

T.R.
GEBZE TECHNICAL UNIVERSITY
GRADUATE SCHOOL

**COLD SINTERING OF Sm DOPED CERIA - SODIUM
CARBONATE NANOCOMPOSITE ELECTROLYTES FOR
SOFC APPLICATIONS**

MURAT MURUTOĞLU

A THESIS OF DOCTORATE
DEPARTMENT OF MATERIALS SCIENCE AND
ENGINEERING

ADVISOR: PROF. DR. HUSEYİN YILMAZ

JUNE 2025

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LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

KOYH UYGULAMALARI İÇİN S_m KATKILI SERYUM
– SODYUM KARBONAT NANOKOMPOZİT
ELEKTROLİTLERİN SOĞUK SİNERLENMESİ

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DOKTORA TEZİ
MALZEME BİLİMİ VE MÜHENDİSLİĞİ
ANABİLİM DALI

DANIŞMAN: PROF. DR. HÜSEYİN YILMAZ

HAZİRAN 2025

DOCTORATE JURY APPROVAL FORM

A thesis submitted by Murat, Murutoğlu, defended on 07/07/2025 before the jury formed with the 27/01/2025 date and 2025/07 numbered decision of the GTU Graduate Administration Board, has been accepted as a DOCTORATE thesis in the Department of Materials Science and Engineering.

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ABSTRACT

This thesis investigates the development of innovative electrolyte materials for Solid Oxide Fuel Cells (SOFCs) through the Cold Sintering Process (CSP). The study aims to address challenges associated with conventional fabrication methods, such as low densification, sodium carbonate decomposition, and grain coarsening, by focusing on ceria-based nanocomposite electrolytes containing varying amounts of Na_2CO_3 . The CSP technique, which operates at low temperatures, aims to achieve high densification while preserving the nanoscale structure that is critical for ionic conductivity.

The densification of samarium-doped ceria (SDC)- Na_2CO_3 nanocomposites via CSP is presented in detail. Experimental results demonstrate that the CSP method achieves relative densities of $\geq 97\%$ at temperatures below 200°C , significantly outperforming conventional sintering techniques.

The effects of carbonate content and different transient solvents (deionized water and ethylene glycol) on microstructural and electrical properties were systematically investigated. It was found that both the humidification method and carbonate concentration play a critical role in determining the densification and conductivity. Electrolytes with 20 %wt. carbonate content tested in a cathode/electrolyte/cathode half-cell configuration exhibited ionic conductivity of 68 mS/cm at 600°C . Under a reducing atmosphere (H_2), this value further increased to 0.13 S/cm .

Furthermore, single-step fabrication of full SOFC cells integrating the anode, electrolyte, and cathode layers via CSP was successfully achieved. Full-cell tests demonstrated a power density of 534 mW/cm^2 .

The study also explored the hypothesized superionic conduction pathway at the ceramic-carbonate interface. However, no direct experimental evidence of this superionic pathway could be obtained, indicating that further investigation is required.

Keywords: Cold Sintering Process (CSP), Nanocomposites Electrolytes, Solid Oxide Fuel Cells (SOFC)s, Low Temperature Sintering, Single Step Fabrication, SDC- Na_2CO_3

ÖZET

Bu tez, Katı Oksit Yakıt Hücreleri (SOFC) için yenilikçi elektrolit malzemelerin Soğuk Sinterleme Prosesi (CSP) aracılığıyla geliştirilmesini araştırmaktadır. Geleneksel üretim yöntemlerinden kaynaklanan düşük yoğunluk, sodyum karbonatın dekompozisyonu ve tane kabalaşması gibi problemlere çözüm getirmeyi amaçlayan çalışmada, farklı oranlarda Na_2CO_3 içeren serya (CeO_2) bazlı nanokompozit elektrolitler üzerine odaklanılmıştır. Düşük sıcaklıklarda çalışan CSP tekniği, iletkenlik açısından kritik olan nano ölçekli yapıyı korurken yüksek yoğunluk elde etmeyi hedeflemektedir.

Samaryum katkılı serya (SDC)- Na_2CO_3 nanokompozitlerin CSP ile yoğunlaştırılması ayrıntılı şekilde sunulmuştur. Deneysel sonuçlar, CSP yönteminin $200\text{ }^\circ\text{C}$ altındaki sıcaklıklarda $\geq 97\%$ kısmi yoğunluklara ulaşarak geleneksel sinterleme yöntemlerini önemli ölçüde geride bıraktığını göstermektedir.

Karbonat miktarı ile farklı çözücülerin (saf su ve etilen glikol) mikro yapısal ve elektriksel özellikler üzerindeki etkisi sistematik olarak araştırılmıştır. Nemlendirme yöntemi ve karbonat konsantrasyonunun hem yoğunluk hem de iletkenlik üzerinde belirleyici olduğu bulunmuştur. Ağırlıkça % 20 karbonat içeriğine sahip elektrolitler, katot/elektrolit/katot yarım hücre konfigürasyonunda test edilerek $600\text{ }^\circ\text{C}$ 'de 68 mS/cm seviyesinde iyonik iletkenlik göstermiştir. İndirgen atmosfer (H_2) altında bu değer 0.13 S/cm 'ye kadar yükselmiştir.

Ayrıca, anot, elektrolit ve katot katmanlarının CSP yoluyla tek adımda üretildiği KOYH hücrelerinin üretimi başarıyla gerçekleştirilmiştir. Yapılan tam hücre testleri 534 mW/cm^2 'lik bir güç yoğunluğu elde edildiğini ortaya koymuştur. Çalışmada ayrıca, seramik-karbonat arayüzünde olduğu varsayılan süperiyonik iletim yolunun varlığı araştırılmıştır. Ancak bu süperiyonik iletim mekanizmasına dair doğrudan deneysel bir kanıt elde edilememiş olup, daha ileri çalışmalara ihtiyaç duyulmaktadır.

Anahtar Kelimeler: Soğuk Sinterleme Prosesi (SSP), Nanokompozit Elektrolitler, Katı Oksit Yakıt Hücreleri (KOYH), Düşük Sıcaklık Sinterlemesi, Tek Adım Üretim, SDC- Na_2CO_3

ACKNOWLEDGEMENTS

I would like to express my deep and sincere gratitude to my supervisor, Prof. Dr. Hüseyin Yılmaz, who not only shared his profound scientific knowledge with me but also taught me great lessons of life. His support, suggestions, and encouragement gave me the drive and will to complete this work.

I would like to express my sincere gratitude to the members of my thesis monitoring committee, Prof. Dr. Cihangir Duran and Prof. Dr. Yahya Kemal Tür, for their guidance and valuable suggestions throughout my doctoral studies.

Also, I would like to express my thanks to Assoc. Prof. Dr. Aligül Büyükaksoy for sharing his scientific expertise with me.

Moreover, I also would like to thank Aygöl Alkan Gültekin, for her support during my research and the writing process.

I am thankful for Ahmet Nazım and Adem Şen for their technical assistance and their support.

I would also like to thank Merve Torman Kayalar for making my time in the workplace more pleasant through her kind presence and sincere friendship.

Finally, I would like to thank my parents, siblings, and nephews for their love and endless support.

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LIST OF SYMBOLS AND ABBREVIATIONS

AFC	: Alkaline Fuel Cell
CSP	: Cold Sintering Process
CS	: Conventional Sintering
CPM	: Co-Precipitation Method
DI	: Deionised
DCO	: Doped Cerium Oxide
DSC	: Differential Scanning Calorimetry
EDS	: Energy Dispersive Spectroscopy
EG	: Ethylene Glycol
EIS	: Electrochemical Impedance Spectroscopy
FWHM	: Full Width at Half-Maximum
FAST	: Field-Assisted Sintering Technique
FAST/SPS	: Field-Assisted Sintering Technology/Spark Plasma Sintering
GDC	: Gadolinium-Doped Ceria
HIP	: Hot Isostatic Pressing
HHP	: Hydrothermal Sintering
HTSOFC	: High Temperature Solid Oxide Fuel Cells
ITSOFC	: Intermediate Temperature Solid Oxide Fuel Cell
LNO	: Lithiated Nickel Oxide
LSCF	: Lanthanum Strontium Cobalt Ferrite
LSM	: Lanthanum strontium manganite
LPS	: Liquid Phase Sintering
MIEC	: Ionic-Electronic Conductor
MCFC	: Molten Carbonate Fuel Cell
min	: Minute
NEE	: Normalised Excess Energy
OCP	: Open Circuit Potential
ORR	: Oxygen Reduction Reaction
PAFC	: Phosphoric Acid Fuel Cell
PEMFC	: Proton Exchange Membrane Fuel Cell
SEM	: Scanning Electron Microscope
SOFC	: Solid Oxide Fuel Cell
SPS	: Spark Plasma Sintering
SSS	: Solid State Sintering
TDB	: Triple-Phase Boundry
TEC	: Thermal Expansion Coefficient
TGA	: Thermogravimetric Analysis
XRD	: X-ray diffractometer
YSZ	: Ytria-Stabilised Zirconia
O ²⁻	: Oxygen Ions
H ⁺	: Hydrogen Ions
BaTiO ₃	: Barium Titanate
ZnO	: Zinc Oxide
Mo ₂ K ₂ O ₇	: Molybdenum Potassium Oxide
V ₂ O ₅	: Vanadium Oxide
Mo ₂ Na ₂ O ₇	: Molybdenum Sodium Oxide
MoO ₃	: Molybdenum Oxide

Zn	: Zinc
P	: Pressure
T	: Time
E_a	: Activation Energy
σ^{ef}	: Effective Conductivity
p	: Pore Volume
σ^o	: Conductivity of Completely Dense Materials
ASR	: Area Specific Resistance
E_a	: Activation Energy
k	: Boltzmann Constant



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1. CHAPTER ONE: MOTIVATIONS

1.1. Motivation

Sintering, a technique that consolidates powder materials through heat without reaching full melting, has origins traced back thousands of years in metallurgy and ceramics [1]. Early applications of sintering were found in ancient civilizations, where it was used to strengthen pottery and metal objects [2]. In the 20th century, sintering became a key industrial process in the manufacturing of complex ceramics, metal alloys, and advanced composites [3]. As industrial needs evolved, sintering technology advanced to achieve higher densification and material stability, forming the foundation of modern sintering methods [4].

The traditional sintering process, typically requiring temperatures above 1000 °C, presents several challenges. High temperatures result in considerable energy consumption and increased costs for industrial applications [5]. Additionally, these elevated temperatures can cause undesirable phase volatility, where components in the material decompose or evaporate, compromising the material's structural integrity [6]. Achieving uniform densification is another significant challenge, especially in complex or large components, often resulting in weak spots within the sintered product [7]. Such densification inconsistencies contribute to mechanical weaknesses, limiting the applications of conventionally sintered materials [8].

To address these challenges, researchers have focused on optimizing energy efficiency and material stability within high-temperature sintering environments [9]. Alternative methods have been developed to reduce energy consumption and improve densification, leading to significant technological advancements in sintering [10].

One example is Spark Plasma Sintering (SPS), which uses electrical discharges to achieve rapid heating, enabling densification at lower temperatures and shorter times than conventional sintering [11]. Microwave sintering, another method, applies microwave energy to selectively heat materials, offering energy savings and faster processing while reducing thermal gradients that can cause structural inconsistencies [12]. Similarly, the Field-Assisted Sintering Technique (FAST) combines pressure and

electric current to enhance densification at reduced temperatures [13]. These advanced methods address issues such as energy efficiency, material stability, and uniform densification, facilitating the production of advanced materials with complex geometries [14].

The increasing demand for energy-efficient processes and novel material requirements has driven the development of new sintering techniques. One of the most notable advancements is the Cold Sintering Process (CSP), introduced by Randall and colleagues in 2016 [15, 16]. CSP represents a breakthrough in low-temperature sintering, addressing the challenges of traditional high-temperature methods. This process involves sintering materials at temperatures below 300 °C, often in the presence of a transient liquid phase that aids particle rearrangement and densification at reduced temperatures [15]. This innovation dramatically reduces energy consumption and allows the sintering of temperature-sensitive materials that would degrade under conventional conditions [16].

CSP is particularly advantageous for fabricating composite materials and hybrid systems, enabling the combination of different material types. This versatility expands its applications in fields such as electronics, biomedicine, and fuel cells [17]. With its low-temperature requirements and broad material compatibility, CSP is emerging as a sustainable and efficient manufacturing technique, paving the way for future advancements in sintering technology [18, 19].

1.2. Problem Statement

Traditional solid oxide fuel cells (SOFCs) typically employ doped ZrO_2 and CeO_2 electrolytes, which require high operating temperatures between 700 °C and 900 °C to achieve sufficient ionic conductivity [20]. These elevated temperatures can adversely affect the long-term stability of fuel cells and increase operational costs, thereby limiting their widespread commercialization. [21, 22]. Consequently, developing new electrolyte materials that maintain high ionic conductivity at lower temperatures, preferably below 600 °C, is of significant importance [21].

One common approach to achieving high conductivity at reduced temperatures involves the use of nanocomposite electrolytes. These are typically prepared by combining cerium oxide (CeO_2)-based ceramics with inorganic salts such as Na_2CO_3

or Li_2CO_3 . The addition of these salts enhances ionic transport and stabilizes the electrolyte, resulting in exceptionally high ionic conductivities even at lower temperatures [21, 23, 24].

In these composites, samarium-doped ceria (SDC) is often used as the ceramic phase, while sodium carbonate (Na_2CO_3) serves as the inorganic salt. SDC- Na_2CO_3 nanocomposites have demonstrated remarkable ionic conductivities of up to 0.1 S/cm and fuel cell performances reaching 0.8 W/cm² at temperatures as low as 550 °C [25, 26, 27].

Although it has not yet been fully elucidated, the conduction mechanism in nanocomposite electrolytes is thought to occur via multi-ionic or co-ionic conduction. According to this mechanism, oxygen ions (O^{2-}) conduct through the ceramic phase, while hydrogen ions (H^+) contribute to conduction along the "super ionic path" postulated to form at the ceramic-carbonate interface [28, 29]. Analysis of this mechanism highlights the critical importance of enhancing the ceramic-carbonate interface to achieve high ionic conductivity. This enhancement can be accomplished through two primary approaches: first, by ensuring that the ceramic phase is composed of homogeneously distributed, fine-grained particles; and second, by maximizing the overall density of the structure.

Even though nanocomposite electrolytes exhibit high ionic conductivity and performance at low temperatures, which makes them promising for the commercialization of solid oxide fuel cells (SOFCs), their production poses significant challenges. Reported conductivity values for nanocomposite electrolytes range widely from 10^{-4} to 10^{-1} S/cm, reflecting the difficulties in achieving high conductivity through reliable manufacturing methods. One of the key issues is the densification challenge associated with traditional fabrication techniques [30, 31]. This difficulty arises due to the low melting and decomposition temperatures of the carbonate phase within the composite, which restrict the sintering temperature and make it challenging to achieve densities suitable for SOFC applications. For instance, in the widely studied SDC- Na_2CO_3 nanocomposite system, traditional methods (sintering at 700 °C for 2 hours) have achieved only 78 % of theoretical density [32]. Even using the expensive and complex "Hot Isostatic Pressing" (HIP) technique, Wang et al. reported achieving a maximum density of 91 % after sintering at 550 °C for 30 minutes [33]. However, this density remains below the minimum 92 % (preferably above 95 %) required for

efficient SOFC performance. Insufficient densification, which results in high porosity, adversely affects mechanical strength, ionic conductivity, and chemical stability, leading to significant performance losses. Additionally, lower density reduces the high ceramic-carbonate interfacial density, a critical factor for conductivity in nanocomposite electrolytes. Another significant issue associated with low density is that an electrolyte with a density below 92 % can not be effectively used in SOFC applications. This is because, below this threshold, porosity in the microstructure may become interconnected, which poses a major challenge for the efficient operation of a fuel cell.

Another major challenge associated with traditional fabrication methods is grain coarsening of the ceramic phase, which further reduces the ceramic-carbonate interfacial density and consequently leads to conductivity and performance losses. To achieve the required densities for SOFC applications, composites are typically sintered at the highest possible temperatures (~ 700 °C), constrained by the carbonate phase's low melting or decomposition temperature. However, sintering at these elevated temperatures induces grain growth. For example, Shuwati and Gülgün reported that, despite starting with nano-sized ceramic particles in SDC- Na_2CO_3 composites, the grains grew to the micron scale after sintering [34]. This grain growth significantly reduces interfacial density, further compromising the performance of nanocomposite electrolytes.

Addressing these densification and grain coarsening challenges is critical for the successful commercialization of nanocomposite electrolytes.

1.3. Objectives

In this doctoral dissertation, it is proposed that the challenges limiting the performance of ceria-carbonate nanocomposite electrolytes-namely, low densification and particle coarsening caused by conventional sintering methods-can be addressed through the Cold Sintering Process (CSP), an innovative production technique that operates at significantly lower temperatures. While the superionic path between ceria and carbonate is a hypothesized phenomenon, maintaining a high interfacial density between these phases is crucial for optimizing ionic conductivity. By employing CSP, which avoids the high temperatures associated with conventional sintering, this study

aims to achieve higher densities and preserve the nano-sized structure of the particles, thereby preventing coarsening. Consequently, it is anticipated that this method will lead to improved performance by overcoming the key limitations of conventional processing techniques.

Another focus of this thesis is the investigation of the conduction mechanism of nanocomposite electrolytes, as proposed in the literature, through an experimental/practical approach. This is because, with CSP, it has been made possible to achieve the optimal conditions for the mentioned mechanism (maximizing the ceramic-carbonate interface) and compare the results with the literature. If such a mechanism exists, the CSP method is expected to yield the best outcomes.

This thesis focuses on the densification of nanocomposite electrolytes using the Cold Sintering Process (CSP) and includes their microstructural and electrical characterizations. Additionally, it involves the fabrication of full cells, consisting of an anode, electrolyte, and cathode, in a single step using CSP, along with the microstructural and electrical characterization of these cells.

2. CHAPTER TWO: LITERATURE REVIEW

2.1. Cold Sintering Process

2.1.1. Introduction

Low-temperature ceramic processing methods are crucial for reducing energy consumption and carbon emissions in material manufacturing. Furthermore, ceramics have progressively been integrated with various materials, including polymers and metals, to form composite systems [35-38]. Nonetheless, the fabrication of such composites via co-firing presents problems that arise from gaps in sintering temperatures, thermal characteristics, and possible chemical incompatibilities among the material components [39, 40]. Therefore, lowering the sintering temperature of ceramics has emerged as a priority. Conventional techniques generally necessitate the sintering of green ceramic materials to attain over 95 % relative density at temperatures ranging from 50 % to 75 % of their melting point [41]. In order to mitigate this issue, many advanced techniques like hydrothermal sintering, spark plasma sintering, microwave sintering, liquid-phase sintering, and cold sintering have been devised to reduce the necessary sintering temperatures [42-46]. Among these methods, the cold sintering process significantly reduces the processing temperature for many ceramics.

The cold sintering process (CSP) eliminates the necessity for elevated temperatures for achieving densification [47]. CSP is a low-temperature, energy-efficient method employed to densify ceramics at ultra-low temperatures such as 25-300 °C within a few minutes under moderate uniaxial pressure, often in the hundreds of MPa. Similar to liquid phase sintering, the CSP occurs due to particle rearrangement, dissolution-precipitation processes, and grain growth, but with the involvement of a transient liquid phase as sintering assistance [48]. Optimally, the transient phase partially dissolves the ceramics, facilitates particle rearrangement, and enables the precipitation of the supersaturated solution within the pores as the transient phase evaporates [47, 48]. The procedure may be graphically represented as seen in **Figure 2.1**.

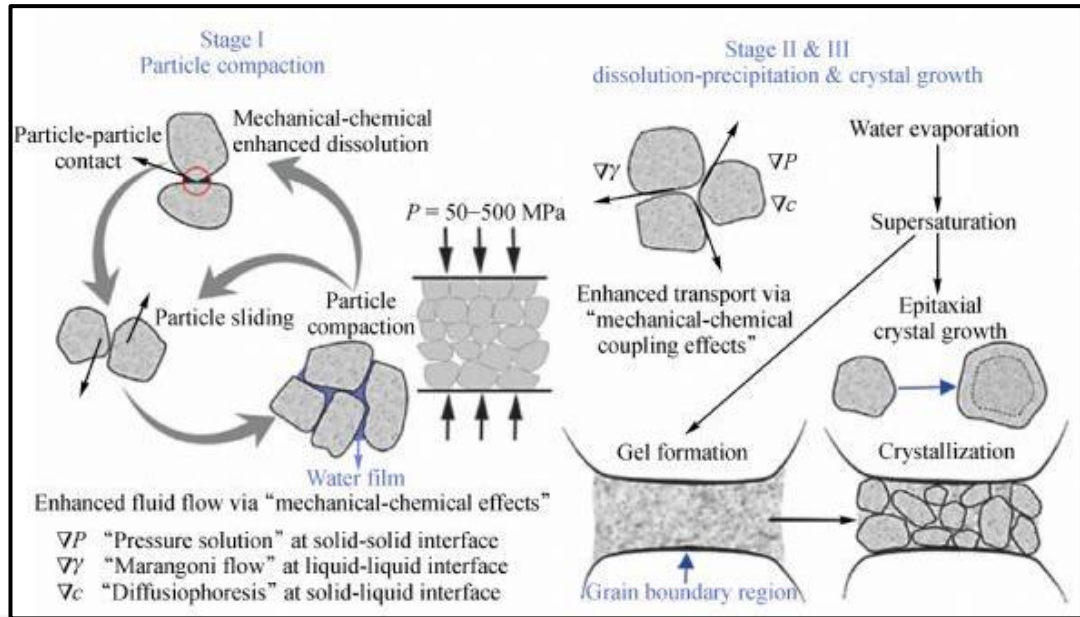


Figure 2.1: Illustration of cold sintering process proposed for BaTiO₃ [49].

The cold sintering process has attracted considerable attention in recent years. The origin of this process dates back to the 1950s, when the influence of moisture on reducing the sintering temperature of specific metal oxides and sulphates was first examined [50]. In the 1970s, additional progress was achieved in examining the influence of pressure combined with heat on the densification of ceramics [51]. Roy et al. [52] conducted the initial investigation into the influence of uniaxial pressures and solvents on the densification of ceramic pastes. During the subsequent decade, Hydrothermal Hot Pressing (HHP) was developed and subsequently applied to densify various compounds including SiO₂, ZrO₂, and TiO₂ [53-57]. A closed system was utilised in HHP, similar to hydrothermal sintering, to limit the evaporation of the liquid phase. In fact, this is one way in which CSP differs from hydrothermal sintering HHP. As opposed to closed systems subjected to hydrothermal pressure, cold sintering occurs in an open system subjected to non-equilibrium circumstances [48].

In more recent research, Kahari et al. [58, 59] shown that the introduction of water into Li₂MoO₄ can facilitate the densification of the material at temperatures close to room temperature when a uniaxial pressure is provided. As a result of this procedure, Guo et al. [47] were able to densify a larger variety of compounds at temperatures less than 400 °C and moderate uniaxial pressures, which ultimately led to the development of the cold sintering process. Water is the sintering aid that is utilised in CSP the most frequently; Nonetheless, additional liquids are also employed.

Research on the cold sintering process has intensified, focusing on the proposed densification processes and the impact of various processing factors on obtaining optimal densification. The interaction of critical parameters, including applied pressure, sintering temperature, transient liquid content, and dwell duration, has been thoroughly examined to optimise the process and broaden its applicability to a diverse array of materials. This section will present a detailed description of the impact of CSP parameters on material densification, emphasising their contributions to the process. The discussion will encompass the evolution of the theorised mechanisms of cold sintering, including particle rearrangement, dissolution-precipitation processes, and transient phase behaviours, highlighting accomplishments and limitations in the area.

2.1.2. Mechanism of CSP

In recent years, a variety of materials were processed by the cold sintering process, as illustrated in **Figure 2.2** [60, 61]. Zinc oxide (ZnO) and barium titanate (BaTiO_3) stand out as key materials, given their significant role in investigating and clarifying the densification mechanism of CSP.

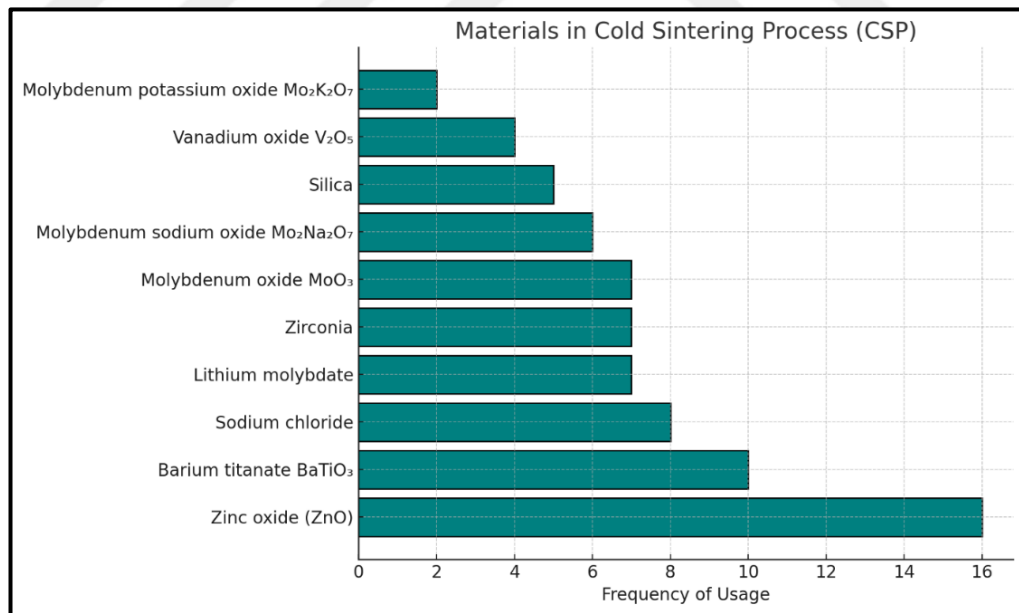


Figure 2.2: Frequency of materials used in the cold sintering process, highlighting zinc oxide and barium titanate as the most commonly utilized materials. (Adopted from references 60 and 61).

These materials are often utilised to explore the process thoroughly, offering important insights into the core principles of particle rearrangement, dissolution-precipitation,

and interfacial dynamics under CSP conditions. This section will focus on demonstrating the cold sintering mechanism through the use of these two materials as prototype examples. CSP represents a novel method, yet the specifics of its densification mechanism remain inadequately understood. The initial model for cold sintering mechanisms, introduced by Randall's group, outlines a two-stage dissolution-precipitation process, which closely resembles the mechanisms identified in liquid phase sintering [47]. This model emphasises the significance of transient liquid phases in promoting particle rearrangement and densification-precipitation throughout the cold sintering process.

According to this model, the initial step of densification is reported to occur by uniaxial pressure facilitated by the liquid phase, which enhances lubrication among particles. Pressure is believed to facilitate the distribution of the liquid phase inside the green body and enhance solubility, with sharp corners and edges dissolving initially to promote more effective packing. Over time, the pressure facilitates compaction, re-arrangement, and grain boundary creep inside the green body. Following the elevation of temperature, a further phase is outlined, whereby the elevated temperature under pressure further enhances solubility. This results in the generation of a supersaturated solution, enhancing mass transport and particle re-arrangement within the material, which, along with the applied pressure, facilitates densification. As the liquid phase is gradually evaporated, supersaturation escalates, hence enhancing mass transport.

The dissolution-precipitation reaction theory has been further established by Ndayishimiye et al., whose research on hydrothermal sintering demonstrated similar interactions occurring between the liquid phase and silica [62].

Nevertheless, additional research indicates that more processes are involved than initially believed, particularly with the liquid phase's function, with some suggesting that the liquid phase sintering (LPS) model inadequately describes CSP. Gonzalez-Julian et al. employed a combination of FAST/SPS (Field-Assisted Sintering Technology/Spark Plasma Sintering) with CSP to densify ZnO using water or a 0.5 % Zn-Ac solution [63].

The conclusion that came about was that the liquid phase plays 4 major roles within the cold sintering process:

- It enables superior initial packing owing to reduced particle friction.

- Dissolution of Zn^{2+} and O^{2-} on particle surfaces, particularly at sharp points and edges.
- Formation of defects because of diffusion of H^+ and OH^- .
- The generation of highly defective new diffusional pathways between grains.

This indicates the presence of other, more complex processes, suggesting that a basic LPS model is inadequate [63].

Biesuz et al. conducted a comprehensive theoretical investigation of CSP that questions the foundational hypotheses of cold sintering based on an LPS-like process [64]. This investigation analyses and evaluates the processes previously presented by Maria et al. (stages 1 and 2), considering various situations, including liquid content. In step 1, Biesuz et al. describe the process as a system of non-interacting particles inside a liquid suspension. Supported by data from Taveri et al., who investigated a comparable hydrothermal method known as isostatic cold press [65].

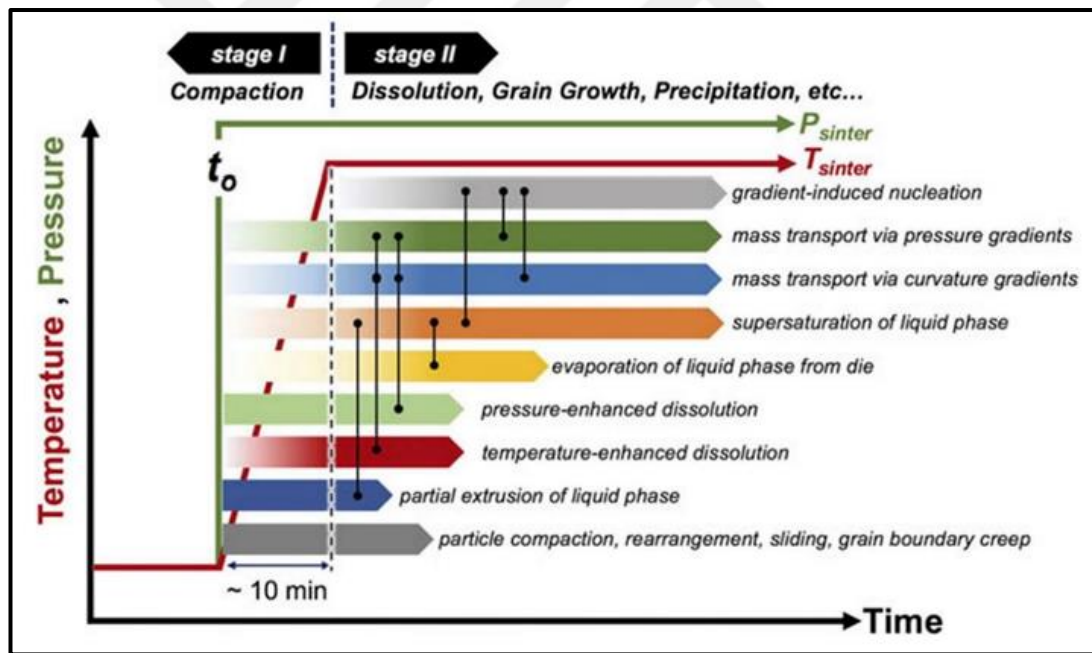


Figure 2.3: Schematic representation of the processes that facilitate compaction, consolidation, densification, and crystallisation during the cold sintering process. In this graphic, temperature rises upon the application of pressure. Vertical black lines denote processes or systems linked by a notably robust interaction [60].

Biesuz et al. indicate that Ostwald ripening may be regarded as the only active process. Biesuz et al. determined that additional inquiry into the CSP processes is necessary, since existing theories are inadequate, hence corroborating Gonzalez-Julian et al.'s

conclusions that other mechanisms, such as plastic deformation, are occurring [63, 64, 65]. Maria et al., have illustrated some of CSP mechanisms to highlight the diverse number of compaction, densification, and densification mechanisms that may contribute to cold sintering in **Figure 2.3** [60].

2.1.3. Materials

The active mechanism for densification may vary based on the material that is cold sintered and/or the liquid phases used. These differentiations have been classified according to the physical and chemical features of the original powder and solvent choices.

The dissolution behavior of particle surfaces may proceed via either a congruent or incongruent mechanism, contingent upon the specific chemical interactions between the solid particles and the solvent liquid phase. In congruent dissolution, the particle surface dissolves uniformly into the liquid medium, facilitating densification through a dissolution-precipitation mechanism [66]. This phenomenon has been extensively examined in the case of ZnO, particularly in systems incorporating zinc acetate or acetic acid, which serve as representative models for chemically driven densification via congruent dissolution. Pioneering work by Funahashi et al. on the cold sintering of ZnO revealed a markedly reduced activation energy for grain growth-measured at 43000 J/mol, which is substantially lower than that observed in conventional high-temperature sintering processes [67, 68].

Materials that undergo congruent dissolution typically experience densification through a singular, dominant mechanism. This process is notably driven by the accumulation of mobile ionic species in the transient phase, which emerge as the particles dissolve. In an effort to assess the role of solvent chemistry in cold sintering behavior, a comparative investigation was carried out using water and zinc acetate/acetic acid as transient media for ZnO compacts [66]. It was found that the greater solubility of ZnO in acetic acid promoted a more pronounced pressure-assisted mass transport, consistent with an accelerated pressure-solution creep mechanism [66, 67].

Perovskite ceramics such as $\text{Pb}(\text{Zr,Ti})\text{O}_3$ and BaTiO_3 tend to exhibit incongruent dissolution behavior in most conventional solvents, posing a significant challenge for

their consolidation via the cold sintering process [69, 70]. In systems where effective dissolution does not occur, achieving sufficient densification typically necessitates an additional high-temperature annealing step. This thermal treatment facilitates mass transport by enhancing diffusion kinetics and aids in the removal or transformation of secondary phases that may accumulate along grain boundaries [47, 71, 72].

In their investigation of cold sintering enhanced-permittivity BaTiO₃, Guo et al. employed water as the transient medium [47]. During processing, Ba²⁺ ions were leached from the BaTiO₃ particle surfaces, subsequently leading to the formation of an amorphous BaCO₃ phase at the grain boundaries. Concurrently, the particle surfaces became coated with an aqueous-phase-derived, Ti-enriched surface that inhibited their reactivity. This unintended formation of BaCO₃ negatively affected the dielectric properties of the material, and its presence within grain boundary regions was found to be unavoidable under the given processing conditions. To address this issue and promote further densification, a post-sintering annealing treatment at 900 °C was required to decompose the BaCO₃ phase and improve microstructural integrity [47, 73].

The eutectic combination of NaOH and KOH may reduce the synthesis temperature of many complex oxides [74, 75]. A notable example in the literature demonstrates the use of alkali flux in a one-step cold sintering route for BaTiO₃, enabling densification at temperatures as low as 300 °C [76]. Despite its sub-melting-point state being characterized by exceptionally high viscosity, which inherently hampers the dissolution-reprecipitation pathway, the flux maintained sufficient chemical aggressiveness at the interparticle contact zones. This localized reactivity was adequate to induce surface degradation on the BaTiO₃ grains, even in the absence of complete flux liquefaction.

In another study, achieving densification of BaTiO₃ at temperatures as low as 225 °C has been made possible through the incorporation of Ba(OH)₂·8H₂O as a flux [77]. The underlying mechanism relies on chemical instability at the particle surface, which facilitates mass transport through a solution-mediated process. Prior to sintering, the BaTiO₃ powders are subjected to acetic acid treatment, triggering the formation of an amorphous, barium-depleted surface layer. This outer structure serves as a reactive site for selective dissolution during compaction. Once dissolved, the exposed crystalline

grain cores, with inherently lower chemical activity, become the deposition sites for reprecipitated species, enabling neck formation and structural densification [77].

2.1.4. Post Heat Treatment

Achieving the required full-scale densification of some materials in a single-step cold sintering procedure is unfeasible. The majority of ceramics exhibit hindered dissolution or incongruent dissolution, characterised by the presence of amorphous or secondary phases through their grain boundaries. These include ZrO_2 , $\text{Pb}(\text{ZrTi})\text{O}_3$, and BaTiO_3 ceramics [78-80]. Consequently, a subsequent post-annealing heat treatment is necessary at a designated temperature and duration, based on the material's crystallisation temperature, to rid it of the secondary phase and obtain the desired enhanced densification.

The limited thermal energy supplied during cold sintering is typically insufficient to restore grain boundary integrity or fully eliminate residual phases. As a result, an additional thermal processing stage is frequently introduced to drive moisture removal, promote microstructural refinement, and improve overall compactness. For instance, in the case of BaTiO_3 , a follow-up annealing step conducted in the intermediate temperature range (typically between 700–850 °C) has been shown to promote grain coalescence and increase relative density by several percentage points [81]. Similarly, while conventional sintering of stabilized zirconia systems generally occurs near 1400 °C, alternative processing strategies have enabled the fabrication of 3YSZ ceramics with up to 85 % theoretical density at significantly reduced thermal budgets. A subsequent thermal treatment below conventional sintering temperatures can elevate this value to approximately 95 %. In contrast, 8YSZ exhibits more modest compaction during initial low-temperature processing, often achieving no more than 56 % density prior to any secondary heating step [16, 82, 83]. Although the incorporation of a thermal post-step might appear to compromise the energy efficiency of cold sintering, the reduced temperature levels and shorter durations still offer a notable advantage. Additionally, such thermal processing aids in eliminating unwanted boundary phases and supports grain development in systems like PZT, KNN, and BaTiO_3 , which are sensitive to interfacial inhomogeneities.

2.1.5. CSP Parameters

The factors that affect the densification of particles have been extensively explored and focused on three key features of CSP: materials, solvents, and processing parameters [84]. The internal properties include composition, particle size, and solubility in transient liquid, whereas the exterior features include the transient medium, including pH, amount, and solvent type. Thirdly, the selection of suitable physical factors, including pressure, temperature, duration, and atmosphere, is shown in **Figure 2.4** [85, 86]. The impact of many critical factors has been determined in several cold sintering investigations. Several critical factors are emphasised and examined comprehensively in this section.

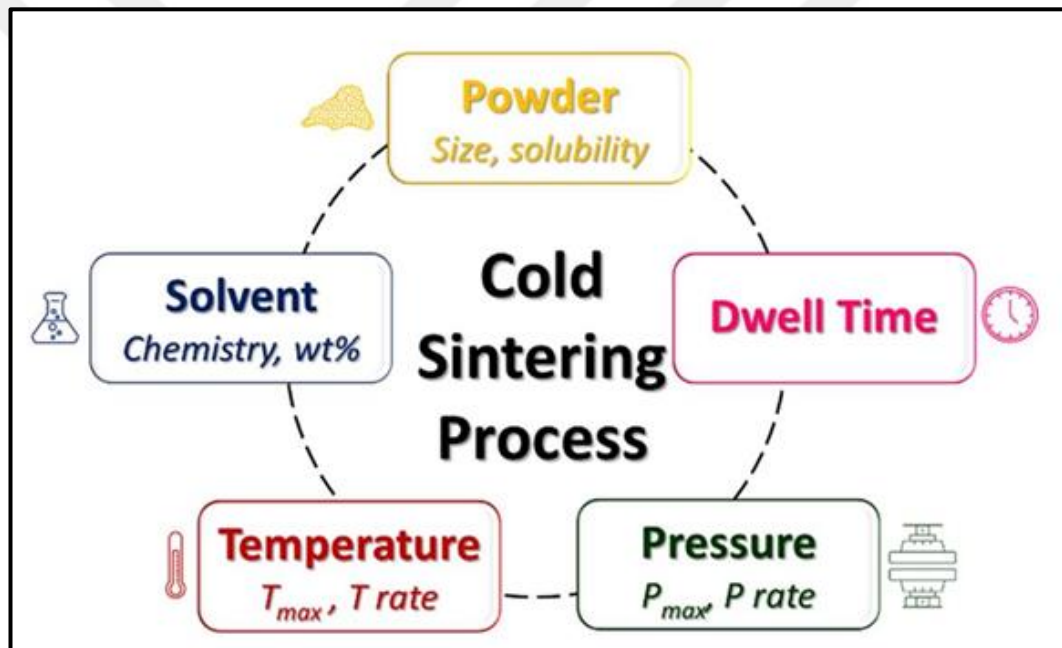


Figure 2.4: Schematic of parameters taking important roles in cold sintering process [85, 86].

2.1.5.1. Temperature

Sintering occurs by the diffusional transfer of material. This diffusional transport involves the movement of atoms or ions accompanied by a counterflow of vacancies. Defects in crystalline materials govern this transport through their concentration gradients. Simultaneously, temperature significantly influences the diffusional processes occurring during sintering [3, 5-7]. The cold sintering process is seen as

having a pressure solution-induced diffusional mechanism for mass transport. An increase in cold sintering temperature supplies more energy necessary for efficient mass movement. However, it is not as successful as conventional sintering due to the much lower temperature of CSP compared to conventional methods. The temperature for CSP is more efficient in facilitating the dissolution and precipitation processes [8]. The rise in temperature enhances densification during CSP, as indicated by some cold sintering investigations; nonetheless, its impact is less significant than that found under pressure [87]. The CSP temperature must exceed the boiling point of the transient liquid to enable full removal, hence preventing pore formation that might diminish densification.

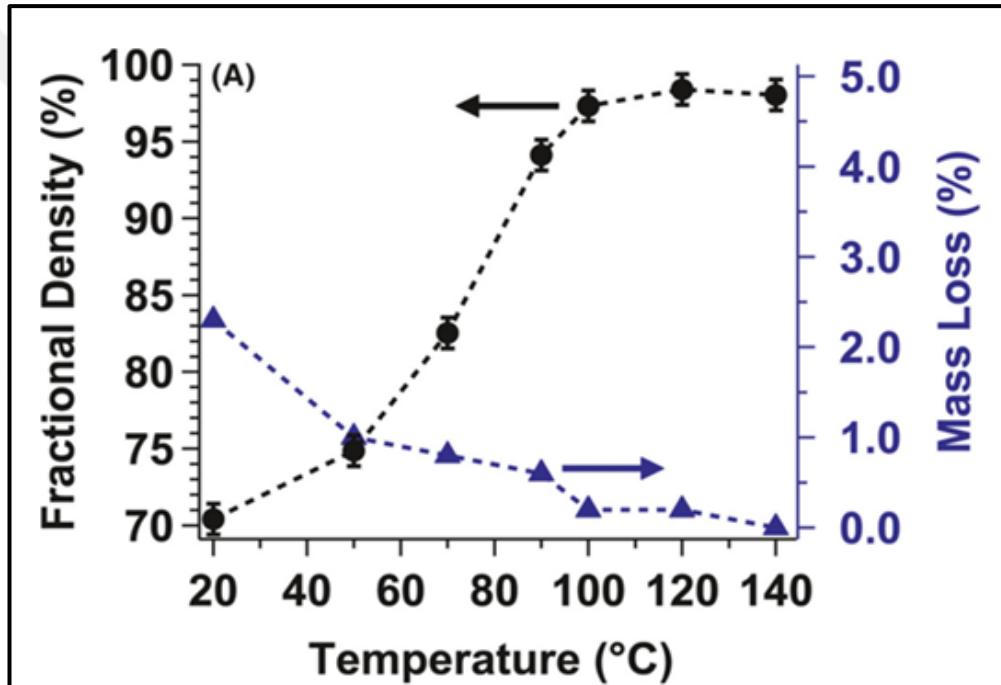


Figure 2.5: Relative density of cold sintered ZnO pellets and as pressed pellets mass loss after drying as a function of temperature [91].

The maximum temperature used for cold sintering in the literature was less than 400 °C [88, 89]. It causes the solvent to evaporate and escape from the die through the clearance areas between the punch and the die [90]. During the final sintering stage, elevated temperatures affect grain development. Kang et al. investigated the influence of CSP temperature ranging from room temperature to 140 °C on the ZnO cold sintering process utilising acetic acid solution at a constant uniaxial pressure of 530 MPa for 30 minutes [91]. A rise in relative density with temperature was seen in

Figure. 2.5, with a high value of 98 % at 120 °C. The most significant increase was noted between 50 and 90 °C, correlating with the enhanced solubility and destabilisation of zinc hydroxide [91].

The literature finds the effect of heating rates controversial. For example, Schwarz et al. and Gonzalez et al. in their cold sintering study of ZnO reported that high heating rates allow water to stay in the structure for longer times and improve the densification at lower pressures. For slower heating rates, water leaves the system earlier, and a comparatively large amount of water and higher pressure were required to activate the cold sintering mechanism [92, 93].

However, in another cold sintering of ZnO study, it was stated that slow heating to reach CSP temperature prolongs sintering time and provides more contacts between the powder and the solvent to enhance dissolution, thus densification [94].

2.1.5.2. External Pressure

External pressure significantly enhances the driving force for the sintering process. Pressureless sintering may lead to insufficient or non-uniform densification in the final sintered specimen. Applying external pressure throughout the heating stage might mitigate this issue. Some advanced densification approaches apply both heat and mechanical force simultaneously, enabling enhanced microstructural densification and improved material properties. Techniques such as hot pressing and/or hot isostatic pressing exemplify this strategy, representing classic cases where external pressure is employed in tandem with elevated temperatures. These pressure-enhanced sintering methods are commonly used in ceramic processing, particularly in cases where conventional thermal treatments alone fail to achieve the desired density and microstructural integrity.

Densification is enhanced under pressure, which also acts to constrain excessive grain coarsening. The primary active processes in pressure-assisted sintering include rearrangement, lattice diffusion, grain boundary diffusion, dislocation movement resulting in plastic deformation, grain boundary sliding, and viscous flow. The primary mechanism for densification depends on the parameters employed during pressure-assisted sintering.

According to the Randall's group, external pressure facilitates liquid phase sintering in CSP. It is less rapid than dislocation creep and occurs at less stress, resulting in the elongation of grains, particularly in the direction of pressing [95]. In the cold sintering process, externally applied pressure is typically preserved during the whole sintering period [49, 64].

Gonzalez et al. emphasized the significance of plastic deformation and grain boundary sliding [93]. They employed pure deionised water and a zinc acetate solution as transient liquids for ZnO, determining the stress exponent to be $n = 2 - 4$ for cold-sintered ZnO in FAST/SPS, which is greater than the reported value ($n = 1$) for ZnO conventionally densified in FAST/SPS or hot pressing at elevated temperatures, or anticipated for liquid phase sintering [96]. This clearly indicates that pressure-induced plastic deformation plays an active part in the cold sintering process, contingent upon the densified materials.

2.1.5.3. Dwell Time

CSP is defined as a very rapid sintering process, often occurring within a few minutes, generally not exceeding 60 minutes [8, 9]. Pressure-solution creep is the primary mechanism of CSP; when the solvent fully evaporates, dissolution ceases, and the temperature is often insufficient to facilitate diffusion [93, 95]. Dwell time is a crucial parameter that greatly influences the cold sintering process of many ceramics and composites. The impact of stay time has been documented in several cold sintering investigations, indicating that extended dwell time often exhibits non-linear behaviour, which can either enhance or hinder densification, contingent upon the initial materials and CSP circumstances.

For example, Ndayishimiye et al. investigated the effect of residence time up to 80 minutes on the cold sintering of ZnO at 155 °C [97]. At a uniaxial pressure of 320 MPa and at time zero, the relative density of the cold-sintered material was greater than 98 %. A non-linear density development is evident, decreasing from 98 % at 0 minutes to 97 % after 20 minutes in CSP. Thereafter, it escalates in a non-linear manner to about full density of 99 %. Simultaneously, they observed a 63 nm increase in grain size, reaching 229 nm from the initial particle size. This was followed by a plateau after

approximately 40 minutes, which remained at this level despite a gradual increase in relative density.

A comparable work involved the cold sintering of ZnO at 250 °C utilising water as a transient liquid, examining the effects of CSP duration ranging from 5 to 60 minutes [98]. The ZnO density exhibits a notable increase from 93 % to 99 % in 55 minutes.

Jiang et al. demonstrated the density progression of cold-sintered ZnO at 150 °C under 200 MPa utilising acetic acid solution over various isothermal stay durations [99]. The relative density rises from around 86 % at 0 minutes to 97.4% after 30 minutes, following which the density stabilises and reaches a plateau. The structural development of cold sintered ZnO demonstrates that increasing dwell time results in a reduction of fine grains, which turn into larger grains, hence decreasing the distance between grains and indicating increased densification in accordance with density evolution.

2.1.5.4. Transient Liquid

The initial fundamental phase in CSP involves selecting a suitable solution and its contents, typically up to 20 %wt., required to establish a non-equilibrium environment for chemical interaction, significantly lowering the sintering temperature until complete evaporation of transient liquids [3, 100, 101]. The solvent operates in two steps: first, it provides lubrication to reduce friction and aid particle re-arrangement during the first CSP stage; subsequently, its chemical interaction with the powder promotes dissolution and diffusion processes in the final sintering step. The aqueous solution facilitates the dissolving of materials, which differs based on the particle species and explains the various CSP scenarios [80, 102]. A substantial amount of CSP research demonstrates that transient aqueous solutions facilitate densification [48, 103-107].

To ensure uniform dispersion, the materials were usually ground with a pestle in a mortar before being introduced into the die. Some existing literature presents limited transient liquid usage. Dargatz et al. and J. Gonzalez-Julian et al. employed just 1 to 3 %wt. aqueous solutions [93, 108]. In certain rare instances, the cold sintering process was conducted without the further addition of any transitory liquids [109]. In a comparable investigation, the densities of ZrO₂ were assessed both in the absence and

presence of an aqueous phase, revealing differences of 48 % and 56 %, respectively [102].

The distinctive features of the transient liquids have a unique role in determining the final sintered density. As previously clarified, it may result in congruent, partial, and incongruent dissolution of the initial particles. The transient liquids may consist of several types, including pure deionised water, acidic solutions, organic solutions, or combinations thereof [14, 102, 110-112].

J. Gonzalez-Julian et al. demonstrated that ZnO achieved a densification of only 57.9 % of the final density without adding any transient liquids. The introduction of water and/or a combination of water and zinc acetate resulted in a density of 84.1% (with water) and 88.3% (with water-zinc acetate) [93]. Numerous other instances further emphasised the need for appropriate transient liquid selection for the system.

2.1.5.5. Particle Size

From a thermodynamic perspective, sintering is a compaction process aimed at reducing surface Gibbs free energy [3, 5, 6]. Consequently, smaller particle sizes would offer a greater specific surface area, which is favourable to the dissolution-precipitation process [113]. The influence of primary particle size on the achievement of final sintered density in the cold sintering process has not been as well examined in the literature compared to other factors such as transient liquid, pressure, and temperature. Nevertheless, nanoparticles were utilised in nearly all studies [13-19].

Furthermore, there are few studies that highlight the significance of nanoparticle size in densification during the cold sintering process. Guo et al. illustrate the function of nanoparticles in an experimental CSP investigation of BaTiO₃ ceramics [14]. The size of nanoparticles facilitates the minimisation of total surface Gibbs free energy, and their superiority over larger particles can be ascribed to the enhanced chemical reactivity resulting from their elevated surface area to volume ratio, which promotes increased dissolution events [14].

However, studies directly investigating particle size effects in densification, such as a comparison of nano and micro initial powders used in CSP, are limited. Furthermore, there is some paper against the common understanding that small particles can be densified better than the larger particles. For example, although both powders used

were in the nano-size range (20–30 nm and 40–100 nm), Nur K. et al., in their study on the sintering of ZnO powders with different particle sizes, reported that ZnO powders with larger particle sizes achieved higher densities at 900 °C of post-annealing temperature after the cold sintering process carried out at 250 °C [114]. This finding is quite controversial against what was commonly proposed for the nanosize effect.

2.1.6. Energy Consumption

Energy consumption is a critical factor to evaluate while assessing the feasibility of cold sintering. Heidary et al. conducted an investigation that compared and contrasted the energy efficiencies of several sintering methods [115].

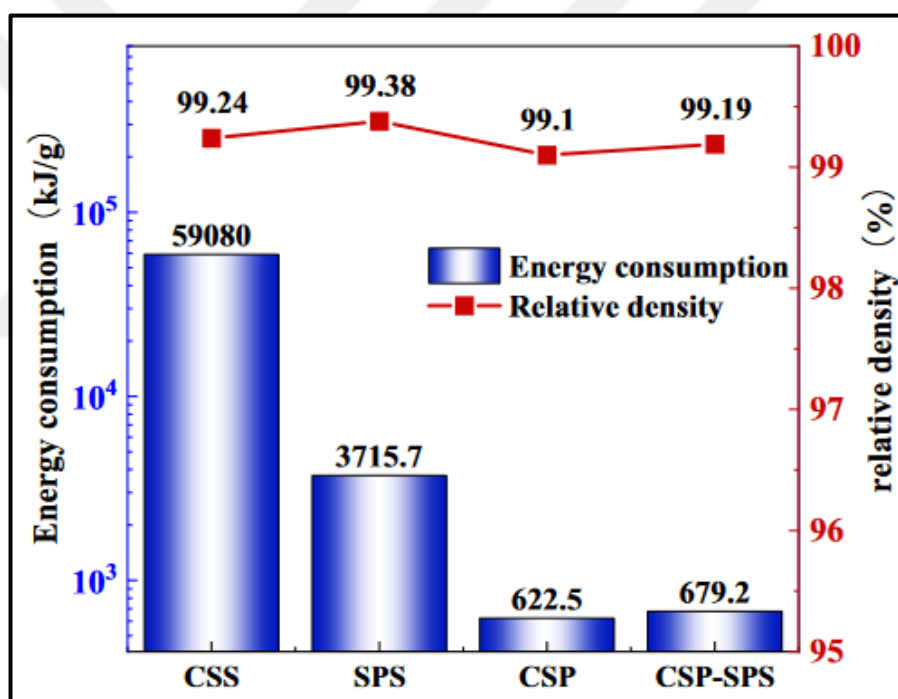


Figure 2.6: Energy consumption comparison for different production methods to densify the ceramic body [115, 116].

The energy consumptions of Solid State Sintering (SSS), Liquid Phase Sintering (LPS), Fast Firing, FAST, Laser Sintering, and CSP were all evaluated. They have defined a novel term, 'Normalised Excess Energy' (NEE), to facilitate the comparison of energy use across various methodologies. A reduced NEE signifies enhanced energy efficiency. NEE values for seven materials were plotted under various sintering instances [115].

Figure 2.6 illustrates that traditional sintering had NEE values of over 400, whereas CSP demonstrated an NEE of around 2.4. The subsequent most efficient approach was laser sintering at around 16.5, markedly surpassing several CSP sintered materials [115]. The research indicated that CSP is significantly more efficient than conventional methods.

2.2. Fuel Cells

2.2.1. Introduction

Energy sustains virtually all human activity and is vital for daily existence. Fossil fuels, comprising natural gas, oil, and coal, provide over 80% of the increasing global energy demand [117, 118]. These energy sources have facilitated industrial and scientific advancements; nonetheless, their rarity and environmental impact are global concerns. The reliance on fossil fuels is unsustainable due to their escalating depletion. In the early 2000s, global fossil fuel reserves were projected to endure less than 250 years for coal, 60 years for natural gas, and 40 years for oil, highlighting the necessity to transition to alternative energy sources [119]. The world faces resource depletion and ecological degradation as fossil fuel use escalates to meet population and economic expansion. The burning of fossil fuels exhausts resources and produces gases like CO₂, CH₄ and N₂O. These emissions significantly affect global warming, air pollution, and public health [120, 121]. The intensification of the greenhouse effect has significantly contributed to climate change, manifesting in rising global heat levels, heightened frequency of severe weather phenomena, and the retreat of polar ice. A shift to greener and sustainable energy alternatives is essential to mitigate environmental issues [122].

Replacing fossil fuels with clean sources like solar and/or wind is increasingly seen as a viable energy transition pathway. Nevertheless, the intermittent nature, geographic constraints, and storage challenges restrict their ability to fully supplant current energy sources [119]. Solar and wind energy production is variable in certain locations and seasons due to climatic conditions and daylight availability. A further obstacle to the deployment of renewables is the lack of efficient and scalable energy storage. Notwithstanding these challenges, hydrogen continues to be a feasible energy carrier. Hydrogen exhibits versatility since fuel cells and electrolysis efficiently facilitate its

conversion to and from energy [121]. Hydrogen's high energy density, accessibility, and clean combustion render it an essential component of the future energy landscape [122]. Upon combustion, hydrogen produces no greenhouse gas emissions, only water. Hydrogen is environmentally benign and sustainable.

Fuel cells stand out as highly efficient systems within the broader spectrum of hydrogen-based energy solutions. Operating through electrochemical redox reactions, they generate electrical power directly by reacting hydrogen with oxygen, eliminating the need for combustion. The hydrogen economy depends on their efficiency, scalability, and versatility across many applications [117, 118]. Fuel cell technology today enables its use in transportation, residential power generation, and industrial processes.

2.2.2. Fuel Cells

Fuel cells function as electrochemical systems that transform the chemical energy stored in fuels into both electricity and heat [123]. Fuel cells offer a benefit compared to fossil fuels, as they do not produce CO₂ emissions from combustion processes. The advantages include reduced emissions, more electrical efficiency, and quiet operation. Fuel cells have significant promise for achieving high energy efficiency, minimal prices, and application to industrial processes due to recent advancements [125].

Numerous fuel cell methods utilise various materials and function over diverse temperature ranges. They consist of two electrodes and an electrolyte that provides strong ionic conductivity while maintaining low electronic conductivity for optimal performance. Fuel cells are categorised based on the types of electrolytes that facilitate ionic conduction.

A comparison of several fuel cell types, including electrolyte, efficiency, operating temperatures, applications, benefits, and drawbacks, is presented in **Table 2.1**.

This study focuses on the fabrication of specific materials used in the solid oxide fuel cell (SOFC), a specific form of fuel cell. SOFCs use the transport of oxygen and hydrogen ions over a solid electrolyte layer, leading to ionic conductivity. This interaction is propelled by the engagement between the oxidant and the fuel, resulting in electrical generation [128-130].

Table 2.1: A comparison of different types of fuel cells [126, 127].

Fuel Cell Type	Electrolyte	Operating Temperature (°C)	Advantages	Disadvantages
Proton Exchange Membrane (PEMFC)	Polymer membrane	60-100	Compact size, quick startup, low-temperature operation	Sensitive to fuel impurities, expensive catalysts
Solid Oxide (SOFC)	Solid ceramic (YSZ, GDC)	600-1000	High efficiency, fuel flexibility, high-quality waste heat	High temperature limits materials, slow startup
Alkaline (AFC)	Aqueous potassium hydroxide	50-200	Simple design, rapid startup, high efficiency	Requires pure hydrogen, corrosion issues
Molten Carbonate (MCFC)	Molten carbonate salts	600-700	Fuel flexibility, high efficiency, scalable	Corrosion issues, complex operation

2.2.3. Solid Oxide Fuel Cells (SOFCs)

A conventional solid oxide fuel cell consists of three elements: the fuel electrode (anode), an electrolyte, and the air electrode (cathode). A dense electrolyte is positioned between a porous cathode and anode, which can be arranged in series to produce sufficient voltage to satisfy the application's specifications [131, 132]. SOFC operate at a typical temperature range of 600-1000 °C, offering a cleaner, low or zero-emission technology, particularly when utilising hydrogen as fuel, and demonstrating superior efficiency relative to alternative technologies. The elevated working temperatures promote internal reforming, hence accelerating electro-catalysis with metals to provide high-quality heat as a by-product for co-generation systems [133].

In a typical solid oxide fuel cell configuration, three primary components form the functional stack: the hydrogen-processing side, the air-processing side, and an ion-conducting ceramic layer sandwiched in between. Hydrogen is directed toward the

hydrogen electrode, while the oxidant reaches the oxygen-side electrode [134]. Acting as a barrier to gas flow yet allowing ion transport, the ceramic separator ensures selective conductivity. The surrounding electrodes, composed of porous solids, allow gaseous reactants to permeate toward the active interface and facilitate the outward transport of reaction by-products. Within this structure, negatively charged oxygen species migrate through the ceramic layer from the oxidant side toward the fuel side, sustaining the electrochemical reaction [135].

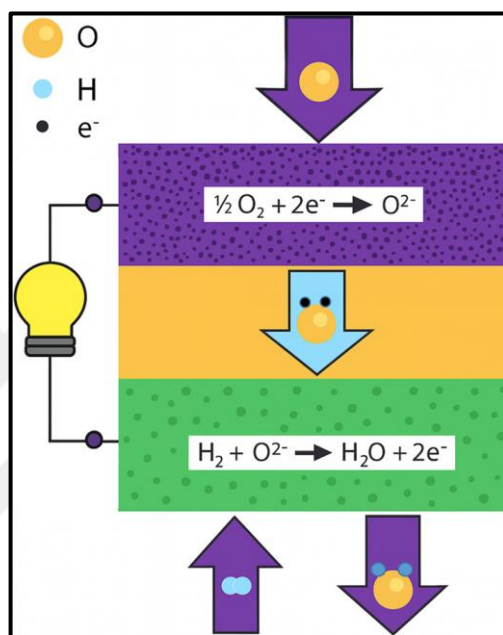


Figure 2.7: A schematic showing the working principle, charge transfer, and gas flow in a solid oxide fuel cell [136].

At the hydrogen-processing electrode, the fuel, typically H₂, undergoes dissociation into electrons and positively charged hydrogen ions (H⁺) [135]. The electrolyte selectively conducts ionic species such as protons, oxygen ions, or a combination of both, depending on its composition, while blocking electron transfer. This ion-conductive medium enables charge transport across the electrochemical cell, linking the oxidation and reduction reactions occurring at opposite electrodes, **Figure 2.7** [136]. The operational principle of the SOFC involves the cathode material receiving electrons from the external circuit (provided by the anode) and reducing O₂ into oxygen ions at the cathode-electrolyte triple-phase boundaries (TPBs) [134, 135]. The generated O²⁻ gets delivered into the electrolyte, which facilitates the transfer of oxygen ions to the triple phase boundaries of the anode/electrolyte to oxidise the supplied fuel (H₂) at the anode side. The reaction products at the anode are clean water

and electrons, which are carried to the current collector and then to the external circuit. The electrolyte material serves not only as an ion link but also functions as a barrier to the internal flow of electrons from the anode to the cathode through the electrolyte, hence facilitating electricity generation in the external circuit [134, 135].

The electrode reactions are given as;



In summary, oxygen molecules in the porous cathode electrode are reduced by accepting electrons from the circuit, resulting in the formation of oxygen ions. The anions are forced to diffuse from the cathodic to the anodic region of the electrodes across the surrounding electrolyte. The catalyst for diffusion is the difference in chemical potential between the electrodes. At the anodic electrode, oxygen ions react with the provided fuel, typically hydrogen (H₂), resulting in the formation of water (H₂O). This combustion process generates electrons, so finalise the external electrical integration of the circuit. Consequently, power, heat, and water are procured [137].

SOFC, whose operational concept is outlined above, has attracted significant interest from the fuel cell research field over the past few decades. Despite extensive research on SOFCs, a significant commercial breakthrough has yet to materialise. A significant barrier for the commercialisation of SOFCs is the elevated operating temperature required to get adequate ionic conductivity in the electrolyte. This establishes severe constraints on the materials employed in cells and supporting structures (e.g., interconnects) and their thermal compatibility. Furthermore, certain degradation pathways emerge more rapidly at elevated temperatures [138,139]. Doped ceria, specifically gadolinium or samarium-doped ceria (GDC or SDC), has been studied as a substitute for the conventional yttria-stabilized zirconia (YSZ) electrolyte, enabling a decrease in operational temperature from 800 to 1000 °C, even with substantial electrolytes; however, additional reductions in operational temperature remain essential [140, 141].

2.2.4. SOFC Components

Solid Oxide Fuel Cells (SOFCs) consist of three essential components: the anode, the electrolyte, and the cathode. These components are essential for delivering the requisite functionalities to an SOFC and must exhibit stability. The specifications for these three components are detailed in the following sections.

2.2.4.1. Anodes

The anode is essential to the operation of the fuel cell. The procedure improves fuel electro-oxidation and facilitates electron delivery throughout the circuit. The conditions for an effective anode are described below [142-144].

- Mixed conductor (ionic and electronic).
- Negligible polarisation resistance.
- Physical and chemical stability in a reductive environment at high temperatures.
- Thermal expansion properties aligned with the electrolyte's characteristics.
- Enhanced catalytic activity to promote the reaction of fuels (including hydrogen) with oxide ions.
- Economically viable.

NiO serves as a commonly used base material in fuel cell anodes and is often combined with ceramic components like YSZ, GDC, or SDC to improve overall performance. In these composite systems, the metal oxide contributes to electronic conductivity, while the ceramic phase facilitates the movement of ions. Such dual-conducting structures typically demonstrate superior electrochemical performance compared to standalone metal oxides.

The anode, sometimes referred to as the fuel electrode, serves as the negative electrode in the SOFC. The hydrogen-rich gas carries across the anode surface to electrochemically oxidise hydrogen at the TPBs. It also facilitates the movement of free electrons generated by oxygen ion molecules migrating from the cathode via the electrolyte, leading to the production of electric current, which is then sent to the cathode via the external circuit. Anode materials must fulfil specific criteria, including adequate ionic and electronic conductivities, optimal grain size distribution, suitable

porosity, superior electrocatalytic activity (for the electrochemical oxidation of hydrogen), compatibility in thermal expansion with other cell components, mechanical robustness, and chemical stability. An anode is a ceramic material consisting of a mixed ionic-electronic conductor (MIEC), which enhances ionic conductivity at TPBs and provides enough electronic conductivity [145, 146].

The composite structure formed by nickel and YSZ has gained prominence in anode design for solid oxide fuel cells, largely attributed to its affordability, thermal compatibility with YSZ ceramics, and remarkable chemical resilience under high-temperature, reducing conditions. Within this composite, nickel plays a dual role: it catalyzes the dissociation of molecular hydrogen and simultaneously forms the electrically conductive network essential for current collection and transport within the electrode architecture [147-149].

2.2.4.2. Cathodes

Functioning as the positive terminal of the cell, the air electrode enables oxygen molecules to adsorb onto its surface, where they are reduced by incoming electrons supplied via the external circuit. This reaction produces O^{2-} ions, which are then transported across the solid electrolyte toward the hydrogen-processing side of the cell. For optimal performance of SOFC, the cathode material must exhibit particular properties such as [145, 150].

- Elevated electrical conductivity and robust stability in an oxidative environment
- Minimal or negligible discrepancy of the cathode's TEC with the cell components.
- High compositional compatibility between the electrolyte and adjoining materials.
- Elevated ionic conductivity (oxide ion conductivity)
- Sufficient porosity to facilitate effective O_2 gas transport from the cathode to the cathode-electrolyte contact
- Elevated catalytic efficacy of redox reactions of O_2 .
- Economically efficient

Lanthanum strontium manganite (LSM) and lanthanum strontium cobalt ferrite (LSCF) are the most extensively studied perovskite cathode materials that possess the perovskite structure ABO_3 for SOFC. In HT-SOFC, LSM is recognised as the prevalent cathode material when co-fired with YSZ or ceria-based electrolytes. Despite elevated temperature applications, the electron conductivity of LSM reduces as the temperature drops in IT-SOFC [151]. Furthermore, perovskite LSCF, exhibiting mixed ionic-electron conductor characteristics, demonstrates an expansion of the TPBs compared to electron-conductive LSM [152, 153]. The MIEC characteristics of LSCF and BSCF enhance the electrocatalytic activity of oxygen. The primary concern with LSCF is its elevated TEC, which surpasses that of the more prevalent electrolytes such as YSZ and GDC [154]. The TEC mismatch leads to concerns regarding the fuel cell's operating temperature and co-firing with the electrolyte during manufacture. Additional drawbacks of cobalt-based cathode materials arise from the interaction between cobalt and YSZ, elevated costs, and the propensity for cobalt to evaporate and reduce, resulting in limited materials that can function stably despite the high oxygen absorption of cobalt-based cathodes [155, 156].

The selection of cathode material in solid oxide fuel cells is predominantly determined by the electrolyte material, operating temperature, and the electrochemical specifications of the cell. Lithiated Nickel Oxide (LNO) is favoured as a cathode material when ceria-based alkali carbonate nanocomposites serve as electrolytes. Ceria-based alkali carbonate nanocomposites generally function at moderate to low temperatures (400–600 °C) and have dual ionic conductivity (O^{2-} , CO_3^{2-} , and H^+). LNO is suitable with these mixed-conducting electrolytes as it facilitates both oxygen reduction and carbonate ion-based electrochemical processes at these temperatures. The thermal expansion coefficient of LNO roughly aligns with that of ceria-based electrolytes, mitigating mechanical stresses during thermal cycling and enhancing the fuel cell's durability [158]. Consequently, LNO was selected over frequently utilised cathode materials including LSM and LSCF in this investigation.

2.2.4.3. Electrolytes

The electrolyte is the element that dictates the working temperature of the SOFC while isolating the anode and cathode to avoid direct electrical contact between the two electrodes, which might result in a short circuit, thereby compelling electrons to move

through the external circuit to produce electricity. While the electrolyte restricts electron transport, it facilitates the transport of ions (O^{2-} , OH^- , H^+) from the cathode to the anode, hence providing the maintenance of overall electrical charge balance. In the SOFC, the electrolyte is subjected to an oxidising agent (air from the cathode side) and a reducing agent (fuel from the anode side) at elevated temperatures. After the oxygen molecule has evolved into oxygen ions at the cathode, it has to cross the electrolyte towards the anode of the cell. To enable this transport process, the electrolyte should have certain characteristics such as [159, 160].

- Exhibit elevated ion transfer but no e^- .
- Dense and impermeable to prevent reactive gases from bypassing
- Minimise resistive losses in the cell by making it as thin as feasible
- Chemical, thermal, and structural stability over a broad temperature spectrum
- TEC compatibility with the anode and cathode

A broad class of well-established oxygen ion conductors are oxides with a fluorite-type structure. These materials adopt a face-centered cubic arrangement where cations occupy the lattice corners and face centers, while oxygen ions fill all tetrahedral sites, producing a network rich in interstitial voids. When aliovalent dopants (i.e., lower-valent cations) are introduced into the lattice, oxygen vacancies form to maintain charge neutrality, which in turn facilitates enhanced ion mobility [161]. Among these, yttria-stabilized zirconia (YSZ) in its cubic phase remains the benchmark electrolyte for solid oxide fuel cells (SOFCs) due to its remarkable chemical durability, mechanical robustness, and negligible electronic conductivity [162]. Beyond zirconia-based systems, doped ceria (DCO) has gained attention as a promising alternative electrolyte for intermediate-temperature SOFCs (IT-SOFCs) [163]. Particularly, samarium-doped ceria (SDC) and gadolinium-doped ceria (GDC) have emerged as leading candidates, demonstrating optimal ionic transport properties at dopant levels of 10–20 mol%. Compared to YSZ, ceria-based electrolytes exhibit higher ionic conductivity and lower activation energy under sub-800 °C operating conditions [163]. However, one drawback of DCO is its tendency to undergo partial reduction of Ce^{4+} to Ce^{3+} under reducing atmospheres or at elevated temperatures (≥ 600 °C), which can compromise the structural integrity of the material. This reduction leads to undesirable

electronic conduction pathways, resulting in current leakage and diminished electrochemical performance across the cell [164].

Despite their widespread use, single-phase electrolyte materials exhibit intrinsic limitations. The strong electrostatic binding within their lattice framework results in a substantial energy barrier for ion displacement, often yielding activation energy values close to 1.0 eV, approximately double the threshold typically associated with superionic conductors. This intrinsic rigidity hinders the formation and movement of mobile charge carriers, making it difficult to achieve efficient ion transport. As a result, high operational temperatures are generally required to overcome these kinetic barriers and sustain adequate ionic conductivity in conventional solid oxide electrolyte systems. [166].

2.2.5. Nanocomposite Electrolytes

Multiple approaches exist to reduce the elevated operating temperatures of SOFCs from 1000 °C to about 600 °C while maintaining large ionic conductivity in the electrolytes. These involve thin films, proton conductors, ceria-based materials, carbon nanowires, and a co-doped method [167-170].

In recent years, an alternative method to enhance material characteristics and performance has been extensively employed. A well-recognized example is the class of composite electrolytes derived from ceria. In recent years, extensive research has focused on designing alternative electrolyte systems tailored for low-temperature SOFCs by adopting this composite strategy [171-173]. These materials typically consist of a cerium oxide-based matrix enriched with a second component, often alkaline carbonates such as Na_2CO_3 , Li_2CO_3 , K_2CO_3 , or their eutectic mixtures. Numerous combinations of doped ceria, including samarium-, gadolinium-, and yttrium-stabilized variants (SDC, GDC, and YDC, respectively), have been systematically paired with various molten salts and hydrated species to improve ionic transport and compatibility within this hybrid framework. [164, 171-173].

Their operational principle was suggested to rely on dual-phase conduction involving oxygen and protons. Qinghua and Bin Zhu proposed that the interface areas between oxide and carbonate phases enhanced ionic conductivities when SDC and Na_2CO_3 were mixed to produce composites. Ionic conduction occurs in the electrolyte via the

passage of H^+ and O^{2-} , hence enabling a dual conduction mechanism in the nanocomposite [174].

An ionic conductivity reaching 0.1 S/cm was observed at 300 °C for a nanocomposite system containing 20 %wt. Na_2CO_3 mixed with SDC [175–177]. Interestingly, neither constituent, when evaluated individually, exhibits significant conductive behavior at this temperature, as both SDC and Na_2CO_3 are known to be poor conductors under such conditions [174]. This suggests that the remarkable transport properties arise not from the bulk phases themselves but rather from the interfacial region formed through their intimate contact. It is hypothesized that this interphase region offers a unique environment that facilitates ion mobility, possibly due to a synergistic effect that increases the local concentration of mobile charge carriers. Multiple theories have been put forward to explain the origin of this enhanced ion transport behavior.

One of the most commonly implied mechanisms in the literature is based on the space charge region. This concept suggests that the interface between the ceria phase (commonly SDC or GDC) and the alkali carbonate phase (mostly Na_2CO_3) generates a space charge area due to variances in chemical potential, oxygen ion concentration, or defect densities between the two materials. The space charge effect is substantiated by research on ceria-carbonate composites [178, 179].

In the space charge area, elevated ionic conductivity networks as a result of a higher density of oxygen vacancy defects [178]. These areas are crucial for ionic transport in nanocomposites and account for the improved conductivity, as evidenced by experimental findings on SDC- Na_2CO_3 and analogous composites [179].

An elevated concentration of mobile oxygen vacancies in this space charge region, induced by defect interactions at the interface [178, 179]. A reduced activation energy relative to bulk ceria or alkali carbonate phases, aligning with the interfacial conduction mechanism [180]. Zhu et al. came across a conductivity of 0.1 S/cm at 300 °C, attributing this elevated conductivity to the space charge process [178]. At elevated temperatures, the carbonate structural lattice may soften or melt, leading to rotational or translational vibrations of the carbonate anions, thus promoting proton transport. Moreover, in the proposed process, H^+ and O^{2-} may coexist and are also transported across the interfacial areas between doped ceria and carbonate phases [181-185].

Consequently, it was suggested that a significant ionic conduction pathway occurs at the interface between doped ceria and carbonate phases in the composite.

Alternative models, in addition to the co-ionic conduction model based on the space charge area, have also been suggested. In one instance, opposing the previously mentioned co-ionic transport mechanism, the elevated ionic conductivity values in the composites have been attributable to the interaction between (O^{2-}) and (Na^{1+}), which enhanced the transport of oxygen ions [186, 187].

Nevertheless, several investigations in the literature state that the multiple conduction mechanism behind high conductivity, which relies on the space charge area, is totally misleading [188-192]. While Nafe contended that the multiple transmission mechanism is a misdirection by citing examples of molten carbonate systems, it is important to recognise that all the aforementioned mechanisms apply equally to both liquid (binary, ternary such as SDC-LN or SDC-LNK) and solid (such as SDC- Na_2CO_3) systems.

Consequently, despite extensive research carried out over several decades showing the synergistic effects of ceria-based alkaline carbonate nanocomposites, the underlying mechanism remains uncertain. The varying conductivity and performance values reported in the literature present a unique subject for debate.

3. CHAPTER THREE: ONE STEP DENSIFICATION OF SDC- Na_2CO_3 NANOCOMPOSITE ELECTROLYTES FOR SOFC APPLICATIONS BY COLD SINTERING PROCESS

3.1. Introduction

To address the escalating energy demands while also preserving the environment, various energy conversion technologies have attracted more focus. Solid Oxide Fuel Cells (SOFCs) represent a very promising sustainable energy technology that efficiently converts the chemical energy held in fuels into electrical energy, achieving efficiencies of up to 70 % [193, 194].

Yttrium Stabilised Zirconia (YSZ), the predominant ceramic oxide electrolyte, necessitates operational temperatures ranging from 800 to 1000 °C to achieve sufficient oxygen ion conductivity for application in Solid Oxide Fuel Cells (SOFCs), thereby categorising it as High Temperature Solid Oxide Fuel Cells (HTSOFCs). However, elevated operational temperatures provide several disadvantages for fuel cells, such as constraining their long-term stability and escalating manufacturing costs, which are the primary barriers to their extensive commercialisation [195-197]. Therefore, it is essential to identify potential innovative electrolyte materials exhibiting excellent ionic conductivities at low temperatures, ideally below 600 °C, categorised as Intermediate Temperature Solid Oxide Fuel Cells (ITSOFCs) [198, 199]. Owing to their elevated ionic conductivities and commendable chemical stabilities, ceria ceramics doped with Sm, Gd, or Y have been extensively investigated as potential electrolyte materials for fuel cells operating at lower temperatures than those based on zirconia [200, 201]. Upon exposure to reducing atmospheres during operation, these doped ceria electrolytes demonstrated mixed conduction, comprising both ionic and some electronic conduction, due to deterioration, ultimately resulting in energy inefficiency of the fuel cell [202, 203].

A prevailing strategy has been the use of composite electrolytes in the fabrication of SOFCs to improve ionic conductivity at reduced temperatures. A notable composite

electrolyte was synthesised by combining doped ceria ceramics with inorganic salts. The use of several inorganic salts significantly impeded electrical conduction while enhancing ionic conduction and stabilising the electrolyte, leading to very high ionic conductivities even at moderate temperatures [204-207]. A variety of ceria-based composite electrolytes including different salts and oxides have been developed [208-211]. The doped ceria-carbonate composites emerged as the most promising candidates, with very high ionic conductivities of up to 0.1 S/cm at low to moderate temperatures (300-600 °C) and superior fuel cell performance [178, 212-214].

A broad spectrum of ionic conductivity values, from 10^{-4} to 0.1 S/cm, in ceria-carbonate composite electrolytes has been published in the literature. Researchers proposed their idea on a novel conduction mechanism at the phase boundaries specific to the composite, as described below, disregarding of the stated conductivity scales.

A co-ionic conduction mechanism was hypothesised in doped ceria-carbonate composite electrolytes. This hypothesis claims that doped ceria-carbonate composite electrolytes demonstrated multi-ion conductivity, namely for O^{2-} and H^+ ions [215-217]. At elevated temperatures, the carbonate structural lattice may soften, leading to rotational or translational vibrations of the carbonate anions, so promoting proton transport. Moreover, in the described process, H^+ and O^{2-} may coexist and are also transported across the interfacial areas between doped ceria and carbonate phases [207, 212, 216, 218, 219]. Consequently, it was suggested that a significant ionic conduction pathway occurs at the interface between doped ceria and carbonate phases in the composite.

Different models, apart from the co-ionic conduction model, have been suggested [220]. In one instance, in contrast to the aforementioned co-ionic transport mechanism, the enhanced ionic conductivity values in the composites have been ascribed to the interaction between (O^{2-}) and (Na^{1+}), which enhanced the mobility of oxygen ions [215, 220].

All suggested conduction pathways for the high conductivity of the doped ceria-carbonate composite necessitate a high interface density. If a highly conductive pathway existed, it would be expected to achieve even greater conductivity values if the composite electrolytes were fabricated from nanosized doped ceria ceramics with a high interface density assured [221- 223]. Such techniques have been described in

the literature and referred to as nanocomposite electrolytes. Nonetheless, these doped ceria-carbonate composite electrolytes required densification at temperatures near or beyond the melting points of the carbonate phase. In instances when eutectic carbonate mixes were employed, the electrolytes were typically densified and characterised at temperatures beyond their eutectic points [203, 208, 218, 224].

It is important to note that molten carbonate environments are highly corrosive and can readily dissolve the inorganic phase. Consequently, the inorganic doped ceria particles might suffer coarsening, leading to a significant reduction in the interface density within the composite. Consequently, the ionic conductivity of these composites might be enhanced if particle growth during processing ceases to maintain a high interface density [203, 225-227]. According to current understanding, a nanocomposite including a nano-sized samarium doped ceria (SDC) phase distributed inside an alkali carbonate matrix would serve as an optimal electrolyte for the fabrication of SOFCs. If a high conduction path exists, there is potential for further increase of the ionic conductivity of these composite electrolytes.

The Cold Sintering Process (CSP) is an innovative densification technique that operates at ultra-low temperatures ($<300\text{ }^{\circ}\text{C}$), introduced by Randall in 2016 [13, 14]. The densification mechanism during CSP occurs in two stages. Initially, the particles rearrange with the aid of an aqueous phase, followed by material transport by dissolution and re-precipitation mechanisms at elevated pressures and temperatures [228, 229]. Since then, other materials have been effectively densified using cold sinter processing, including piezoelectrics, semiconductors, and ionic conductors [229-234]. The efficacy of cold sintering processing in achieving complete densification of materials, such as ZnO, BaTiO₃, and NASICON, is based on the selected material [13, 229, 233]. In certain instances, a subsequent heat treatment phase in conventional ovens may be required for densification, as reported with materials like YSZ and CeO₂ [14, 235, 236]. Nonetheless, the densification temperatures in traditional furnaces were significantly lower than those typically employed in the sintering of these materials. For instance, GDC could achieve 96 % of its theoretical density with initial cold sintering followed by normal sintering at $1100\text{ }^{\circ}\text{C}$ [237]. The sintering of GDC in traditional furnaces necessitates temperatures over $1450\text{ }^{\circ}\text{C}$ [238].

This work demonstrates that Sm-doped CeO₂-Na₂CO₃ nanocomposite electrolytes have been densified at far lower temperatures than traditionally stated in the literature,

utilising an innovative method known as cold sintering processing in a single step. Primarily, this approach preserves the authentic nanostructure of the composite electrolyte throughout the production phase. The nano-composites were typically densified near the melting temperatures of the carbonate phase, whether the carbonate phase was pure or a eutectic mixture, resulting in the coarsening of the inorganic ceramic phase, which reduces the interfacial area density and consequently diminishes ionic conductivity. These nanocomposites have an interface that provides a low-resistance pathway for diffusing ions, resulting in them being very suitable for fuel cell applications. This innovative technology ensures that the electrolyte remains below its service temperature, typically under 600 °C, at all stages of operation.

The carbonate phase appears to be one of the most promising candidate materials for investigation through cold sintering processes. Initially, it is pliable with a melting temperature significantly lower than that of the inorganic ceramic phase and readily dissolves in water at advanced concentrations, facilitating a material transport process through dissolution and re-precipitation, analogous to the densification mechanism observed in liquid phase sintering during CSP. Ceria-based carbonate nanocomposite electrolytes are notoriously challenging to densify using traditional sintering techniques [237, 239-241]. Kumar et al. indicated that traditional approaches achieved just 78 % density [242]. This degree of densification is insufficient due to the interlinked porosities that allow fuels and gases to mix up and react without generating energy. Consequently, it is vital to densify these electrolytes to at least 92 % of their theoretical densities to guarantee isolated porosities.

CSP is a method for achieving high electrolyte density at much reduced processing temperatures. Furthermore, it is a well-established fact that the nano-CeO₂ phase in the CeO₂-Na₂CO₃ composite system readily coarsens to micron sizes because of the requirement for elevated densification temperatures in typical furnaces, leading to a microcomposite rather than a nanocomposite [243, 244]. The absence of stated densities in the majority of analogous research in the literature served as an additional impetus for investigating the densification of these nanocomposites by CSP.

To address the issues mentioned earlier and maintain the intrinsic properties of the nano-composite during processing, a task that conventional methods struggle to accomplish, a novel technique known as cold sinter processing was employed to

densify ceria-carbonate nanocomposite electrolytes to over approximately 97 % of their theoretical density in a single step at temperatures below 200 °C.

3.2. Experimental Method

3.2.1. Materials Preparation

The electrolytes SDC- Na_2CO_3 were made using commercially available powders of $\text{Ce}_{1.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (20SDC, Inframat, USA) and Na_2CO_3 (Alfa Aesar, USA), with a maximum weight ratio of 30 % Na_2CO_3 . First, the powders were ball-milled separately for 48 hours to break any agglomerates that may have formed. A nano-composite electrolyte powder consisting of SDC and Na_2CO_3 was made by first adding the SDC powders with the Na_2CO_3 , then ball-milling the mixture for 24 hours in an isopropanol medium, and then calcining it for 1 hour in an air environment at 650 °C. In the calcination procedure, a heating rate of 5 °C/min was used. After the calcined powder mixes cooled to room temperature, they were pulverised using a mortar and pestle. They were subsequently placed in an airtight container and tagged as SDC-30N.

3.2.2. Cold Sintering Process

Figure 3.1 shows the CSP investigations that were conducted using a 100-ton hydraulic press from HIDROTIM, Turkey. The press was outfitted with a PID-controlled mica band heater that externally clamped the steel die. A K-type thermocouple was used for temperature monitoring. Temperatures ranging from 50 to 250 °C, pressures from 75 to 675 MPa, and times from 1 to 180 minutes were all used for cold sintering. As a "spacer" between the top and lower die punch surfaces, YSZ powders from TOSOH, Japan, prevented the sample from clinging during the CSP.

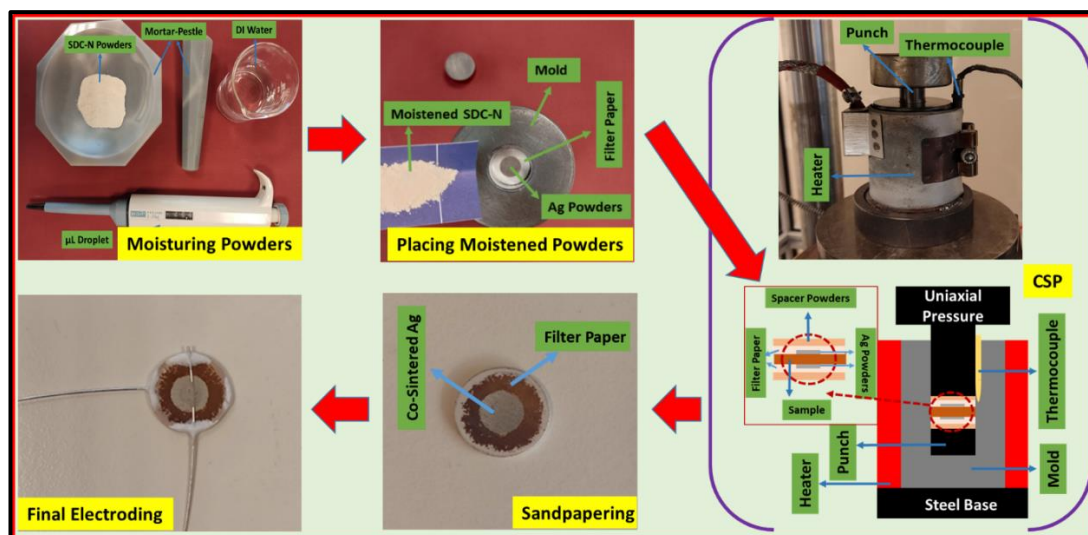


Figure 3.1: Illustration of the experimental procedure in preparing the SDC-30N nanocomposite electrolytes by the cold sintering process.

Before being cold sintered, the SDC-30N composite powder was mixed with deionised (DI) water up to 10 % by weight and then homogenised using a mortar and pestle. The next step was to pour the composite powders that had been moistened into a steel die chamber that was originally filled with YSZ spacer particles, filter paper, and Ag powders, in that order. After the die cavity was filled with the humid composite powders, the same process was performed in the opposite sequence. **Figure 3.1** illustrates the cold sintering stacking sequence, which includes the following layers: YSZ spacer powders, filter paper, Ag powders, composite electrolyte particles, Ag powders, filter paper, and YSZ spacer powders. Next, the die was subjected to a controlled heating process using the mica band heater, at a rate of around 20 °C per minute, until it reached the cold sintering temperature, where it was maintained isothermally. Before being removed from the die, the cold sintered SDC-30N composite samples were cooled naturally to temperatures below 50 °C. **Figure 3.2a** shows the heating regime, whereas **Figure 3.2b** details the whole cold sintering process setup.

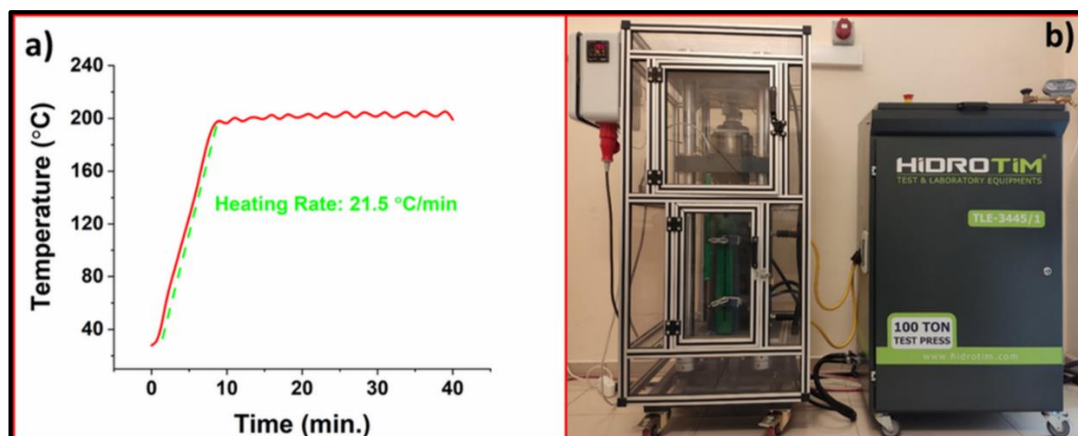


Figure 3.2: (a) Heating regime and (b) full setup of cold sintering process.

From the same composite powder mixture, reference composite samples were made. These samples were dry-pressed at 120 MPa for 2 minutes and sintered in standard furnaces at 700 or 800 °C for 1 hour. The samples were labelled as SDC-30NR700 and SDC-30NR800, respectively. Reference samples were produced similarly, however their sintering was done in a conventional furnace at 1450 °C for 5 hours.

3.2.3. Materials Characterization

The densities of disc-shaped SDC-30N samples were determined from their masses and dimensions. The theoretical density of the composite was determined using the mixing rule, using the theoretical densities of SDC and Na_2CO_3 as 7.19 and 2.54 g/cm³, respectively. The crystallinity and phases were examined using an X-ray diffractometer (XRD) (Rigaku D-Max 2200, Japan) using Cu-K α radiation (1.54056 Å) throughout the range of 20-70° (2 θ). Crystallite sizes were determined using the broadening of X-ray peaks (Full Width at Half Maximum, FWHM) and the Scherrer equation. Standard silicon powders were used to calibrate the diffractometer. The microstructures of SDC-30N nano-composites were examined with a Scanning Electron Microscope (SEM) (Philips XL 30 SFEG, Eindhoven, Netherlands) on the shattered surfaces. Elemental analysis and mapping of materials were conducted using Energy Dispersive Spectroscopy (EDS, JEOL JEM-ARM200CF with a Centurio EDS detector). Differential scanning calorimetry (DSC, Netzsch 404 C Pegasus, Germany) and thermogravimetric analysis (TGA, Netzsch STA 449 F3 Jupiter, Germany) were used for the thermal analysis. The temperature measurement range ran from ambient temperature to 600 °C, with a heating rate of 10 °C/min for both DSC and TGA.

Electrochemical Impedance Spectroscopy (EIS) with a Gamry Reference 3000 potentiostat/ galvanostat/ ZRA analyser was used to assess the electrical conductivity of cold-sintered SDC-30N nanocomposite samples at temperatures between 300 °C and 600 °C. EIS measurements were obtained in humidified airflow, achieved by passing air through water at ambient temperature. The excitation voltage was established at ± 10 mV, and the frequency range was assigned from 5×10^{-2} to 10^5 Hz. EIS measurements were conducted by co-sintering Ag current collectors on the parallel sides of the nanocomposite electrolyte, as seen in Figure 3.1. Silver wires were affixed to the co-sintered silver electrode layers with silver inks prepared by combining silver and aluminium oxide powders in α -terpineol and 2-butoxyethanol. The connection was ultimately accomplished using Ceramabond adhesives (Aremco, USA), which also facilitated effective electrical connections.

3.2.4. Results and Discussions

3.2.4.1. Densification by Cold Sintering of SDC-30N Nanocomposites

The cold sintering of SDC-30N nanocomposite powders was investigated in terms of temperature, pressure, time, and moisture content to determine the optimal sintering parameters for achieving maximum density, as seen in **Figure 3.3a-d**. It is crucial to note that these studies were conducted to achieve a minimum density of 92 % of the theoretical density for the SDC-30N nanocomposite ceramic, beyond which porosities were anticipated to be isolated, thereby qualifying it for use as an electrolyte in the fabrication of SOFCs, a primary requirement. Otherwise, fuels and oxides would meet and react without generating any electrical energy, making the SOFCs ineffective.

To investigate the influence of temperature on the cold sintering of SDC-30N nanocomposite powders, the powders were mixed with 4 wt. % water and then cold sintered under 450 MPa of uniaxial pressure for a period of 30 minutes. Temperatures between 50 and 250 °C were examined. Theoretical relative density values of the cold-sintered nanocomposites as a function of sintering temperature are shown in **Figure 3.3a**. It was observed that with an increase in processing temperature, the relative density of the samples correspondingly rose, reaching 97 % of its theoretical density at 225 °C.

The densification rate accelerated below 110 °C; nonetheless, the subsequent density values were insufficient to satisfy the criteria for an electrolyte.

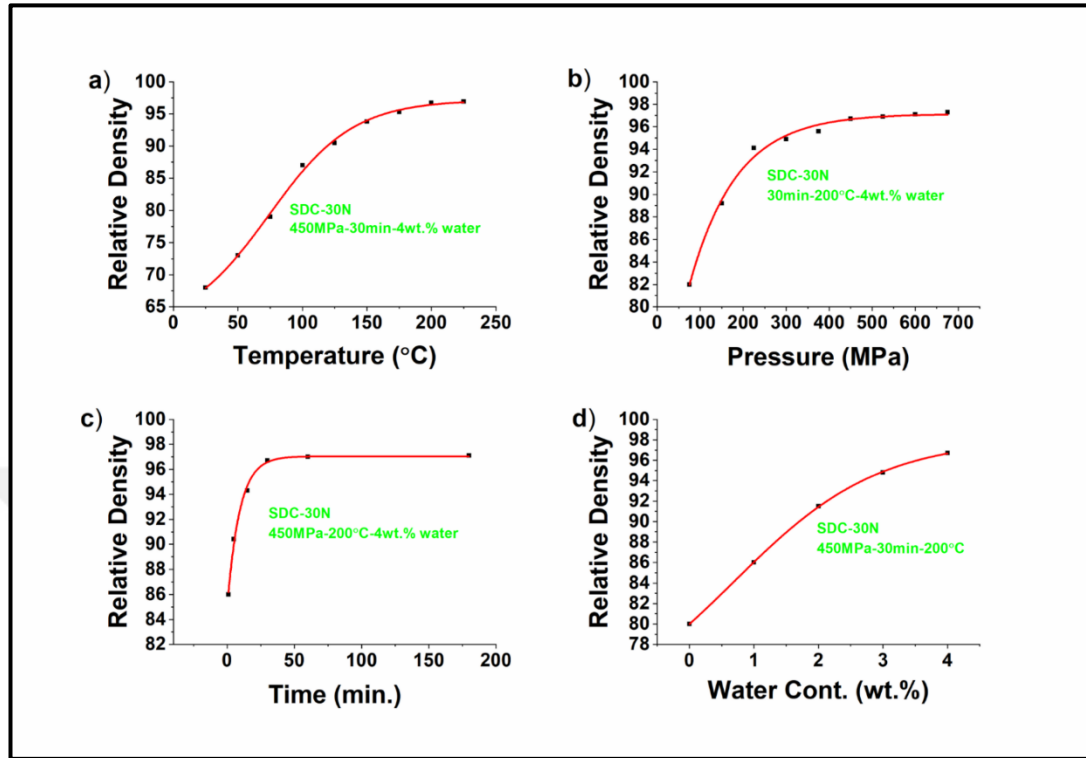


Figure 3.3: The effect of cold sintering parameters (a) temperature, (b) pressure, (c) time, and (d) moisture content on the relative density of SDC-30N nanocomposite electrolytes.

The cold sintering conditions in this work are analogous to those of semi-open hydrothermal synthesis. The hydrothermal conditions favoured densification as temperature increased. It was anticipated that the evaporation-induced loss of water from the system resulted in a reduced densification rate of the samples at temperatures over 110 °C. Investigations at temperatures over 250 °C were excluded, not because of insufficient density, but because they could not be extricated from the mould without sustaining damage. There was no need to elevate the processing temperatures further, since around 97 % of the theoretical density values had already been attained. The significance of uniaxial pressure on the densification response of SDC-30N nanocomposite powders was examined, as seen in **Figure 3.3b**. The densification rate was observed to be more rapid below 300 MPa; however, the resulting density values were insufficient to satisfy the requirements for an electrolyte. In contrast, at pressures exceeding 300 MPa, the densification rates became less influenced by pressure, yet the resulting density values were satisfactory, approximately 97 %. The densification rate

was seen to have a modest dependence on the applied pressure. It is a well-established fact that when pressure increases, particles typically become more tightly packed via rearrangement, which also accelerates dissolution and re-precipitation processes, facilitating more material transport to the neck area. The two processes were identified as the material transport mechanisms in the cold sintering process [228, 245].

Besides the proven effects of pressure on densification during CSP, literature indicates that pressure may facilitate densification via creep and plastic deformation in certain soft materials, such as NaCl and LiF, particularly in the later stages of CSP and in the absence of water [246, 247]. The low hardness of Na₂CO₃ (1.3 on the Mohs hardness scale) likely facilitated densification by creep and plastic deformation under elevated uniaxial pressure. Its elevated solubility limit in water and limited hardness make Na₂CO₃ an excellent potential material for densification using CSP in engineering applications.

SDC-30N nanocomposite powders were cold sintered with varying quantities of deionised water while maintaining constant processing pressure, duration, and temperature, as seen in **Figure 3.3d**. The relative densities of the samples exhibited an approximately linear rise with increasing moisture content. Minor fluctuations in moisture content led to a significant increase in the achieved theoretical density values. CeO₂ ceramics have little solubility in water, in contrast to Na₂CO₃, which has a high solubility of around 34 gr/100 mL at 25 °C [234, 248].

Consequently, it was posited that the carbonate phase, which readily dissolved in substantial amounts in water and facilitated fast mass transport via pressure and temperature, was accountable for the density increases. Owing to its elevated solubility limit in water, some dissolved carbonates during processing leached with the water from the mould; hence, water concentrations over 4 %wt. could not be examined. The measured density value of around 97 % achieved with 4 %wt. water was sufficient for use as a nanocomposite electrolyte.

Various CSP durations, spanning from minutes to days, have been published in the literature for diverse materials. This investigation revealed that density values of around 97 % were achieved in the SDC-Na₂CO₃ nano-composite powders in under one hour. Elevated solubility limits at high pressure facilitated rapid densification in SDC-Na₂CO₃ nanocomposites during CSP. The density of reference samples SDC-

30NR700 and SDC-30NR800 (fabricated conventionally as given in literature) was determined to be around 70 % only [249].

Therefore, it can be said that the densification process in CSP parallels that of liquid-phase sintering [13, 14]. Sodium carbonate likely assisted densification by serving as a binding and filling agent among SDC particles, aided by mass transfer influenced by temperature, pressure, and particularly water. In addition to plastic deformation and creep resulting from elevated pressure, temperature, and duration [13, 14], it was determined that water significantly contributed to desiccation due to the high solubility of sodium carbonate in it.

3.2.4.2 Thermal Analysis of Composite Powders

Figure 3.4 presents the differential scanning calorimetry (DSC) results for SDC-30N composite powders. The endothermic peak slightly above 100 °C was ascribed to the evaporation of water. Na_2CO_3 exhibits a phase transition from δ -monoclinic to β -monoclinic form (alpha modification) around 340 °C [250]. Additionally, at around 480 °C, a second-order ferroelastic phase transformation from monoclinic to hexagonal was seen [251-253].

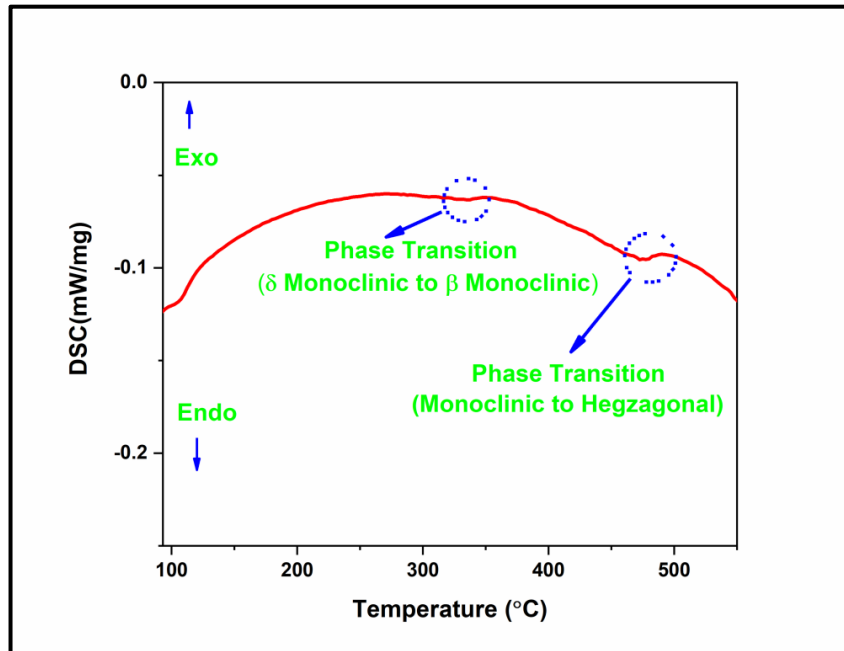


Figure 3.4: DSC curve of SDC-30N nanocomposite powders.

3.2.4.3. Phase Analysis

Figure 3.5 displays the results of an XRD analysis regarding the crystallinity and phase of SDC and Na_2CO_3 powders both before and after cold sintering. The phase and crystallinity of SDC and Na_2CO_3 powders, before and after cold sintering, were studied by XRD and were given in **Figure 3.5**. Diffraction peaks from the SDC phase were assigned to the cubic fluorite structure of CeO_2 (JCPDS 34-0394). The XRD peaks corresponding to the Na_2CO_3 phase, indicated by an asterisk (*), were seen to be minor nevertheless demonstrate the crystallinity of this phase. Additional minor peaks were identified that correspond to either NaHCO_3 or $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$ phases. These phases were believed to result from the interaction between Na_2CO_3 and H_2O in the environment. Figure S1 presents a more detailed study of the X-ray diffraction pattern. In the literature, particularly when the Na_2CO_3 phase composition was below about 25 % in the composite powder combination, their XRD peaks were hardly discernible. Perhaps, in those investigations, this was one of the reasons cited for the Na_2CO_3 phase being characterised as amorphous. Nonetheless, tiny diffraction peaks, as seen in this work, have been observed in the composite powders containing above about 25% carbonate phase [250, 254, 255]. The nano-composite developed in this work included 30 % wt Na_2CO_3 phase. **Figure 5** indicates that the XRD peaks corresponding to the Na_2CO_3 phase exhibited increased intensity after CSP, likely due to enhanced crystal structure.

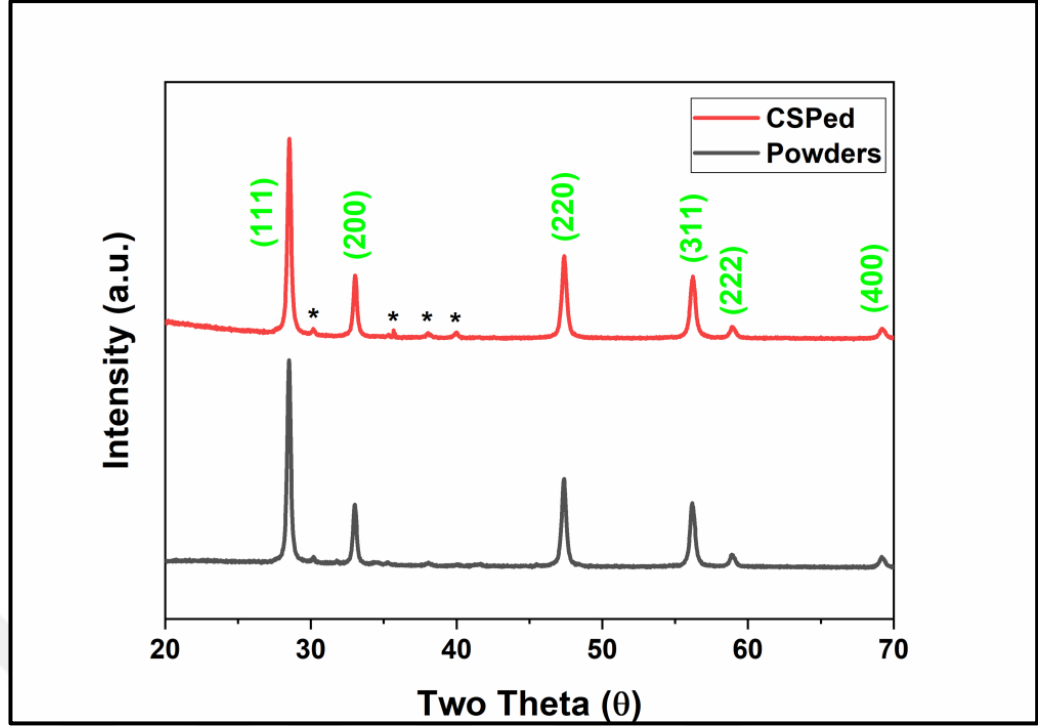


Figure 3.5: XRD patterns of SDC-30N composite powders and cold sintered SDC-30N composites.

The average crystallite size of SDC powders in the nanocomposites, determined from XRD peak broadening using the Scherrer equation (Equ. 1), was around 25 nm, both before to and after CSP.

$$D = 0.9\lambda/\beta\cos\theta \quad (3.1)$$

where λ indicates the X-ray wavelength of Cu-K α , 1.5406 Å, and β represents the full width at half-maximum (FWHM) of the most intense (hkl) reflection at the Bragg angle θ . The calculated crystallite sizes before and after cold sintering were close to identical, suggesting that SDC particle growth did not occur during CSP. Consequently, SDC-Na₂CO₃ nano-composites were consolidated to very high densities without particle coarsening for the first time at much lower temperatures than those mentioned in the literature by the use of CSP. The crystallite size of SDC powders in the reference SDC-30NR700 samples was determined to be around 34 nm. This clearly indicated that particle coarsening occurred during high-temperature sintering in conventional furnaces. It is important to note that, despite the processing temperatures of the reference samples being about 500 and 600 °C higher than that used in CSP, the samples either did not achieve densification (70 %) or were highly

fragile, likely owing to the decomposition of the Na_2CO_3 phase. Utilising CSP, SDC- Na_2CO_3 nanocomposite electrolytes may be densified to increased quantities at much reduced temperatures for SOFC applications. Moreover, the growth of SDC particles in the nanocomposite may be restricted, thereby preserving the authentic nanostructure of the composite. A substantial SDC- Na_2CO_3 interface density could also be attained, which is severely unattainable with traditional methods.

3.2.4.4. Microstructural Analysis

Figure 3.6 illustrates the scanning electron microscopy pictures of the shattered surfaces of SDC-30N nanocomposite samples that underwent cold sintering at 200 °C. The pictures were obtained at three distinct magnifications (**Figure 3.6x-y**), demonstrating a crack-free microstructure. The structure exhibited considerable density, aligning with the density data documented in Section 3.3.1 of this work, as seen in **Figure 3.6x**. The picture mostly features grey and light grey areas, distributed alongside darker parts inside the microstructure.

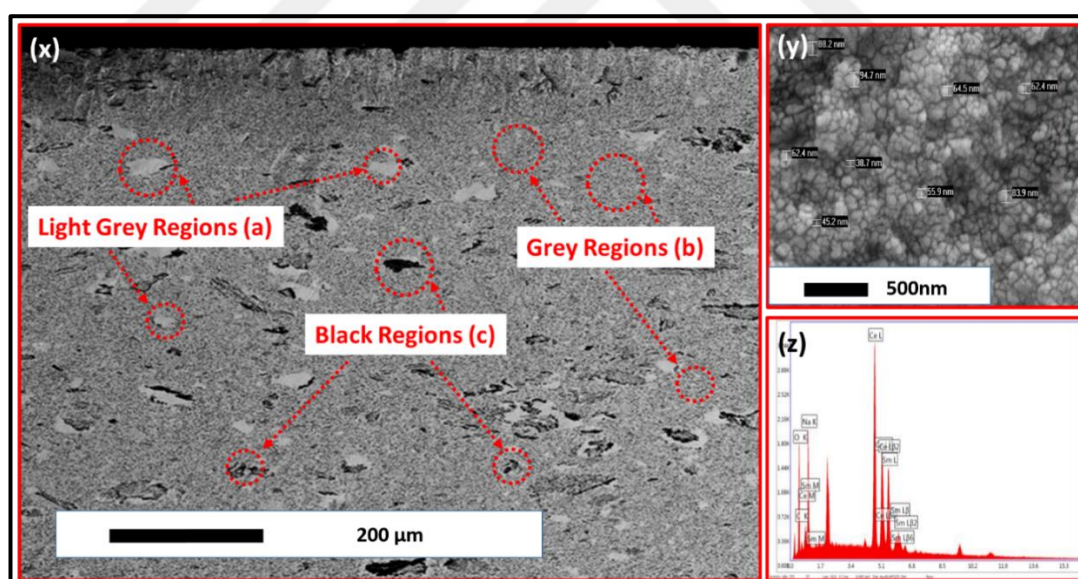


Figure 3.6: The cross sectional-SEM images of the SDC-30N composites fabricated via cold sintering process at 200 °C. x) General microstructure showing dark and light/gray regions y) Average particle size of SDC ceramics in the composite z) EDS analysis of the composite.

Utilising CSP, dense and fine-grained (**Fig. 3.6y**) SDC-30N nanocomposite electrolytes were fabricated, which typically need elevated temperatures for processing, where particle coarsening is inevitable. The grain sizes in the nano-

composite were mostly seen to range from 50 to 100 nm. It was shown that CSP is an effective alternative method for treating materials with precise microstructural specifications. Bin Zhu et al. used hot isostatic pressing, a costly and rather complex technique, to densify the SDC- Na_2CO_3 composites at 550 °C for 30 minutes; nevertheless, only 91 % relative density was attained in this investigation [256]. The pioneering CSP investigation of the ceria-carbonate system was conducted by Hui-Zhen et al. [257]. Nevertheless, with a density of 84 %, it suffered from an inadequacy of the theoretical density of 92 %, which is the requisite barrier for SOFC applications. This work managed to develop a ceria-carbonate system with a high density (~97 %) suitable for SOFC applications for the first time.

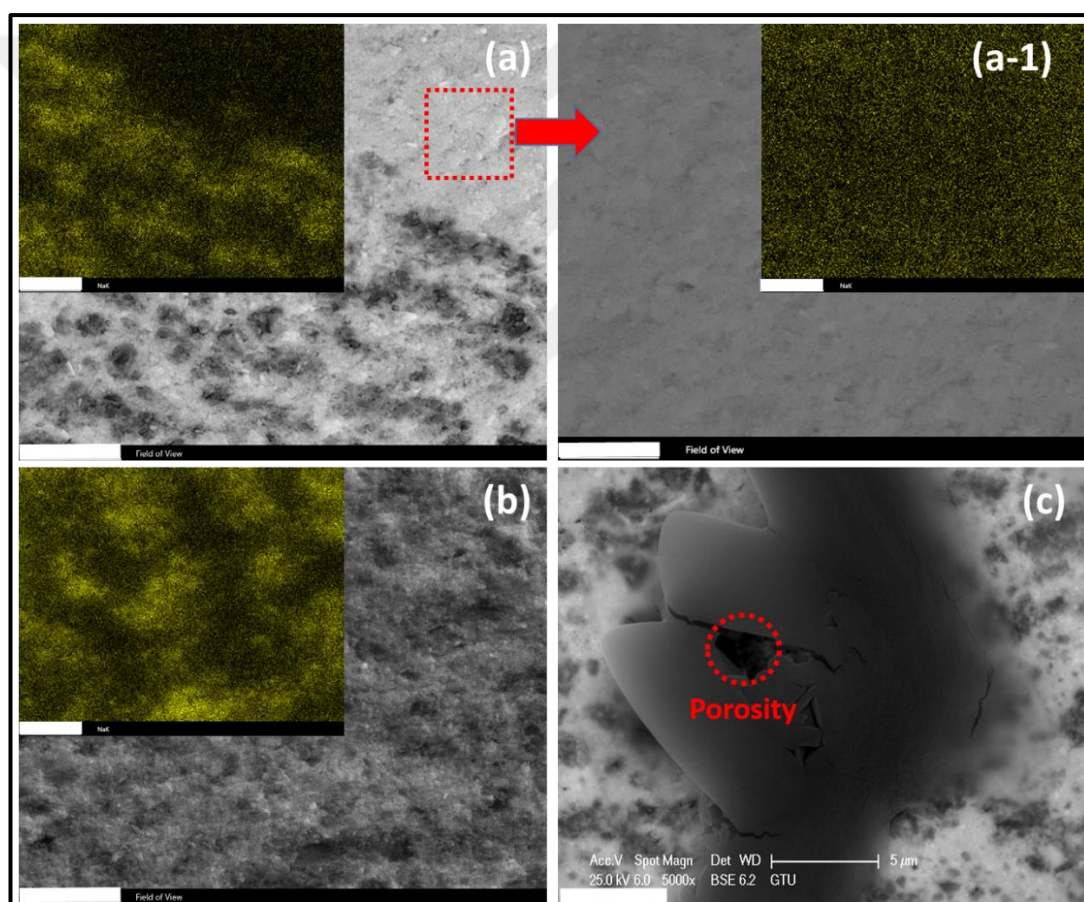


Figure 3.7: SEM images of the SDC-30N nanocomposites fabricated via cold sintering process at 200 °C a) Na-EDS mapping at the border of grey and light-grey region (a-1) Na-EDS mapping from the grey region only b) Na-EDS mapping from the dark region only c) A crystalline Na_2CO_3 phase with porosity [All bars are 5 μm].

The EDS spectra shown in **Figure 3.6z** confirms the presence of Na, C, and O with Ce and Sm throughout the nanocomposite. The microstructural phases were

indistinguishable using EDS due to their fine nature. **Figure 3.7** presents the detailed SEM images and EDS maps of the areas with varying contrasts, labelled as a, b, and c in **Figure 6**. In the grey and light grey areas, the SDC and Na₂CO₃ phases were seen to be somewhat uniformly distributed, as shown in **Figure 3.7a-b**. **Figure 3.7a** may be falsifying since it depicts areas deficient in Na and hence Na₂CO₃. EDS mapping of that location demonstrated a uniform distribution of the Na₂CO₃ phase, as seen in **Figure 3.7a-1**.

The areas had lower carbonate concentration and demonstrated considerable density. The additional water for CSP was predicted to significantly contribute to the emergence of these grey and light grey areas. Higher amounts of the carbonate phase were detected inside the grey areas. The creation of these zones is believed to result from water evaporation during CSP, including the dissolution and subsequent precipitation/crystallization of dissolved carbonate phases. The existence of crystalline carbonate phases, a few microns in size and exhibiting a faceted shape, as seen in **Figure 3.7c**, clearly indicates carbonate phase growth. As shown in **Section 3.3.1**, the introduction of water was the principal element facilitating densification during CSP; yet, it resulted in an inhomogeneous microstructure. To our knowledge, a comprehensive microstructural picture illustrating the homogeneity or inhomogeneity of the nanocomposite, as seen in **Figure 3.6x**, has not been provided in the literature to date for comparison.

3.2.4.5. Electrical Conductivity

Figure 3.8a shows the resulting Nyquist and Bode graphs, which originated from the EIS data of SDC-30N at 600 °C. Area specific resistance to ion transport through the electrolyte (ASR1) is represented by the first intercept value on the horizontal axis of the Nyquist curve, while the area specific resistance associated with the inverse of the rate of electrochemical processes at the electrodes (ASR2) is the sum of the diameters of the several arcs (**Figure 3.8a**). Therefore, the electrolyte's electrical conductivity was calculated using Equation 3.2, where σ represents the electrical conductivity and t represents the thickness.

$$\sigma = \frac{t}{ASR1} \quad (3.2)$$

Figure 3.8b illustrates the temperature dependence of the electrical conductivity of SDC-30N, measured in flowing, humidified air, alongside conductivity data obtained from the literature. The electrical conductivity of the SDC-30N electrolyte increased with temperature in the 350 – 600 °C range, suggesting a thermally active process.

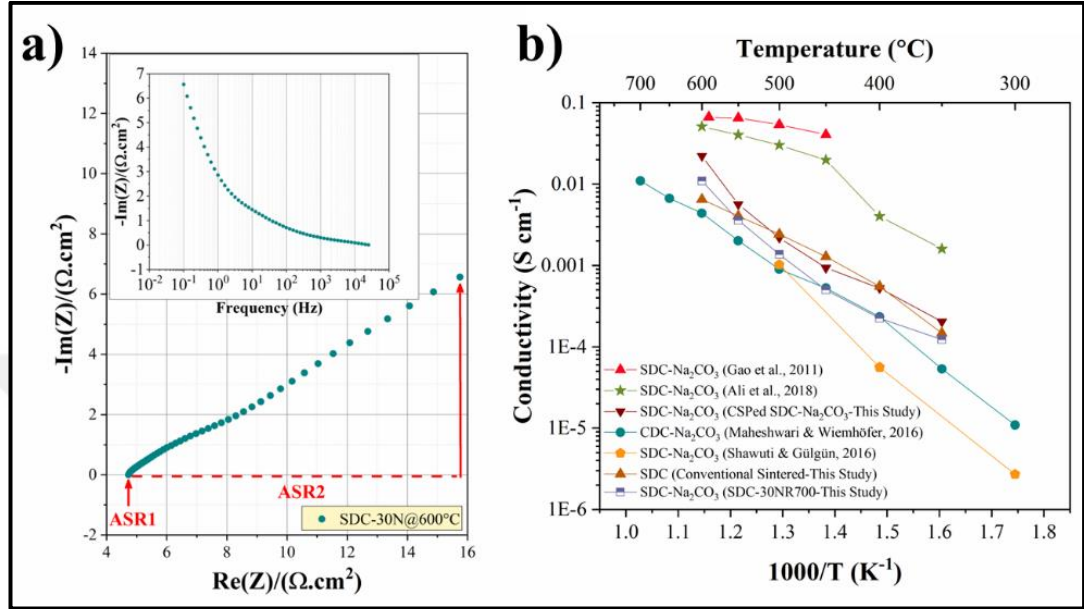


Figure 3.8: a) Nyquist and Bode (insert) plots of SDC-30N sample at 600 °C in air flow, b) the conductivity of cold sintered SDC-30N nanocomposite electrolyte obtained from AC impedance as a function of temperature (350-600 °C) and its comparison to the related literature.

An electrical conductivity of 22 mS/cm was recorded at 600 °C. The result is within the broad spectrum of electrical conductivity values, approaching the top results published in the literature for ceria-carbonate composite electrodes [220, 250, 252, 258].

To further understand the impact of the cold sintering method on the electrical performance of the nanocomposite electrolytes (SDC-30N), their electrical conductivity values were compared with those of conventionally sintered analogues (SDC-30NR-700). The SDC-30NR-700 sample exhibited about half the electrical conductivity of SDC-30N, although it had a comparable temperature dependency (**Figure 3.8b**). The observed enhancement in conductivity may be ascribed to two primary factors: firstly, the advanced density resulting from cold sintering, and secondly, the maintained high interfacial area density between SDC and the carbonate phase, accomplished by limiting grain growth through the utilisation of a low-

temperature process. This work used the Bruggeman approximation, as presented in Equation 3.3, to analyse the influence of porosity on electrical conductivity in composites produced by traditional or cold sintering methods [259].

$$\sigma^{\text{ef}} = \sigma^0 (2-3p)/2 \quad (3.3)$$

where σ^{ef} indicates the effective conductivity obtained experimentally from bulk samples, p represents the pore volume fraction, and σ^0 denotes the conductivity of completely dense materials. The calculations assume that the pores are spherical and that their conductivity is zero. The conductivity ratios of composites with 0.3 (conventionally treated) and 0.03 (CSP) percent porosities were estimated using the Bruggeman approach and experimental observations, yielding values of 0.58 and 0.5, respectively. This study was conducted without considering the variance in interfacial area density of the alternatively handled electrolytes, as outlined following.

The prevalent consensus in the literature regarding the ionic conduction mechanism in ceria-carbonate composite electrolytes is that predominant proton conductivity occurs at the ceria/carbonate interface, while oxygen and carbonate ions also contribute through the respective ceria and carbonate phases [204, 213, 215, 216, 260]. To evaluate this theory, the electrical conductivities of pure SDC and pure Na_2CO_3 were measured, yielding values of 6.3 mS/cm (95 % dense) and 1 mS/cm (98 % dense), respectively, at 600 °C (**Figure 3.8b**). Composites produced using both traditional and CSP processes had superior electrical conductivities compared to pure SDC and pure Na_2CO_3 , suggesting a synergistic impact rather than a mere rule of mixing.

The traditional processing procedure at high temperatures led to an increase in the crystallite size of SDC from 25 to 34 nm, which was not included in the Bruggeman approximation. The composites detailed in reference 220, in **Table 3.1**, may be categorised as micro-composites because to the SDC phases being within the micron size range. The conductivity value was found as 4 mS/cm, which was five times lower than the result observed in this investigation, despite both composites having comparable densities [220]. It was shown that nanocomposites exhibited elevated conductivity owing to their high interfacial area density, which might serve as a fast ion conduction pathway. Moreover, the influence of water use on the relationship between microstructure and electrical characteristics in samples produced by CSP was

also overlooked. The Bruggeman approximation was a primitive assessment of electrolyte conductivity in this investigation.

The first findings indicate that the long-term durability of the nano-composite electrolytes was evaluated by EIS measurements conducted over 24 hours at 600 °C, revealing no significant changes in the conductivity.

Table 3.1. A comparative analysis of processing parameters and conductivity levels of doped ceria samples demonstrated in the literature.

Material	Processing Condition	Density (%)	Crystallite or Grain Size (nm)		Conductivity (S cm ⁻¹)	Reference
			Initial	Final		
Doped ceria carbonate	CS at 700 °C for 1h	71	25	34	0.011 @ 600 °C	This study
Doped ceria carbonate	CSP	97	25	25	0.022 @ 600 °C	This study
Doped ceria carbonate	CSP	85	-	20-50	0.0063 @ 600 °C	Hui-Zhen et. al., 2022 ²⁵⁷
Co-doped ceria carbonate	CPM/CS at 700 °C for 2h	78	-	15	0.0023 @ 600 °C	Kumar et. al., 2018 ²⁴²
Doped ceria carbonate	CPM/CS at 700 °C for 2h	-	-	-	0.06 @ 600 °C	Gao et. al., 2011 ²⁵¹
Doped ceria carbonate	CS at 600 °C for 20h	95	-	1000	0.004 @ 600 °C	Maheshwati & Wiemhöfer, 2016 ²²⁰
Doped ceria carbonate	CS at 700 °C for 1h	98	150	1000	0.0028 @ 550°C	Shawuti & Gülgün, 2014 ²⁴⁴
Doped ceria carbonate	CPM/CS at 800 °C for 4h	-	-	36	0.052 @ 600°C	Ali et. al., 2018 ²⁵⁸

CS: Conventional Sintering, CSP: Cold Sintering Process, CPM: Co-Precipitation Method

3.2.5. Conclusions

This work demonstrates that the densification challenges of samarium-doped ceria-sodium carbonate nanocomposite electrolytes may be resolved without particle growth. The findings indicate that the cold sintered samarium doped ceria-sodium carbonate nanocomposites achieved densification at much lower temperatures than those necessitated by traditional processing methods. Consequently, this novel production technique may serve as an efficient means to prepare electrolytes for LT-SOFCs. Cold-sintered nanocomposite electrolytes exhibited conductivity values of 22 mS/cm at 600 °C, aligning with existing research. The present work demonstrated that the use of CSP resulted in improved densification of nano-composite electrolytes to over 92 % of their theoretical density, a feat difficult to accomplish by traditional processing techniques. Consequently, these electrolytes may be used in the fabrication of solid oxide fuel cells (SOFCs). We assert that our study will provide a foundation for further investigations into the development and optimisation of ceria-carbonate electrolytes for high-performance LT-SOFCs. Future research will investigate nanocomposites with varying ceria to carbonate ratios and diverse powder synthesis methods, including co-precipitation, using the cold sintering process.

4. CHAPTER FOUR: CARBONATE CONTENT AND LIQUID PHASE EFFECTS ON MICROSTRUCTURAL AND ELECTRICAL PROPERTIES OF COLD SINTERED SDC- Na_2CO_3 NANOCOMPOSITE ELECTROLYTES

4.1. Introduction

The growing worldwide energy demand, combined with a growing emphasis on environmentally sustainable alternatives, has positioned solid oxide fuel cells (SOFCs) as a prominent technology in the field of clean energy. This is due to their notable efficiency and ability to produce electricity by converting fuel into electricity through electrochemical processes, with water and heat being the primary byproducts. Consequently, researchers globally are investigating innovative materials and electrolytes in order to augment the efficiency of SOFCs and facilitate the progression towards a more sustainable energy landscape [261-263].

SOFCs have been extensively studied for many decades as a viable solution to address the increasing energy demands while simultaneously mitigating the adverse environmental consequences. They possess remarkable characteristics that make them very promising in the field of clean energy. These properties include elevated operational temperatures, generally ranging from 800 to 1000 °C, long-term stability, and the capacity to use a variety of fuels. Consequently, SOFCs emerge as a serious challenger within the clean energy sector. Nevertheless, the use of traditional SOFCs is hindered by their high operational temperature, which often exceeds 800 °C. This characteristic renders the technology impractical for commercial purposes and poses challenges in integrating SOFCs into the worldwide energy market [264-266].

Consequently, a wide range of attempts have been performed to reduce the operational temperature within the intermediate region of 400–600 °C [267]. Scientists have devoted significant importance to the study of electrolytes due to the recognition that the ionic conductivity of the electrolyte plays a crucial role in determining the performance of SOFCs [268]. Gadolinium-doped ceria (GDC) and samarium-doped

ceria (SDC) have gained major attention as highly encouraged and conductive electrolytes in the context of intermediate-temperature solid oxide fuel cell (IT-SOFC) applications [269-271]. Despite the significant progress made by the researchers in reducing operating temperatures and enhancing ionic conductivity, the conductivity of ceria-based ceramics (GDC, SDC, etc.) remained constrained within the range of 1 mS/cm to 10 mS/cm at intermediate temperatures, pointing to the need for further improvement [272-274].

Ceria-based carbonate electrolytes have emerged as a potential solution for intermediate-temperature SOFCs, which typically operate in the range of 400 °C to 600°C. These composite materials, often comprising cerium oxide (ceria, CeO_2) and carbonate compounds like sodium carbonate (Na_2CO_3), grab great attention due to their high conductivities at low temperatures [274-277]. One of the pioneer researches in this field was done by Bin Zhu et al., they introduced a two-phase ceria-based carbonate composite and suggested that the ionic conductivity of ceria can be further enhanced by introducing a secondary carbonate phase where the ceramic ceria phase is glued by a sodium carbonate phase [278]. Based on this theory, it is suggested that oxygen ions (O^{2-}) facilitate conduction throughout the ceramic phase, while protons (H^+) contribute to conduction via the "super ionic path" reported to exist at the interface between the ceramic and carbonate [279, 280]. Following evaluation of the conduction approach, it becomes evident that enhancing the ceramic-carbonate contact is crucial for achieving high conductivity. It is important to acknowledge that the augmentation of the interface may be achieved by two means: firstly, by ensuring that the ceramic phase comprises particles that are as homogeneous and finely grained as possible, and secondly, by maximizing the density of the structure.

The existence of conflicting conductivity values for comparable systems in the literature led to an impression of doubt about the conduction mechanism. For instance, Bin Zhu reported a value of 0.1 S/cm, whereas Maheshwari and Wiemhöfer recorded a value of 4 mS/cm for the SDC- Na_2CO_3 composite at 600 °C [178, 220]. Notwithstanding a lack of comprehension of the conduction mechanism, several experiments have consistently shown that the conductivity of the composite system surpasses that of the single ceramic phase [273-275].

In our previous research we also seen that there is a composite effect that ceria-carbonate composite showed two times higher conductivity than the single phase

doped-ceria. But it is hard to come to a solid conclusion on the conduction mechanism based solely on this finding.

Additionally, conventional fabrication processes encounter challenges related to the densification of ceria based-carbonate nanocomposite electrolytes [206, 237, 238]. It has been reported that, even with relatively complex and expensive methods such as hot isostatic press (HIP), only 91 % can be achieved [33].

The cold sintering process (CSP) is an innovative technique for densifying ceramic materials and ceramic-based composites at temperatures that are notably lower than those required for traditional sintering methods [13, 14, 15]. The process generally involves the use of a minimal quantity of solvent, often water, together with the application of significant pressure, up to 700 MPa, at moderate temperatures ranging from room temperature to 400 °C. The phenomenon of densification in cold sintering process (CSP) is widely theorized to result from a beneficial combination of re-arrangement of particles and dissolution-precipitation mechanisms. The induced pressure promotes the densification of ceramic particles, leading to their close contact, while the transient liquid in the dissolution and subsequent re-arrangement of material at the interfaces between particles. This procedure results in the establishment of strong interparticle connections and an elimination of porosity [16-19].

Cold sintering, an innovative and promising technique, offers a potential solution to address the hard densification challenges and increasing ceria-carbonate interface by preventing coarsening in ceria-based carbonate electrolytes. The first study of cold sintering of ceria-based carbonate electrolyte was carried out by Wang et. al., however, the highest relative density of samples, 84 %, were not applicable for a SOFC application due to the possible interconnected porosities [257]. In our previous study we have successfully solved the densification issue by reaching 97 % of relative densities at 200 °C, utilizing cold sintering process [281]. So, densification of ceria-carbonate composite electrolyte at very low temperature was made possible. However, that study was conducted with only 30 wt. carbonate content and in the presence of water only as the transient liquid for densification, which resulted in a partially inhomogeneous microstructure due to the high solubility character of sodium carbonate in it. Furthermore, the effect of carbonate content and liquid phase on densification of the composite electrolyte was missing. In this study, the variation of carbonate content (up to 30) and the type of transient liquid phase, in which Na_2CO_3

is partially soluble (PEG) or highly soluble (H_2O), on the microstructure was studied. Composite electrolytes were also cold sintered without any added liquids as a reference. It was also revealed that there was a strong correlation between the humidification method and both densification and microstructure. This study is a contribution to the growing body of knowledge in the realm of ceria-based-carbonate electrolytes for intermediate-temperature solid oxide fuel cells, with the ultimate aim of advancing sustainable energy technologies with this research.

4.2. Experimental

4.2.1. Material Preparation

SDC- Na_2CO_3 nano-composite electrolytes were prepared from commercial powders of $\text{Ce}_{1.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (20SDC, Inframat, USA) and Na_2CO_3 (Alfa Aesar, USA) powders. The powders were first subjected to separate ball milling for a duration of 48 hours in order to crush down possible agglomerates. Nano-composite electrolyte powders were prepared by mixing the previously ball-milled SDC and Na_2CO_3 powders, containing 10, 20, or 30 % Na_2CO_3 in weight, and then ball-milling them for 24 hours again in an isopropanol medium. Subsequently, the mixtures were calcined at $650\text{ }^\circ\text{C}$ for 1 hour in air atmosphere. The calcined powders were directly cooled down to room temperature and then ground using mortar and pestle. After sieving, they were kept in an oven at $80\text{ }^\circ\text{C}$ to prevent moisture condensation. Prepared powders were labeled as SDCN10, SDCN20 and SDCN30 depending on their Na_2CO_3 content.

4.2.2. Cold Sintering Process

CSP studies were conducted using a specially designed hydraulic press with a 100 tons capability (HIDROTIM, Turkey). A steel mould equipped with a PID-controlled mica band heater that tightly clamps it from the outside was used to cold sinter powders.

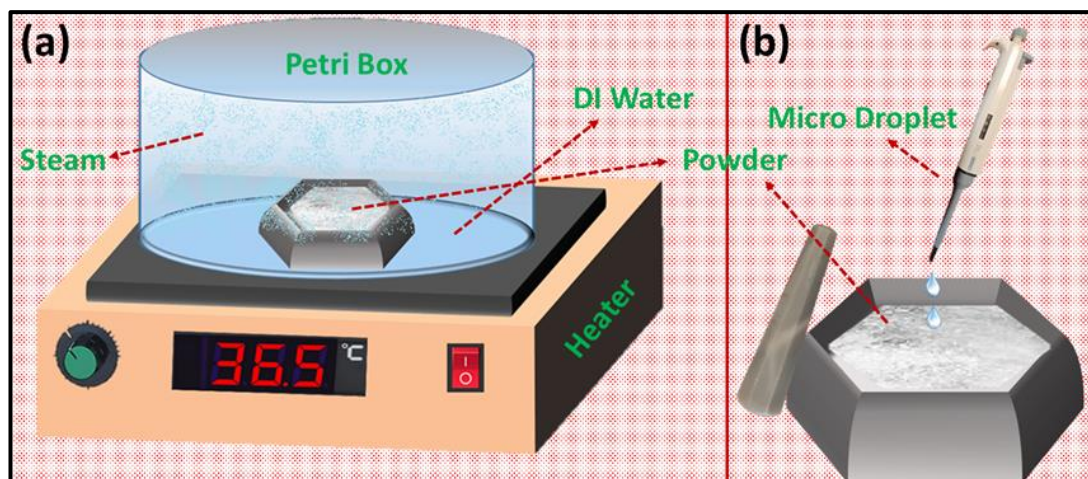


Figure 4.1: Illustration of humidification method by a) petri holder and b) mortar-pestle.

Temperatures were monitored using a K-type thermocouple placed on the mould surface. The cold sintering process was carried out within a temperature range of 50 to 250 °C, at pressures ranging from 75 to 675 MPa, and for varying periods lasting from 1 to 180 minutes. Yttrium stabilized zirconia (YSZ) powders sourced from TOSOH in Japan were used as a "spacer" in order to avoid the sticking of the sample to the upper and lower die punch surfaces during the process.

Deionized (DI) water and Ethylene Glycol (EG) up to 10 % by weight were used as transient solvents for CSP. Furthermore, two different methods were used to adjust the moisture content of the nanocomposite powders with the DI water; i) water was allowed to reach an equilibrium moisture level in a closed environment by evaporation and condensation at 40 °C. ii) DI water was added to the composite powder mixture using a pipette. The solvent addition methods were illustrated in **Figure 4.1**. Afterwards, the liquids, either DI water or EG, added to the composite powders were homogenized in a mortar and pestle, which were then sandwiched between a four-layer structure consisting of cathode powder, silver powder, filter paper, and YSZ spacer powder on each side, respectively, in the die cavity during cold sinter processing. The mica band heater was utilized to heat the mould to the required temperatures, after which it was allowed to dwell isothermally.

4.2.3. Characterization

The densities of the samples were calculated from their masses and dimensions after surface polishing. In calculating the theoretical density of the composites, the mixture law was used, and the densities of SDC and Na_2CO_3 were taken as 7.19 and 2.54 g/cm³, respectively. The crystallinity and phase analysis were done by using an X-ray diffractometer (XRD) (Rigaku D-Max 2200, Japan). The microstructures of nanocomposites were analyzed using a scanning electron microscope (SEM) (Philips XL 30 SFEG, Eindhoven, Netherlands) from the fractured or polished surfaces. Electrochemical Impedance Spectroscopy (EIS) (Nowatech Zive MP2 Potentiostat, South Korea) was used to measure the electrical conductivity of the cold sintered samples at temperatures ranging from 500 to 600 °C. EIS measurements were done under humidified air flow, which was ensured by bubbling the air through water at room temperature. The excitation voltage and frequency range were set to 10mV and 5×10^{-2} to 10^6 Hz, respectively. Silver paste was used as the current collector.

4.3 Results and Discussions

4.3.1. Densification via Cold Sintering Process

A detailed study was conducted on the cold sinterability of nanocomposite powders as a function of processing temperature, applied pressure, processing duration, the type and amount of transient liquid phase as well as how they were added, and carbonate content in the composite powder. They are all summarized in **Table 4.1**. In determining the optimum cold sintering process conditions, two main outcomes were always a priority. First was the densification; that is generally, a minimum relative density required in solid oxide fuel cells was above 92 % in order to eliminate the possibility of interconnected porosities in electrolyte materials. It was crucial to hinder mixing of fuels by flowing through these interconnected porosities and reacting without producing any electricity, leading to inefficient fuel cells. Second was that a functioning solid oxide fuel cell should be able to be made out of it: that is, samples should be free from defects like cracks, delamination, etc. For example, a sample that could be densified by cold sintering at very high pressures and very low temperatures but could not be characterized for its electrical properties was considered as a failure.

Tablo 4.1: A brief of the processing of nanocomposites depending on their carbonate contents and achieved density values.

Carbonate Cont. (% wt.)	CSP Conditions	Transient Liquid	Liquid Adding Method	Density (%)
10	250 °C 600 MPa 30 min	-	-	78
		DI (% 4wt.)	Mortar-Pestle	82
		DI (% 4wt.)	Petri Holder	91
		EG (% 6wt.)	Mortar-Pestle	84
20	250 °C 600 MPa 30 min	-	-	82
		DI (% 4wt.)	Mortar-Pestle	88
		DI (% 4wt.)	Petri Holder	98
		EG (% 6wt.)	Mortar-Pestle	92
30	200 °C 450 MPa 30 min	-	-	86
		DI (% 4wt.)	Mortar-Pestle	97
		DI (% 4wt.)	Petri Holder	96
		EG (% 6wt.)	Mortar-Pestle	94

DI: Deionized Water, EG: Etylne Glycol

The densification results given in **Figure 4.2-3** showed that relative densities were found to increase with increasing carbonate content in the mixture as expected.

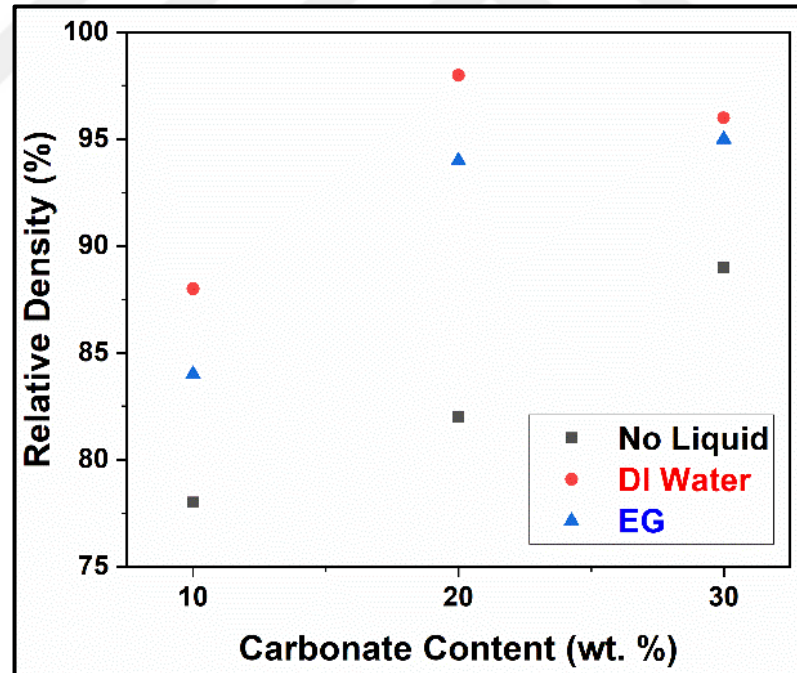


Figure 4.2: Relative densities as a function of carbonate content with different transient liquids.

Because carbonate, being the soft phase, should promote denser compaction under cold sintering conditions. It was so whether or not a liquid in which the carbonate phase was soluble was employed. For example, in samples denoted as SDC10N (no

liquid phase), the relative density was measured as 78 % which was inadequate for constructing a solid oxide fuel cell out of it, but with increasing carbonate content (SDC20N, SDC30N), it was found the relative densities were well above the required minimum densities.

In a previous study, it was emphasized that the water might be the main reason for the high level of inhomogeneity in SDC-sodium carbonate nano-composites due to the high solubility of sodium carbonate in water [281]. That is why the effect of another different transient liquid, namely ethylene glycol, in which sodium carbonate has limited (~3 gr/100 mL) solubility, was also studied. Because sodium carbonate being highly soluble in water might be the reason for the microstructural inhomogeneity. Maybe with the employment of low solubility of solvents, EG, the severity of the microstructural inhomogeneity problem might be reduced. Furthermore, it was expected that the possible contribution of the problem to the overall fuel cell performance could be eliminated. Therefore, a systematic study of the effect of EG on relative densities of nanocomposite electrolytes was conducted. Surprisingly, the results revealed that especially at higher carbonate contents, EG was almost as effective as DI water in increasing densities of the composites. Relative densities of SDC20N and SDC30N composite electrolytes prepared with 6 %wt. EG transient liquid were measured as 94 % and 95 %, respectively, as shown in **Figure 4.2**. The minimum density criteria for SOFC applications were satisfied by these values. In the literature, the cold sintering mechanism of carbonates and salts was based on their easy dissolution in water (second stage of cold sintering: dissolution-precipitation) and plastic flow due to their soft character [282, 283]. The reason for obtaining such high densities with EG, where even the solubility of sodium carbonate is limited, is thought to be contrary to the conclusion in our previous study; the densification may have been more dominant in the first stage of cold sintering, the 'particle rearrangement' stage. It is because EG has a higher boiling point (~197 °C) than that of water, and therefore, the transient liquid must be present in the system for longer durations, thus promoting the particle rearrangement, which may have had a greater effect on densification.

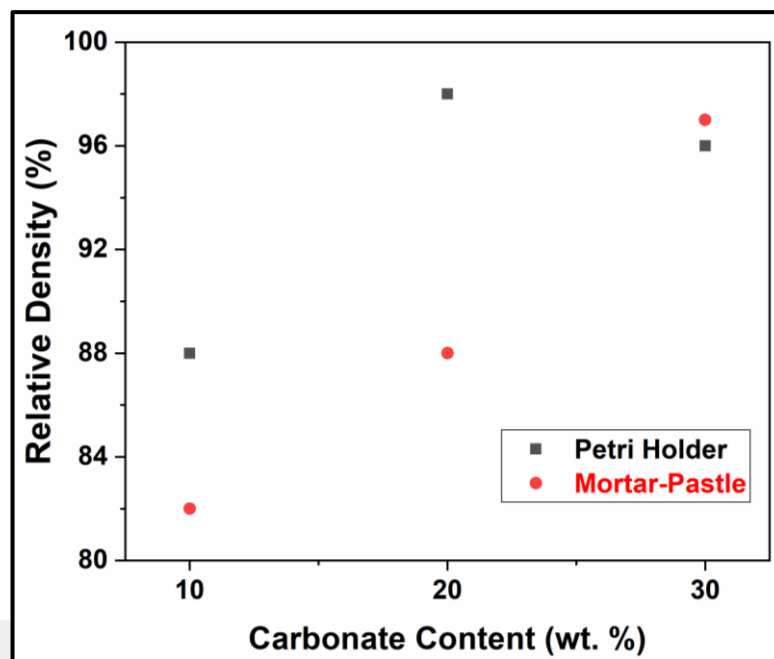


Figure 4.3: Effect of the humidification method on relative densities.

The carbonate content was found to be a major variable in densification by cold sintering. When there was enough carbonate (≥ 20 %wt.) in the system, transient liquids and the method of the humidification became dominant for the densification (**Figure 4.2-3**). It is worth underlining the effect of humidification method on densification; likewise, especially for the SDC20N samples, which contain wt. 20 % sodium carbonate, the relative densities increase drastically from 88 % to 98 % with the changing humidification method from mortar-pestle to petri holder, **Figure 4.3**. The reason for more densification was attributed to homogenous humidification in the petri-holder. In humidification using mortar-pestle, DI water was just added drop by drop on the powder mixture. Even though it was quickly mixed for 5 minutes, the water distribution still remained local, that is inhomogeneous. It could be one of the reasons for reduced densification. Petri holder, on the other hand, lead to more homogeneous liquid distribution due to condensation from the gas phase.

At the end, while 10 % carbonate containing sample could be densified to 91 %, the 20 and 30 % carbonate containing ones could be densified to well above to 92 % with the help of H_2O and EG as the source of the liquid phase.

4.3.2. Phase Analysis

Figure 4.4 shows the XRD patterns of SDC10, SDC20N, and SDC30N nanocomposite electrolyte samples. The main diffraction peaks were associated with the SDC phase with a cubic fluorite structure (JCPDS 34-0394). While the small peaks labelled with asterisks (*), at 30 and 38, were found to correspond to the Na_2CO_3 and/or NaHCO_3 phases in the SDC30N nanocomposites. NaHCO_3 phase was probably formed by the reaction between Na_2CO_3 and moisture in the air.

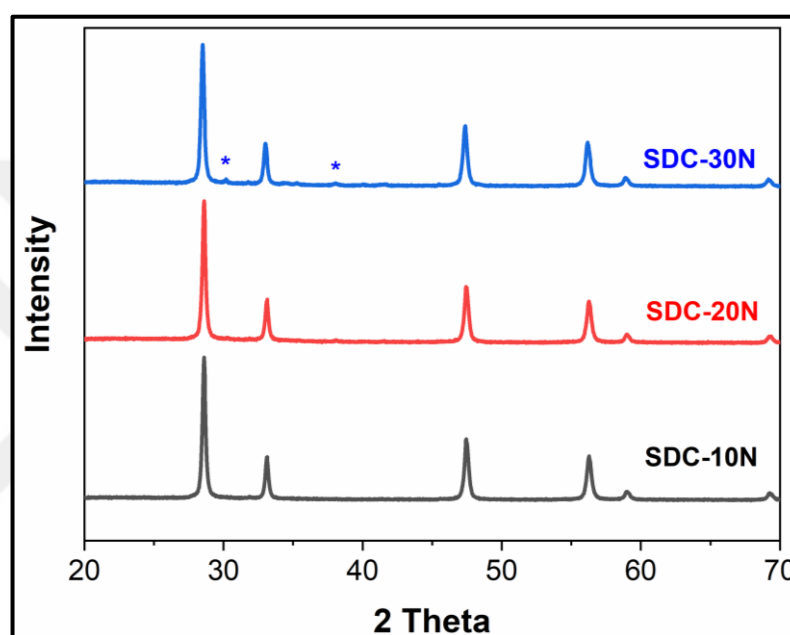


Figure 4.4: X-ray diffractometer (XRD) patterns of SDC10N, SDC20N, and SDC30N nanocomposite electrolyte samples.

However, there were no observed small peaks for the samples containing lower carbonate amounts, SDC10N and SDC20N. This is considered to be due to the high 'structure factor' difference caused by the SDC phase's higher average atomic number (Z) than the carbonate phases. Apart from oxygen, the main constituents of SDC are heavy atoms such as Sm ($Z = 62$) and Ce ($Z = 58$), whereas the average Z of Na_2CO_3 is just 14 [244, 281]. This could explain why the associated peaks were hidden in the background noise until a specific amount of carbonate phase was exceeded. In our previous work, SDC crystallite size was calculated around 25 nm and showed that there was no grain growth after CSP at 200 °C.

4.3.3. Microstructure Analysis

At small magnifications, as in **Figure 4.5**, the cold sintered sample microstructures look dense. However, densities calculated from the mass and macroscopic geometry of the samples were found to be quite different. This might be caused by the soft nature of the carbonate phase and/or the size of the particles that could not be seen at low magnifications. Even during surface preparation for SEM analysis, small particle fragments may fill the cavities, giving the surface a falsely smooth appearance.

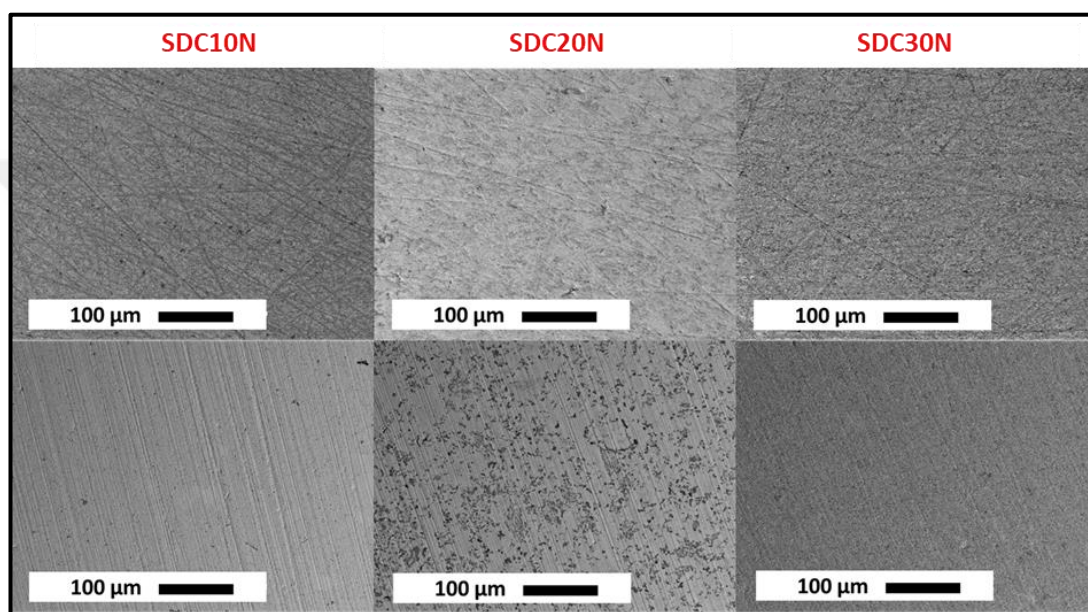


Figure 4.5: SEM images of SDC10N, SDC20N, and SDC30N (left to right) nanocomposite electrolytes CSPed without any transient liquids (up) and with EG (down). Images were taken from the polished surfaces.

As it was stated previously, samples could not be densified over 92 % without the utilization of any transient liquids such as DI water and EG. These liquids promoted densifications for almost all samples at all carbonate content levels. However, they also caused inhomogeneity in the microstructures. **Figure 4.5** shows the effect of EG on the microstructure for the samples of SDC10N, SDC20N, and SDC30N in comparison with the ones without the addition of any liquids.

In the absence of any liquid, the microstructures look homogeneous. Having said that, irrespective of the carbonate content, all samples with the added liquid phase showed inhomogeneity to the same extent, see in **Figure 4.S1**. This could easily be seen at high magnifications.

Figure 4.6 shows the humidification method effect on the microstructure for the samples of SDC10N, SDC20N, and SDC30N prepared with % 4wt. DI water in mortar-pestle or in a petri-holder. In Section 4.2.1, it was mentioned that humidification method has a significant effect on the densities. The analogic drastic level evolution was also observed in the microstructural analysis. In all carbonate content, changing the humidification method from mortar-pestle to petri-holder led high level of inhomogeneity and the inhomogeneity level increased with the increasing carbonate content. Such a drastic change in the microstructure is difficult to attribute solely to a change in the humidification method. However, a possible explanation may be consistent with the mechanism proposed in **Section 4.3.1** for densification.

In the dropwise method, sodium carbonate rapidly absorbs water, leading to the partial, localized trapping of water. Although composite powders containing water are mixed and distributed using a pestle, the distribution remains limited to the micron scale. This may partially reduce the densification effect of the water.

In contrast, in the Petri dish method, the composite powder spread over a wide surface is humidified through condensation from the vapour phase, resulting in more homogeneous humidification. In samples humidified using this method, carbonate-containing phases are observed to be closer to one another. This homogeneous humidification may have facilitated the easier merging of carbonate phases under CSP (Cold Sintering Process) conditions during water removal.

The intensification of this effect with increasing carbonate content supports this interpretation. An increase in carbonate content would trap water more effectively, delaying its evaporation. Consequently, the dissolved carbonates in the water would have more time to combine and grow through mass transfer. This effect may explain the formation of interconnected, carbonate-rich large regions, as more clearly observed in the SDC30 sample in **Figure 4.6**. Additionally, the effect might not only be due to the duration of water removal but also the enhanced gathering of carbonates during water evaporation.

It was obvious that the distinct microstructures seen in **Figure 4.5** and **Figure 4.6** were caused by the transient liquid phases. It was found that without transient liquids, the microstructures of all composite samples were quite homogeneous; however, the introduction of a liquid phase like EG or DI water resulted in inhomogeneity

depending on the sodium carbonate solubility level in these liquids used as sintering aids during cold sintering.

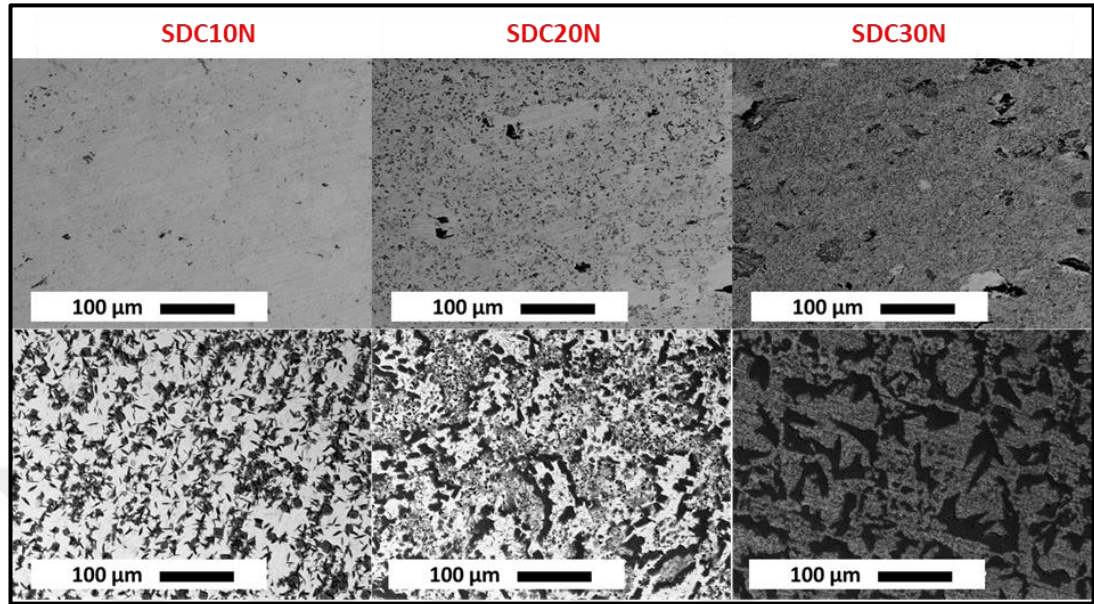


Figure 4.6: SEM images of SDC10N, SDC20N, and SDC30N (left to right) nanocomposite electrolytes humidified with DI water in mortar-pestle (up) and in petri-holder (down). All samples contain an equal amount of DI water (% 4wt.). Images were taken from the polished surfaces.

On the other hand, without the presence of transient liquids, regardless of the carbonate contents, samples could not be densified over 92 % of their theoretical densities, rendering them suitable for efficient SOFC applications.

4.3.4. Electrical Measurements

Table 4.2 presents the conductivity values with the relative densities of nanocomposite samples prepared through various liquid mixing methods. Conductivity values only for those samples that were eligible for fuel cell production were reported. For SDC10N samples, enough densification was achieved only when DI water was used as the solvent and humidification was done in petri-holder. The maximum achieved conductivity was found to be 51 mS/cm at 600 °C. Among all samples, the maximum conductivity recorded was 68 mS/cm for the SDC20N sample, which was also humidified in a petri-holder. In our previous work, conductivity of the SDC30N sample was reported as 22 mS/cm. Its conductivity was further improved to 50 mS/cm

by enhancing the current collection ability of the electrode system explained in the experimental section.

Table 4.2: Conductivity and density values of the CSPed samples with different preparation methods.

Samples	Liquid Adding Method	Relative Density (%)	Conductivity @ 600 °C (mS.cm ⁻¹)
SDC10N	-	78	-
	Mortar-Pestle (DI Water)	82	-
	Petri-Holder (DI Water)	91	51
	Mortar-Pestle (EG)	84	-
SDC20N	-	82	-
	Mortar-Pestle (DI Water)	88	61
	Petri-Holder (DI Water)	98	68
	Mortar-Pestle (EG)	92	50
SDC30N	-	89	56
	Mortar-Pestle (DI Water)	97	50
	Petri-Holder (DI Water)	96	49
	Mortar-Pestle (EG)	94	42

Nanocomposite electrolytes with different carbonate contents were prepared, among which the one with wt. 20 % carbonate showed the highest conductivity of 68 mS/cm. When compared to SDC10 and SDC30, SDC20 samples prepared with DI water or EG still showed the highest conductivity. The reason for that was believed to be that in SDC20N samples ensured the maximum carbonate-ceria interfacial area according to the proposed high conductive path in the literature and minimum insulating carbonate materials in between [279, 280]. Another clear indication of the results is that introducing EG as a transient liquid did not bring much improvement in conductivity even though it increased the density of samples and resulted in better homogeneity in the microstructure, as compared to DI water utilization. For instance, the lowest conductivities of 50 and 42 mS/cm achieved for the SDC20 and SDC30 samples, respectively.

It was clear that the carbonate content and the use of EG affected the conductivity; however, the effect of homogeneity and density was found to be negligible. For example, in SDC20 samples, as the relative densities increased from 88 % to 98 %, a minor increase in conductivity was observed. For the SDC30N samples, such an effect

did not exist at all. Even though inhomogeneity was improved by employing a different humidification method, the conductivity was unaffected.

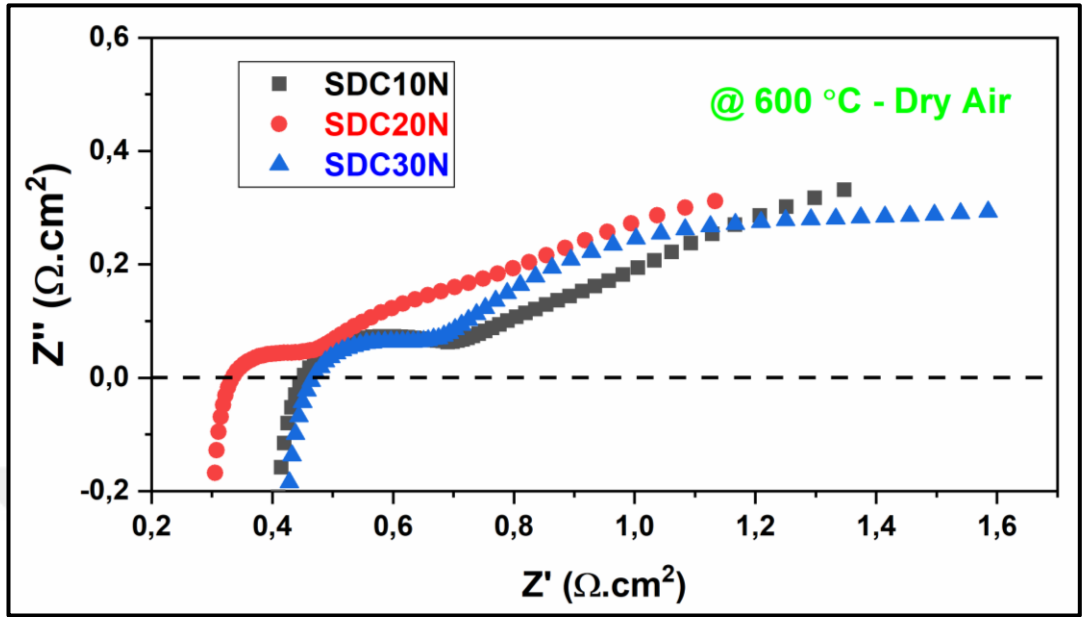


Figure 4.7: Nyquist plots of cold sintered SDC10N, SDC20N and SDC30N samples measured at 600 °C in humidified air.

Figure 4.7 shows Nyquist plots obtained from EIS measurements of SDC10, SDC20, and SDC30N at 600 °C. The horizontal axis intercept values on the Nyquist curve correspond to the area specific resistance (ASR1) of ion transport through the electrolyte, whereas the total diameters of the several arcs represent the area specific resistance (ASR2) correlated with the electrochemical processes that occur at the electrodes. Equation 4.1 was used to calculate the electrolyte's electrical conductivity, where σ represents electrical conductivity and t denotes the thickness of the electrolyte.

$$\sigma = t/\text{ASR1} \quad (4.1)$$

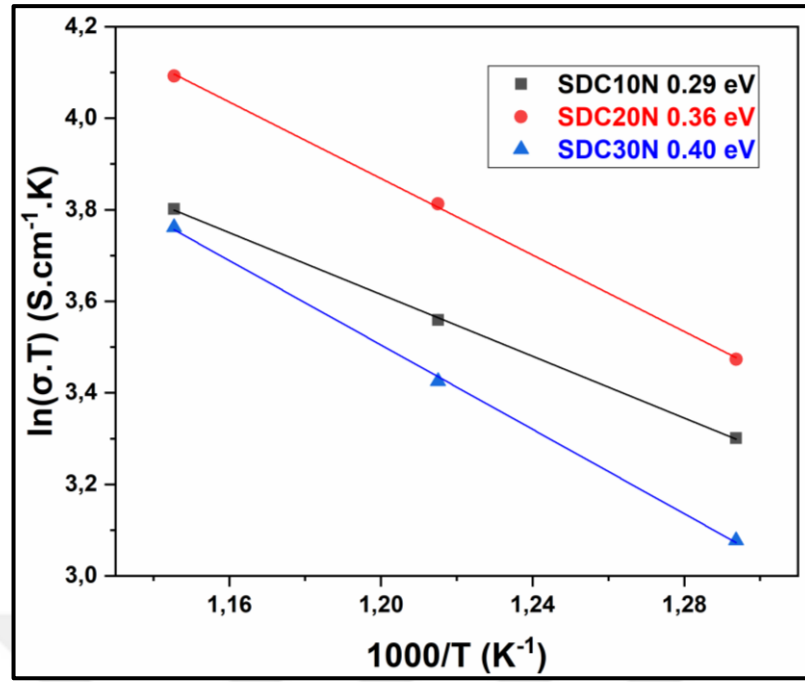


Figure 4.8: Arrhenius plots of cold sintered SDC10N, SDC20N and SDC30N samples measured in the range of 500 - 600 °C in humidified air.

Arrhenius plots were derived from the conductivity data by linear fitting to calculate the activation energies (E_a) of the SDC10N, SDC20N, and SDC30N nanocomposite electrolytes in humidified air in the temperature range 500 – 600 °C and results were shown in **Figure 4.8**. The activation energies (E_a) of the nanocomposite electrolytes were calculated using the following equation:

$$\sigma = A/T \exp(-E_a/kT) \quad (4.2)$$

where σ is related to the ionic conductivity of the samples, A is a pre-exponential factor, k is Boltzmann's constant, T is the temperature in Kelvin, and E_a is the activation energy of the nanocomposite electrolytes. The calculated values of the activation energies for the SDC10N, SDC20N, and SDC30N nanocomposite electrolytes in the humidified air were 0.29 eV, 0.36 eV and 0.40 eV, respectively. The above activation energy results could be an indication that the nanocomposite electrolytes have dual conductive characteristics since the SDC alone normally shows activation energy in the range of 0.6 to 0.9 eV [284-287].

4.4. Conclusion

The findings of this study demonstrated that the cold sintering process (CSP) can significantly enhance the densification and conductivity of SDC- Na_2CO_3 nanocomposite electrolytes, making them promising candidates for intermediate-temperature solid oxide fuel cell applications. Increasing the carbonate content improved densification, with 20 wt % carbonate identified as the optimal level for achieving the highest conductivity (68 mS/cm at 600 °C). The use of deionized water in the petri holder method yielded homogenous humidification that plays a crucial role in densification. Although ethylene glycol as a transient liquid also improved densification, it led to reduced conductivity, potentially due to organic residues at the carbonate-ceria interface. Overall, this research contributes to advancing the development of efficient electrolyte materials for sustainable energy technologies.

5. CHAPTER FIVE: ONE-STEP FABRICATION OF FULL SOFCs VIA CSP

5.1. Introduction

Nanocomposite electrolytes have been widely studied for several decades due to their high conductivity at low temperatures, addressing the challenges associated with the high operating temperatures of traditional electrolytes (YSZ, GDC, SDC). These nanocomposites are typically prepared by mixing CeO₂-based ceramics with inorganic salts (e.g., Na₂CO₃, Li₂CO₃). It has been reported that the addition of inorganic salts improves ionic conduction and stabilizes the electrolyte, providing exceptionally high ionic conductivities even at low temperatures [288, 289]. SDC-Na₂CO₃ nanocomposites have demonstrated extraordinary ionic conductivities of up to 0.1 S/cm even at ultra-low temperatures, such as 300 °C, and high fuel cell performance of approximately 0.8 W/cm² [290, 291].

The cold sintering process (CSP) is an innovative technique that enables the densification of ceramics at significantly reduced temperatures, typically below 300 °C, by utilizing a transient aqueous environment under uniaxial pressure.

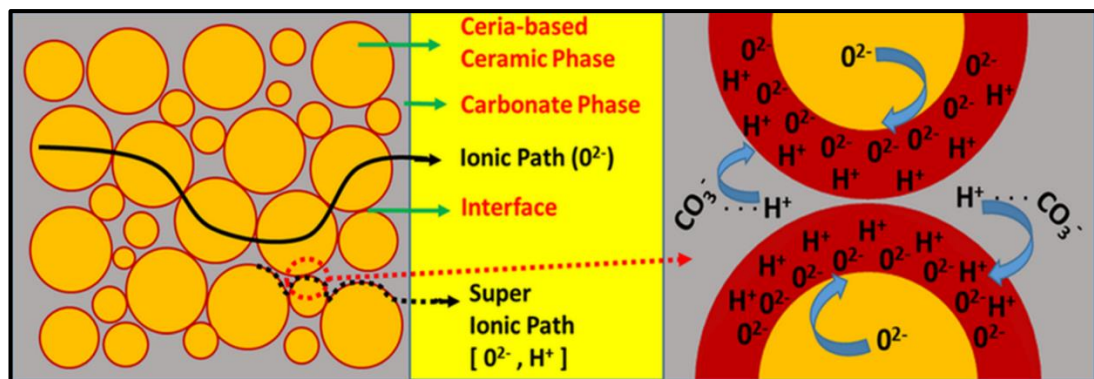


Figure 5.1: Illustration of proposed co-ionic conduction mechanism.

This method contrasts sharply with traditional sintering, which requires temperatures exceeding 1000 °C [13-15]. It is proved in multiple research that CSP facilitates the single-step fabrication of electrolyte materials such as SDC-Na₂CO₃, and NASICON [233, 281]. The ability of CSP to produce these materials in a single step not only reduces energy consumption but also maintains the fine microstructures essential for

optimal electrochemical performance, marking a significant advancement in the fabrication of efficient and cost-effective electrolyte materials for energy applications.

The conduction process in nanocomposite electrolytes remains incompletely understood; nonetheless, it is proposed that multi-ionic or co-ionic conduction takes place at the ceramic-carbonate interface. This process posits that oxygen ions (O^{2-}) facilitate conduction through the ceramic phase, while hydrogen ions (H^+) enhance conduction via a "super ionic path" believed to exist at the ceramic-carbonate interface [292, 293]. The assumed conduction mechanism is illustrated schematically in **Figure 5.1**. Analysis of this mechanism reveals that improving the ceramic-carbonate contact is essential for achieving high conductivity. Increasing the interface may be accomplished in two ways: first, by ensuring the ceramic phase consists of consistently small-grained particles; second, by improving the structural density. The Cold Sintering Process (CSP) can ideally fulfil these parameters, producing up to 97% density at a low temperature of 200 °C, hence minimizing particle coarsening. Consequently, according to the suggested conduction mechanism, it is feasible to expect that electrolytes produced through CSP would demonstrate superior performance.

In this study, we present a pioneering fabrication of a three-layered solid oxide fuel cell (SOFC) comprising anode, electrolyte, and cathode layers, synthesized in a single step at 200 °C using the CSP. This novel approach offers a unique opportunity to evaluate the conduction mechanisms in ceria-based alkali carbonate nanocomposite electrolytes. By maximizing the interface between ceramic and carbonate phases, it is anticipated that ionic conductivity and overall electrochemical performance will be significantly enhanced. CSP facilitates this by enabling densification at low temperatures, preserving the nanostructure, and promoting extensive interfacial contact. The electrochemical performance of the single-step fabricated full cell was evaluated and benchmarked against existing literature, providing valuable insights into the conduction mechanisms within ceramic-alkali carbonate nanocomposite electrolyte systems. We hope that the findings contribute to a deeper understanding of these mechanisms, potentially guiding the development of more efficient and cost-effective SOFCs.

5.2. Experimental

5.2.1. Material Preparation

Commercial 20 mol % Sm-doped ceria (SDC20) powders (Inframat, USA) with particle size ≈ 80 nm, and Na_2CO_3 (Alfa Easer, USA) were used in electrolyte preparation. Electrolyte powders were quenched to room temperature from 650°C after 1 hour dwelling time for the thermal stability. The anode powders were prepared by mixing commercial NiO powders (Inframat, USA) with a particle size of ~ 20 nm with the electrolyte powders using ball milling for 24 hours. NiO/electrolyte ratio was chosen as 60:40 in volume. For the cathode preparation, lithiated NiO ($\text{Li}_{0.3}\text{Ni}_{0.7}\text{O}$ - LNO) was synthesized by the combustion method with lithium and nickel salts. LNO powders were then mixed with the electrolyte powders in 50:50 volume ratio in a ball mill for 24 hours. Pore formers were added to the anode and cathode powders, with 20 %vol. starch and 10 %vol. PMMA for the anode, and 20 %vol. starch and 20 %vol. PMMA for the cathode. All powders, including anode, electrolytes, and cathode, were sieved using a $190\ \mu\text{m}$ mesh and stored in an oven to prevent moisture prior to use.

5.2.2. Full Cell Pellet Preparation and Cold Sintering

A set of experiments was undertaken to evaluate the effects of the cold sintering parameters. The formerly prepared electrolyte powders were mixed with different quantities of deionized water up to 10 %wt., then manually ground using a mortar-pestle. Anode and cathode powders were not subject to any moisture.

The anode, wetted electrolyte, and cathode powders (0.2 gr from each) were transferred into a steel die with a diameter of 15 mm in an order as shown in **Figure 5.2** and then uniaxially pressed using pressures ranging from 75 to 600 MPa. In order to secure better current collection, Ag powders were co-cold sintered at the surface of both side of the cell.

The final cell before measurement was 5 layered structure as Ag-Anode-Electrolyte-Cathode-Ag fabricated in one step without further processing except connecting Ag wires with Ceramobond ceramic adhesive. Filter paper was also used for two reasons: first, to serve as a spacer preventing sticking, and secondly (as a form with a hole in the middle), for providing a specific area for the Ag powders on top of the anode and

cathode electrodes. A heater jacket was wrapped around the die while pressing, and the temperature was ramped up at ~ 20 °C/min rate and held isothermally for 30 min.

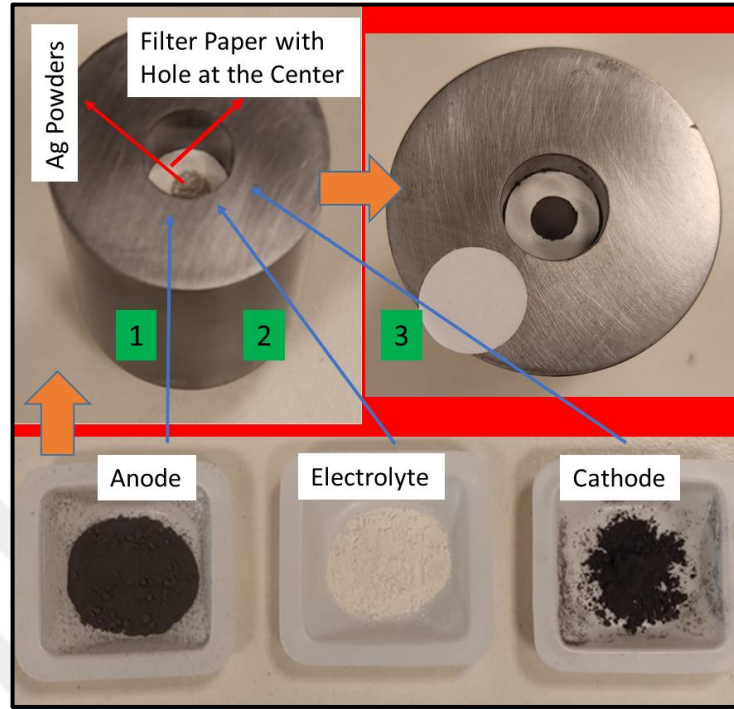


Figure 5.2: Schematic of preparation of 5 layered structure for full cells.

For the sake of comparison, same 5 layered structured samples, considered as reference samples, were just dry pressed at room temperature without water at 150 MPa for 2 minutes. The reference samples were sintered at 700 °C for 2 hours in a conventional furnace. In order to evaluate the effect of cold sintering on structure and conductivity, cold-sintered samples were compared to those prepared by conventional routine.

5.2.3. Characterization

X-ray diffraction (XRD) patterns were recorded on the pellets at room temperature using a Rigaku D-Max 2200, Japan diffractometer with a Cu anode X-ray source ($\lambda_{\text{Cu}} K_{\alpha 1} = 1.5406 \text{ \AA}$) in the $20\text{-}70^\circ 2\theta$ range with a step size of 0.02° and a time per step of 1 s. The microstructure and morphology of composite samples was investigated by scanning electron microscopy (SEM, Philips XL 30 SFE, Eindhoven, Netherlands). Sample densities were calculated by measuring the mass and the geometric dimensions of the pellets. Theoretical densities of anode, electrolyte, and cathode were calculated by the mixture rule of composite and determined as 5.8 gr/cm^3 , 5.28 gr/cm^3 and 5.28

gr/cm³, respectively. Transmission Electron Microscopy (TEM) was used to investigate the interface between SDC and Na₂CO₃.

5.2.4. Electrochemical Measurements

Electrochemical impedance spectroscopy (EIS) was performed using a frequency response analyzer Wonatech Zive MP2 Potentiostat in the frequency range of 1 MHz - 0.05 Hz. Measurements were recorded at OCP (Open Circuit Voltage, zero bias voltage), with a perturbation signal amplitude of 10 mV, under humidified atmospheres. Measurements were done from 500 to 600 °C every 50 °C with a stabilization time of 10 min. The gas humidification was provided by bubbling gas through water at room temperature.

Cold sintered cells in a form of Ag|SDC-Na₂CO₃/NiO| SDC-Na₂CO₃| SDC-Na₂CO₃/LNO|Ag were used for fuel cell characterisation. S/A/E/C/S where S: silver paste, A (Anode): SDC-Na₂CO₃/NiO, E (electrolyte): SDC-Na₂CO₃, and C (cathode): SDC-Na₂CO₃/LNO. Cells were 15 mm in diameter and around 0.6 mm in thickness (anode thickness 0.20 mm, electrolyte 0.20 mm and cathode 0.20 mm). The cell performance was measured at 550 and 600 °C and H₂ gas was used as a fuel with a flow rate of 100 ml/min at atmospheric pressure, and air was used as an oxidant.

5.3. Results and Discussion

5.3.1. Full Cell Fabrication via CSP

Prior to the fabrication of full cell samples, the composite electrolyte-NiO anode (60 % by volume) and the composite electrolyte-LNO cathode (50 % by volume) underwent cold sintering under identical circumstances as the electrolyte manufacture, with the objective of achieving densities greater than 70 %. The anode and cathode densities were calculated to be 75 % and 78 %, respectively, after a separate cold sintering process without any transient liquid utilised. The full cells were effectively constructed in a single step in a "sandwich" configuration of "anode-electrolyte-cathode," by cold sintering at 200 °C and 450 MPa for 30 minutes.

5.3.2. Phase Analysis

XRD patterns of anode (NiO-SDC20N) and cathode (LNO-SDC20N) samples are given in **Figure 5.3**.

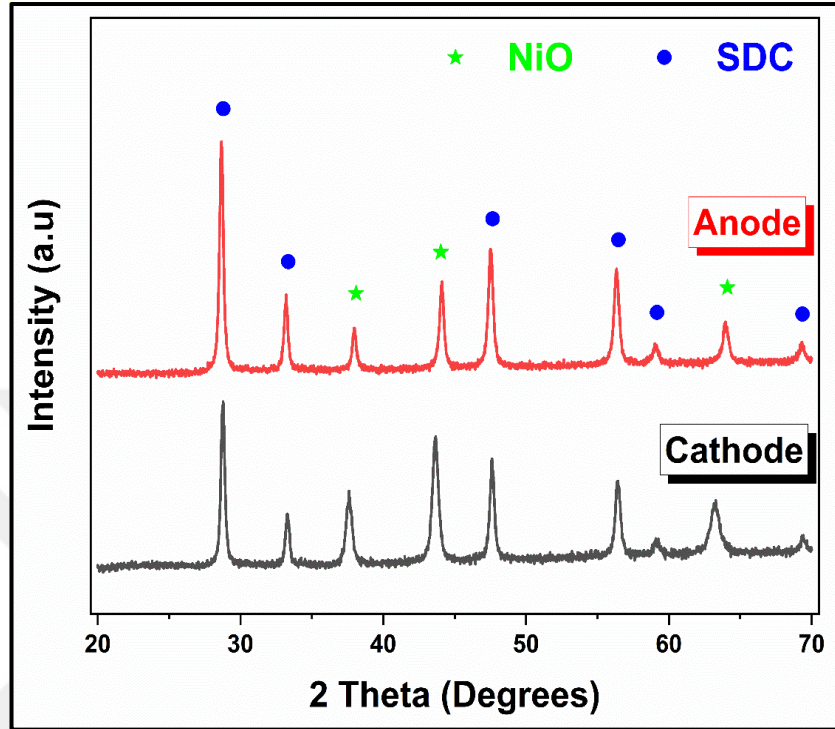


Figure 5.3: XRD patterns of anode and cathode electrodes.

The main diffraction peaks were associated to the SDC and NiO phases. There were no detected peaks related to the Na_2CO_3 phases.

5.3.3. Microstructure Analysis

Figure 5.4 demonstrates SEM images of cold sintered fuel cells in one step at 200 °C. The most significant aspect of this image is there is no separation at the interface between the anode and the electrolyte, as well as between the cathode and the electrolyte. The anode-electrolyte-cathode was sintered as a singular entity at 200 °C in a single step, reaffirming that the layered structures were successfully produced with the cold sintering process [82, 236]. A smooth and continuous contact was achieved between the electrolyte, anode, and cathode using the cold sintering technique. The comparatively dark areas seen in the electrolyte phase were identified as sodium carbonate-rich regions, originating from water with high amounts of dissolved sodium carbonate, as explained in previous chapters.

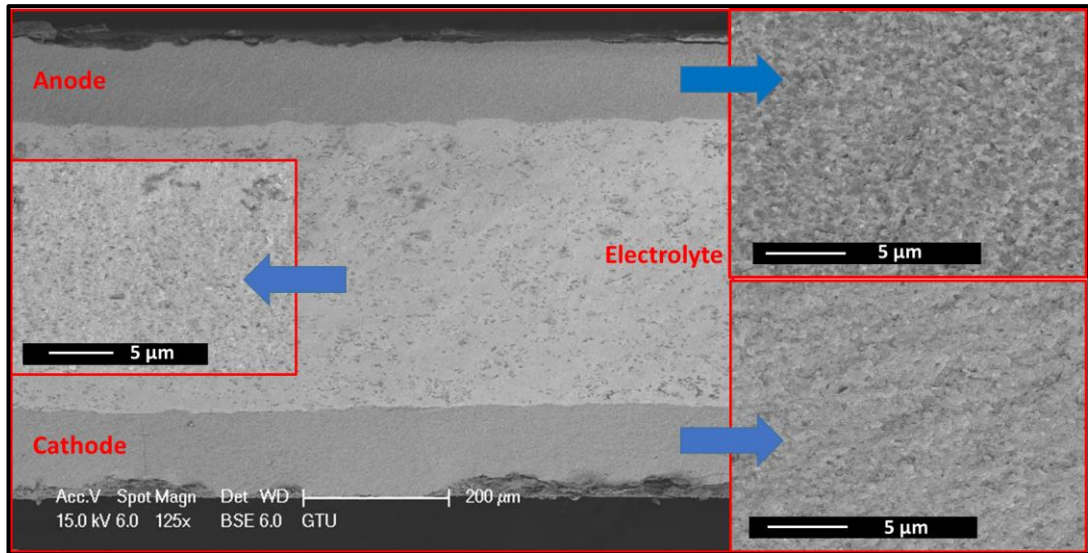


Figure 5.4: SEM images of cold sintered full cell in a single step at 200 °C.

5.3.4. Electrical Analysis

The electrochemical performances of full cells produced with CSP in the form of anode (NiO-electrolyte) – electrolyte (SDC- Na_2CO_3) – cathode (LNO-electrolyte) were measured.

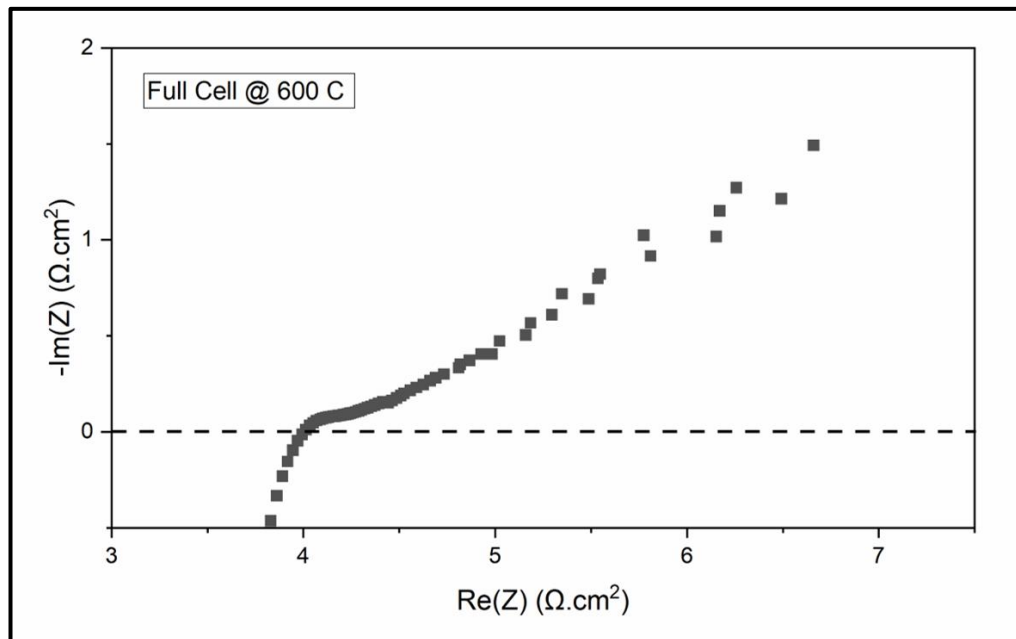


Figure 5.5: Nyquist plots of full cell, produced without pore formers at 600 °C.

The first full cell performance studies revealed that the largest resistance of the cell comes from the electrodes (anode and cathode), as shown in **Figure 5.5**. In this context, firstly, anode-electrolyte-anode and cathode-electrolyte-cathode symmetric half cells were produced, and their performances were examined. Nyquist curves of the anode-electrolyte-anode symmetrical half cell were examined, and it was observed that both ohmic and polarization resistances were quite high; see **Figure 5.6**.

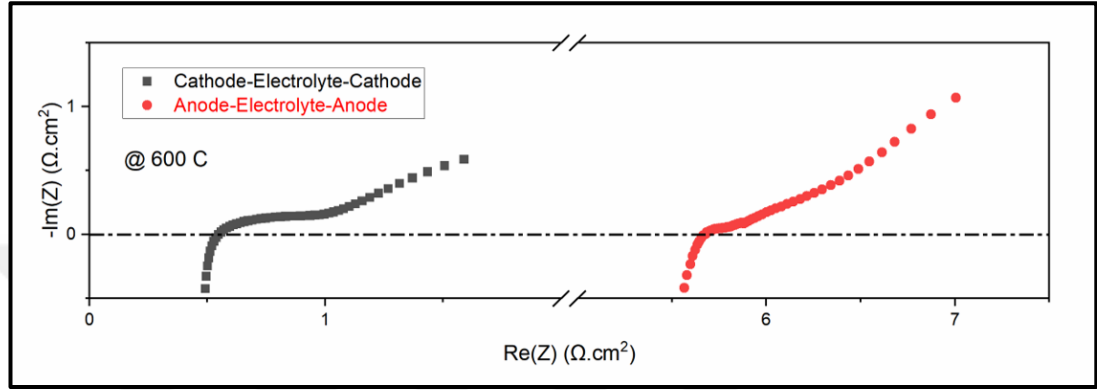


Figure 5.6: Nyquist plots of cold sintered symmetric half cells of cathode-electrolyte-cathode and anode-electrolyte-anode samples measured at 600 °C [Cathode half cell under ambient air and anode half cell under H₂ % 10 – Ar % 90 gas mixture].

It is thought that the difference in ohmic resistance with the full cell is probably due to the fact that the NiO in the anode is not completely reduced and the cell behaves like a thick cell with low density. For this reason, only the anode was produced in bulk, and its impedance spectroscopy was examined. It has been observed that the total resistance of the bulk anode improves over time in the reducing atmosphere. This case explains that the anode could not be completely reduced. It was thought that there may be two reasons. Firstly, the reduction may not be complete because the anode is very dense and does not allow gas flow. Secondly, since the amount of NiO in the anode is below the percolation limit, it may not be able to establish a three-dimensional (3D) contact in the bulk. In order to solve the reduction problem of the anode, the amount of NiO in the anode was first increased from 50 % to 65 % and then to 80 % by volume in order to provide the percolation limit. The samples were produced with CSP and subjected to reduction in H₂ atmosphere at 600 °C for 2 hours and cooled again in H₂ atmosphere. Then, it was checked whether contact/short circuit could be detected on the surfaces of the samples with the help of a voltmeter. While anodes containing 50 % and 65 % NiO by volume did not give contact, contact was obtained from samples

containing 80 % NiO. For this reason, subsequent studies were continued with anodes containing 80 % NiO by volume.

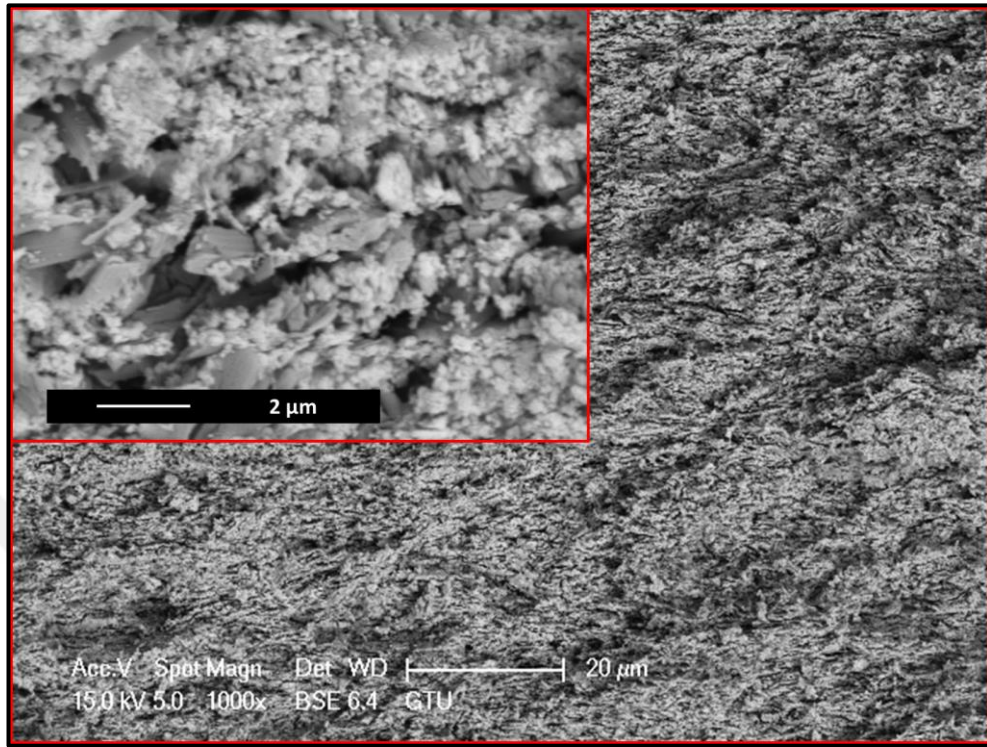


Figure 5.7. SEM image taken from the cracked surface of the anode containing 20 % graphite by volume, after the graphite was evaporated at 600 °C for 2 hours and then the samples were reduced in the hydrogen environment.

To increase the performance of anodes and cathodes, first graphite and then starch were used as pore formers. In this way, it is aimed to increase catalytic activity and increase full cell performance by facilitating gas diffusion. In this context, graphite was tried first. Anodes and cathodes, to which 20 % graphite by volume was added, were mixed in a ball mill for 24 hours to achieve a microstructure with homogeneous porosity. **Figure 5.7** shows the microstructure after evaporating the graphite. When the microstructure was examined, the targeted homogeneous porosity structure was obtained, but the performance measurements made with these samples could not be taken due to the removal of the current collector silver on the surface, which is estimated to have formed during the evaporation of the graphite. In addition, as the graphite moved away from the structure, it weakened the samples structurally and caused the samples to break easily. For this reason, starch $(C_6H_{10}O_5)_n$ of technical purity, which is thought to volatilize at lower temperatures and have a binding effect on the structure, was used.

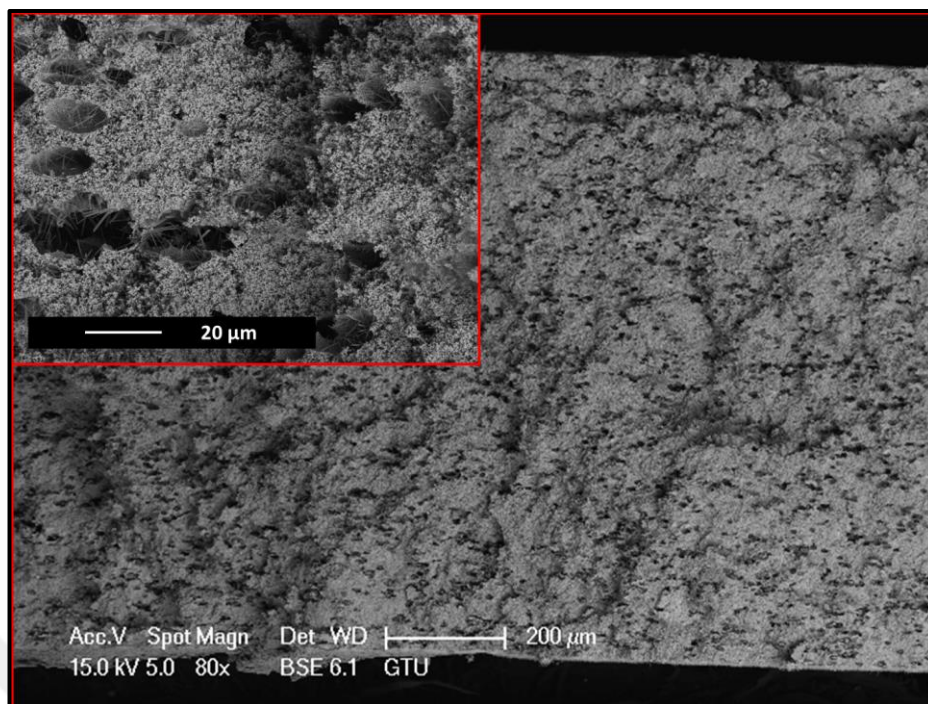


Figure 5.8. SEM image taken from the cracked surface of the anode containing 20 % starch by volume, where the starch was evaporated at 600 °C for 2 hours and then reduced in the H₂ atmosphere.

The anodes and cathodes, to which 20 % starch by volume was added, were mixed in a ball mill for 24 hours to achieve a microstructure with homogeneous porosity. **Figure 5.8** shows the microstructure after starch evaporation. When the microstructure was examined, the targeted homogeneous porosity structure was obtained. Unlike graphite, the porosities are nearly 10 times larger. Additionally, it was observed that the samples did not lose their structural strength as in graphite. For this reason, it was decided to use starch as a pore former.

Full cells were produced using 20% by volume starch as a pore former with good structure. However, this time, separations were observed at the electrolyte-anode and electrolyte-cathode interfaces in the majority of the samples after CSP. It has been determined that the majority of separations occur at the anode-electrolyte interface, **Figure 5.9a-b**. Performance measurements were attempted to be taken from samples in which there was no separation after CSP. However, these samples could not protect their integrity after reaching measurement temperatures. It is thought that the reason for the separations is the local stresses caused by the pore formers moving away from the structure and possible expansion differences at the electrolyte-anode and electrolyte-cathode interfaces with temperature. In addition, it is thought that the

separations generally occur at the electrolyte-anode interface, which may be due to the fact that the anode contains a high amount of NiO, such as 80 %. When high amounts of NiO transform into Ni in a reducing environment, it is likely that it may create tensile incompatibilities with the electrolyte due to its metallic character.

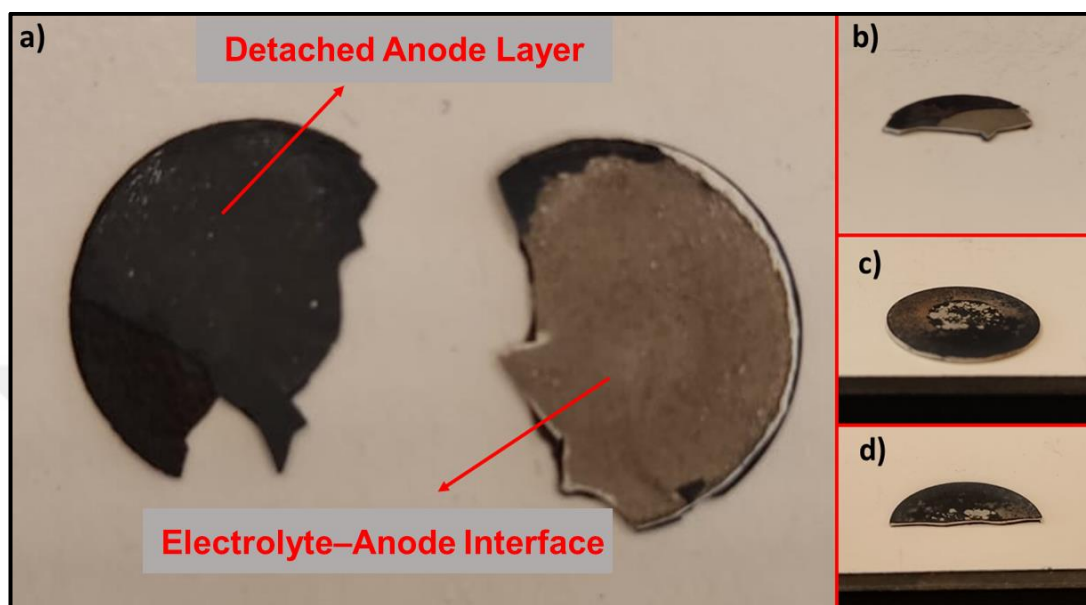


Figure 5.9 SEM images of full cells produced using starch as a pore former after CSP; a-b) Samples with interlayer separation after CSP, c-d) without separation.

The performances of complete cells containing anode-cathode with 30 and 40 % vol. pore formers, respectively, produced in a single step with CSP, were measured. The impedance results obtained at 600 °C are given in **Figure 5.10**. Nyquist plots show that both ohmic and total resistances are not significantly enhanced when compared to full cells, with and without pore formers.

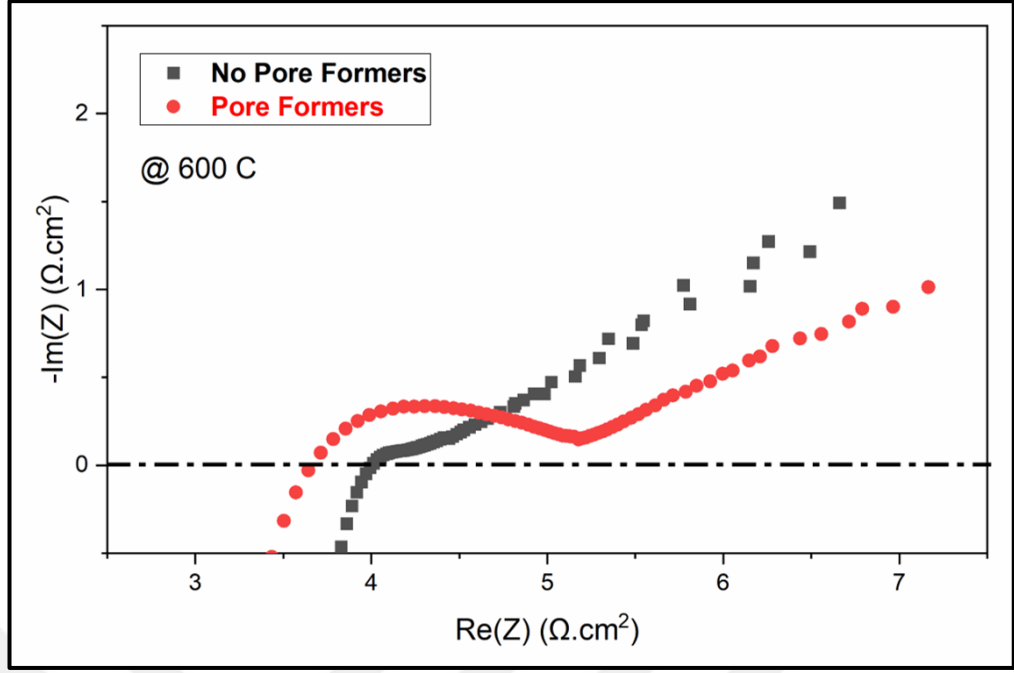
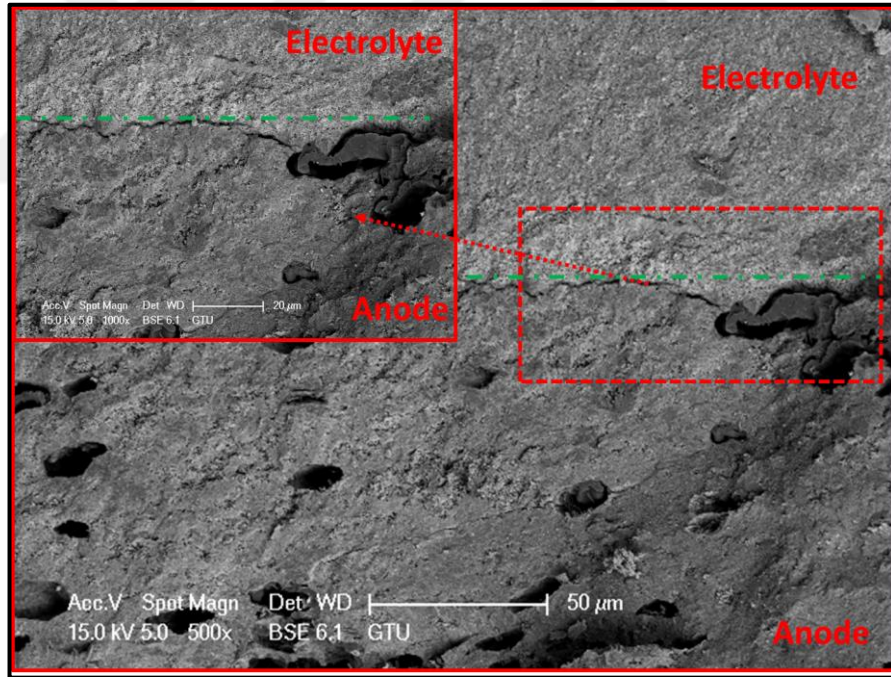


Figure 5.10: Nyquist plots of full cells produced with electrodes with and without pore formers, taken at temperatures between 600 °C.



Şekil 5.11. SEM image taken from the electrolyte-anode interface of a full cell that was heat treated (not reduced) at 600 °C for 1 hour in air atmosphere.

SEM images taken from the samples examined in this context are given in **Figure 5.11**. When the SEM images are examined, it is clearly seen that cracks have formed at the electrolyte-anode interface.

It should be noted that these SEM images were taken after only the pore formers were evaporated in the air at 600 °C, and no reduction was made in the hydrogen environment. In reduced samples, these cracks are large enough to disrupt the structural integrity of the sample, making microstructural characterization of the samples difficult after measurement.

High resistances due to interfacial cracks were observed in the impedance analysis of full cells produced with electrodes containing pore formers (anode-cathode). IV measurements taken at 600 °C are given in **Figure 5.12**. This effect is clearly seen in the IV measurements. Maximum power density at 600 °C was measured as 24 mW/cm² which is very low when compared to literature.

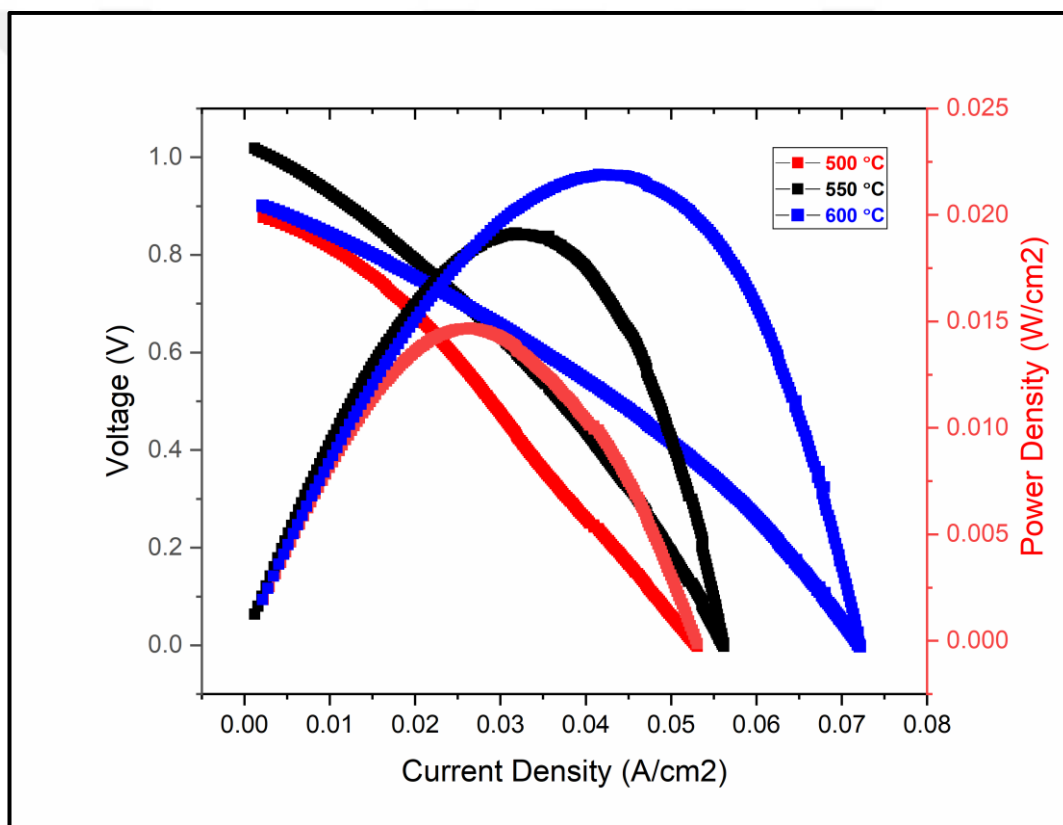


Figure 5.12. IV measurements of full cells produced with electrodes using pore formers, taken at temperatures between 500-600 °C.

Microstructural enhancements have been achieved in anode and cathode optimizations aimed at improving full cell performances, but it has been observed that these cause new problems (separation at the electrolyte-anode and electrolyte-cathode interfaces) in the full cell combination.

5.3.5. Investigation of the Low Cell Performance

In order to determine the root causes of the low electrochemical performance observed in the cold-sintered fuel cells, an alternative measurement system was employed. Measurements obtained using the newly adopted setup (Fiaxell) for symmetrical anode half-cells showed significantly improved results compared to those previously recorded with the earlier setup (**Figure 5.13 vs. Figure 5.6**).

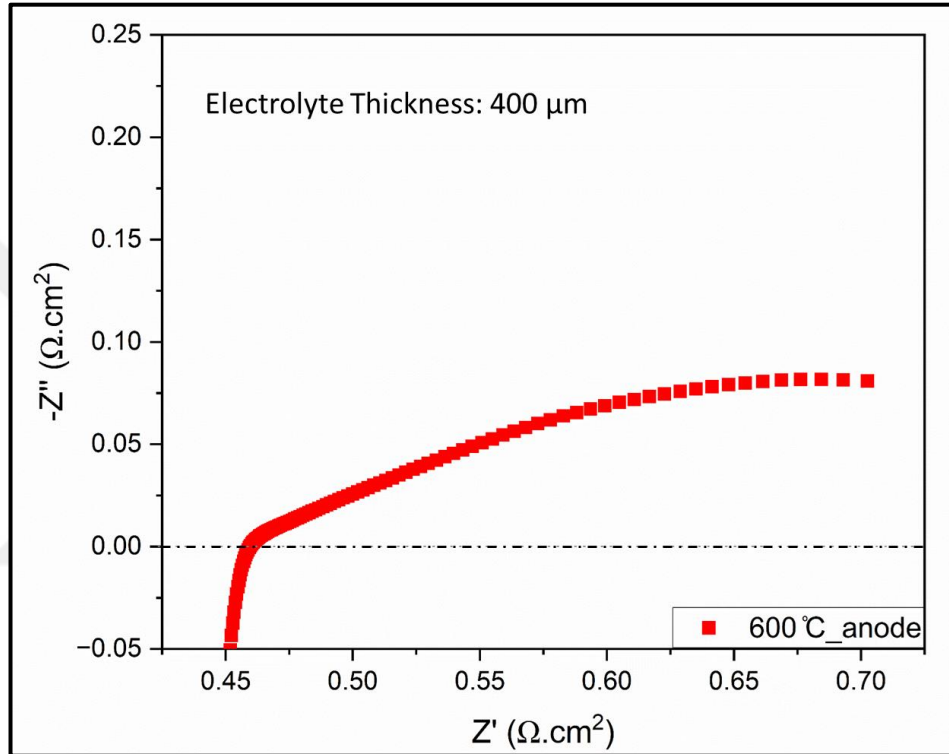


Figure 5.13. Nyquist plots of anode symmetrical half cell taken at temperature 600 °C.

In the earlier configuration, the test furnace had a relatively large internal volume ($\sim 6400 \text{ cm}^3$), and the reducing atmosphere was composed of a diluted 90 % Ar – 10% H_2 gas mixture. It is therefore likely that the insufficient hydrogen partial pressure in the chamber may have hindered the full reduction of NiO in the anode, thereby increasing polarization resistance. In contrast, the Fiaxel setup delivered pure H_2 directly to the sample surface, likely enabling more effective reduction of the NiO phase and resulting in markedly lower polarization resistance.

These updated measurements yielded two critical insights. First, the ohmic resistance was significantly lower than previously reported, with values around $0.45 \text{ } \Omega.\text{cm}^2$, suggesting that the conductivity of the electrolyte is substantially enhanced under

reducing atmospheres compared to ambient air. Indeed, the conductivity approached 0.1 S/cm, which aligns with values reported for highly conductive co-ionic systems such as SDC-carbonate nanocomposites.

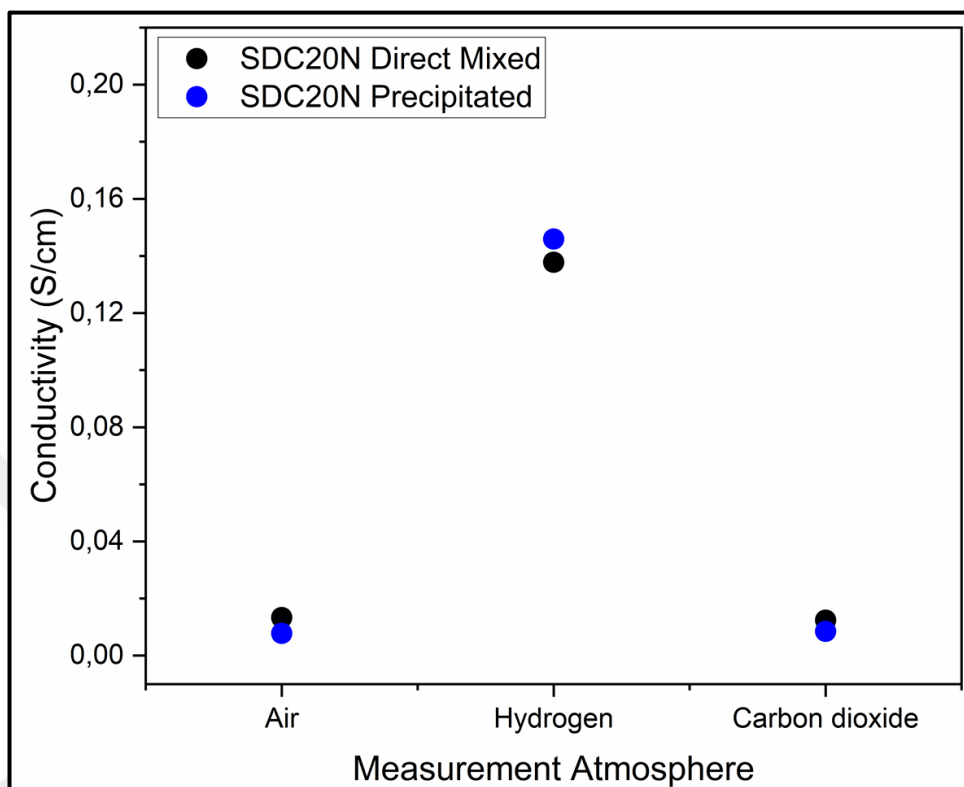


Figure 5.14. Conductivity values at 600 °C of SDC20N samples fabricated with two different methods, direct mixing and precipitation.

Following the conductivity value approaching 0.1 S/cm obtained from the anode/electrolyte/anode symmetric half-cell under a reducing atmosphere (**Figure 5.13**), further measurements were conducted to compare the conductivity of the electrolyte under different atmospheric conditions (**Figure 5.14**). When measured in an air atmosphere using a Ag/electrolyte/Ag configuration, the conductivity values were noticeably lower than those reported in Chapter 4 for cathode/electrolyte/cathode symmetric cells. As previously discussed, this discrepancy is attributed to a contact issue; the silver electrodes tend to detach from the electrolyte surface during measurement in air, leading to loss of current collection.

In contrast, the same electrolyte samples, when measured in a reducing atmosphere, exhibited conductivity values that were up to ten times higher. This exceptional enhancement strongly supports the hypothesis that the SDC-carbonate composite

behaves as a robust proton conductor under reducing conditions. The dramatic increase in conductivity indicates the presence of a proton-dominant co-ionic conduction mechanism, likely facilitated by the ceramic–carbonate interface, which becomes highly active in a hydrogen atmosphere.

Second, the values suggested that the major contribution to polarization resistance in the full cell does not originate from the anode. When comparing symmetrical impedance measurements of the anode and cathode (**Figure 5.6 vs. Figure 5.13**), the cathode appears to be the dominant source of polarization. This led to the exploration of alternative cathode materials. Given that the conductivity of SDC- Na_2CO_3 composites increases by up to an order of magnitude in reducing atmospheres, implying proton-dominant transport behaviour cathode materials common in proton-conducting fuel cells, such as BSCF ($\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$) and BCFZY ($\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$), were investigated.

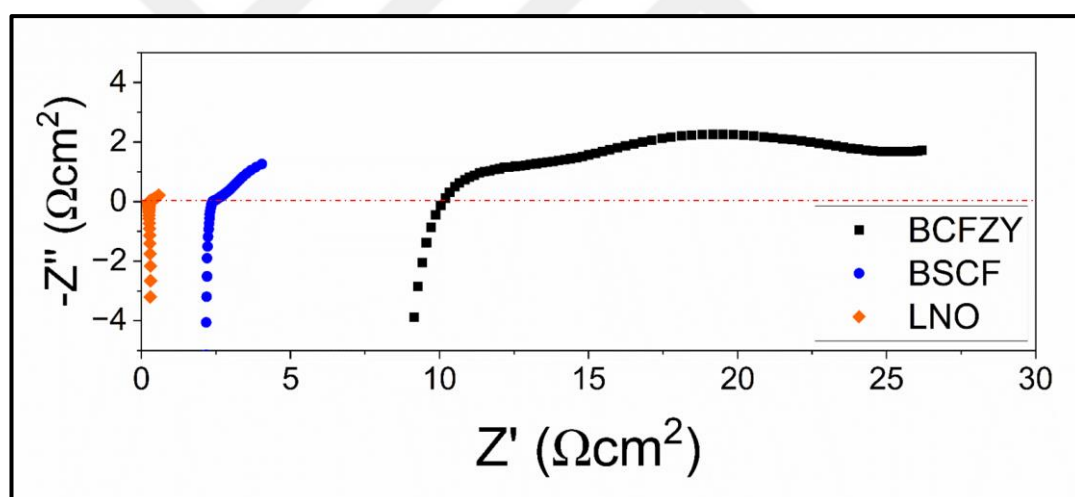


Figure 5.15. Comparison of Nyquist plots of cathode symmetrical half cells taken at a temperature of 600 °C.

These alternative cathodes were mixed with the SDC-carbonate composite (60 %vol. electrolyte) and tested in symmetrical cathode half-cell configurations. However, the resulting impedance spectra (**Figure 5.15**) revealed that their polarization resistances were substantially higher than those observed for the original lithiated NiO (LNO)/SDC- Na_2CO_3 system. Therefore, the LNO-based composite cathode was retained for full-cell tests due to its superior performance under the tested conditions. In the literature, such high ionic conductivities (greater than 0.1 S/cm) are often

attributed to a superionic conduction pathway at the ceramic–carbonate interface [21, 212, 213]. This pathway is believed to arise from the formation of an amorphous carbonate shell around the ceramic particles, resulting in a core-shell microstructure that facilitates co-ionic (O^{2-}/H^+) transport [207, 215-219]. Numerous studies have reported that this type of structure is typically achieved through co-precipitation or direct precipitation synthesis methods, which promote intimate mixing and interfacial bonding between the ceramic and carbonate phases [33, 294-297].

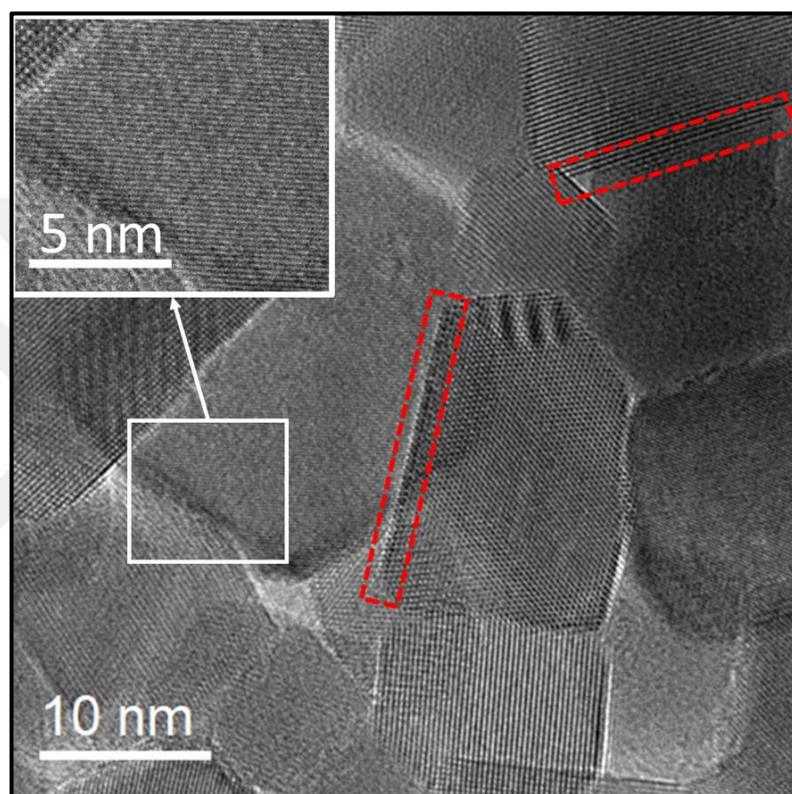


Figure 5.16. TEM image of SDC20N nanocomposite powders fabricated with the precipitation method.

In the present work, however, the SDC- Na_2CO_3 nanocomposite powders were simply prepared by direct mechanical mixing of commercial SDC and Na_2CO_3 powders using ball milling. To allow meaningful comparison, the electrical conductivities of nanocomposites produced by both the precipitation route (as reported in the literature) and the ball-milled route (this study) were measured under various atmospheric conditions at 600 °C (**Figure 5.14**). Remarkably, the results showed that both types of powders exhibited comparable ionic conductivities, suggesting that the formation of an amorphous carbonate shell may not be a strict requirement for achieving high performance.

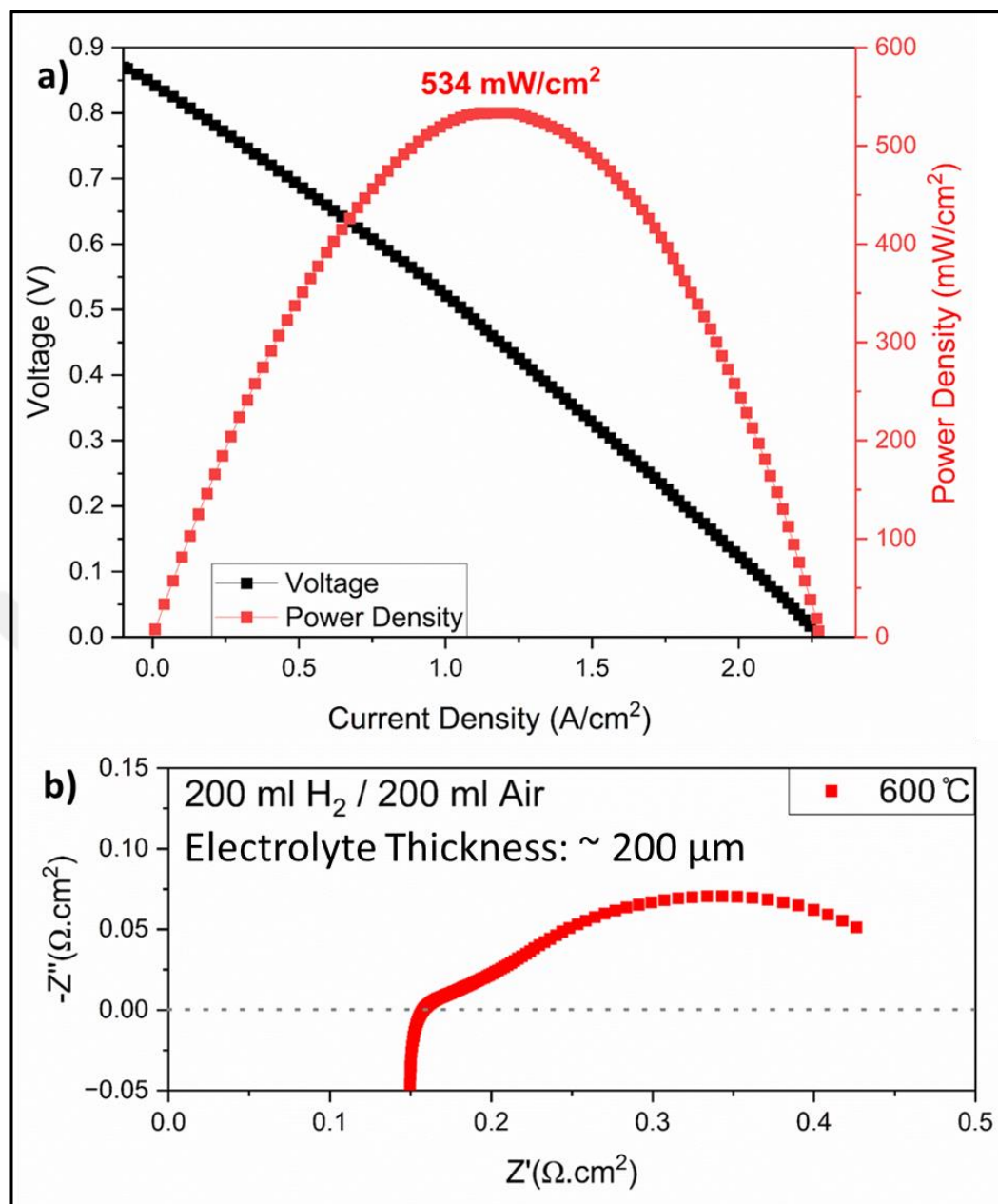


Figure 5.17. a) IV and b) Nyquist plot measurements of fuel cell taken at a temperature of 600 °C.

To further investigate this, TEM analyses were performed on the nanocomposite powders to detect the presence of an amorphous carbonate layer at the ceramic surface, previously suggested as the key factor enabling the superionic pathway [33, 298-300].

However, as shown in **Figure 5.16**, the TEM results did not reveal any clear evidence of an amorphous interfacial layer, suggesting that high conductivity in these composites may instead arise from effective phase connectivity and interfacial percolation achieved during cold sintering, rather than from structural features like

core-shell structure. Electrochemical performance of the fabricated fuel cells was evaluated using I-V and impedance spectroscopy measurements. **Figure 5.17a** displays the current-voltage (I-V) and power density characteristics of a full cell comprising a cathode/SDC–Na₂CO₃/anode configuration tested at 600 °C.

The cell achieved a peak power density of 534 mW cm⁻², indicating efficient ionic transport through the nanocomposite electrolyte. The voltage is relatively low compared to similar cells. It is probably because of the measurement setup, which is non-sealed. The bell-shaped power density curve highlights the optimal operating range of the cell, with minimal internal resistive losses near the peak. The achieved current density is quite comparable with the literature [295, 301-303].

Complementary electrochemical impedance spectroscopy (EIS) data is shown in **Figure 5.17b**, providing insights into the interfacial and bulk resistances under fuel cell operating conditions (200 ml min⁻¹ H₂ / 200 ml min⁻¹ air). The Nyquist plot reveals a well-defined semicircular arc, with a total polarization resistance below 0.4 Ω.cm², further supporting the high-performance nature of the cell. The high-frequency intercept corresponds to the ohmic resistance of 0.15 Ω.cm² indicating 0.13 S/cm conductivity with the 200 μm electrolyte thickness, dominated by the electrolyte and contact contributions, while the arc represents the polarization resistance arising from electrode processes. The achieved conductivity is very high and well comparable with the data in the literature [33, 300, 302, 304]. The combination of high power output and low impedance confirms the effectiveness of the cold-sintered SDC–Na₂CO₃ nanocomposite as a promising co-ionic conductor for intermediate-temperature solid oxide fuel cells.

5.3.6. Conclusion

In this study, a novel approach to fabricate solid oxide fuel cells in a single step via the cold sintering process at 200 °C was demonstrated using a ceria-sodium carbonate (SDC–Na₂CO₃) nanocomposite as the electrolyte. The results confirm that CSP is not only capable of producing highly dense electrolyte layers but also enables direct integration of anode and cathode layers without the need for high-temperature post-

sintering, thus significantly reducing energy consumption and preserving nanoscale microstructures.

Electrochemical characterizations revealed promising performance, with the best full cell reaching a peak power density of 534 mW.cm^{-2} at 600°C and a total polarization resistance below $0.4 \Omega.\text{cm}^2$. Impedance spectroscopy further indicated that the electrolyte exhibited a high ionic conductivity of $\sim 0.13 \text{ S/cm}$, attributed to co-ionic transport pathways at the ceramic-carbonate interface. Comparative measurements under different atmospheres confirmed that conductivity increased by up to an order of magnitude in reducing conditions, consistent with proton-dominated conduction mechanisms.

Although improvements in porosity and electrode microstructure were achieved through pore former optimization, mechanical and interfacial challenges, such as delamination and cracking at high NiO content, emerged as limitations. Moreover, no amorphous carbonate shell was detected via TEM in the composites, suggesting that enhanced conductivity can be achieved without core-shell structures, likely due to effective phase connectivity and interfacial contact promoted by CSP.

Overall, this work highlights the feasibility of single-step CSP fabrication of complete fuel cells with high performance and structural integrity and positions SDC- Na_2CO_3 nanocomposites as a viable co-ionic electrolyte system for intermediate-temperature SOFCs. Further advancements in cathode-electrolyte compatibility and optimised setup design may enable even greater performance and commercial applicability.

6. CHAPTER SIX: FUTURE WORK

6.1. General Results and Recommendations

This study demonstrated that the Cold Sintering Process (CSP) is a viable and highly effective method for fabricating high-density SDC- Na_2CO_3 nanocomposite electrolytes at temperatures significantly lower than those used in conventional sintering. Relative densities of $\geq 97\%$ were achieved at just $200\text{ }^\circ\text{C}$, addressing one of the most critical limitations in the fabrication of ceria-carbonate electrolytes. Furthermore, the low processing temperature prevented grain coarsening and helped maintain the nanoscale structure of the ceramic phase, maximizing the interfacial area between SDC and the carbonate phase. This enhancement of the ceramic-carbonate interface is considered to play a key role in the observed conductivity improvements.

Compositional optimization revealed that 20 %wt. Na_2CO_3 content offered the most balanced performance, providing sufficient carbonate phase continuity while preserving the mechanical and microstructural integrity of the electrolyte. Transient liquids such as deionized water and ethylene glycol were used to further promote densification during CSP, and the method of application, whether via petri holder or mortar mixing, was shown to have a significant influence on both microstructure and conductivity. In half-cell tests with a cathode/electrolyte/cathode configuration, the electrolyte with 20 %wt. carbonate exhibited an impressive ionic conductivity of 68 mS/cm at $600\text{ }^\circ\text{C}$. Under reducing conditions (H_2 atmosphere), this value further increased to 0.13 S/cm , indicating the potential of the CSP-fabricated electrolytes for real SOFC environments.

A major contribution of this work is the successful single-step fabrication of full SOFC cells via CSP. By co-sintering the anode, electrolyte, and cathode layers in one process at $200\text{ }^\circ\text{C}$ and 450 MPa , the need for sequential sintering or post-assembly treatments was eliminated. The resulting integrated interface between cell components reduced processing complexity and showed good electrochemical integrity. Electrochemical characterizations of the full cells yielded a maximum power density of 534 mW/cm^2 at $600\text{ }^\circ\text{C}$.

Further optimization of the anode and cathode layers revealed that although microstructural tailoring such as the use of graphite or starch pore formers improved electrode porosity and gas diffusion, it also introduced mechanical challenges like delamination at the electrode-electrolyte interfaces.

In light of these observations, one recommended strategy for enhancing full cell performance is to develop an electrolyte-supported structure. This would involve depositing a thin anode layer by spray coating onto a robust, dense electrolyte substrate, followed by CSP and final cathode application using prepared or commercial ink. This configuration could reduce the thicknesses of both the anode and cathode layers below 10 μm , minimizing the polarization losses and thereby increasing overall power output.

In conclusion, the cold sintering process shows great promise for low-temperature fabrication of nanocomposite SOFC electrolytes and integrated full cells. Nevertheless, future studies should focus on refining electrode formulations, improving interfacial bonding, and exploring scale-up strategies for industrial application. The methodology and findings of this research pave the way for more energy-efficient, cost-effective, and high-performance SOFC systems.

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BIOGRAPHY

Murat Murutoğlu received his Bachelor of Science degree in Metallurgical and Materials Engineering from Sakarya University in Spring 2012, and his Master of Science degree in Materials Science and Engineering from Gebze Technical University in Spring 2018. In the same year, he began his Ph.D. studies in Materials Science and Engineering at Gebze Technical University.

During his Ph.D. studies, he also engaged in international research activities, conducting visits to both Gdańsk University of Technology and Tampere University. At Gdańsk University of Technology, through the Erasmus mobility program, he worked on spray coating and infiltration techniques. He later visited Tampere University twice: first under the Erasmus program, where his research focused on metal-supported and proton-conductor solid oxide fuel cells (PC-SOFCs), and then through a European Ceramic Society scholarship, where he carried out research on the cold sintering of PC-SOFCs.

His research has resulted in several publications in peer-reviewed journals, covering a wide range of studies in the field of cold sintering process and solid oxide fuel cells.