the surface. To further understand Ba loss, a MATLAB simulation based on Fick's second law provides optimal values for D_0 ($7.328 \times 10^{-9} \text{ cm}^2/\text{s}$) and E_a (127.80 kJ/mol) that align with experimental results. Additionally, a gas-tightness experimental setup is developed to evaluate the airtightness of the dense electrolyte layer in the bi-layer membrane, revealing that increased layer thickness enhances airtightness. This systematic approach underscores the progress made in optimizing the fabrication and performance of SOC membranes.

Chapter 5

Conclusion and Recommendations for Future Work

This chapter summarizes the research on the manufacturing of solid oxide electrochemical cells using proton-conducting materials in a perovskite structure, and it also provides recommendations for future work.

5.1 Conclusion

In this thesis, proton conducting BZCY172 ceramics bi-layer membrane are fabricated. The BZCY172 powder synthesis, bi-layer fabrication processing, sintering, and characterization works are reported.

Chapter 1 offers a comprehensive overview of SOC, including their definition, benefits, and drawbacks. It explores proton-conducting materials that enhance SOC performance and reviews different powder synthesis methods, underscoring the importance of choosing the right method for applications. The chapter also delves into membrane production techniques, stressing the need for advanced equipment and methods to create high-quality membranes. Moreover, it outlines the challenges in membrane fabrication, highlighting the complexities and obstacles in developing effective and reliable SOC membranes.

Chapter 2 provides an overview of the apparatus and methods used in synthesizing proton-conducting material powders and fabricating membranes. It details combustion and sol-gel techniques for powder synthesis, emphasizing precise control of conditions and using equipment like analytical balances, temperature probes, and furnaces. For membrane fabrication, it explains die pressing for substrates and screen printing and manual blade coating for deposition of electrolyte layers. Sintering methods are introduced to address issues such as warpage, Ba loss, and adhesion in bi-layer membranes. Characterization techniques, including XRD and SEM, are also discussed, highlighting their importance in analyzing the structural and morphological properties of the materials.

Chapter 3 outlines the BZCY172 powder synthesis using combustion and sol-gel methods, focusing on the effects of calcination temperatures on the resulting material. The combustion method involves two recipes: one using nitric acid (initial recipe) and the other using all-nitrates precursors. The sol-gel method, similar to combustion, simplifies the process by eliminating the need for precursor

solution neutralization. After synthesis, the powders are calcinated at various temperatures, with optimal results achieved at 1000°C. Characterization of the powders, including XRD and SEM analyses, reveals that the all-nitrates recipe produces more porous powders with better crystallinity and phase purity, compared to the initial recipe. The combustion method gives finer particles compare with sol-gel method. The chapter concludes that the all-nitrates recipe with combustion method is more effective in achieving the desired stoichiometric ratios and material properties.

Chapter 4 outlines the fabrication and optimization of bi-layer membranes for solid oxide fuel cells, starting with the mixing of BZCY172 powder with NiO and starch as substrate, followed by pressing, pre-sintering, and screen printing of an electrolyte layer using a binder. Challenges with uniformity and adhesion lead to the adoption of manual blade coating and the use of a planetary ball mill to create a thicker paste. Sintering at controlled temperatures improves layer density and defect minimization. The investigation into sintering conditions reveals issues with Ba loss and material segregation, mitigates by employing sintering aids like NiO and optimizing temperature and sintering processes. X-ray diffraction analysis confirms the presence of BZCY, YSZ, and CZ phases on the surface bulk of electrolyte layer. Ba loss in the electrolyte layer is modeled using Fick's second law, highlighting a correlation between Ba concentration and layer thickness. And gas-tightness testing indicates that thicker electrolyte layers enhance performance, though manual blade coating still posed issues with paste spread.

5.2 Recommendations for Future Work

The recommendations provide primarily revolve around the sintering stage of the process, as it is observed that issues related to Ba loss and segregation tend to occur in the sintered membrane.

1. Experimenting with sinter the membrane under conditions of low CO₂, it is worth noting that the materials BaZrO₃ and BaCeO₃ are susceptible to the phenomenon of Ba segregation occurring outside the structural framework. This occurrence is partly stimulated by the preferential formation of BaCO₃ in the presence of CO₂. Moreover, the existence of BaCO₃ serves to impede the diffusion of cations and consequently complicates the sintering process.
2. The other methods involve utilizing sintered aids such as NiO and implementing a two-step method to decrease the sintering temperature in order to prevent Ba loss and address the issue of segregation more effectively.

3. Another potential approach involves addressing the issue of agglomeration in the BZCY172 powder, as reducing the particle size of BZCY172 has the potential to facilitate the sintering process of the material. This method focuses on mitigating the challenges associated with powder agglomeration, thereby enhancing the sintering capabilities of BZCY172 through the utilization of smaller particles.
4. Finally, it should be noted that the presence of aluminum contamination within the BZCY172 paste, from the ball mill process, has the potential adverse effects on the sintering ability of the BZCY172 material; therefore, it is imperative that a revised recipe be implemented specifically for the roller mixing stage in order to ensure the attainment of a homogeneous paste.

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Appendix: MATLAB Code for Barium Concentration Model

```
% Load the Excel file with preserved column headers

filename = 'powder covered membrane ba loss copy.xlsx';

opts = detectImportOptions(filename, 'VariableNamingRule', 'preserve');

% Load the data from each sheet

sheet1 = readtable(filename, opts, 'Sheet', 'line (240425)');
sheet2 = readtable(filename, opts, 'Sheet', 'line1 (240425)');
sheet3 = readtable(filename, opts, 'Sheet', 'line1 (240506)');

% Extract the Barium concentration (y) and distance (x) from each sheet

y1 = sheet1{:, 1}; % Barium Concentration
x1 = sheet1{:, 2}; % Distance in meters
y2 = sheet2{:, 1}; % Barium Concentration
x2 = sheet2{:, 2}; % Distance in meters
y3 = sheet3{:, 1}; % Barium Concentration
x3 = sheet3{:, 2}; % Distance in meters

% Average the x and y values

y_avg = mean([y1, y2, y3], 2);
x_avg = mean([x1, x2, x3], 2);

% Ratio between relatively concentration and actual concentration of barium

MW = 137.327; % molecular weight of barium (g/mol)
```

```

mass = (MW / 6.022e23) * 1; % mass of one barium atom in BZCY bulk (g)

a = 4.263e-10; % lattice constant of BZCY (m)

V = a^3; % volume of one BZCY bulk

x_real = mass / V; % real concentration of Ba in one BZCY bulk

r = 148.037 / x_real; % the 148.037 is the average value from stablized region of barium
concentration profile (4.22um to 22.31um)

% Convert C_data to actual concentration of barium in kg/m^3

y_avg = y_avg / r;

% Calculate the standard deviation (error bars) for x and y

y_err = std([y1, y2, y3], 0, 2);

y_err = y_err / r; % actual concentration

x_err = std([x1, x2, x3], 0, 2);

% Convert distance from meters to micrometers

x_avg = x_avg * 1e6; % Convert to micrometers

x_err = x_err * 1e6; % Convert to micrometers

% Save the averaged data and error bars into a .mat file

save('averaged_data.mat', 'x_avg', 'y_avg', 'x_err', 'y_err');

% Extract the variables: Convert experimental data to model units

x_data = x_avg;

C_data = y_avg;

```

```

% Parameters

R = 8.314; % J/(mol·K) universal gas constant

Ci = 148.037 / r; % g/m^3

Cs = 2.717e5; % g/m^3


% Time span

tspan = linspace(0, 127680, 127680);


% Spatial grid

x = linspace(1e-6, 21.71e-6, 100);


% Define the PDE function with continuous T(t)

function [c, f, s] = pdeFunc(x, t, u, DuDx, Ea, D0, R)

    % Define the temperature T(t) as a continuous function; T in degree C

    if t < 29280

        T = (1/30) * t + 25;

    elseif t < 59280

        T = (1/60) * t + 512;

    elseif t < 73680

        T = 1500;

    elseif t < 103680

        T = -(1/60) * t + 2728;

    else

```

```

    T = -(1/30) * t + 4456;

end

D = D0 * exp(-Ea / (R * (T + 273.15))); % Convert T to Kelvin
c = 1 / D;
f = DuDx;
s = 0;
end

% Define the initial condition
function u0 = initialCondition(x, Ci)

    u0 = Ci;
end

% Define the boundary conditions
function [pl, ql, pr, qr] = boundaryConditions(xl, ul, xr, ur, t, Ci, Cs)

    pl = ul - Cs;
    ql = 0;
    pr = ur - Ci;
    qr = 0;

    % ul and ur are the solution values at the left and right boundaries, ql and qr Dirichlet boundary
    conditions, which specify the values of the solution at the boundaries directly, without involving the
    flux term
end

```

```

% Define the objective function (for optimization)

function error = objectiveFunction(params, x, tspan, x_data, C_data, Ci, Cs, R)

    Ea = params(1);

    D0 = params(2);

    % array (or vector) of parameters that the optimization function fminsearch is trying to optimize


    % Solve the PDE with current parameters

    m = 0; %Cartesian coordinates

    sol = pdepe(m, @(x, t, u, DuDx) pdeFunc(x, t, u, DuDx, Ea, D0, R), ...
        @(x) initialCondition(x, Ci), ...
        @(xl, ul, xr, ur, t) boundaryConditions(xl, ul, xr, ur, t, Ci, Cs), ...
        x, tspan);

    C_final = sol(end, :);

    % pdeFunc is defined to take additional parameters (Ea, D0, R) along with the standard arguments
    x, t, u, and DuDx. pdeFunc calculates the coefficients c, f, and s used in the PDE.

    % initialCondition is defined to take additional parameters (Ci) along with the standard argument x.
    initialCondition returns the initial value of the solution u at the spatial position x.

    % boundaryConditions is defined to take additional parameters (Ci, Cs) along with the standard
    arguments xl, ul, xr, ur, and t. boundaryConditions returns the values of pl, ql, pr, and qr that define
    the boundary conditions at the left (xl) and right (xr) boundaries.


    % Interpolate the PDE solution to the data points

    C_interp = interp1(x, C_final, x_data, 'linear', 'extrap');

    % Ensure C_interp and C_data are column vectors for compatibility

```

```

C_interp = C_interp(:);
C_data = C_data(:);

% Calculate the error as a scalar value
error = sum((((C_interp - C_data)./ C_data).^2);

end

% Initial guess for Ea and D0
initialGuess = [1e5, 1e-12]; % Activation energies often range from 10^3 to 10^5 J/mol, Do ranges
from 10^-12 to 10^-6 m^2/s.

% Perform the non-linear optimization (fminsearch is iterative method that start with an initial guess
and improve the parameters step by step, to minimize the objective function)

bestParams = fminsearch(@(params) objectiveFunction(params, x, tspan, x_data, C_data, Ci, Cs, R),
initialGuess);

% objectiveFunction is the function that calculates the error (or objective) value that fminsearch tries
to minimize.

% Extract the best parameters, bestParams will hold the values of Ea and D0 that minimize the
objective function.

Ea_best = bestParams(1);
D0_best = bestParams(2);

disp(['Best Ea in J/mol: ', num2str(Ea_best)]);
disp(['Best D0 in m^2/s: ', num2str(D0_best)]);

```

```

% Solve the PDE with best parameters, These lines solve the PDE using the optimized parameters
and store the final concentration profile in C_final

m = 0;

sol = pdepe(m, @(x, t, u, DuDx) pdeFunc(x, t, u, DuDx, Ea_best, D0_best, R), ...
    @(x) initialCondition(x, Ci), ...
    @(xl, ul, xr, ur, t) boundaryConditions(xl, ul, xr, ur, t, Ci, Cs), ...
    x, tspan);

C_final = sol(end, :); %selects the last row of the solution matrix sol, which represents the solution at
the final time point. (final row ensures that the boundary conditions and the PDE have been satisfied
over the entire time span)


% Plot the results

figure;

% Plot the model prediction

plot(x * 1e6, C_final, 'r', 'LineWidth', 2); % Convert x to micrometers for plotting

hold on;

% Plot the experimental data with error bars

errorbar(x_data, C_data, y_err, y_err, x_err, x_err, 'bo', 'MarkerFaceColor', 'blue', 'CapSize', 10);

xlabel('Distance (micrometers)', 'FontSize', 14);

ylabel('Barium Concentration (g/m^3)', 'FontSize', 14);

legend('Model', 'Data');

```

```
set(gca, 'FontSize', 14);
```

```
grid off;
```

```
hold off;
```