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YSZ/NiO membranes manufactured by aqueous tape casting and freeze drying

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YSZ/NiO membranes manufactured by aqueous tape casting and freeze drying

Master's dissertation submitted to the Graduate Program in Materials Science and Engineering of the Federal University of Santa Catarina as a partial requirement for obtaining a master's degree in ceramic materials.

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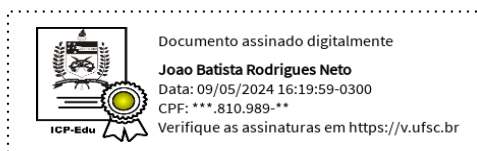
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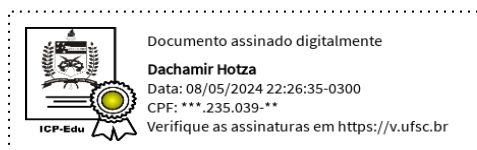
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Coordenação do Programa de Pós-Graduação



Prof. Dachamir Hotza, Dr.
Orientador

Florianópolis, 2024.

To my dear grandmother,

Neilde

and to my beloved parents,

Dagoberto e Mônica.

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*“Science is just a way to read a universe
written by God.”*

(Bruno Assis da Rocha)

ABSTRACT

The present work aims to develop, investigate, and characterize a processing route for anode-supported SOFC components manufacturing, particularly, electrolyte, functional, and structural anode. Combining aqueous tape casting and freeze drying, it was possible to obtain thin and flexible green tapes, while generating highly directional pores within structural anodes. Different casting techniques were also tested, such as screen printing and manual tape casting. The suspensions were assessed by their rheological behavior, comparing the effects of varying composition, reaching a pseudoplastic behavior. Freeze-drying was performed with the aid of liquid nitrogen to promote fast freezing. However, the freezing velocity was so high that the directional pores were not perfectly formed. A different freezing condition was also tested, at a lower freezing speed, which provided a better result. The green tapes were evaluated by their morphological aspects, aiming for flexible, resistant, and defect-free tapes. A new delamination technique was developed to separate the tapes from the carrier film, by using stearic acid. As a result, the tapes were much more easily removed, when compared to using silicone spray. The tapes were joined by vacuum assembling, which provided a good bond, thus, dismissing the use of lamination techniques. Finally, the assembled tapes were debinded and sintered by using a constraining technique, which led to their breakage. SEM images were taken to assess pores morphology, assembling quality, and thickness of the tapes. To obtain one of the raw materials for anode manufacturing, nickel oxide was synthesized by sol-gel route, obtaining a highly crystalline powder, as shown by XRD results.

Keywords: tape casting; freeze drying; solid oxide fuel cell; aqueous processing.

RESUMO

O presente trabalho tem como objetivo desenvolver, investigar e caracterizar uma rota de processamento para a fabricação de componentes de SOFC suportadas no ânodo, especialmente o eletrólito, o ânodo funcional e o ânodo estrutural. Combinando colagem de fita aquosa e liofilização, foi possível obter fitas verdes finas e flexíveis e, ao mesmo tempo, gerar poros altamente direcionados nos ânodos estruturais. Também foram testadas diferentes técnicas de colagem, como impressão em tela e colagem manual de fitas. As suspensões foram avaliadas por seu comportamento reológico, comparando os efeitos da variação da composição, chegando a um comportamento pseudoplástico. A liofilização foi realizada com o auxílio de nitrogênio líquido para promover o congelamento rápido. No entanto, a velocidade de congelamento foi tão alta que os poros direcionais não se formaram perfeitamente. Uma condição de congelamento diferente também foi testada, com uma velocidade de congelamento menor, o que proporcionou um resultado melhor. As fitas verdes foram avaliadas por seus aspectos morfológicos, com o objetivo de obter fitas flexíveis, resistentes e sem defeitos. Uma nova técnica de delaminação foi desenvolvida para separar as fitas do filme de suporte, usando ácido esteárico. Como resultado, as fitas foram removidas com muito mais facilidade, em comparação com o uso de spray de silicone. As fitas foram unidas por montagem a vácuo, o que proporcionou uma boa união, dispensando, assim, o uso de técnicas de laminação. Por fim, as fitas montadas tiveram seu material orgânico removido e foram sinterizadas por meio de uma técnica de contenção, o que levou à sua quebra. Foram feitas imagens de MEV para avaliar a morfologia dos poros, a qualidade da montagem e a espessura das fitas. Para obter uma das matérias-primas para a fabricação do ânodo, o óxido de níquel foi sintetizado pela rota sol-gel, obtendo-se um pó altamente cristalino, conforme demonstrado pelos resultados de DRX.

Palavras-chave: colagem de fita; liofilização; célula a combustível de óxido sólido; processamento aquoso.

RESUMO EXPANDIDO

Membranas de YSZ/NiO produzidas por colagem de fita aquosa e liofilização

Introdução

É amplamente conhecido que o uso de combustíveis fósseis traz vários impactos ambientais, incluindo o efeito estufa, a poluição do ar e da água, o uso extensivo da terra, a perturbação do habitat, a acidificação dos oceanos, o derretimento das geleiras, o aumento da temperatura global, os impactos negativos sobre a saúde e, finalmente, o esgotamento destes recursos naturais, uma vez que se trata de uma fonte de energia limitada. Uma alternativa para reduzir o uso de combustíveis fósseis foi o desenvolvimento de carros elétricos. A ideia é substituir os motores de combustão convencionais, que queimam combustíveis fósseis, por motores elétricos, que convertem a corrente elétrica fornecida por uma bateria, proporcionando, assim, movimento mecânico. Embora os carros elétricos possam percorrer centenas de quilômetros sem liberar gases nocivos, quando as baterias chegam ao fim de sua vida útil, seu conceito verde desaparece. Se forem descartadas em aterros sanitários, as baterias podem liberar substâncias problemáticas, inclusive metais pesados. Até mesmo a reciclagem é um desafio, pois pode ser custosa, perigosa e requer a infraestrutura e a tecnologia corretas para ser feita. Uma possível forma de evitar o uso de baterias enormes e ao mesmo tempo manter as vantagens sustentáveis dos veículos elétricos, é usar um dispositivo que gera eletricidade dentro do veículo. Esse tipo de tecnologia é chamado de tecnologia embarcada e permite o uso de baterias convencionais menores, já que não seria mais necessário armazenar grandes quantidades de energia. A tecnologia em questão é chamada de célula de combustível e, assim como em qualquer gerador de energia, um combustível é necessário para ser convertido em energia elétrica. Uma célula a combustível converte a energia química dentro de um combustível, como o hidrogênio ou hidrocarbonetos, diretamente em eletricidade. Entre os vários tipos de células a combustível, a célula a combustível de óxido sólido (SOFC), é uma candidata bastante estudada como tecnologia embarcada. As SOFCs demonstraram alta eficiência elétrica, com faixas entre 65% e 85%, além de poderem operar com uma grande variedade de combustíveis, incluindo hidrogênio, metano, biogás, etanol e outros hidrocarbonetos. Também apresenta baixas emissões de poluentes, de acordo com cada tipo de combustível, e tem operação silenciosa. Embora as SOFCs demonstrem ser a resposta definitiva para as preocupações ambientais causadas pelos veículos, seu uso em larga escala ainda é dificultado por alguns pontos fracos, como por exemplo, problemas relacionados à degradação de seus componentes, decorrente de sua alta temperatura de operação.

Objetivos

O escopo do presente trabalho está focado no desenvolvimento de uma nova rota de processamento que combina tape casting e montagem a vácuo, com liofilização, ao mesmo tempo em que investiga os efeitos da variação de alguns parâmetros de processamento, visando melhores propriedades morfológicas e mecânicas, o que consequentemente proporcionará maior vida útil à SOFC. O uso da montagem a vácuo visa a fixar as camadas da SOFC umas às outras, como eletrólito, ânodo

funcional e ânodo estrutural, preservando os poros do ânodo. Enquanto a liofilização visa investigar e comparar a geração de poros altamente direcionados no ânodo estrutural, contra o uso de formadores de poros, melhorando a difusão do etanol.

Metodologia

A síntese de óxido de níquel (II) empregou o método sol-gel. Inicialmente, a água foi aquecida a 70 °C, em seguida, o cloreto de níquel hexahidratado foi adicionado, dissolvido, e o pH ajustado para 12 com o uso de NaOH 1M. O gel resultante foi centrifugado, filtrado e lavado para remover o cloreto de sódio (subproduto). Em seguida foi seco a 110°C por 24 horas e cominuído manualmente. A calcinação foi realizada em dois patamares, 400°C e 900°C por 2 horas, produzindo óxido de níquel, sendo NiOx não estequiométrico (400°C), e NiO estequiométrico (900°C). O preparo das suspensões inicia-se com a mistura manual de dispersante e água deionizada, seguida pela adição do pó e esferas de zircônia em um pote de polipropileno. Em seguida, a mistura é dispersada em uma máquina de moagem excêntrica por 5 minutos. Posteriormente, o ligante, o surfactante e o antiespumante são adicionados sequencialmente com etapas de mistura independentes de 5 minutos, exceto pelo antiespumante, com uma mistura de 1 minuto. A suspensão é então posicionada em um dessecador a vácuo por 2 minutos a uma pressão negativa de 600 mmHg para remoção de bolhas. As suspensões foram caracterizadas por suas propriedades reológicas usando um viscosímetro Thermo HAAKE VT550, variando a taxa de cisalhamento de 0 a 1000 s⁻¹ com uma duração de análise de 180 s. Foram avaliados três métodos de conformação de fita: colagem de fita tradicional usando uma lâmina fixa com abertura de 200 µm e uma velocidade de filme transportador de 6 cm/min, serigrafia manual com um estêncil de 210 µm de espessura, e colagem de fita manual com uma lâmina móvel de aço inoxidável, com aberturas variáveis entre 200 – 1000 µm. Diferentes condições de superfície do filme carreador foram testadas para avaliar a facilidade de remoção da fita, sendo elas, Mylar padrão, revestido com silicone e revestido com ácido esteárico. As superfícies dos filmes foram preparadas da seguinte forma: padrão (limpa com etanol), revestida com silicone (aplicado e espalhado com spray de silicone), e revestida com ácido esteárico (ácido esteárico é derretido em uma placa térmica a 60 °C, e espalhado uniformemente sobre o filme, sendo em seguida solidificado por resfriamento natural). Todas as fitas foram secas ao ar, em temperatura ambiente (22 – 30 °C) e umidade de 70 – 75%. A liofilização foi realizada para gerar poros altamente direcionados. O equipamento utilizado foi da JJ Científica, do modelo LJJ. Foram realizadas duas rotas para comparar a taxa de congelamento, a espessura da fita e a presença de um gerador de poros. A primeira barbotina, sem gerador de poros, foi conformada com uma abertura de lâmina de 1 mm e colocada diretamente em um freezer a -80 °C, sobre uma base de acrílico para congelamento mais lento, por 7 horas. A segunda barbotina, com formador de poros, foi conformada com uma abertura de lâmina de 0,5 mm e imediatamente colocada em uma superfície metálica previamente resfriada com nitrogênio líquido a cerca de -195 °C, para congelamento rápido, e posteriormente, colocada dentro do freezer a -80 °C por 7 h. Em seguida, ambas as amostras foram colocadas dentro do liofilizador a -50 °C para aplicação de vácuo, com a liofilização sendo realizada por 24 h. A remoção do material orgânico contido nas fitas verdes individuais foi realizada em um forno a 600 °C por 1 h, com uma rampa de aquecimento de 1 °C/min, enquanto a sinterização contida foi realizada a 1430 °C por cerca de 4 h. Já para as fitas montadas, diferem-se apenas na remoção do material orgânico que se deu por 3h. A montagem a vácuo

das fitas foi realizada umedecendo a superfície das fitas com água deionizada, com a ajuda de um pincel, unindo-as e aplicando vácuo para garantir a remoção de qualquer ar preso entre as fitas.

Resultados e discussão

O hidróxido de níquel (II) precipitado, fez com que a viscosidade da solução aumentasse para o estado de gel, exigindo uma mudança da agitação magnética para a agitação por hélice. O óxido de níquel obtido demonstrou ser altamente cristalino, conforme demonstrado pelos resultados de DRX, apresentando um tamanho médio de partícula de 895 nm. As suspensões apresentaram comportamentos reológicos pseudoplásticos, o que é altamente desejável para colagem de fitas. Combinando a colagem aquosa de fitas e a liofilização, foi possível obter fitas verdes finas e flexíveis e, ao mesmo tempo, gerar poros altamente direcionados nos ânodos estruturais. Entretanto, para a rota com o uso de nitrogênio líquido, a velocidade de congelamento foi tão alta que os poros direcionais não se formaram perfeitamente. Por outro lado, um congelamento mais lento, proporcionou um resultado melhor. A nova técnica de delaminação com o uso de ácido esteárico foi um sucesso, sendo que as fitas foram removidas com muito mais facilidade, em comparação com o uso de spray de silicone. A montagem a vácuo proporcionou uma boa união das fitas, dispensando assim, o uso de técnicas de laminação (termoprensagem). Por fim, a remoção dos orgânicos e sinterização contida, resultou na quebra das fitas, que pode ter sido causada pela fragilidade do material cerâmico após a remoção dos orgânicos, ou pela diferença de coeficiente de expansão térmica das fitas, durante a sinterização.

Conclusões

A otimização do teor de aditivos em suspensões cerâmicas, como ligantes, plastificantes e surfactantes, deve ser acompanhada experimentalmente pela sua conformação, pois somente com a fita formada será possível afirmar se aquela composição foi boa. Por outro lado, os dispersantes podem ser otimizados por testes reológicos, sem a necessidade da colagem. As suspensões altamente viscosas muitas vezes podem ter problemas com bolhas remanescentes, e os métodos típicos para removê-las não são tão eficazes. Recomenda-se dar preferência a suspensões de viscosidade moderada. Caso não seja possível resolver o problema das bolhas remanescentes, pode-se fazer uma laminação para cobrir os buracos com fitas adjacentes, resultando em uma fita multicamadas. No entanto, deve-se levar em conta que isso aumentará a espessura do conjunto final. Os buracos que aparecem nas fitas frescas, logo após a colagem, provavelmente estão associados à alta tensão superficial. Esse problema pode ser resolvido com a redução da tensão superficial, usando surfactantes, ou com o aumento da viscosidade, aumentando a carga de sólidos. O uso de ácido esteárico como revestimento lubrificante no filme transportador foi um sucesso. A nova técnica demonstrou ser muito eficaz para facilitar a remoção da fita do filme de suporte. São necessárias análises adicionais para verificar como o revestimento de ácido esteárico afeta a rugosidade e a textura da fita final. O uso de nitrogênio líquido como auxiliar para o congelamento rápido, pode ser excessivamente rápido, levando ao aprisionamento de partículas sólidas dentro dos cristais de gelo. É importante avaliar a rapidez do congelamento e, ao mesmo tempo, preservar a geração de poros altamente direcionados. No entanto, um congelamento excessivamente lento também pode resultar em poros excessivamente largos.

Enquanto verdes, as fitas altamente porosas não devem ser manuseadas, afim de evitar rachaduras nas paredes internas, que podem reduzir a resistência da fita. A remoção de orgânicos de forma contida (com carga), não é adequada para fitas cerâmicas, pois elas se tornam extremamente frágeis nesta etapa, de modo que a carga pode causar sua quebra. A laminação (prensagem térmica), não foi necessária para montar as fitas, pois a montagem a vácuo foi bastante eficaz. A reologia de uma suspensão pode ser bastante alterada com o uso de pós de diferentes tamanhos médios de partículas. Além disso, suspeita-se que o pó tetragonal usado neste trabalho seja aglomerado por atomização, com o uso de um agente aglutinante, já que os pós de YSZ tetragonais são comumente usados para fins de prensagem. Outra forte evidência é que as imagens de MEV dos eletrólitos mostram a presença de muitos poros arredondados, que podem ser os vazios deixados por tais aditivos aglomerantes.

Palavras-chave: colagem de fita; liofilização; célula a combustível de óxido sólido; processamento aquoso.

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LIST OF ABBREVIATIONS AND ACRONYMS

AFC	Alkaline Fuel Cell
APS	Average Particle Size
BSE	Backscattered Electron
CMC	Carboxymethyl Cellulose
CVD	Chemical Vapor Deposition
C-YSZ	Cubic Yttria-Stabilized Zirconia
DCO	Doped Ceria Oxides
DEA	Diethanolamine
DLS	Dynamic Light Scattering
DMFC	Direct Methanol Fuel Cell
FC	Fuel Cell
FCC	Face-Centered Cubic
GDC	Gadolinium-Doped Ceria
HT-SOFCs	High Temperature Solid Oxide Fuel Cells
IEP	Isoelectric Point
IT-SOFCs	Intermediate Temperature Solid Oxide Fuel Cells
LSGM	Lanthanum Strontium Gallium Magnesium
LSM	Lanthanum Strontium Manganite
MCFC	Molten Carbonate Fuel Cell
MIEC	Mixed Ionic and Electronic Conductors
NASA	National Aeronautics and Space Administration
NPF	No Pore Former
PAA	Polyacrylic Acid
PAFC	Phosphoric Acid Fuel Cell
PEG	Polyethylene Glycol
PEMFC	Proton Exchange Membrane Fuel Cell
PF	Pore Former
PP	Polypropylene
PSD	Particle Size Distribution
PVD	Physical Vapor Deposition
SDC	Samaria-Doped Ceria
SE	Secondary Electron
SEM	Scanning Electron Microscopy
SOFC	Solid Oxide Fuel Cell
T'	Tetragonal Metastable Phase
T-YSZ	Tetragonal Yttria-Stabilized Zirconia
USA	United States of America
XRD	X-ray Diffraction
YSZ	Yttria-Stabilized Zirconia
ZP	Zeta Potential

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1 INTRODUCTION AND OBJECTIVES

1.1 MOTIVATION AND CHALLENGES

It is widely known that the use of fossil fuels brings several environmental impacts (QUEIROZ et al., 2020), including greenhouse effect, air and water pollution, land use and habitat disruption, ocean acidification, glaciers melting, global temperature increasing, negative health impacts and finally resource depletion, since it is a limited energy source (JURADO et al., 2021; KAYODE; KAZEEM; ENOCK, 2022; SHAHEEN SHAH et al., 2022; WU et al., 2014; ZHANG; SHEN; CHAN, 2012).

The main gases or dust released by using these fuels are carbon monoxide (CO), carbon dioxide (CO₂), methane (CH₄), nitrogen oxides (NO_x), sulfur dioxide (SO₂), particulate matter and volatile organic compounds (VOCs) (CAMARGO-CAICEDO; MANTILLA-ROMO; BOLAÑO-ORTIZ, 2021). The effects respectively related to these pollutants can be seen in Table 1.

CO and CO₂ are mainly released by combustion processes, such as coal, oil, and natural gas combustion at power plants, vehicles, and industrial processes (ETIM; SONG; ZHONG, 2020). While CO₂ highly contributes to the greenhouse effect, CO is toxic to living beings (ARANTHADY et al., 2022). CH₄ is mainly released by oil and natural gas systems as well as by anaerobic decomposition of organic matter at landfills and is also a powerful greenhouse gas, contributing to global warming (MOHAMEDALI; HENNI; IBRAHIM, 2018). SO₂ is mainly released by coal power plants and causes acid rain, harming aquatic ecosystems, soil, and vegetation (ZHANG; YANG; CUI, 2016). Nitrogen oxides, such as nitric oxide (NO) and nitrogen dioxide (NO₂) are mainly released by combustion vehicles, as well as power plants, during fossil fuels burning. NO_x also contributes to acid rain formation and atmospheric pollution (PANWAR; OBER; PINKSE, 2023). Particulate matter is very fine particles, like dust, released to the atmosphere during fossil fuel combustion, and has great potential to harm our respiratory system and general health (BROOK et al., 2010). Finally, VOCs are released during the burning of fossil fuels, industrial processes, and evaporation of petroleum products, such as solvents and fuels. VOCs are harmful to health since they can be carcinogenic (CIPOLLA et al., 2016).

Table 1 – Greenhouse gases and dust released by fossil fuel use.

Gases	Effect
CO	Toxic
CO ₂	Global warming
CH ₄	Global warming
NO _x	Acid rain
SO ₂	Acid rain
Particulate	Toxic
VOCs	Toxic

Source: Author.

An alternative to reduce fossil fuel usage was the development of electric cars. The idea was to substitute conventional combustion engines which burn fossil fuels, with electrical ones, which convert the electrical current supplied by a battery, thus, providing mechanical movement (YUAN; WANG; COLOMBAGE, 2012).

One of the main bottlenecks of this alternative is that the energy that is provided to recharge the car's batteries can have different sources, and it depends on the region where the cars are operating. Each region has a specific mix of different energy sources, where sometimes the major electrical energy of a region comes from fossil fuels, such as coal or natural gas (COHEN, 2022; DERUYCK et al., 2018). Therefore, thinking about reducing fossil fuel usage, and electrifying vehicles is not a straightforward solution for many countries.

Another necessary evaluation is a comparison between the efficiency of combustion engines and electrical generation from fossil fuel burning. Since the electrical generation efficiency from power plants is higher than combustion engines, it is reasonable to reduce greenhouse gas emissions by using electrical cars in countries supplied by fossil fuel power plants (LI et al., 2020b). Therefore, this is an essential and complex assessment to be made. Other factors that should be taken into account are battery degradation, the environmental impact of battery manufacturing, and its end-of-life assessment (CHOUDHURY, 2021; STARK et al., 2017).

Although electric cars can travel hundreds of kilometers without releasing harmful gases, when batteries reach the end of their life, their green concept fades. If it is disposed of in landfills, batteries can release problematic substances, including heavy metals. Even recycling is a challenge since it can be expensive, and dangerous,

and requires the correct infrastructure and technology to do it. Another problem is that the batteries are not being designed thinking on their recycling, since they differ widely in chemistry and construction, making it difficult to develop an efficient recycling system. It is also known that it is cheaper to buy new raw materials for battery manufacturing, rather than recycling an old one. Therefore, it will not be as simple to ensure that every battery will be recycled, without government support creating regulatory laws (MORSE, 2021).

Another challenge is that usually lithium-ion batteries are used in electric vehicles (EVs), and they have a limited lifespan, since throughout their useful life, batteries suffer degradation and reduce their ability to retain energy (CHEN et al., 2022; ZHU et al., 2022). Therefore, the lifespan of an electric car can be shorter than a combustion vehicle. Table 2 brings some advantages and disadvantages of electrical vehicles over combustion ones.

Table 2 – Advantages and disadvantages of electric cars.

Advantages	Disadvantages
Reduced maintenance	Limited driving range
Engine higher lifespan	Charging infrastructure
Zero emissions	Charging time
Higher energy efficiency	Battery degradation
Environmental consciousness	Environmental impact of batteries
Technological innovation	Electrical energy demand increase

Source: Author.

A possible way to avoid the use of huge batteries while keeping the sustainable advantages of electric vehicles is using a device that generates electricity inside the vehicle. This type of technology is called embedded technology and allows the use of conventional smaller batteries since it is no longer necessary to store large amounts of energy. The technology in question is called a fuel cell, and just like any power generator, fuel is necessary to be converted into electrical energy. A fuel cell converts the chemical energy inside a fuel, such as hydrogen and hydrocarbons, directly into electricity (ZARABI GOLKHATMI; ASGHAR; LUND, 2022). The advantage here is that this reaction releases only water vapor to the atmosphere, thus, being a sustainable device.

Since hydrogen is the original fuel for the cell to function when using hydrocarbons, it is necessary to convert them to hydrogen, by using steam reform or internal conversion in the fuel cell itself (SUZUKI et al., 2011).

Ethanol is already a widely used fuel for combustion vehicles, which can be reformed into hydrogen. Ethanol is a renewable energy source since it can be produced from sugar cane, corn, oat, rice, barley, wheat, and sorghum (KIM; DALE, 2004). In Brazil, ethanol is mainly produced from sugar cane. Brazil has the most modern and competitive sugar and alcohol complex in the world, making fuel cell technology very promising for the country (GOES; MARRA; SOUZA SILVA, 2008).

Among various types of fuel cells, solid oxide fuel cells (SOFCs) are a well-studied candidate for embedded technology. SOFCs have shown high electrical efficiency, with ranges between 65% to 85% (CHEN; JIANG, 2020), while they can operate with a variety of fuels, including hydrogen, methane, biogas, ethanol, and other hydrocarbons (SONG et al., 2019). They also produce low pollutant emissions, according to each type of fuel, and have a silent operation (BAQUERO et al., 2013).

Although SOFCs appear to be the answer to environmental concerns caused by vehicles, their usage on a large scale is still hampered by some weaknesses, such as degradation-related issues that come from their high operating temperature (ZARABI GOLKHATMI; ASGHAR; LUND, 2022).

1.2 OBJECTIVE

The scope of the present work is focused on developing a processing route combining tape casting and vacuum assembling with freeze drying, at the same time it investigates the effects of varying some processing parameters, aiming for suitable morphological and mechanical properties, which will provide a longer lifespan to the SOFC.

The use of vacuum assembling aims to attach SOFC layers, such as electrolyte, functional anode, and structural anode, preserving anode pores. Moreover, freeze drying aims to generate highly directional pores in the structural anode, instead of using pore formers, enhancing ethanol diffusion.

1.3 SPECIFIC OBJECTIVES

Identify the effect of different suspension compositions on slurries rheology and morphological aspects of the tapes, aiming for pseudoplastic suspensions and defect-free tapes. Identify the effect of different freeze casting temperatures on generated pores morphology. Assess if stearic acid is efficient as a delamination facilitator, and develop a new coating technique. Develop a new assembling technique which provides a good adhesion of the tapes, free of entrapped air.

2 LITERATURE REVIEW

2.1 FUNDAMENTALS OF SOLID OXIDE FUEL CELLS

2.1.1 History

Fuel cells are electrochemical devices that can generate electricity through a redox reaction that occurs through an ion-conducting membrane (BRANDON; RUIZ-TREJO; BOLDRIN, 2017). The first fuel cell was developed in 1842 by William Robert Grove, a British physicist, who was the first to offer proof of the thermal dissociation of atoms within a molecule. His invention, also called a gas battery, was able to generate an electric current from hydrogen and oxygen gas, releasing water (BRITANNICA, 2023). Not long after, in 1965, the first practical application of fuel cells was found by NASA in their Project Gemini, where they used liquid oxygen and liquid hydrogen to generate electricity, with water as a byproduct. In this case, a thin permeable polymer sheet coated with a platinum catalyst was used (NASM, [n.d.]). Figure 1 shows the fuel cell used by NASA at Project Gemini.

Figure 1 – Fuel cell used by NASA during Project Gemini.



Source: NASM, (n.d.).

Following the timeline, it was in the 1890s when Walther Nernst studied the conductivity increasing of mixed oxides over their pure constituents, conceiving the first technological implication of ion conduction through solids. Schottky and Frenkel developed the concept of ion conduction through lattice defects in 1930, leading to the submission of the first solid oxide fuel cell patent by Siemens and Halske. The first cell with a similar configuration to that of modern days, was proposed by Baur and Preis, which used yttria-doped zirconia for the electrolyte, combining with metal oxide

electrodes. However, their system failed due to high Ohmic losses but was enough to encourage a new wave of investigation into conducting mixed oxides. Over the next 30 years, many scientists performed systematic research into ion-conducting materials aiming to optimize the mechanical and electrochemical properties required for a durable fuel cell. Since 1990, many companies, majorly from the USA, Western Europe, and Japan, have focused their efforts on bringing a range of SOFC configurations to the market, aiming for residential combined heat and power, commercial grid-independent generators, and industrial SOFC gas turbine hybrids. At the moment, state-of-the-art SOFC devices can already achieve electrical efficiencies above 50%, reaching up to 90% with combined heat released. Nonetheless, SOFCs will not be able to deliver their full potential unless the main bottleneck gets solved, in other words, degradation issues (BRANDON; RUIZ-TREJO; BOLDRIN, 2017).

2.1.2 Main types of fuel cells

In the present day, there are many types of fuel cells being developed and manufactured, each one with their characteristics and principles. Table 3 brings some of the main existing types of fuel cells, respectively with their characteristics, and applications.

Table 3 – General information on the main types of fuel cells.

(continue)

Acronym	Name	Operating temperature (°C)	Electrolyte Material	Efficiency (%)
PEMFC	Proton exchange membrane FC	50-100	Polymer	50 - 60
SOFC	Solid oxide FC	800 - 1000	Ceramic	45 - 85
AFC	Alkaline FC	80-120	Liquid alkaline electrolytes	50 - 60
DMFC	Direct methanol FC	≤ 60 - 130	Polymer	20 - 45
MCFC	Molten carbonate FC	620 - 660	Molten carbonate salts	60 - 65
PAFC	Phosphoric acid FC	160 - 220	Liquid phosphoric acid	55 - 80

*FC – Fuel Cell

Table 3 – General information on the main types of fuel cells.

(end)

Acronym	Applications	Advantages	Disadvantages	References
PEMFC	Transportation, portable power, and stationary power generation	Quick startup, high power density	Sensitive to impurities and low-quality heat	ZHAN, (2022)
SOFC	Large-scale power production	High-quality heat, fuel flexibility	Slow startup, safety concerns, and degradation issues	
AFC	Stationary, transport, and portable devices	High-efficiency and low-cost electrodes	Stability, activation issues, and impurities	(DAWSON et al., 2017; YU et al., 2012; ZHAN, 2022)
DMFC	Small portable power sources and transportation	Fed with liquid fuel	Low efficiency	(PAIK; KIM; HAN, 2008; SHUDO; SUZUKI, 2008; SUTTER; VAN DER SPEK; MAZZOTTI, 2019)
MCFC	Stationary power generation systems	High efficiency, fuel flexibility, and high-quality heat	Degradation issues	(AHMADI et al., 2019; CHOI; KIM; YI, 2014)
PAFC	Stationary applications	Fuel flexibility	Larger size and expensive	(AHMADI et al., 2019; HE et al., 2010)

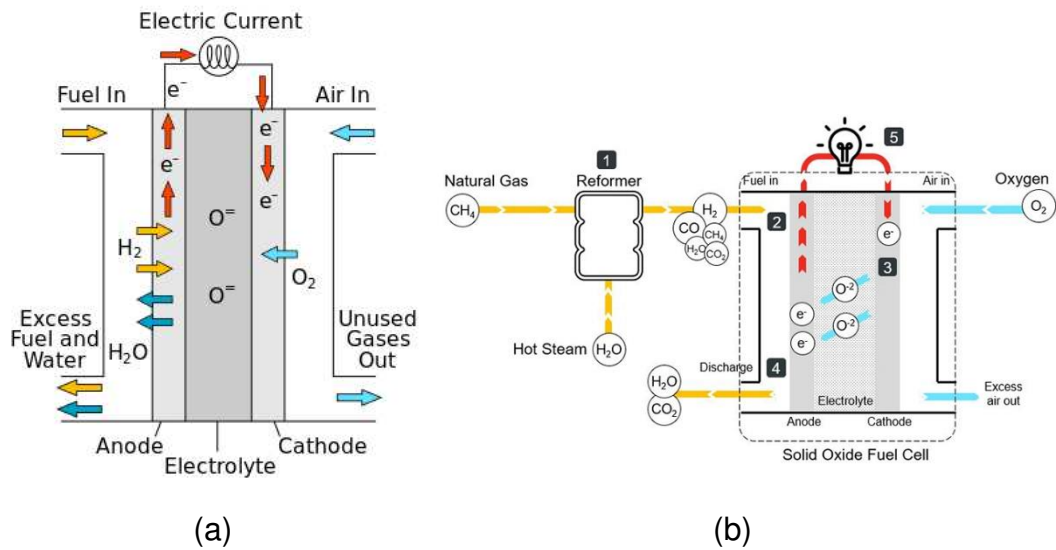
Source: Author.

2.1.3 Structure and parts

Solid oxide fuel cell (SOFC) is a promising technology and one of the most efficient for energy generation, since it employs different fuels, shows low, or no, CO₂ emissions, and has a relatively long lifespan (ZARABI GOLKHATMI; ASGHAR; LUND, 2022).

The structure of an SOFC is comprised of many essential parts, such as electrolyte, anode, cathode, current collectors, interconnects, and sealants, where all of them are fundamental for the efficiency of the cell (DELÍBAS et al., 2022). The structure of a SOFC and its operating principle can be seen in Figure 2. Each part requires a specific combination of properties to work well and provide a long lifespan to the cell. The layout of the fuel cell follows as a stack, where the core is comprised of the electrolyte separating the anode and cathode, while interconnects and sealants, ensure the perfect assemble, directing the gas along the electrodes, in the way that no gas leaks or short circuits occur.

Figure 2 – SOFC scheme for different fuels: (a) hydrogen, (b) methane.



Source: WIKIPEDIA, (n.d.); YUKSEL, (2020).

2.1.3.1 Electrolyte

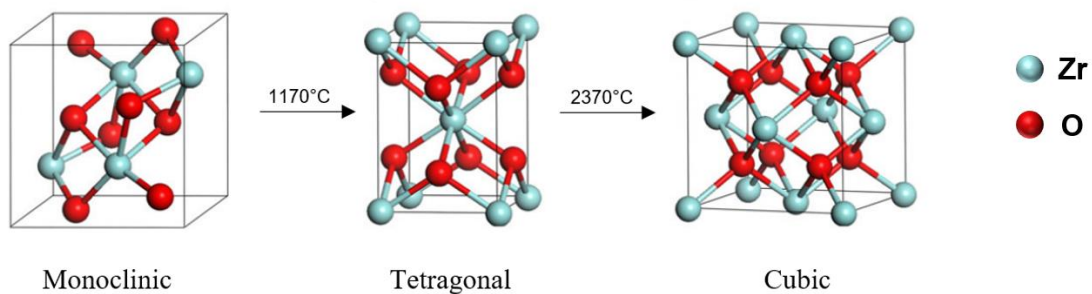
The main role of the electrolyte is to provide ionic conduction of oxygen ions from the cathode to the anode direction while being an electronic insulator and dense enough to prevent gas mixing. Other requirements for electrolytes are chemical and physical stability under reducing and oxidizing atmospheres, and high mechanical resistance to withstand the harsh operating conditions of the SOFC (SAMMES; DU, 2005; ZAKARIA et al., 2020b). Commonly used materials for SOFC electrolytes include yttria-stabilized zirconia (YSZ), scandia-stabilized zirconia (ScSZ), ceria-based materials, lanthanum gallate-based materials (e. g., LSGM) and gadolinium-doped ceria (GDC) (ANIL V. VIRKAR, 2001; FABBRI; PERGOLESI; TRAVERSA, 2010; HUSSAIN; YANGPING, 2020; JADHAV; PAWAR; CHOURASHIYA, 2007; ZAKARIA; KAMARUDIN, 2021).

The mechanism of oxygen ion conduction is possible thanks to oxygen vacancies in the electrolyte crystal structure and the very high operation temperature. The ion conductivity is dependent on the concentration of these vacancies and their mobility. Therefore, specific crystal phases are required to provide a high number of oxygen vacancies, such as cubic YSZ (HOLTAPPELS; VOGT; GRAULE, 2005).

The transport of oxygen ions through the solid electrolyte results in thermally-activated hopping, moving from one crystal lattice site to another in the direction of the electric field. The most common oxygen ion conducting materials have a fluorite crystal structure, XO_2 , where X is a tetravalent cation. In this structure, the cations occupy face-centered cubic positions (FCC), while the anions occupy the eight tetrahedral sites between them. The best oxygen ion conductor, with a cubic fluorite structure, is doped zirconia (ZrO_2) (TSAMPAS; SAPOUNTZI; VERNOUX, 2015).

At room temperature, pure zirconia has a monoclinic phase. At 1170 °C, it undergoes a phase transition to a tetragonal structure causing a decrease in volume. Above 2370 °C, another phase transition occurs to the cubic fluorite structure, which is stable up to the melting point around 2680 °C, Figure 3. Since cubic zirconia only exists at higher temperatures, it is possible to stabilize it at room temperature by doping it with a lower-valence cation, such as Y^{3+} . In addition, doping also leads to an increase in oxygen vacancies, thus enhancing the ionic conductivity (HAN; ZHU, 2013; TAROCO et al., 2011).

Figure 3 – Crystal structures of ZrO_2 .

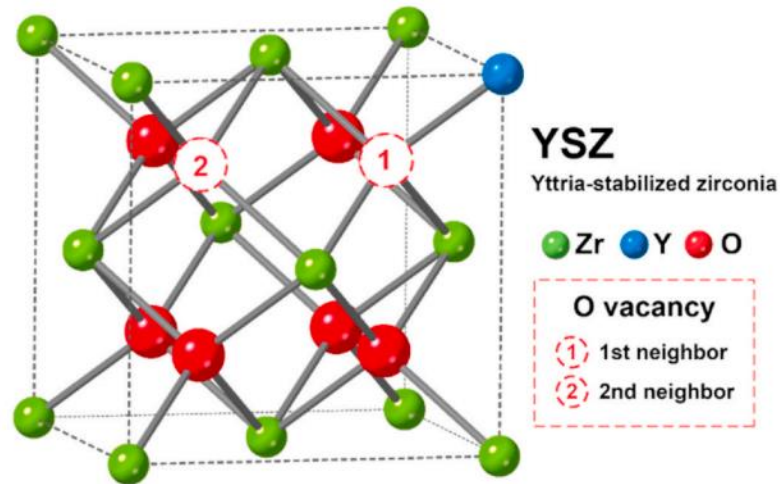


Source: adapted from HAN; ZHU, (2013).

Pure zirconia has poor ionic conductivity, however, when a small number of lower valence cations are introduced into the crystal structure, oxygen ion vacancies are generated, which provide a path for oxygen ions conduction. Figure 4 represents that, to compensate for charge changes caused by the introduction of an aliovalent cation, oxygen vacancies are generated in the crystal lattice. As the concentration of dopant increases, the ion conductivity also increases reaching a maximum of 8% of dopant concentration. Nevertheless, the conductivity greatly decreases if dopant amounts continue to increase by more than 8%, especially at lower temperatures (SHI et al., 2020).

YSZ has enhanced chemical stability compared to other ceramic conductors, exhibiting extremely low thermal conductivity at high temperatures and considerably high oxygen ion conductivity. Therefore, is the most common material used as an electrolyte in solid oxide fuel cells (TSAMPAS; SAPOUNTZI; VERNOUX, 2015).

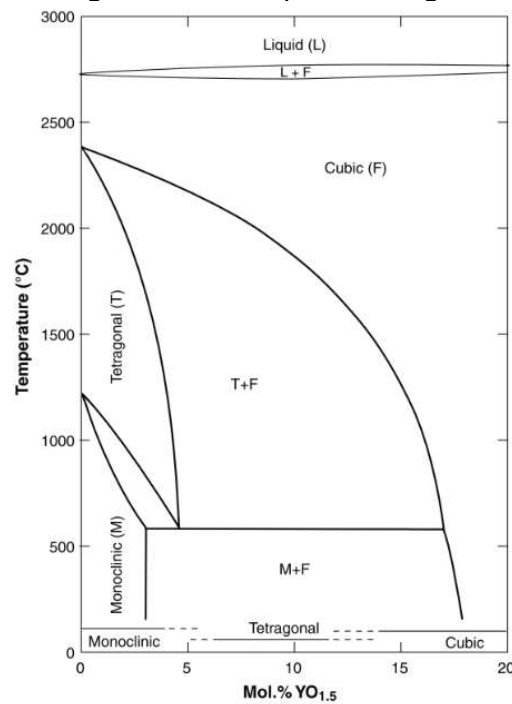
Figure 4 – Schematic of the defect cubic structure in YSZ.



Source: SHI et al., (2020).

During the phase transition from tetragonal to monoclinic pure zirconia, a large volume increase occurs, leading to internal shear stresses and strains. As a result, fractures during cooling from the sintering temperature are expected. It is possible to lower this phase transition temperature by doping the zirconia with yttria (Y_2O_3), enabling the stabilization of the tetragonal phase to some extent at room temperature, which is called a metastable phase (T') (BRANDON; TAYLOR, 1991; BUTZ, 2009; CHEVALIER; GREMILLARD; DEVILLE, 2007; REN; PAN, 2014). In Figure 5 is possible to see the metastable phases, retained at room temperature, indicated just above the horizontal axis.

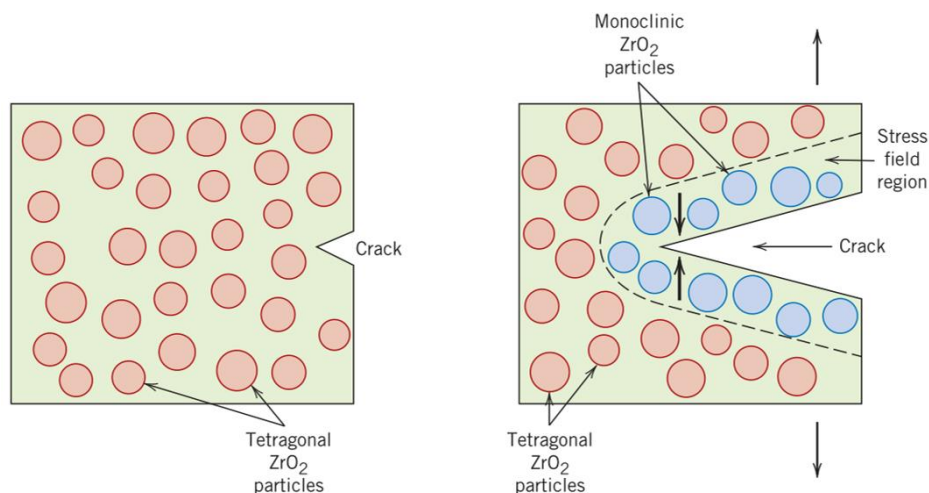
Figure 5 – YSZ phase diagram.



Source: adapted from CHEVALIER; GREMILLARD; DEVILLE, (2007).

T' as a metastable phase, is temporarily stable until some disturbance of energy transforms it back to a more stable state, i.e., monoclinic. This disturbance can be the stress caused by a crack, and since the monoclinic phase has a greater volume, compressive stresses are established on the crack surface, thereby ceasing its growth and even closing it. This phenomenon is known as transformation toughening, Figure 6, (DENRY, 1996; HABIB; ABOUSHELIB; HABIB, 2021).

Figure 6 – Schematic demonstration of transformation toughening.



Source: CALLISTER; RETHWISCH, (2018).

2.1.3.2 Anode

The main function of the anode is to electrochemically oxidize the fuel while conducting and releasing the electrons into the system. There are two types of anodes, functional and structural. The functional anode has the duty of offering active sites for fuel oxidation providing a path for the electron to be transported from the reaction sites to the external circuit, and since is very thin, does not provide mechanical improvement. On the other hand, the structural anode is much thicker and porous, providing not only the active sites but also mechanical resistance for the fuel cell stack, while allowing good diffusion of fuel and by-products to be delivered and removed from the reaction sites (AGUILAR ARIAS, 2012; DING et al., 2010).

The main properties that anodes must have include, a high electronic conductivity, for good electron transmission, high catalytic activity for electrochemical oxidation of fuels, and interconnected pores for effective transportation of fuel and by-product gases. Other properties are common to those of electrolytes, such as mechanical strength, chemical stability, and thermal compatibility with other cell components, providing high resistance to operation conditions (MUKHOPADHYAY; MUKHOPADHYAY; BASU, 2013).

One of the most common materials used as an anode for SOFCs, is a nickel-based composite, such as Ni/YSZ, which exhibits high catalytic activity and effective current collection (JIANG; CHAN, 2004; YANG et al., 2021; ZOUHRI; LEE, 2016). Other materials investigated as alternative anode materials for SOFCs are based on perovskite oxides including chromite, vanadate, titanate, and mixed ionic and electronic conductors (MIEC) (HUSSAIN et al., 2018; WANG et al., 2019).

Furthermore, ceria-based materials have been identified as potential anodes, such as NiO/SDC and NiO/GDC, when using DCO as electrolytes, which provides mixed conductivity (high ionic and electronic conductivity), while improving the chemical compatibility, matching thermal expansion coefficient (CHENG et al., 2007; LIN et al., 2010).

2.1.3.3 Cathode

The main function of the cathode is to electrochemically reduce the oxygen gas to O^{2-} ions while conducting and receiving the electrons from the system (IRSHAD et al., 2016).

Some properties of cathodes that are essential include high electrical and ion conductivity, high electro-catalytic activity towards oxygen reduction, and high chemical stability in an oxidizing environment without the formation of resistive reaction by-products with the electrolyte and current collector. Furthermore, the material should have compatible thermomechanical properties as the electrolyte to prevent mechanical stresses developed during heating and cooling cycles (KAMBLE; FULARI; NIMAT, 2018). Just like the anode, the cathode must be porous allowing good diffusion of oxygen and by-product gases.

The most commonly used cathode material for SOFC application is a composite of YSZ and Sr-doped $LaMnO_3$ (LSM). Although LSM shows a relatively poor oxygen reduction catalytic activity at intermediate temperatures (600 – 800 °C), therefore, being suitable for high-temperature SOFCs (HT-SOFC), it shows a good compatibility of thermal expansion coefficient with YSZ. Other candidates as cathodes with higher catalytic activity at intermediate temperatures are perovskite-type cathodes (IMANISHI et al., 2009).

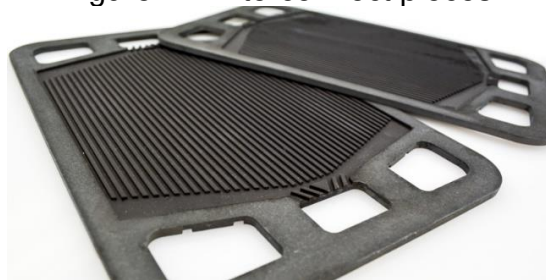
2.1.3.4 Interconnects and sealants

Considering a planar-type SOFC design, where the cells are stacked to each other, interconnects work as a separator plate, physically separating the fuel at the anode side from the air or oxidant at the cathode side, between neighboring cells. Moreover, it also works as a bipolar plate, electrically connecting several ceramic cells in series in the stack. The interconnects must be hermetically sealed to the adjacent components, to prevent not only mixing of fuel and air but also leaks out of the stack. This sealing is provided by sealing materials, such as sealing glass. Therefore, it is possible to state that seal performance not only affects the structural integrity and stability of the stack but also influences the overall SOFC performance (YANG; MEINHARDT; STEVENSON, 2003).

Other properties that interconnects must have include being electronically conducting, having low ionic conductivity, being gas impervious, having a good thermal conductivity, being stable under oxidizing and reducing atmospheres, and having a compatible coefficient of thermal expansion with SOFC other components (ORLOVSKAYA et al., 2004).

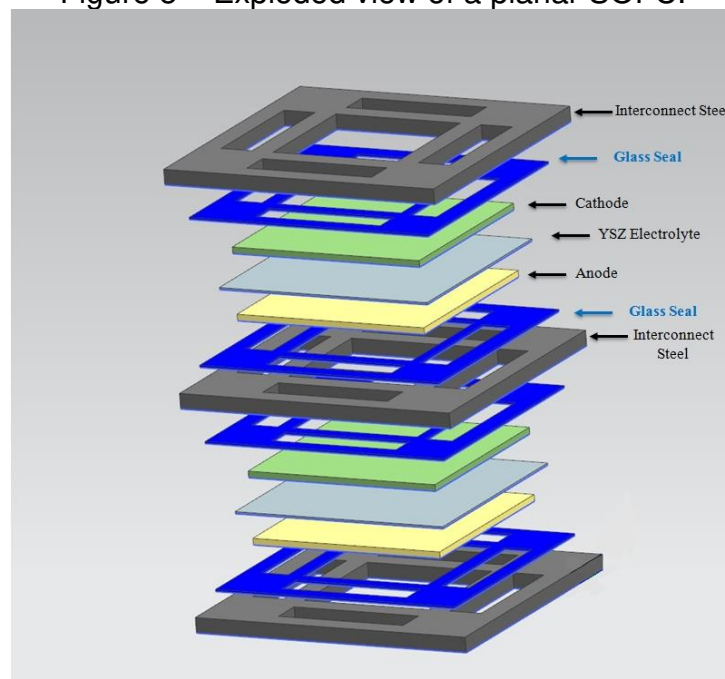
Sealing materials also have the function of electrically isolating the interconnects, preventing them from short-circuiting. Glass and ceramics are popularly used as SOFC sealing materials, while stainless steel ferritic based on chromium is typically used as interconnects. One of the required properties for sealants is that they must be thermochemically compatible with other parts of the SOFC (GUNAWAN; SULISTYO; IWAN SETYAWAN, 2021).

Figure 7 – Interconnect pieces.



Source: CORWIN, (2017).

Figure 8 – Exploded view of a planar SOFC.

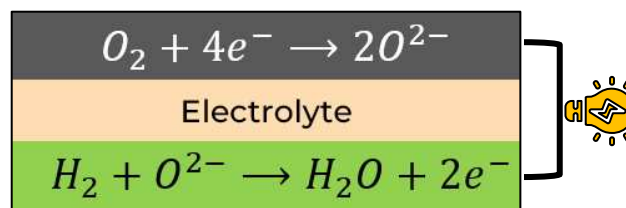


Source: MO-SCI, (n.d.).

2.1.4 Working principle

The basics of SOFC can be described in Figure 2, where an oxidant gas (oxygen), enters the right chamber so that the electrons being supplied by the cathode reduce the oxygen molecules to oxygen anions (O^{2-}). Then, the oxygen ions pass through the electrolyte layer reaching the anode. On the opposite side, a fuel gas (hydrogen), enters the left chamber, where hydrogen molecules are split into hydrogen cations (H^+) by anode active sites, releasing its electron to be conducted by the anode. Then, H^+ ions react with O^{2-} ions, thus generating water vapor. The electrons released through the anode are conducted to an external circuit, until reaches the cathode, thus completing the cycle (KENDALL; KENDALL, 2016).

Figure 9 – Global reactions of a SOFC.

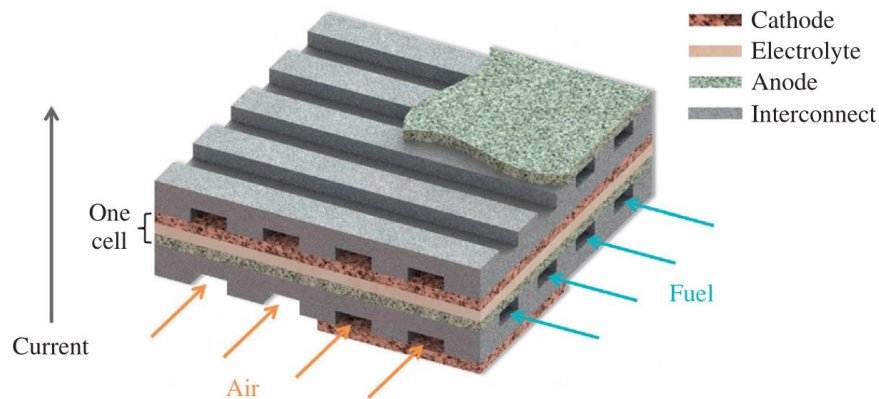


Source: Author.

2.1.5 Configurations

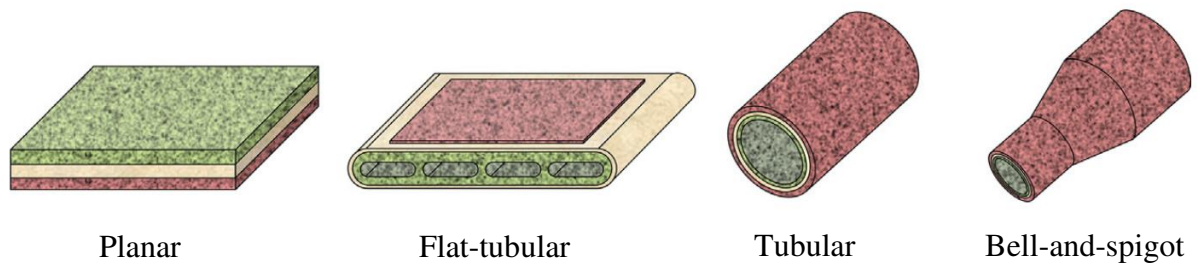
Since the fuel cell is comprised of a few parts, many dispositions or designs are possible while respecting the restrictions and required properties of each part. The first fuel cells were predominantly tubular, since these systems were much easier to seal, and are still used today. Nonetheless, most commercially available systems follow a planar configuration, Figure 10, due to their ease of manufacture, optimal volumetric power density, and being easily stackable. Stacking allows the system to achieve higher voltage (series stack) or current (parallel stack) compared to a single cell. Many other configurations have also been developed, Figure 11, such as flat-tubular, which combines the sealing and mechanical advantages of a tube, while remaining stackable as planar cells. (COOPER; BRANDON, 2017).

Figure 10 – Planar design schematic of a single cell.



Source: COOPER; BRANDON, (2017).

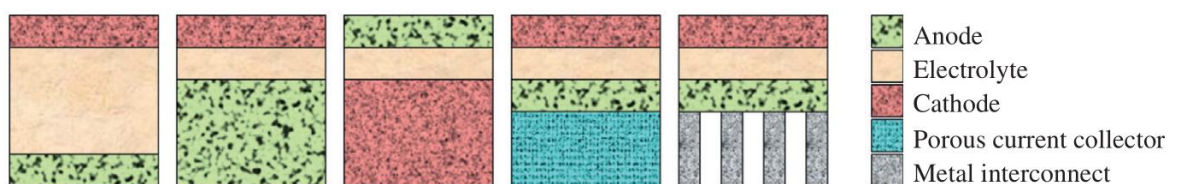
Figure 11 – SOFC geometries.



Source: adapted from COOPER; BRANDON, (2017).

For increasing the mechanical resistance of the set, one of the SOFC components can be chosen to be thicker, being called a support. Since an increase in layer thickness can change its properties, it is important to carefully optimize it to maintain the original functions of the layer. For instance, an anode-supported SOFC, requires an anode with a higher porosity, compared to a regular anode, since increasing the thickness can lead to diffusion resistance, hindering fuel transportation (KAGOMIYA et al., 2015; NGUYEN et al., 2004).

Figure 12 – Schematic of common cell support configurations in SOFCs.



Source: COOPER; BRANDON, (2017).

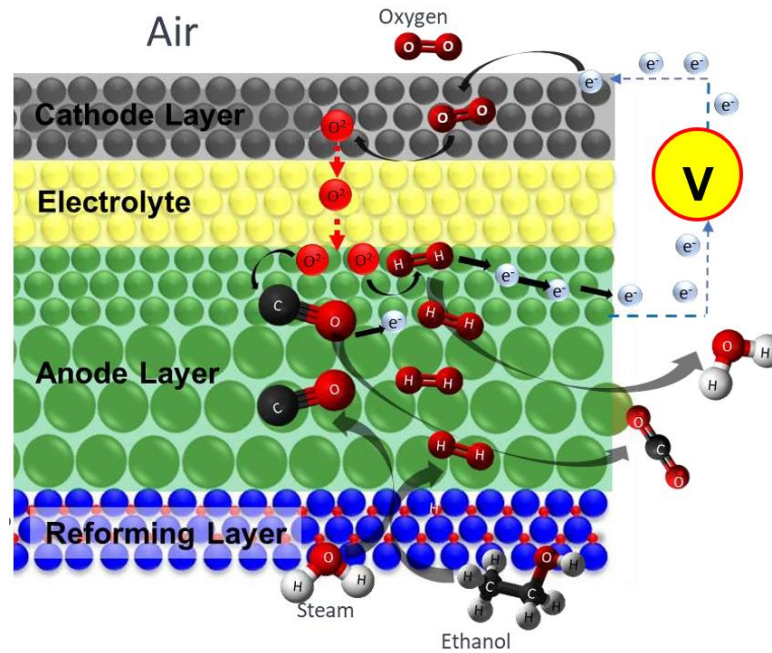
2.1.6 Steam reform

One of the advantages of SOFC is its ability to function with different fuels, including hydrocarbon gases such as methane from natural or biogas, and also liquids for instance, methanol and ethanol, with the latter having an advantage of having much superior energy storage density compared to hydrogen gas. Thanks to the high operating temperature and the abundance of active sites in the porous nickel-based anode, these fuels can be reformed directly on the anode, being converted to hydrogen and byproducts, thus, not being necessary to have an external reforming step (CAI et al., 2022; KENDALL; KENDALL, 2016).

In the case of direct internal reforming of ethanol, steam is added to the fuel to reform the ethanol on the surface of the anode and produce hydrogen, which then will be electrochemically oxidized, provided that a high steam-to-carbon ratio is used to prevent the deposition of carbon. Carbon deposition is one of the biggest disadvantages of using hydrocarbons for internal reforming, which can block active sites and decrease the performance of the cell. Although increasing the steam-to-ethanol molar ratio is carried out to mitigate carbon deposition, the introduction of water vapor with the fuel lowers the power output of the cell. Additionally, free-sulfur fuel is required to avoid irreversible poisoning of nickel (CIMENTI; HILL, 2009).

Although Ni/YSZ cermet is a technology that has already been optimized and matured as SOFC anodes, it has a high tendency for carbon deposition under direct ethanol-fed conditions. Another approach to solve this problem is to use a high-performance catalytic reforming layer, directly over the conventional Ni/YSZ anode, Figure 13. This layer, which is specially developed for internally reforming the ethanol into H₂-rich gas, prevents the ethanol from getting into direct contact with the anode. Catalytic functional layers comprised of rhodium supported on ceria-zirconia (Rh/CeO₂-ZrO₂), have shown promising carbon deposition resistance and phase stability under harsh ethanol steam reforming conditions (ELHARATI et al., 2020).

Figure 13 – Schematic representation of a SOFC with ethanol internal reforming.



Source: ELHARATI et al., (2020).

2.1.7 Challenges

It is widely stated that the main challenge related to SOFCs is the high operating temperature, required for achieving high efficiencies, leading to a short lifetime of the SOFC (KONG et al., 2019). Such high temperatures (600 – 1000 °C), are necessary to ensure a moderate-to-good ionic conductivity of the solid ceramic electrolyte (LIU et al., 2023). However, this can pose significant material stability and durability challenges, making SOFCs not so practical for portable power sources, thus, requiring to use of expensive ceramic interconnects and heat exchangers (BAHOUT et al., 2015; CHAO et al., 2011).

Challenges related to materials are mainly a result of degradation issues Table 4, therefore, the development of intermediate temperature solid oxide fuel cells (IT-SOFCs), which are operated between 500 and 800 °C, aims to minimize premature aging of SOFC components. Nevertheless, low operation temperatures decrease the electrode kinetics, increasing polarization losses during oxygen reduction on the cathode. Thus, the performance of cathodes is a limiting factor for IT-SOFCs (DAI et al., 2013). The reduction in the operating temperature is possible by using mixed ionic and electronic conductors (MIEC), as cathodes (DING et al., 2013).

Another very important challenge of SOFCs is ohmic loss. Ohmic losses are the resistance to the flow of electrons and ions, in the electrodes and the electrolyte respectively, so that the power drop caused by the ohmic losses is proportional to the current density (ZHAO; XU, 2009). In the case of electrolyte ohmic losses, a thicker electrolyte results in a greater distance between the electrodes, therefore, creating a longer pathway for oxygen ions transportation. As a result, greater ohmic losses occur (CUI; MURRAY, 2015). It is expected that for electrolytes thicker than 50 μm , ohmic resistance dominates and becomes the major source of the performance loss. Nevertheless, when reducing electrolyte thickness to below 10 μm , ohmic losses of the electrolyte decrease in the way that the cathode starts to be the major source of voltage loss (SHRI PRAKASH; SENTHIL KUMAR; ARUNA, 2017). Thin film YSZ electrolytes are possible to be used when adopting an anode-supported SOFC (AS-SOFC) architecture, thus, strongly reducing ohmic losses and increasing fuel cell performance (MILCAREK et al., 2016).

Usually, at lower operation temperatures, the cathode leads most of the power losses, associated with oxygen reduction reactions, which are also called activation polarization issues (CHOI et al., 2011). Activation polarization also needs attention as a bottleneck for SOFCs, since is caused by the slowness of the reactions that take place on the surface of the electrodes. This can include not only the resistance to electrochemical oxidation/reduction of fuel/oxygen associated with the electron transportation to or from the electrode but also physicochemical processes associated with the surface adsorption of reactant species (ZHAO; XU, 2009).

The geometry of the SOFC can also pose a challenge, with planar interconnects being one of the major ones. Since interconnects have the function of gas distributors and current collectors, the interconnect optimal design must provide a uniform fuel velocity distribution among channels on the anode side, while doing the same for oxygen in the cathode side. Interconnect design parameters, such as channel height and width, can be decisive for improving fuel cell performance, thus being recognized as a crucial challenge in SOFC development (LIN et al., 2015).

Sealants also have their challenges, such as chemical incompatibility and instability, which pose the necessity of adjusting thermal expansion coefficients to match them with interconnect materials and electrodes during SOFC operation, thus ensuring durability and no gas leakage. In addition, the sealant glass transition

determines the maximum working temperature of the SOFC. (GUNAWAN; SULISTYO; IWAN SETYAWAN, 2021).

Table 4 – Main degradation mechanisms of SOFC components.

Degradations	Cathode	Electrolyte	Anode	Interconnect	Sealant
Poisoning	•		•		•
Microstructural changes	•		•		
Delamination	•		•		
Phase transition		•			
Mechanical failures		•		•	•
Dopant diffusion		•			
Carbon deposition			•		
Corrosion				•	•
Leakage					•

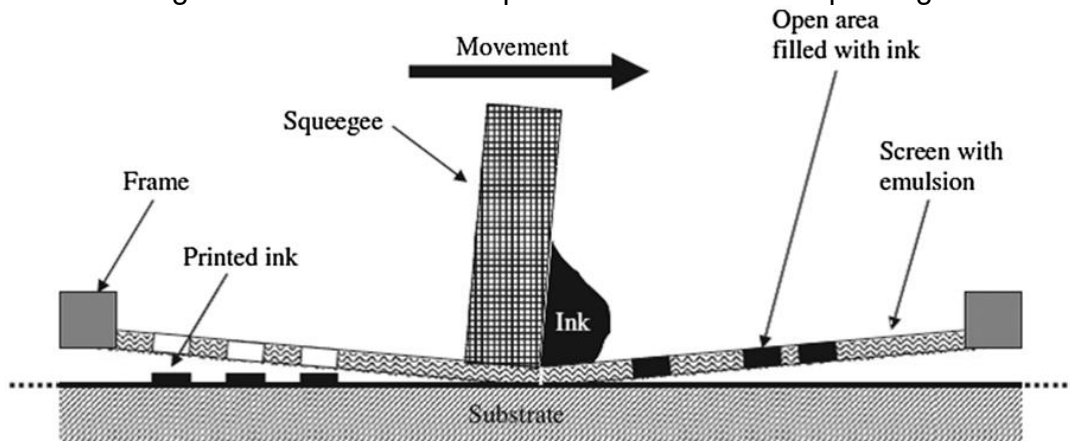
Source: ZARABI GOLKHATMI; ASGHAR; LUND, (2022).

2.2 TAPE MANUFACTURING

2.2.1 Screen printing

One of the most simple and cost-effective manufacturing techniques is screen printing. This technique allows the casting of thin ceramic film in the range of 10 to 100 μm , thus being very suitable for SOFC components manufacturing, such as the electrolyte, anode, and cathode. The basics of screen-printing boil down to feeding the open screen meshes with the suspension and spreading it with a squeegee, thus forming a flat thin film on the substrate (ZAKARIA et al., 2020a).

Figure 14 – Schematic representation of screen printing.



Source: ZAKARIA et al., (2020a).

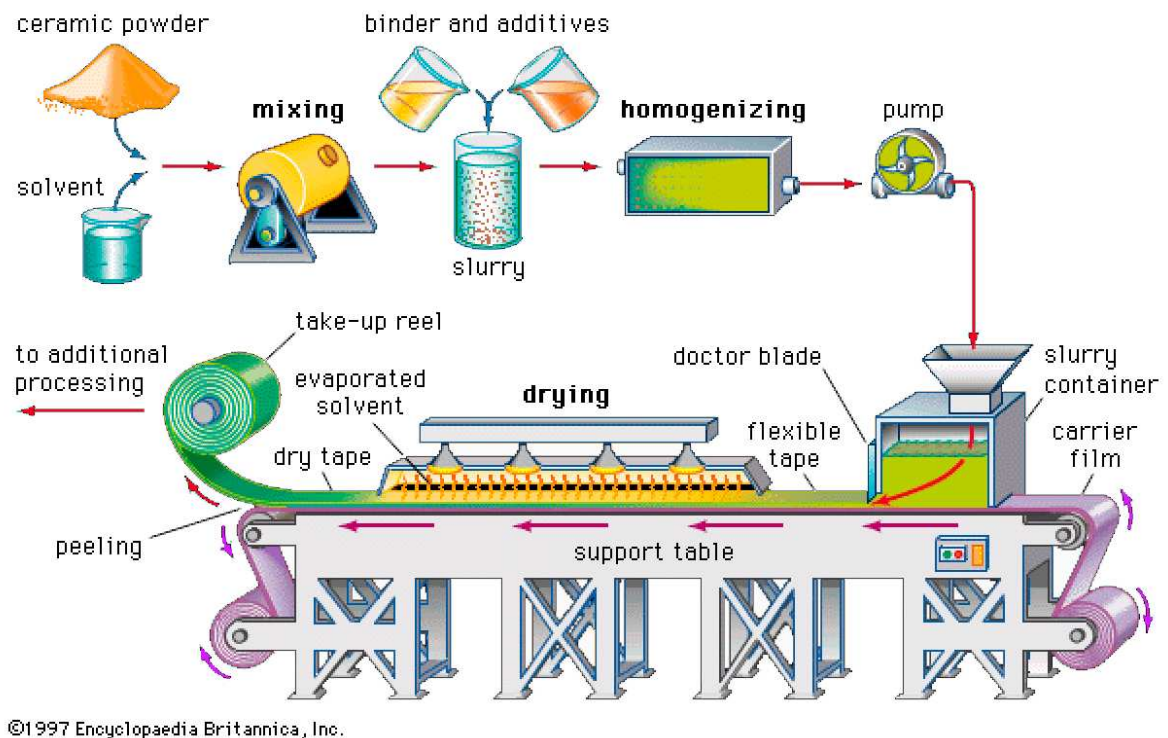
2.2.2 Tape casting

Tape casting is a well-established, wet-shaping technique for manufacturing large, thin, flat, and uniform ceramic tapes with a controllable thickness range between 1 – 1000 μm . One of the main advantages of tape casting is its scalability, which enables large-scale, low-cost production of SOFC components, such as electrolyte, anode, and cathode membranes (NIE et al., 2015).

The procedure consists of adding the slurry into a reservoir called a hopper. The hopper has a blade, called a doctor blade, that can precisely determine the thickness of the desired tape by adjusting the height of the blade, Figure 16. A polymeric conveyor film constantly carries the suspension out of the doctor blade gap, thus giving shape to the tape. The ceramic tape is then dried and removed from the

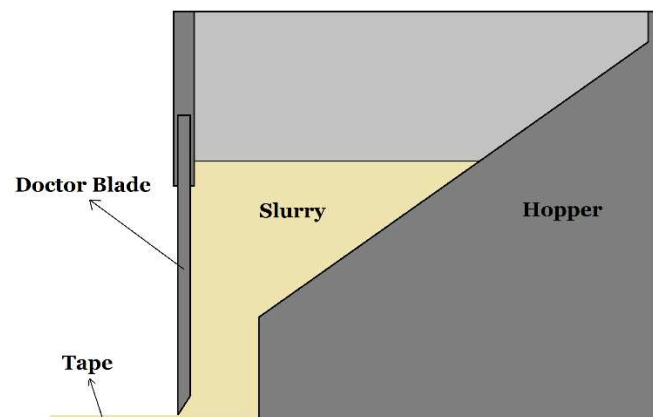
support by delamination, and subsequently subjected to thermal treatment (GARDINI et al., 2010). Figure 15 shows the complete processing route, including the steps of suspension preparation, casting, drying, delamination, and storage for further processing steps.

Figure 15 – Schematic flowchart of the tape casting processing route.



Source: adapted from ENCYCLOPAEDIA BRITANNICA, (1997).

Figure 16 – Schematic details of a hopper.



Source: Author.

Slurries are comprised of ceramic powders, a liquid (organic solvent or water), and additives, with the latter being added to provide the required rheological properties. Typically, tape casting is carried out from slurries based on organic solvents, but due to environmental and safety issues, researchers are focusing on water-based slurries, since water is widely available, nontoxic, nonflammable, and cheap. However, replacing organic solvents with water brings significant challenges related to the rheological and drying behavior of the slurry (GOULART; DE SOUZA, 2017; HOTZA et al., 2019).

Other manufacturing techniques for SOFC components can include physical vapor deposition (PVD) and chemical vapor deposition (CVD). PVD is related to the vaporization or sputtering of a solid target in a vacuum chamber while depositing the vaporized particles on a substrate surface. On the other hand, CVD technologies are based on the deposition of gaseous precursors on a substrate surface, followed by a chemical interaction to produce the film (DUNYUSHKINA, 2022).

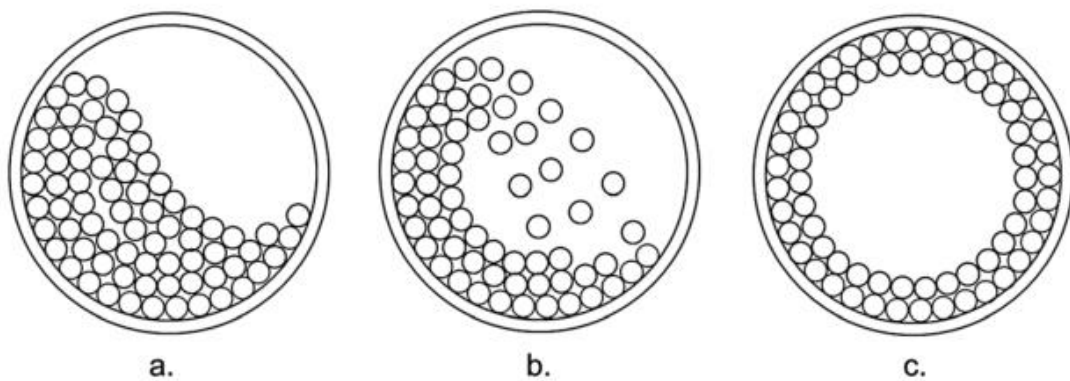
2.2.3 Ball milling

Before tape casting, the slurry needs to be prepared. Ball milling is typically used for comminuting dry powders, and to deagglomerate and mix ceramic slurries. A ball mill consists of a rotating cylinder internally lined with a hard and wear-resistant material, partially filled with media, which are most often made of the same material as the lining and the feed material, to prevent contamination during wear. There is a great variety of media shapes, including rods, short cylinders, balls, pebbles, and granular, all of them being called grinding or tumbling media. Mills can range in diameter from several centimeters to several meters, with capacities ranging from many grams to a few tons. The working principle of a rotating mill is based on the grinding action caused by impacting and shearing the particles between their surfaces. The main operating variables include the diameter and angular velocity of the mill, the size of the grinding media relative to the size of the feed material, the loading of the mill, and in the case of wet milling, the viscosity of the slurry being mixed (REED, 1995).

The motion pattern of the grinding media changes depending on the operation parameters, showing cascading, cataracting, or centrifugation behavior, with increasing mill loading or increasing angular velocity. In the cascading regime, the media balls unroll upon each other from the bulk top to its base, while in the cataracting

regime, the balls detach from the mill wall impacting the bulk media with high intensity. Finally, during the centrifuging regime, balls align with each other, attaching to the wall, with almost no relative velocity. When comparing the grinding forces among these three regimes, cascading exhibits higher shear stress forces, cataracting has higher normal stress forces (compressive forces), and centrifuging shows virtually no stresses between particles and media (BURMEISTER; KWADE, 2013).

Figure 17 – Ball milling regimes – (a) cascading, (b) cataracting, (c) centrifuging.



Source: BURMEISTER; KWADE, (2013).

2.2.4 Rheology

The most important factor for any casting technique is the slurry rheology. Since tape casting requires appropriate rheology to successfully produce high-performance tapes, it is important to assess and optimize the rheology of the suspensions (REN; LUO; ZHOU, 2018).

Slurries for tape casting typically present a shear thinning behavior, where its viscosity decreases under the shear rate produced by the doctor blade during casting. After cast, with no shear rate, the viscosity increases back, thus keeping the shape of the tape, ensuring a homogeneous and smooth surface (MORENO; BERNARDINO; HOTZA, 2014).

The rheology of a slurry is defined during the suspension preparation step, which includes defining the composition, dispersing, and mixing steps. The suspension preparation starts by dispersing ceramic powder in a solvent, using a suitable dispersant to fully deagglomerate and stabilize the particles, into a homogeneous suspension. Usually, the dispersant is added first to the solvent, and the mixture is

homogenized before incorporating the powder and mixing again. This sequence ensures obtaining a homogeneous suspension (GAUDON et al., 2006; LICHTNER et al., 2013; NAYAK et al., 2011). Then, other additives can be added, with additional mixing time, to adjust the required rheological and mechanical properties of the suspension and the final tape, respectively.

Finally, a de-airing step can be performed, if necessary, to remove remaining air bubbles before casting, to avoid defects caused by entrapped bubbles. However, the result may not always be satisfactory, especially when working with dense slurries with fine powders, since in these cases, the suspension has a relatively high viscosity so bubbles are difficult to remove completely (JIANG et al., 2007). Deairing of slurries can be done by applying a vacuum, ultrasonic bath, or simply letting the suspension rest for a few h (BARROS, 2021; ZAMANIAN et al., 2014).

Typical additives used in tape casting are dispersants, binders, plasticizers, surfactants, and antifoams. Generally, a solvent is used to dissolve the additives and uniformly mix them with the powders, providing that the dispersant will generate electrostatic repulsion between particles, stabilizing the suspension. Binders and plasticizers are used to hold the particles together during drying, increasing flexibility and maintaining the strength of the green tape, while preventing cracks (REN; LUO; ZHOU, 2018).

Surfactants are used to reduce the surface tension of the slurry, improving wettability over the carrier film, while antifoam is added to prevent foam formation. It is important to distinguish antifoam from defoamer so that defoamer can eliminate foam already present (TADROS, 2005). Table 5 shows the most commonly used solvents and organic additives for tape casting.

Table 5 – Typical organic additives used for tape casting.

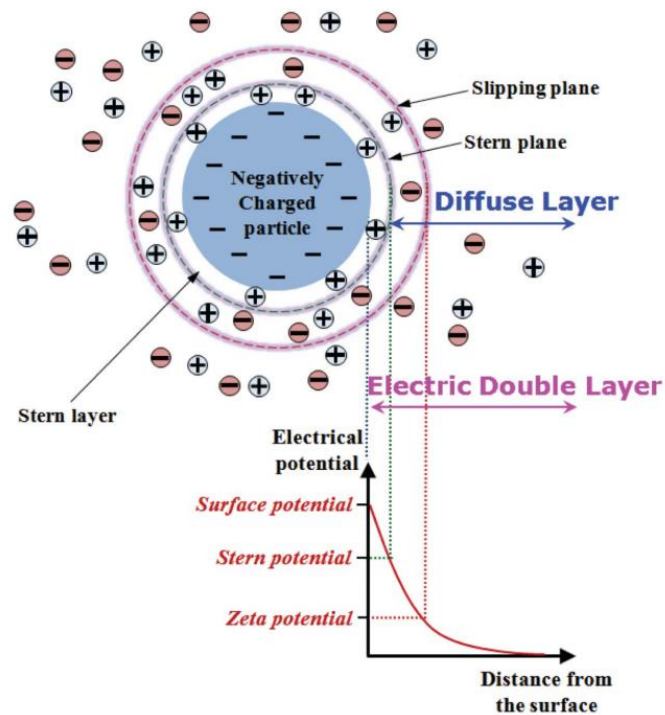
Solvents	Dispersants	Binders	Plasticizers
Butanone	Fish oil	Polyvinyl alcohol	Benzyl butyl phthalate
Acetone	Castor oil	Polyvinyl butyral	Dibutyl phthalate
Ethanol	Corn oil	Polyvinyl acetate	Dimethyl phthalate
Isopropanol	Tributyl phosphate	Methylcellulose	Dioctyl phthalate
Toluene	Triethanolamine	Ethyl cellulose	Polyethylene glycol
Cyclohexanone	Phosphate ester	Polymethyl methacrylate	Polypropylene glycol
Water	Ammonium polyacrylate	Polymethyl acrylate	Butyl stearate
...	Ammonium polymethacrylate	Polypropylene carbonate	...
	Sodium CMC	Polyacrylic acid	
	...	Acrylic resin	
		Ammonium polyacrylate	
		...	

Source: HOTZA; GREIL, (1995); REN; LUO; ZHOU, (2018).

2.2.4.1 Dispersant

Dispersants are additives that coat ceramic particles, increasing the repulsive forces between them, and keeping them in a stable suspension in the slurry. The repulsion forces between particles can occur due to two mechanisms, electrostatic repulsion and steric hindrance (HOTZA; GREIL, 1995). The electrostatic repulsion originated when the molecules of the dispersant adsorb on the particle surface changing the net charge of the particles, thus making all the particles carry an electrostatic charge of the same sign, which will make particles repel each other. In addition, the charge of the particles attracts other counterions and polar molecules surrounding the particle, creating an electrostatic double layer, Figure 18 (PARK; SEO, 2011). It is also important for the amount of charge to be sufficient to surpass the attractive forces. On the other hand, steric hindrance is caused by the thickness of the adsorbed layer which is comprised of long chain dispersant molecules, which becomes a physical barrier preventing particles from getting close to each other, Figure 19 (WANG; KAYALI; LIOW, 2019). The combination of the two effects is also possible, and is called electrosteric repulsion (BISCHOFF et al., 2017).

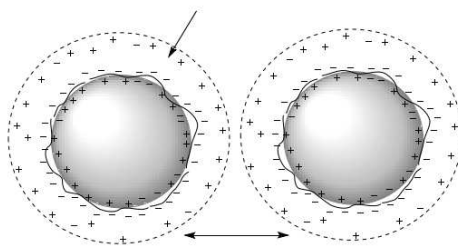
Figure 18 – Electric double layer.



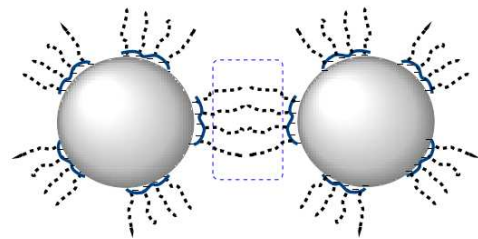
Source: PARK; SEO, (2011).

Figure 19 – Dispersing mechanisms.

Electrical double layer of charged particles, contain counterions



Electrostatic Effect



Steric Hindrance

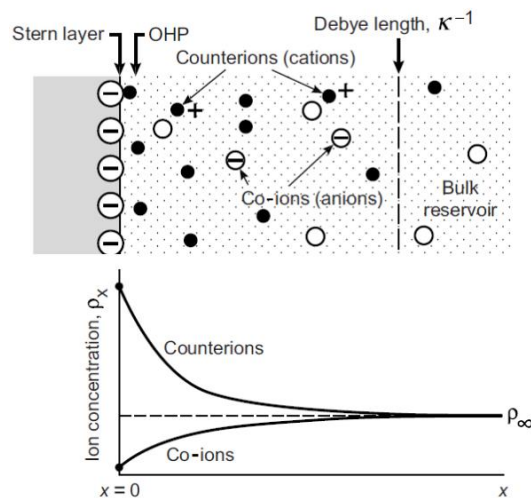
Source: WANG; KAYALI; LIOW, (2019).

Varying the pH is another effective method for dispersing aqueous suspensions, as it directly affects the electrical potential of the particle double layer. In this case, surface charging is due to the protonation or hydroxylation of hydroxide groups on the particle's surface (HOTZA; GREIL, 1995).

As seen in Figure 18, an electrically charged particle will have a layer of ions (counterions), strongly bound to its surface, being called as Stern layer. Right above the Stern layer, there is a second layer which is thicker called the diffuse layer. This layer is majorly comprised of the same counterions of the Stern layer, with a few co-ions. As we move away from the particle, the concentration of counterions decreases, until reaching an equilibrium between counterions and co-ions, Figure 20. Exactly at this point, the end of the diffuse layer is reached, and from there on begins the bulk phase (GONG, 2019).

One fact about the diffuse layer is that, as the particle moves (due to Brownian motion), ions that are closer to the particle move together with the particle, while those that are far remain with the bulk media. The distinction between these two groups of ions is called the slipping plane, and the electrostatic potential at this plane is called the zeta potential. Particles with a zeta potential between -10 and +10 mV are considered approximately neutral, being highly susceptible to agglomeration, while zeta potentials greater than +30 mV or lesser than -30 mV are considered strong, thus providing a well-dispersed and stable suspension (CLOGSTON; PATRI, 2011).

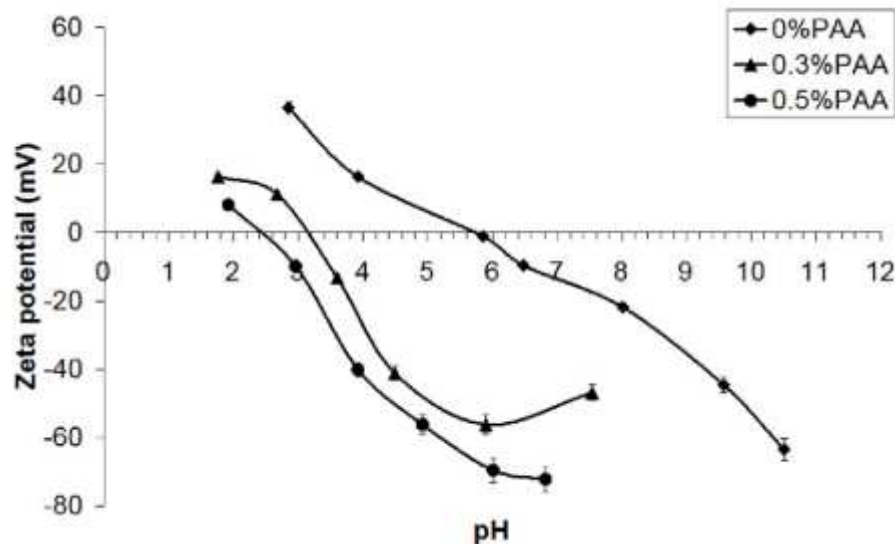
Figure 20 – Ion gradient through the diffuse layer.



Source: GONG, (2019).

Since varying the pH affects the surface charge of the particles, measurements of pH in the function of zeta potential can also give important information about suspension stability regarding pH and dispersant amounts (HOTZA; GREIL, 1995). Figure 21 shows zeta potential curves of YSZ powder, for different dispersant contents. The point where the curve crosses the zero potential is known as the isoelectric point (IEP) and represents the pH at which particles are neutral. It is possible to see that with the addition of dispersant, the IEP is dislocated, and at pH 6, which was previously a point of instability, becomes a quite stable suspension. Although polyacrylic acid (PAA), is most commonly used as a binder, at very low concentrations it can also be used as a dispersant, since it is a polyelectrolyte (CARPIO et al., 2015).

Figure 21 – Zeta potential curves of YSZ particles at different dispersant content.



Source: CARPIO et al., (2015).

Finally, a summary of the main advantages of using dispersants can be highlighted (REN; LUO; ZHOU, 2018):

- increase interparticle repulsive forces, stabilizing suspensions and allowing binders to coat particles more uniformly;
- enable higher solid loadings, increasing the density of green tapes;
- decrease the required solvent content, providing a faster drying with less shrinkage.

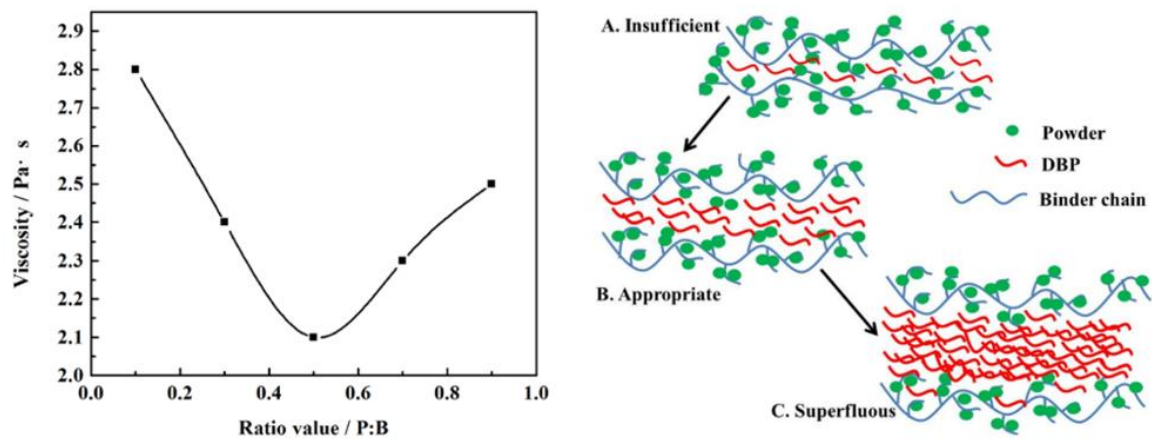
2.2.4.2 *Binder and Plasticizer*

Binders and plasticizers are used respectively to provide strength and flexibility to green tapes after evaporation of the solvent. Through the formation of organic joins between ceramic particles, binders are also used so that the green tapes can be easily handled and retained in the desired shape before sintering. Binders also affect the rheology of the suspension, increasing the viscosity and generating a pseudoplastic behavior, which is essential for tape casting. The absence of binders (or its scarcity), leads to the formation of cracks in the green tape, while its plenty can cause holes, due to the excessive high surface tension. Usually, the optimal amount of binder is determined experimentally (HOTZA; GREIL, 1995; MURALIDHARAN et al., 2011; SHEN et al., 2012).

On the other hand, plasticizers have the effect of softening the binders, by reducing the attractive forces between adjacent binder chains, thus preventing the formation of hard and fragile green tapes. In other words, the plasticizer reduces the overall strength while promoting flexibility. The efficiency of the plasticizer depends on the size of its molecules and the active groups. Plasticizers with low molecular weight and few active groups, generally are more efficient, since their effect is achieved through their mobility. Nevertheless, the efficiency of a plasticizer can be reduced or even lost if the plasticizer is excessively small compared to binder molecules, or if crosslinking occurs between them, which would cause the stiffening of the green tape (FOGHMOES et al., 2016).

Figure 22 shows the effect of adding a plasticizer to a slurry-containing binder. It is possible to see that, as the plasticizer content increases, the viscosity of the suspension decreases to a certain extent, since the small molecules of the plasticizer are inserted between the long chains of binder molecules. As a consequence, the interactions between binder chains are weakened, thus increasing the distance between them and promoting a better fluidity to the slurry. However, if the plasticizer content continues to increase, the excess molecules will start to agglomerate, causing flocculation and an increase in slurry viscosity (LI et al., 2020a).

Figure 22 – Plasticizer/binder ratio impact on viscosity and schematic of interaction.



Source: adapted from LI et al., (2020a).

2.2.4.3 *Viscosity*

While talking about additives and their principles, it is important to evaluate how this information will be collected, treated, and interpreted. Rheological measurements can be performed in most of the cases by rotational viscometers of two types, controlled shear rate and controlled stress instruments. Both of them usually offer the same range of measuring geometries, having concentric cylinder, cone-and-plate, and parallel plate systems as the main ones (CHHABRA; RICHARDSON, 1999).

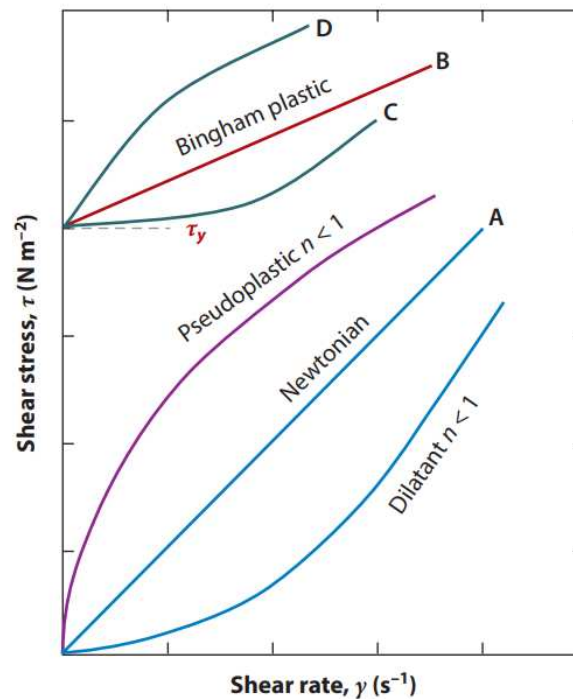
Fluids can show different behaviors that can be classified as Newtonian and non-Newtonian fluids. A Newtonian fluid has constant viscosity regardless of shear rate, while non-Newtonian fluid is any fluid that deviates from this constant behavior. Rheological data is majorly studied by graphics of shear stress in the function of shear rate, which is the best representation for well understanding the fluid. Non-Newtonian fluids are those in the flow curve (shear stress x shear rate), that are non-linear or do not pass through the origin. Therefore, the apparent viscosity is dependent on flow conditions, such as flow geometry and shear rate. The fluids can be grouped into three general classes:

- time-independent, also called purely viscous or inelastic, which shear rate at any point is determined only by the value of the shear stress at that point, at that instant;
- time-dependent, in which the relation between shear stress and shear rate depends, in addition, on the duration of shear and kinematic history;
- viscoelastic, which exhibits characteristics of both ideal fluids and elastic solids, showing partial elastic recovery after deformation.

Most of the real fluids often present a combination of two or even all three types of behaviors. However, it is possible to identify the dominant behavior, taking this as the basis for the subsequent analysis (CHHABRA; RICHARDSON, 2008).

Figure 23 shows the rheological representation of time-independent curves. Curve A, which represents the Newtonian behavior, shows its linearity while crossing through the origin. Since the slope of the curve is the viscosity, it is possible to note that the viscosity is the same for any shear rate, and the flow starts as soon as shear stress is applied. Curve B, known as Bingham plastic behavior, also shows linearity, but now there is a minimum stress τ_y , required for the liquid to flow, called yield stress. The yield stress is the critical shear stress that must be exceeded before irreversible deformation and flow can occur. Pseudoplastic and dilatant curves are also known as shear-thinning and shear-thumping, respectively, and do not present yield stress. It is possible to see that both curves show a slope variation concerning the shear rate, indicating that the viscosity changes with the shear rate. Pseudoplastic represents the decrease of viscosity with increasing shear rate, while dilatant represents the increase of viscosity with increasing shear rate. Finally, the last curves D and C are very similar to pseudoplastic and dilatant curves, but now a yield stress is present. D is also called Bingham pseudoplastic or Herschel-Bulkley fluid, while C is simply called yield stress shear-thickening or yield-dilatant (BOGER, 2013).

Figure 23 – The shear stress–shear rate behavior of time-independent fluids.



Source: BOGER, (2013).

Different models were developed for each behavior, to describe a set of experimental data with an appropriate equation that best fits a flow curve. Table 6 shows the most common, respectively with their equations and applications (MALKIN; ISAYEV, 2022).

Table 6 – Typical rheological models.

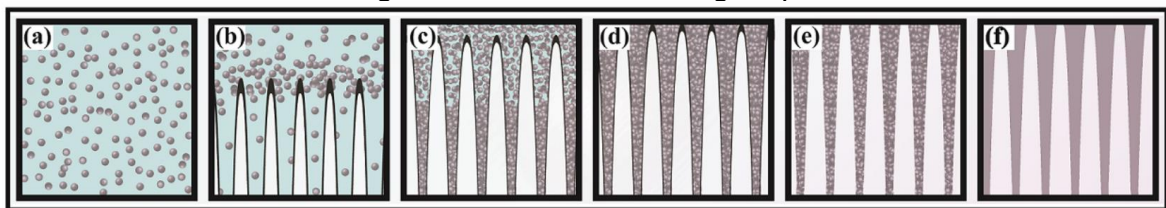
Model	Equation	Application fluid
Newton	$\tau = \eta \dot{\gamma}$	Newtonian
Bingham	$\tau = \tau_y + \eta_p \dot{\gamma}$	Bingham plastic
Herschel-Bulkley	$\tau = \tau_y + K \dot{\gamma}^n$	Bingham pseudoplastic
Ostwald de Waele	$\tau = K \dot{\gamma}^n$	Pseudoplastic + Dilatant
Casson	$\tau = \left[\tau_y^{0,5} + (\eta_p \dot{\gamma})^{0,5} \right]^2$	Bingham pseudoplastic

Source: MALKIN; ISAYEV, (2022).

2.3 FREEZE DRYING

Freeze drying is the most popular technique for making porous ceramics with highly directional pores, in this case, being called freeze casting. The process, which can be seen in Figure 24, starts with a ceramic slurry well dispersed, being frozen by a cold surface (a). During freezing, a temperature gradient is created, so that ice crystals grow in the direction of it while pushing particles away (b). As ice crystals continue to grow, particles are forced to organize themselves between the crystals (c). After complete solidification (d), ice crystals are sublimated by freeze drying, leaving behind empty spaces with the exact shape of the crystals (e). Finally, the porous ceramic is ready to be heat-treated to densify the particles (f), (SCOTTI; DUNAND, 2018b).

Figure 24 – Freeze casting steps.

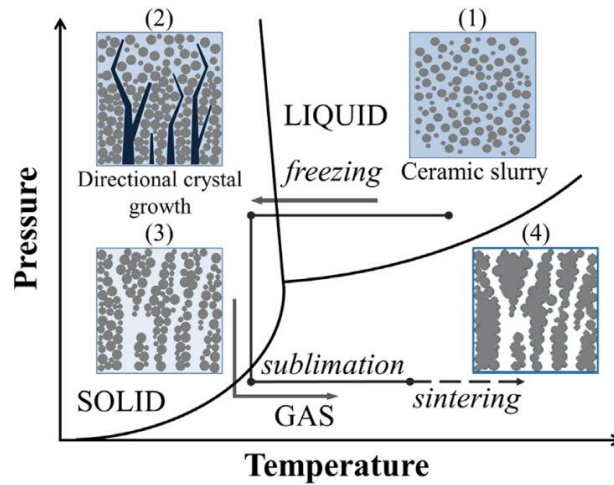


Source: SCOTTI; DUNAND, (2018a).

Important properties of the pores, such as porosity, size, morphology, tortuosity, and orientation, can be controlled by the processing parameters, such as solids loading, freezing rate, freezing temperature, and dispersion medium. Porosity linearly increases with lowering solids loading, while pore size decreases by increasing the freezing rate, i.e., lowering the freezing surface temperature. In addition, pore morphology is primarily dependent on the dispersion medium, for instance, samples cast from water-based slurries have lamellar pores (MILLER; XIAO; FABER, 2015).

Figure 25 shows the freeze casting process regarding the water phase diagram, following three main steps, (1→2) freezing the suspension, (2→3) applying vacuum for sublimation, and (3→4) sintering.

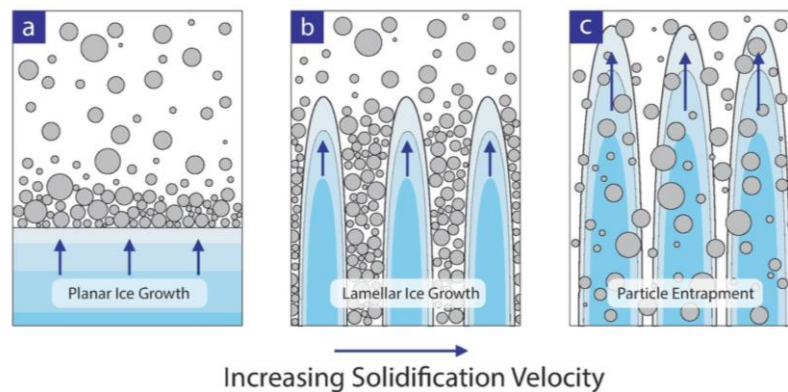
Figure 25 – Freeze casting steps through the water phase diagram.



Source: MILLER; XIAO; FABER, (2015).

The freezing rate, which dictates the crystal growth rate (freezing front velocity), requires extra attention since entrapped particles can occur if the freezing rate is higher than a critical speed, Figure 26. When the freezing front speed is higher than the critical speed, the particles are “swallowed” and trapped by the ice crystals rather than being pushed (c). Without particle orientation, directional pores are inexistent in the final structure. Moreover, if the freezing front speed is lower than the critical speed, lamellar and columnar geometries are produced, since there is enough time for the rearrangement of the particles during crystal growth (b). On the other hand, if the freezing front speed is extremely low, the lamellar structures may disappear, since the low solidification speed makes the crystal growth more stable, with flat morphology, thus pushing all the particles horizontally (a), (SANTOS et al., 2021).

Figure 26 – Effect of freezing front velocity on particle rearrangement.



Source: SCOTTI; DUNAND, (2018a).

3 MATERIALS AND METHODS

3.1 MATERIALS

For the manufacturing of the first electrolyte and anode tapes, tetragonal yttria-stabilized zirconia (YSZ), from Innovnano was used to acquire ceramic processing skills and develop an idea of the appropriate composition for tape casting. For the final electrolyte tape, cubic YSZ from Sigma Aldrich was used, providing the chance to compare the processing of tapes using powders with different particle sizes and manufacturers. For zeta potential assessment, cubic YSZ from Innovnano, and synthesized nickel oxide (NiO), were used. All other materials and additives, respectively with their functions and brands, are shown in Table 7.

Table 7 – Materials, additives, and their functions.

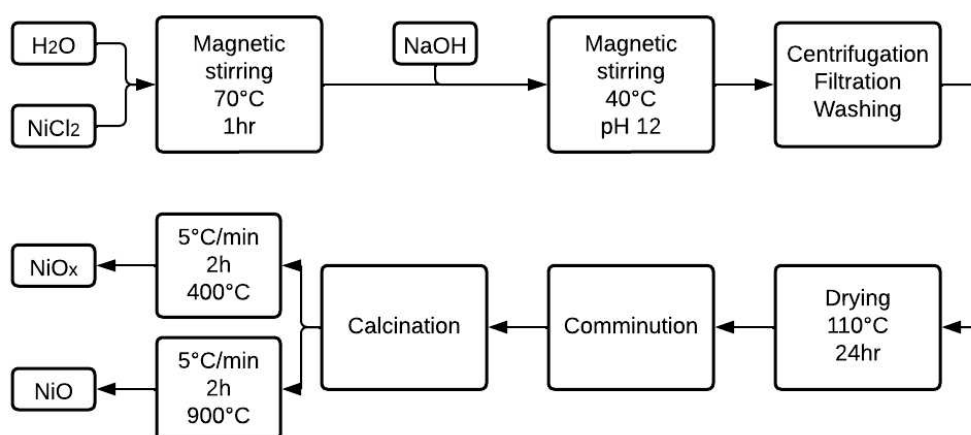
Materials / Additives	Function	Manufacturer
Corn Starch	Pore former	Maizena
YSZ 8% mol (cubic)	Electrolyte	Sigma Aldrich
YSZ 8% mol (cubic)	Zeta Characterization	Innovnano
YSZ Tetragonal	Electrolyte/Anode	Innovnano
NiO	Anode	Author
NiCl ₂ ·6H ₂ O	NiO precursor	NEON
NaOH	Precipitating agent	NEON
Ammonium polymethacrylate	Dispersant	Vanderbilt Minerals
Mowilith LDM 6138	Binder	Claritex
Polyethylene glycol	Binder	NEON
Diethanolamine	Surfactant	N/A
Y-30 Silicone emulsion	Defoamer	Sigma Aldrich
Stearic acid	Mylar lubricant	Gramalux
Silicone spray	Mylar lubricant	Orbi Química

Source: Author.

3.2 METHODOLOGY

3.2.1 Synthesis of Nickel (II) Oxide

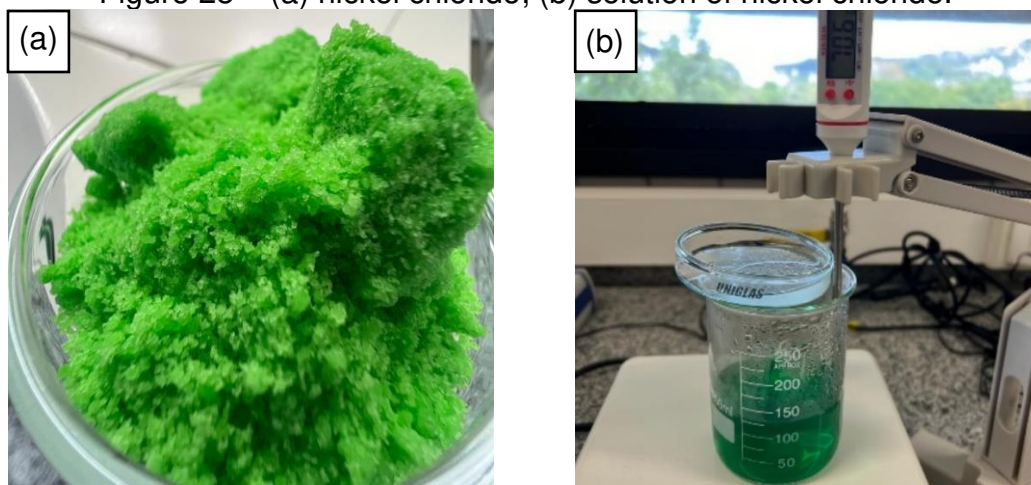
Figure 27 – Sol-gel route of nickel (II) oxide synthesis.



Source: Author.

For the synthesis of nickel (II) oxide, was used the sol-gel route. First, water was heated until reached 70 °C, and then nickel chloride hexahydrate, NiCl₂·6H₂O, was added as the precursor. Nickel chloride was dissolved instantaneously in a dark green solution, while magnetic stirring was left for 1 hour to ensure full dissolution. A petri plate filled with cold water was placed on top of the beaker to mitigate water losses by evaporation, and stabilize the concentration of the solution, Figure 28.

Figure 28 – (a) nickel chloride; (b) solution of nickel chloride.



Source: Author.

After that, the heat was turned off, and while the solution cooled, a solution of NaOH 1M was added dropwise, under magnetic stirring, until reaching a pH of 12, ensuring that the reaction had been completed. The NaOH reacts with the Ni^{2+} and Cl^- ions, precipitating nickel (II) hydroxide, $\text{Ni}(\text{OH})_2$, which is insoluble in water. The average temperature during the precipitation was 40 °C. The balanced chemical equation can be seen below.

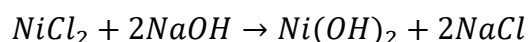


Figure 29, shows fine membranes of $\text{Ni}(\text{OH})_2$ formed by NaOH drops, while stirring is off, and its shape reminds a jellyfish. With stirring, these shapes are destroyed by shear stresses.

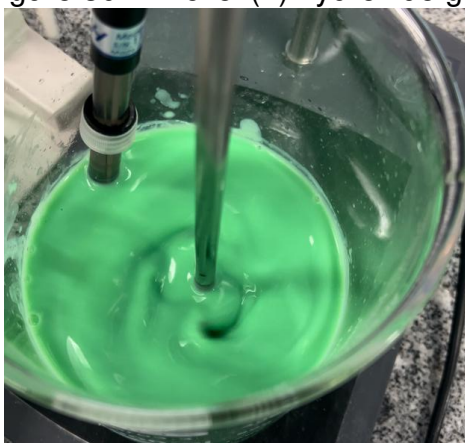
Figure 29 – Nickel (II) hydroxide “jellyfish”.



Source: Author.

It is important to note that, while the $\text{Ni}(\text{OH})_2$ is being precipitated, the solution viscosity increases until a certain point where magnetic stirring is no longer effective. This point is where the solution becomes a gel, thus being necessary to change the mixing method to a propeller disperser. A digital propeller disperser IKA RW 20 was used at 380 rpm, using an anchor impeller. Figure 30 shows a light green gel of $\text{Ni}(\text{OH})_2$ being stirred by an anchor impeller while measuring its pH with a probe.

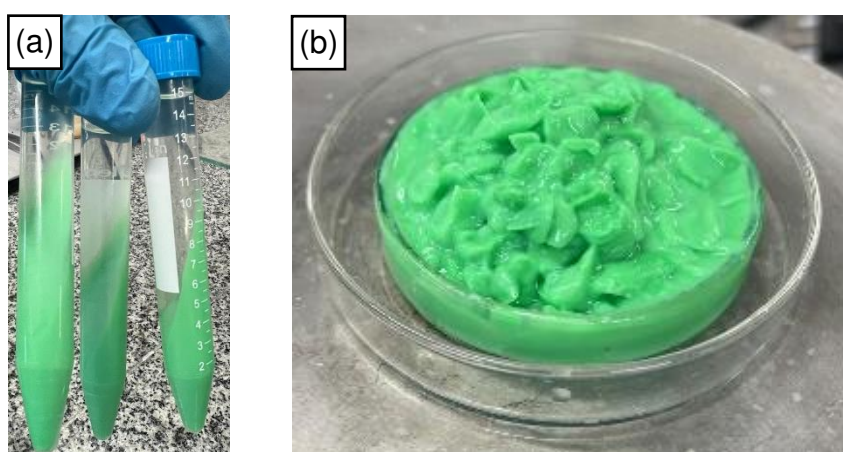
Figure 30 – Nickel (II) hydroxide gel.



Source: Author.

The next step was the centrifugation of the gel, followed by filtration to remove the excess water and concentrate the $\text{Ni}(\text{OH})_2$ gel. After centrifugation, the supernatant liquid was discharged, and the gel was removed with a small spatula. The remaining gel on the falcon tube walls was recovered by washing with distilled water and performing a vacuum filtration with filter paper and a Buchner funnel. Figure 31 shows the centrifuged gel and the final appearance of the concentrated gel. It is important to note that the other product of the reaction is sodium chloride, NaCl , which can be completely removed by consecutive washing steps, with distilled water.

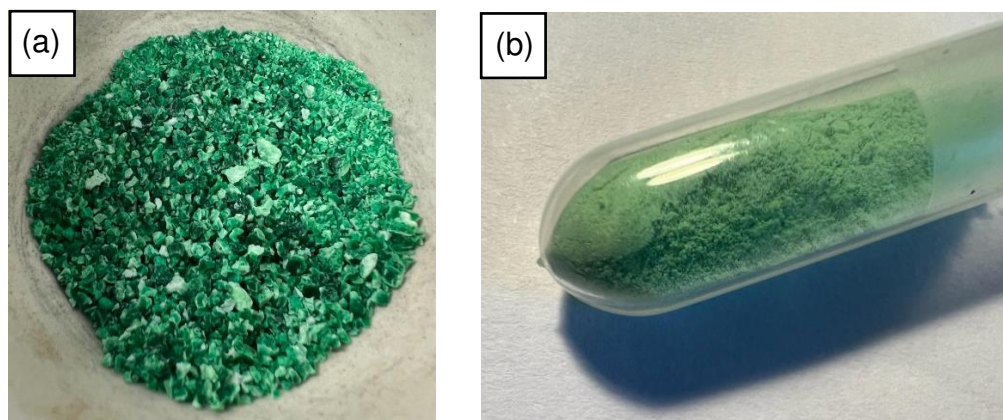
Figure 31 – (a) centrifuged gel; (b) nickel (II) hydroxide gel.



Source: Author.

After that, the drying step was performed inside an oven at 110 °C for 24 h to remove all water content, followed by a manual comminution step with a ceramic mortar and pestle. Figure 32 shows the $\text{Ni}(\text{OH})_2$ solids before and after the comminution.

Figure 32 – $\text{Ni}(\text{OH})_2$ (a) coarse fragments, (b) fine powder.



Source: Author.

The last step is the calcination inside a kiln, where the $\text{Ni}(\text{OH})_2$ becomes nickel oxide, NiO . At this step, 2 temperature levels were tested, 400 and 900 °C, for 2 h, with a heating ramp of 5 °C/min. Figure 33 shows the resulting powders of NiO_x (black), and NiO (olive green), respectively, where NiO_x is the non-stoichiometric form of nickel (II) oxide, while NiO is the stoichiometric form.

Figure 33 – NiO_x and NiO powders.



Source: Author.

For the calcination, it was necessary to use an alumina crucible, big enough to support the amount of powder desired. Since there was no one available, a crucible was produced. The alumina base was manufactured by slip casting following the composition shown in Table 8. After 24 h drying at room temperature, the casted bases were placed in the oven at 80 °C for 24 h. Finally, the bases were sintered in a kiln at 1400 °C for 10 h.

Table 8 – Suspension composition for slip casting.

Component	Wt %
Water	54
Alumina	43
Bentonite	2
Dispersant	1

Source: Author.

Figure 34 – Alumina base after slip casting (green body).



Source: Author.

3.2.2 Powder characterization

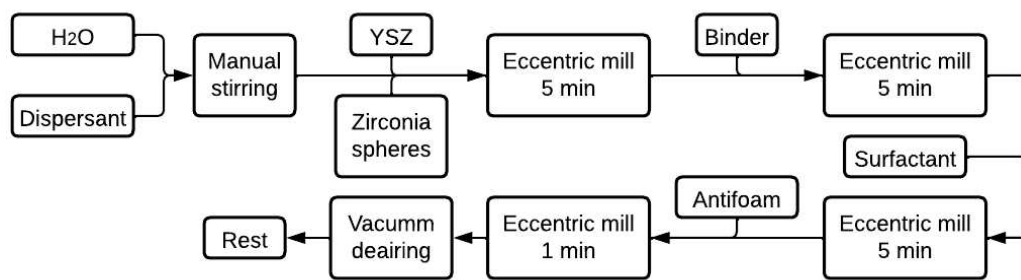
The powders were characterized by their particle size distribution (PSD), and zeta potential (ZP), by using the dynamic light scattering technique (DLS), with a Malvern Zetasizer Nano ZS. The powders were diluted in distilled water, at a concentration around 0.01 %wt. Its crystalline phases were characterized by the x-ray diffraction technique (XRD), with a Rigaku MiniFlex600.

3.2.3 Electrolyte green tape manufacturing

The electrolyte, which is made from yttria-stabilized zirconia (YSZ), was manufactured by tape casting, starting with the suspension preparation followed by casting, drying, debinding, and sintering.

3.2.3.1 Suspension preparation

Figure 35 – Electrolyte suspension preparation route.



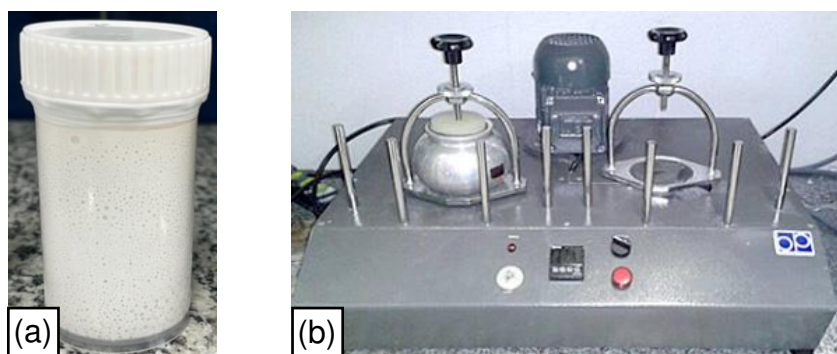
Source: Author.

The suspension preparation was performed by first, manually mixing dispersant and deionized water inside a beaker. YSZ powder and zirconia milling spheres were added into the milling pot, made of polypropylene (PP), with a 4.5 cm diameter, 8.6 cm height, and 100 mL volume.

Then, the mixture of water and dispersant was poured into the pot. Before taking the pot to be mixed by eccentric milling, vigorous manual shaking was performed to make a pre-mixing, preventing the powder from remaining stuck at the bottom of the pot. The first mixing step was performed by ball milling in an eccentric milling from BP Instrumentec, which is a high-energy milling machine, for 5 min.

Then, binder, surfactant, and antifoam were added to the pot, separately in this order, with a mixing step between each addition. The mixing steps were performed at the same conditions (eccentric milling; 5 min), except for the antifoam which was mixed for 1 min. Figure 36 shows the PP pot and the eccentric mill used.

Figure 36 – Milling/mixing: (a) PP pot, (b) eccentric mill.



Source: (a) author; (b) CERMAT-UFSC, (n.d.).

Finally, the suspension was placed into a desiccator coupled to a vacuum pump, where deairing was performed for 2 min, with a negative pressure of 600 mmHg, to remove bubbles. Since the vacuum was not enough to remove all bubbles, the suspension was left to rest for 12 h.

3.2.3.2 Casting

For tape casting, 3 methods were performed and evaluated. Traditional tape casting with a tape caster machine, in which a polyester film (carrier film, Mylar) pulls the suspension through a fixed doctor blade gap, adjusted at 200 μm . The velocity of the carrier film was set to be 6 cm/min. Screen printing was also manually performed by using a stencil with a 4 cm square shape and 210 μm thickness. Finally, manual tape casting was performed, where now, the polyester film is fixed, while the doctor blade manually moves on it. In this case, a simpler stainless steel doctor blade was used, called binil, Figure 37, with random casting velocity and the same 200 μm gap. For all cases, a stainless steel sieve was used in the moment of pouring the suspension, to retain the milling spheres.

Figure 37 – Doctor blade manual device (binil).



Source: SERVITECH, (n.d.).

The suspensions were cast on 3 film surface conditions: standard, silicone coated, and stearic acid coated, to assess the difference in ease of tape removal (delamination). The standard surface is the Mylar surface without lubricant, cleaned with ethanol. The silicone-coated Mylar is made by applying silicone spray and then using paper to remove excess, passing the paper unidirectionally until it has a thin coating layer. Finally, for creating a uniform stearic acid coating, it was necessary to heat the Mylar on a thermal plate up to 60 °C, for the stearic acid powder to melt. Now, with melted stearic acid, the thermal plate was turned off, and while it cooled, a cloth was used to spread the liquid uniformly on the Mylar film. As the temperature lowers, the stearic acid starts to solidify, but now, on a fine and uniform layer shape.

During all cases, all tapes were left to dry overnight at room temperature and humidity. The room temperature varied between 22 and 30 °C, depending on the day. And the humidity was measured to be 70 to 75%.

3.2.4 Anode green tape manufacturing

The anodes, which are made by a mixture of yttria-stabilized zirconia (YSZ) and nickel oxide (NiO), were manufactured by manual tape casting, starting with the suspension preparation followed by casting, drying (or freeze-drying), debinding, and sintering. The methodology used is pretty much the same as that of the electrolyte.

3.2.4.1 *Freeze drying*

Freeze drying was performed to generate highly directional pores. The equipment used was from JJ Científica, of model LJJ, Figure 38. Two routes were performed to compare the freezing rate, thickness of the tape, and presence of pore former. The first sample, with no pore former, was cast with a 1 mm doctor blade gap, and placed directly in the freezer at -80 °C, over an acrylic base for slower freezing, for 7h. The second sample, with pore former, was cast with a 0.5 mm doctor blade gap, and immediately placed on a metal surface previously cooled with liquid nitrogen at around -195 °C, for fast freezing, and later, placed inside a freezer at -80 °C for 7 h. Then, both samples were placed inside the freeze dryer at -50 °C for vacuum application, with freeze drying being performed for 24 h.

Figure 38 – Freeze drying equipment.

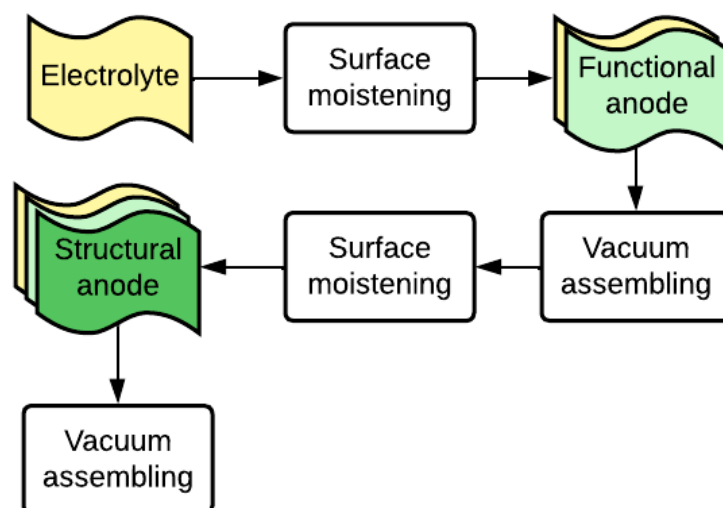


Source: JJ CIENTÍFICA, (n.d.).

3.2.5 Vacuum assembling

For the vacuum assembling of the green tapes, a wet soft brush was used to moisturize the tapes surface, in order to ensure a good adhesion between tapes. Then, vacuum was applied in order to remove any remaining entrapped air between the layers, and to unclog pores that could be clogged by the water.

Figure 39 – Vacuum assembling technique.

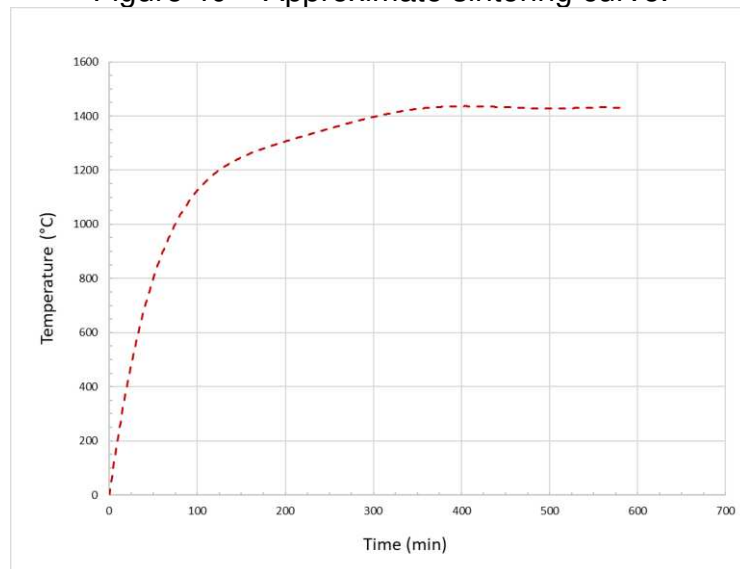


Source: Author.

3.2.6 Debinding and sintering

Tapes were individually debinded and sintered to generate individual SEM images. Debinding of individual green tapes was performed in a kiln at 600 °C for 1 h, with a heating ramp of 1 °C/min, while sintering at 1430 °C for around 4 h. The sintering heating ramp can be seen in Figure 40, which is an approximate curve. Assembled tapes were also manufactured to generate SEM images of the stack. In this case, constrained debinding and sintering were performed, at the same conditions (temperature and time), of individual tapes, except for the 3 h of debinding.

Figure 40 – Approximate sintering curve.



Source: Author.

3.2.6.1 Vacuum assembling

Vacuum assembling of the tapes was performed by moistening the surface of the tapes with deionized water, with the help of a brush, joining them together, and applying a vacuum to ensure the removal of any entrapped air between the tapes.

3.2.7 Suspension characterization

The suspensions were characterized by their rheological properties by using a Thermo HAAKE VT550 viscometer, Figure 41, varying the shear rate from 0 to 1000 s^{-1} with an analysis duration of 180 s.

Figure 41 – Viscometer equipment.



Source: AKRIBIS SCIENTIFIC LIMITED, (n.d.).

4 RESULTS AND DISCUSSION

4.1 POWDER CHARACTERIZATION

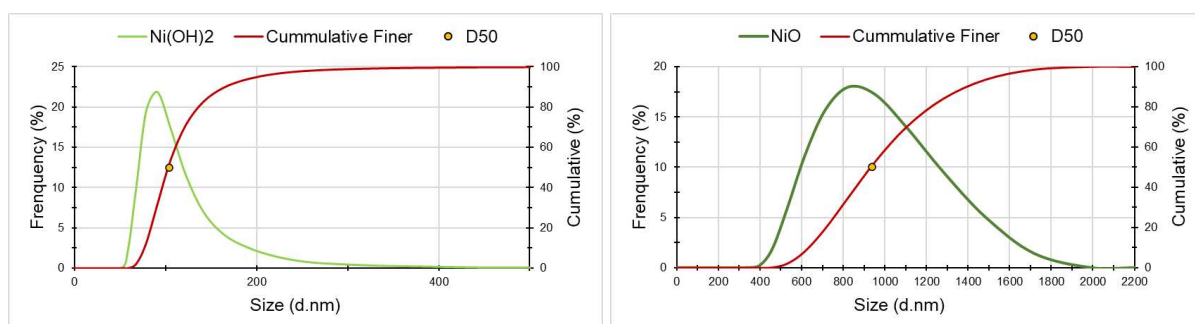
4.1.1 Particle size distribution

4.1.1.1 *Nickel oxide*

The particle size distributions of nickel powders are shown in Figure 42. Nickel hydroxide was synthesized with an average particle size (APS), of 214 nm, which after calcination at 900 °C, generated nickel oxide particles of an APS of 895 nm. The increase in the APS was expected since at this high calcination temperature, diffusion and grain growth may start to occur, making smaller particles agglomerate by getting in contact, forming larger particles, as stated elsewhere (BOŠKOVIĆ; ŽIVANOVIĆ, 1974; IRSHAD et al., 2022). The sintering temperature of nickel oxide is expected to be at 1400 °C since above this temperature no grain growth is noticed. However, at 1200 °C grain growth is already present, inducing that 900 °C can be considered as a pre-sintering temperature. Table 9 also shows the standard deviation of the measurements.

An incongruity was found between the measured APS of $\text{Ni}(\text{OH})_2$ and the graphic generated by the equipment. While the presented APS value was 213.5 nm, the D50 value of the cumulative finer curve is around 100 nm, without explanation. However, based on the manufacturer information, the 213.5 nm displayed number is the value to be considered.

Figure 42 – Particle size distribution of $\text{Ni}(\text{OH})_2$ and NiO .



Source: Author.

Table 9 – Average size and standard deviation (nickel powders).

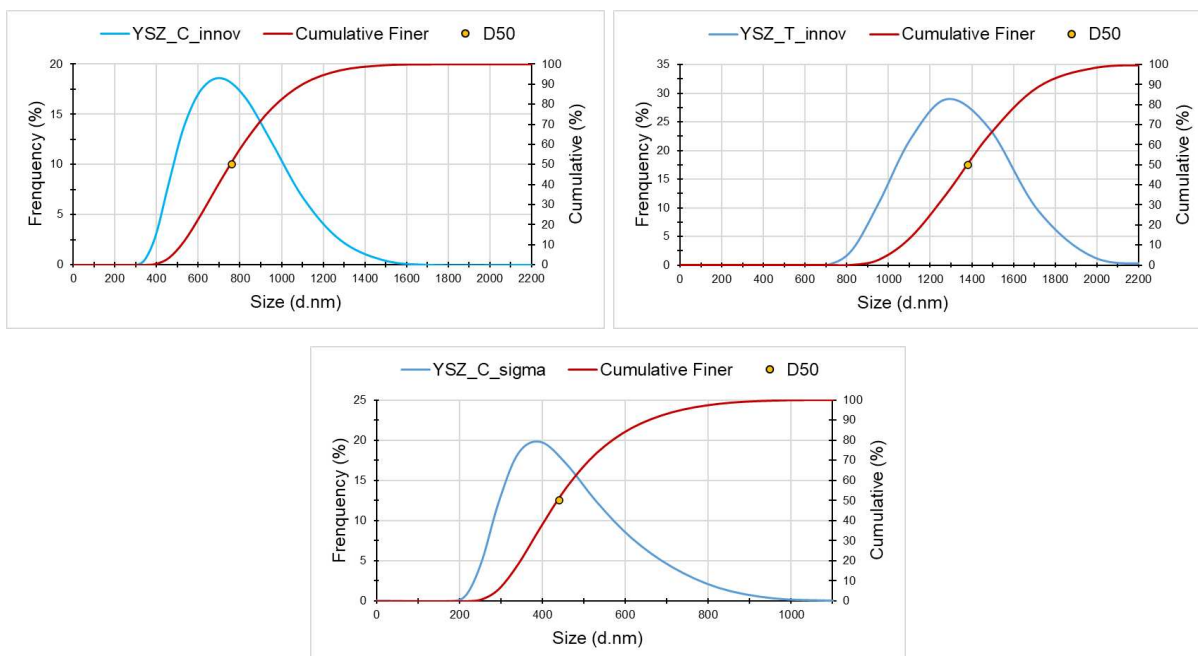
Powder	Size (nm)	Std. Dev.
Ni(OH) ₂	213.5	5.02
NiO	895.2	44.06

Source: Author.

4.1.1.2 Yttria-stabilized zirconia

The particle size distributions of YSZ powders are shown in Figure 43, while Table 10 shows the average particle size and standard deviations displayed by the equipment. It is possible to note a slight deviation between APS and D50 values for cubic powders. This can be explained because APS was based on the mean of all measures of a sample (which was done in triplicate), while only one measure was chosen to plot the graphic. Nevertheless, the incongruity generated by the equipment during Ni(OH)₂ measures, may be also present here but to a lesser extent.

Figure 43 – Particle size distribution of YSZ powders.



Source: Author.

Table 10 – Average size and standard deviation (YSZ powders).

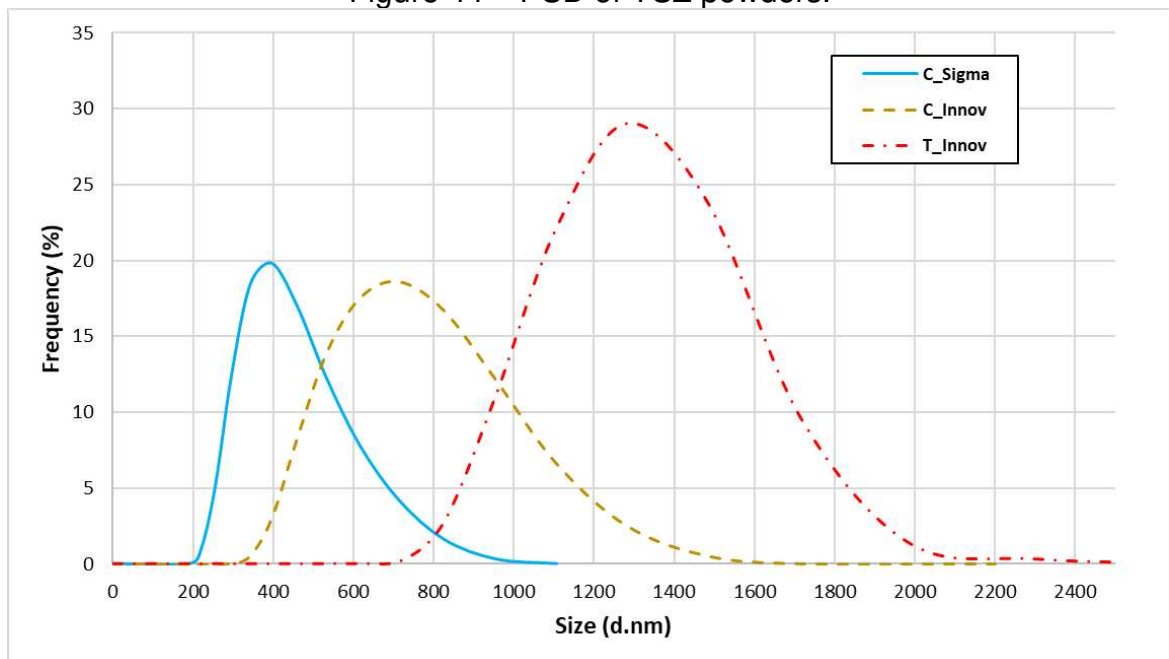
Powder	Size (nm)	Std. Dev.
YSZ_C_Sigma	429.8	23.32
YSZ_C_Innovnano	820.5	5.32
YSZ_T_Innovnano	2003.0	32.79

*C – cubic T – tetragonal

Source: Author.

On the other hand, the measure for the tetragonal powder was not good, since the incongruity was expressive, showing an APS of 2003 nm, with a D50 around 1400 nm. Since these particles are much greater, dynamic light scattering (DLS), may not be the most suitable technique for measuring this powder with accuracy, but the displayed value of ~2000 nm remains somewhat trustworthy, giving the idea of a much greater particle compared with others. Figure 44 shows a comparison between all three powders.

Figure 44 – PSD of YSZ powders.



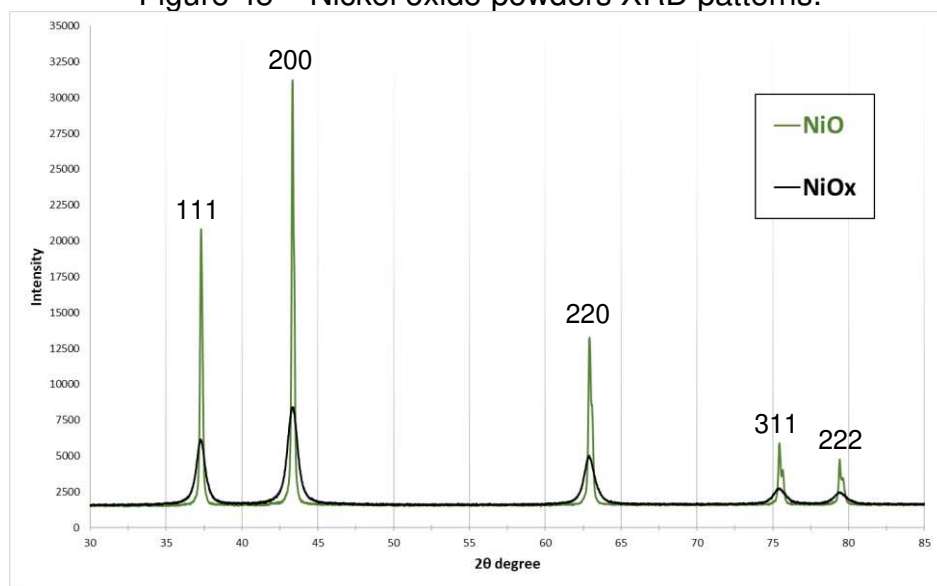
Source: Author.

4.1.2 Crystallographic phases

4.1.2.1 Nickel oxide

Figure 45 brings the XRD curves for the synthesized nickel oxide powders, respectively with the Miller indices (hkl), while Table 11 brings the data of diffraction angle and intensity associated with each index.

Figure 45 – Nickel oxide powders XRD patterns.



Source: Author.

Table 11 – XRD data of nickel oxide powders.

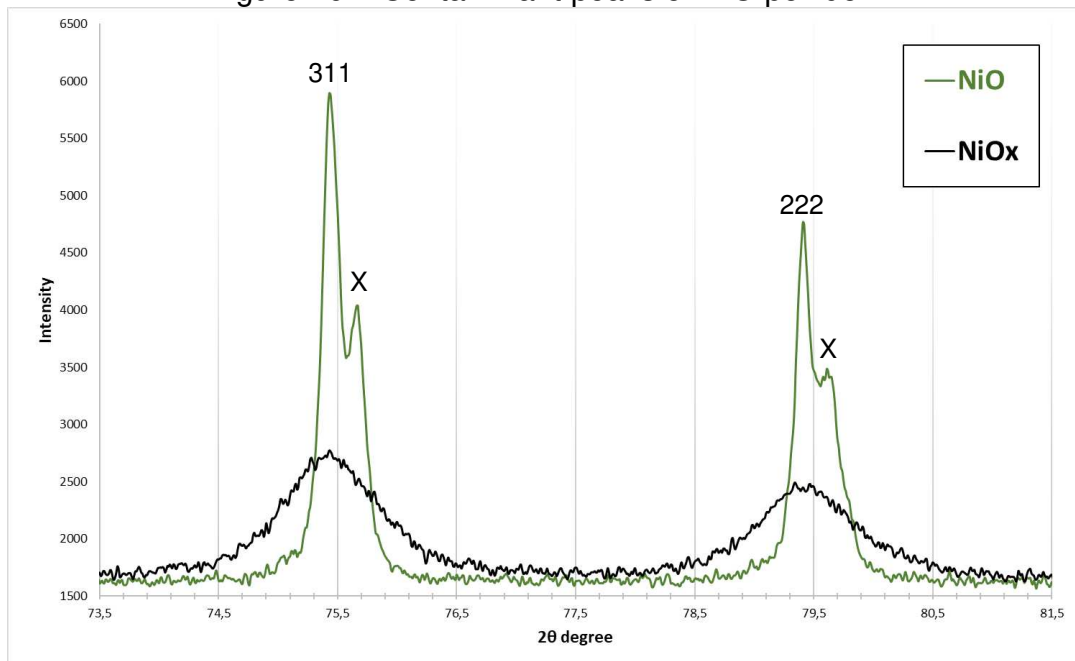
Powder	(hkl)	Diffraction angle 2θ	Intensity
NiO	111	37.31	20832
	200	43.34	31208
	220	62.91	13258
	311	75.43	5894
	222	79.41	4770
NiO _x	111	37.27	6174
	200	43.39	8413
	220	62.89	5044
	311	75.43	2773
	222	79.34	2492

Source: Author.

The results were consistent with patterns found elsewhere (FARDOOD; RAMAZANI; MORADI, 2017; RAHDAR; ALIAHMAD; AZIZI, 2015). The diffraction peaks are associated with a pure cubic phase of NiO. The strong and sharp peaks indicate a high crystallinity.

However, extra peaks found, in Figure 46, indicate that there are some impurities in NiO powder. This is expected since the production of stoichiometric NiO was performed in large quantities, and during the process and handling some contamination may have occurred. On the other hand, non-stoichiometric nickel oxide (NiO_x), was synthesized in another batch, and in a very small quantity, which allowed greater care in handling, thus, showing a higher purity.

Figure 46 – Contaminant peaks of NiO powder.

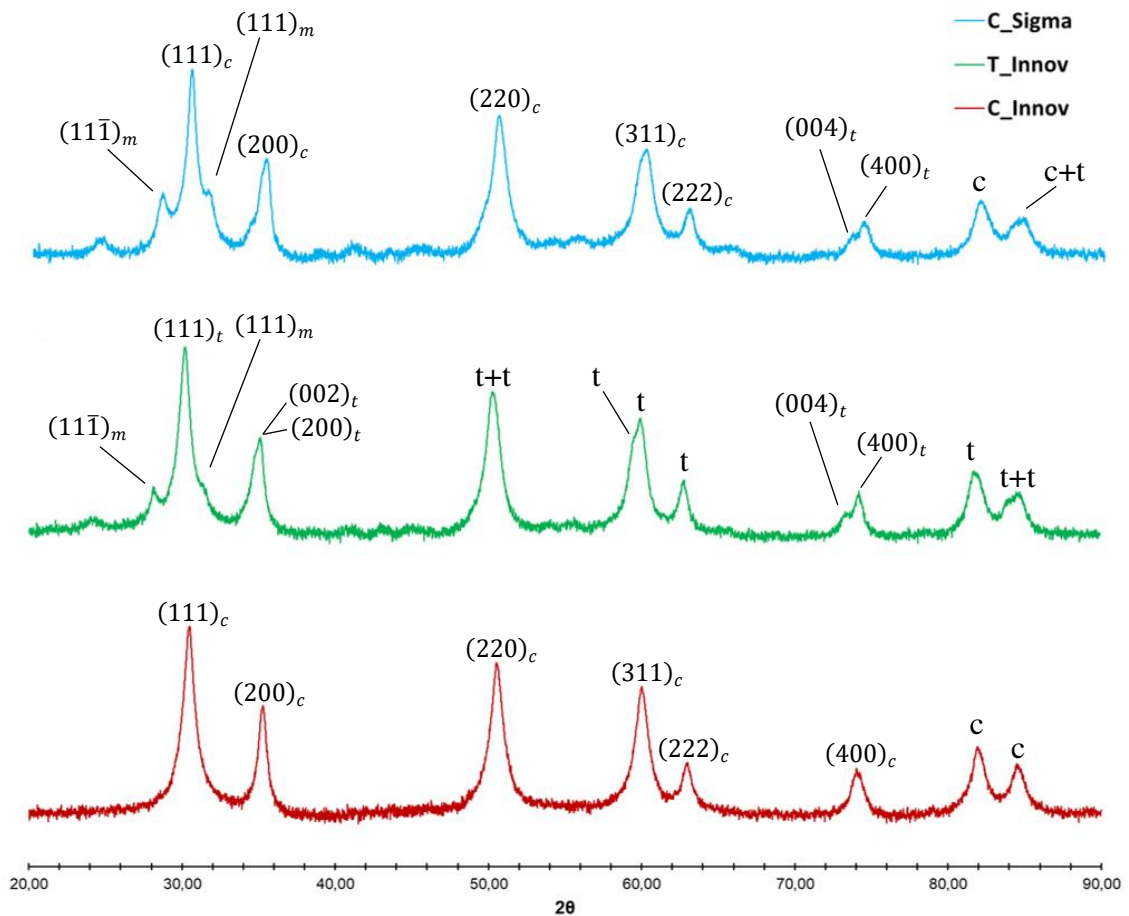


Source: Author.

4.1.2.2 Yttria-stabilized zirconia

Figure 47 shows the XRD curves for the YSZ powders, respectively with the Miller indices (hkl), while Appendix A, brings the data of diffraction angle and intensity associated with each index.

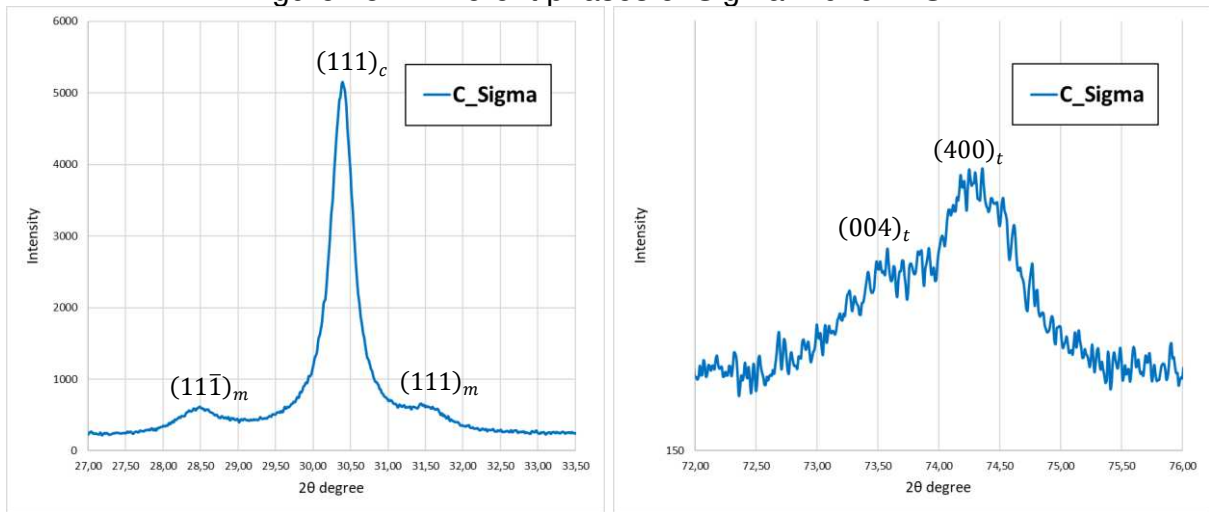
Figure 47 – YSZ powders XRD patterns.



Source: Author.

Starting with Sigma Aldrich powder, which was supposed to be cubic, it is possible to identify monoclinic peaks between the range of $27^\circ - 33^\circ$, and also a tetragonal phase is pronounced between the range of $72^\circ - 76^\circ$. These peaks are more clearly with a zoomed view, Figure 48. Tetragonal powder from Innovnano, also showed the presence of monoclinic phases, between the same range of $27^\circ - 33^\circ$. Finally, cubic YSZ from Innovnano showed to be the purest, without unexpected peaks.

Figure 48 – Different phases of Sigma Aldrich YSZ.



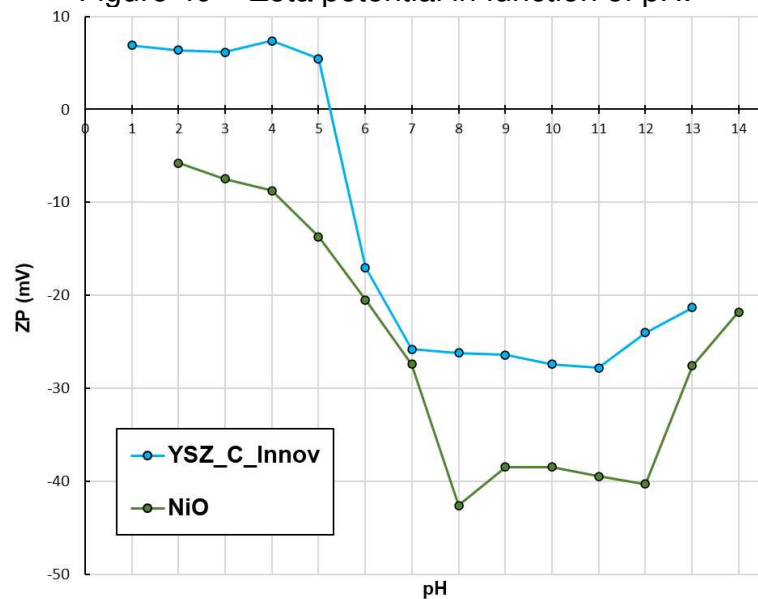
Source: Author.

All phases and Miller indices were identified based on the literature elsewhere (PARK et al., 2022; SATHISH et al., 2011; SRINIVASAN et al., 1991; VLADIMIR et al., 2017; ZHANG et al., 2019).

4.1.3 Zeta potential

The zeta potential in the function of the pH was measured for the synthesized NiO and cubic YSZ from Innovnano, Figure 49.

Figure 49 – Zeta potential in function of pH.



Source: Author.

It is possible to see that YSZ has an isoelectric point (IEP), between a pH of 5 and 6, and only can be considered well dispersed and stabilized for pHs greater than 7, where its ZP gets closer to -30 mV. On the other hand, NiO appears to have an IEP at harsh acid conditions, getting close to pH 0. However, it gets easily stable at pHs greater than 7. Both powders show reverse behavior at pHs greater than 11 to 12, returning to a state of weak stability as a suspension.

It is possible to see that, at neutral conditions (pH = 7), both powders show very similar ZP values with the same negative charge. This is very welcome since both particles are going to repel each other with the same intensity, thus generating a more homogeneous dispersed suspension. Nevertheless, from pH 5 or less, the particles will show opposite charges, leading to a strong agglomeration between YSZ and NiO.

It is important to consider that this analysis was performed only with deionized water. With the addition of a dispersant, the scenario would change, probably reducing the IEP of YSZ, and allowing a good dispersion at lower pHs for both powders. By looking into the literature, it is possible to state that the found IEP for YSZ is similar to other authors (AGUILAR ARIAS, 2012; GHIASI et al., 2023). For NiO is also possible to find similar results, but different ones are also present (EL-KEMARY; NAGY; EL-MEHASSEB, 2013; RAMANATHAN et al., 2004).

Therefore, it is not recommended to base yourself on ZP curves from other authors without building your curve, since many factors can affect the ZP values, in a way that your results can be very different from others. For instance, particle size, surface area, morphology, powder manufacturing process, brand, temperature, and adsorption of ions, molecules, or contaminants onto the surface of ceramic particles, can lead to variances in ZP measurements.

4.2 ELECTROLYTE TAPE MANUFACTURING

4.2.1 Tetragonal YSZ

4.2.1.1 *Screen printing*

Initially, an assessment of the presence of bubbles was made. Figure 50 shows the suspension before (A) and after (B), the resting step, where it is possible to notice that the first pots on the left side of image A, already have larger bubbles (coalescence), while the last pots (freshly mixed), has an aspect of foam with very small bubbles. In an attempt not to use antifoam, after 58 h of rest, it is possible to see that foam strongly reduced, but since these suspensions have a relatively high viscosity, the long resting period was not enough to eliminate all bubbles, as seen in image C. Marks at the bottom of the B pots are grinding spheres.

By casting with the presence of bubbles, the tape will also have bubbles, as we can see in Figure 51. Which is bad, since bubbles can be a precursor of cracks.

Figure 50 – Bubbles assessment.



Source: Author.

Figure 51 – Screen printed wet tape with bubbles.



Source: Author.

Figure 52 shows 4 wet tapes cast by screen printing, with 4 cm width and 210 μm thickness. It was tried to assess the ease of removal of the tape from the Mylar, comparing a silicone coating with no silicone applied. The composition is the same for all tapes (SP1) and can be seen in Table 12. Now, the antifoam was added, so there are no more visible bubbles. A very small amount of binder was applied for assessing what happens.

Figure 52 – Screen printed SP1 electrolyte tapes.



Source: Author.

Table 12 – Composition of screen-printed tapes.

Components		SP1 wt%	SP2 wt%
Powder	YSZ (Innovnano)	54.9	47.2
Water	Distilled water	39.6	34.2
Dispersant	Ammonium polymethacrylate	2.2	1.9
Binder	Mowilith LDM 6138	0.7	15
Surfactant	Diethanolamine	2.4	1.5
Defoamer	Y-30 Silicone emulsion	0.2	0.2
TOTAL	-	100	100

Source: Author.

Figure 53 shows the tape drying at room temperature and humidity. This image is important to see the shrinking phenomena occurring, where while the water evaporates, tape suffers shrinking in all directions, including thickness. In the image, it is possible to see that the drying is radial, from the edges to the center, where the part

that remains wet has a higher thickness. It is also noticeable that some cracks are being born, since shrinking causes internal stresses.

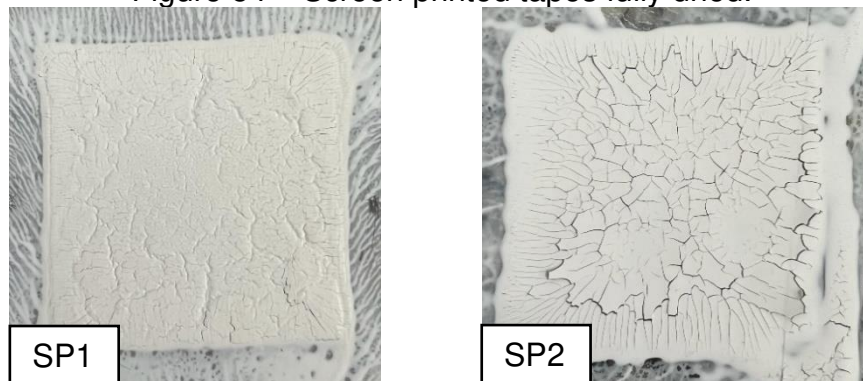
Figure 53 – Screen printed tape drying.



Source: Author.

After fully drying, SP1 tape shows a lot of cracks Figure 54. The low binder content is an important factor that induces the appearance of cracks. Another attempt was performed with a higher binder loading, SP2. As a consequence of increasing the binder, other components will have your content reduced, for total mass.

Figure 54 – Screen printed tapes fully dried.



Source: Author.

When looking at SP2 dried tape, Figure 54, expressive cracks are noticeable, while in SP1 the fragments didn't disconnect from each other, even having almost no binder content. This can be explained since composition SP1 has a greater solid content. Nevertheless, the absence of a binder made SP1 very brittle and friable, while SP2 has a plastic aspect.

It is also noticeable that the crack density is higher for SP1, i.e., the fragments are much smaller, while SP2 shows larger fragments and lower crack density. The reason for that is when increasing the binder content, the particles of the powder will attach strongly, with void spaces filled by the binder, making it more difficult to generate a crack between them. However, even with a higher binder content, cracks were shown, and this can be explained by the reduction of the solid content, and/or, the insufficiency of binder, which may be needed to fully “embrace” all particles.

When comparing SP1 and SP2 compositions, it is possible to see that while the binder content increased, the solid load decreased. With fewer solid particles, the space between them is greater, thus generating internal stresses when the water evaporates, which may lead to cracks. In this case, 15% of binder content was not enough to stabilize 47% of solid content after shrinking. However, when taking one of the fragments of SP2 tape and attempting to break it in half by hand, the plastic behavior was noticeable, resulting in a tape with much greater tenacity. Another possible way to end cracks without adding more binder is adding a plasticizer since its presence would weaken binder interactions making them more flexible during shrinkage.

Because of too many cracks, it was not possible to evaluate which tape was delaminated easier from the Mylar, since all of them broke with any attempt to remove them.

4.2.1.2 Manual tape casting

The exploratory study of binder content was performed by subsequent experiments by manual tape casting, thus generating larger tapes. The next compositions tested are in Table 13.

Table 13 – Electrolytes composition (T-YSZ).

Component		MT1 wt%	MT2 wt%	MT3 wt%	MT4 wt%	MT5 wt%
Powder	YSZ (Innovnano)	54	50	50	44.53	48.82
Water	Distilled water	15.3	22.8	22.8	23.66	22.23
Dispersant	Ammonium polymethacrylate	2.7	2.7	2.7	1.78	2.05
Binder	Mowilith	25	22.7	22.7	27.83	24.90
Surfactant	Diethanolamine	2.5	1.3	[†] 1.3	1.63	1.37
Defoamer	Y-30	0.5	0.5	0.5	0.56	0.63
TOTAL	-	100	100	100	100	100

* Approximated values.

[†] PEG

Source: Author.

To overcome the problems found with screen-printed suspension compositions, binder, and solid content were increased simultaneously (composition MT1 of Table 13). As a consequence, water content was reduced. Figure 55 shows MT1 tapes made by manual tape casting using a binil.

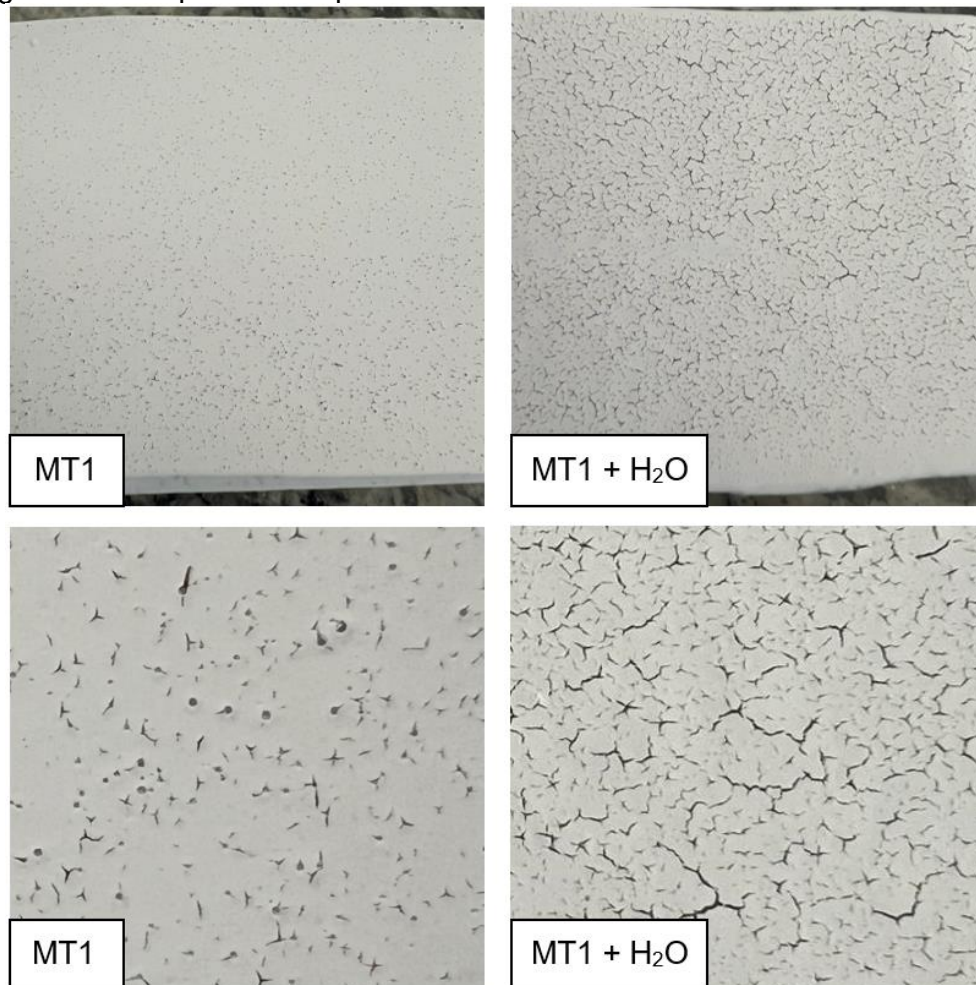
In the left images, is possible to see that now, the crack density has greatly decreased, so that we no longer have the formation of fragments. However, we still have some cracks (“chicken feet” type), which originated from remaining bubbles. With the zoom view, it is possible to see that the cracks were generated from the bubbles.

Manual tape casting facilitates the casting of more viscous suspensions, since the doctor blade runs over the fixed film, forcing the suspension to spread through the gap, while in traditional tape casting, with the doctor blade fixed, the suspension needs to be carried by the film through the gap. For more viscous suspensions, if there is no adequate adherence of the suspension by the Mylar, the suspension can get stuck and not flow well through the gap. Therefore, traditional tape casting is suitable for less viscous suspensions.

During the casting of MT1 tape, it was noticed that the viscosity was slightly high (almost a spackling paste), which could compromise the effectiveness of traditional tape casting. Hence, it was tried to add a small amount of water to check if the suspension would flow better. The amount of water added was not measured.

The right images of Figure 55 show the previous composition of MT1 tape, with more water added. With water content increased, the content of all other constituents decreases, i.e., the solid and binder content decreases, favoring the emergence of shrinking internal stresses. Therefore, it is possible to see that now, the tape has greater cracks and some fragments.

Figure 55 – Tapes of composition MT1 and MT1 with the addition of water.



Source: Author.

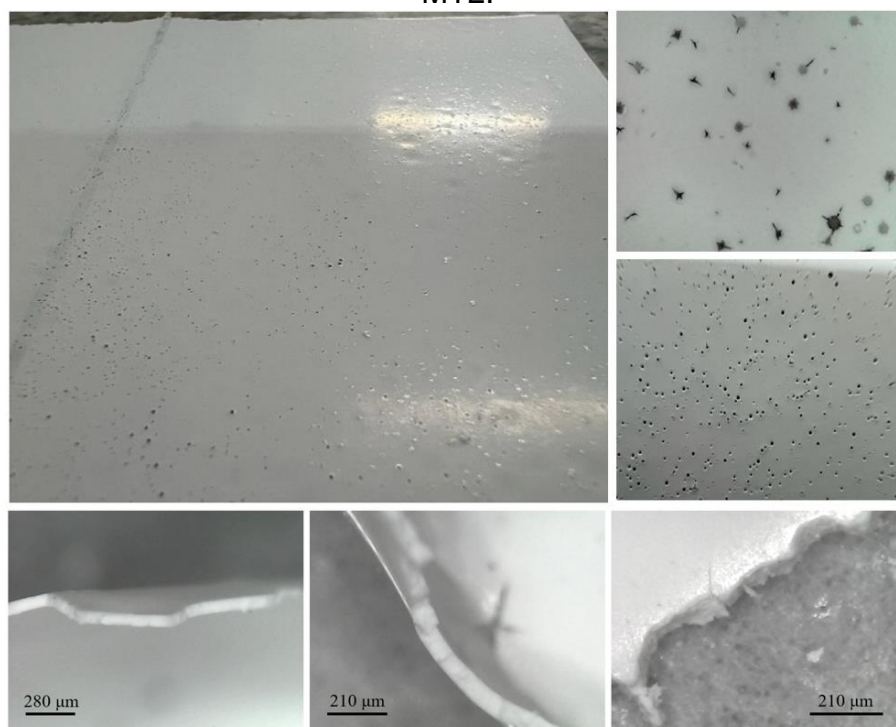
Since the viscosity of suspension MT1 became excessively high, suspensions MT2 and MT3 were an attempt to correct it. By slightly reducing binder and solids

content, new tapes were cast. Now, a comparison of different types of surfactants was made, between diethanolamine (DEA) and polyethylene glycol (PEG).

Both suspensions MT2 and MT3 have the same amount of each component, only differing on surfactant type. Both suspensions showed high plasticity and shiny aspect, and this time, was possible to start removing the tape from the silicone-coated Mylar. However, after some mm were removed, the tape broke because of the high concentration of pores (bubbles). Both tapes presented a high number of bubbles, and even with the cracks practically not being present, the presence of bubbles affected the density of the tape. Electrolyte tapes must be dense to hinder gas passage.

No significant difference was visually noticed between using DEA or PEG, however, since PEG is also a plasticizer, MT3 flexibility is expected to be higher. Further analysis is needed to better assess the mechanical properties comparing the usage of DEA and PEG, for instance, tensile and flexing tests. Figure 56 shows one of the tapes, with zoom images of its bubble holes and cross-section with approximately 70 μm , taken with a digital microscope.

Figure 56 – Tape manufactured with diethanolamine as a surfactant, composition MT2.



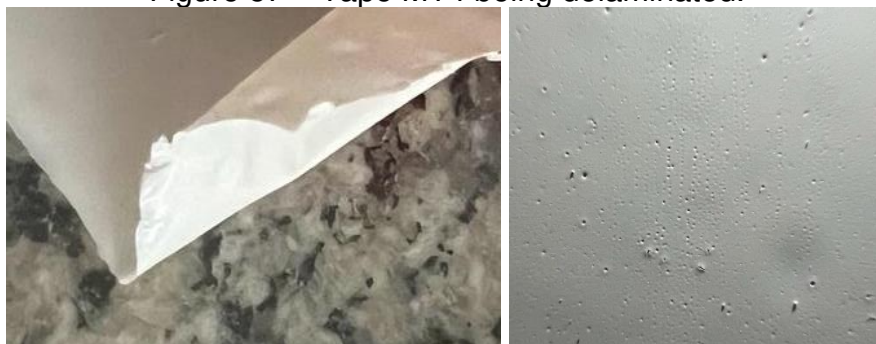
Source: Author.

Up to this point, the castings with manual tape casting were being performed just as soon as the suspensions were prepared, with no resting time. Only vacuum de-

airing was being performed for 2 min. Although this may be one of the reasons for the presence of so many bubbles, another more relevant factor that hinders bubble removal is the viscosity of the suspension. The higher the viscosity, the more difficult it is to get rid of bubbles. This problem was also common for other authors (GANESH et al., 2006; MALEKSAEEDI; PAYDAR; MA, 2010).

For this reason, two more attempts were performed slightly reducing solids content and increasing the binder to compensate for it, thus, getting suspensions MT4 and MT5 with a lower viscosity. The antifoam content was also slightly increased, in an attempt to remove remaining bubbles. Comparing MT4 and MT5, MT4 showed a higher plastic behavior being the first tape that could be fully perfectly delaminated from the silicone-coated Mylar without breaking, Figure 57. Although the Mylar was coated with a silicone layer, the delamination needed to be cautious, since the tape is very thin, delicate, and still presenting a relatively strong attaching to the Mylar. Unfortunately, the tape continues to present bubbles, but in smaller quantities and sizes.

Figure 57 – Tape MT4 being delaminated.



Source: Author.

On the other hand, the tape cast from suspension MT5 presented more bubbles, which were sufficient to bring “chicken feet” cracks back. It is interesting to see that, suspension MT5 has a higher solid content, but this was not enough to avoid cracks formation, showing that, between binder and solids content, the binder has a stronger efficiency concerning cracks hindering. The most likely reason for MT5 tape to have more bubbles is related to its greater solid content, which brings an increase in viscosity, thus hindering bubble removal.

Using silicone spray, showed a slight improvement in tape delamination, but not enough to be called an easy delamination. For this reason, a new technique for

lubricating the Mylar was performed by using stearic acid. Tapes MT5 were cast on 3 surface conditions: standard, silicone-coated coated, and stearic acid coated. Knowing that this tape is fragile, because of the cracks, this comparison was very revealing. For standard and silicone-coated surfaces the tape was not able to be delaminated without breaking apart, but for the stearic acid-coated surface, the tape was delaminated in the easiest way possible, just like lifting a sheet of paper from the table. This experiment showed that using stearic acid as a lubricant for tape delamination works very well. Further analysis is needed to check how the stearic acid coating affects the surface roughness and texture of the tape.

4.2.2 Cubic YSZ

Cubic YSZ from Sigma Aldrich was used to manufacture electrolytes, in an attempt to check how the rheology could change, by using a powder from another manufacturer and with a different particle size distribution. Four compositions were needed until a good tape was reached. The compositions can be seen in Table 14.

Table 14 – Electrolytes composition (C-YSZ).

Component		MC1 wt%	MC2 wt%	MC3 wt%	MC4 wt%
Powder	YSZ (Sigma Aldrich)	44.5	55	54.9	55.0
Water	Distilled water	23.7	17.1	16.9	16.0
Dispersant	Ammonium polymethacrylate	1.8	1.3	1.0	1.0
Binder	Mowilith	27.8	25.0	25.0	25.0
Surfactant	Diethanolamine	1.6	1.2	1.7	2.5
Defoamer	Y-30	0.6	0.4	0.5	0.5
TOTAL	-	100	100	100	100

Source: Author.

The first composition MC1, was based on composition MT4 of tetragonal powder, which was the best previous result. When the suspension was prepared, it was noticed that the viscosity was much different from suspension MT4, having a very aqueous behavior. Knowing that the casting would not work, it was decided to increase the viscosity by increasing the solids loading (suspension MC2). At this time, the viscosity showed to be acceptable for tape casting, and the tape was manufactured

over a stearic acid-coated film. Unfortunately, holes appeared in the tape while wet, caused by the bad interaction of the suspension with the carrier film, probably caused by the high surface tension of the suspension, Figure 58.

Figure 58 – Electrolyte MC2 tape.



Source: Author.

To improve the affinity of the suspension with the Mylar, and increase the wettability, it was decided to increase surfactant content, MC3 and MC4. It was also noticed that the dispersant content could be reduced to 1% while keeping a very good dispersion during the dispersing step. This was expected since cubic Sigma Aldrich powder is less than $\frac{1}{4}$ the size of tetragonal Innovnano.

Although MC3 tape showed the same problem of holes, tape MC4 was a success, Figure 59. The tape could be easily removed from the Mylar thanks to stearic acid coating. It is important to know that even this tape had some microbubbles in some regions, caused by the absence of a resting step before casting.

Figure 59 – Electrolyte MC4 tape.

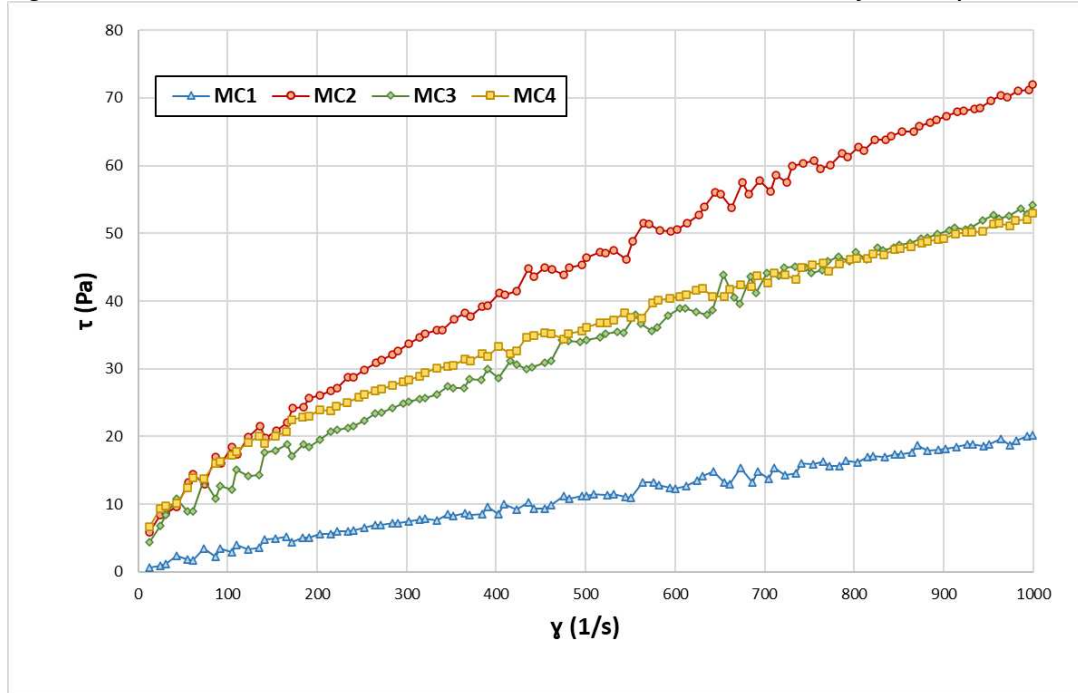


Source: Author.

4.2.2.1 Rheology of YSZ

For assessing the effect of increasing solids content and adding surfactant to the suspensions, a rheological test was performed with suspensions MC1 to MC4, Figure 60.

Figure 60 – Shear stress x shear rate assessment of electrolyte suspensions.

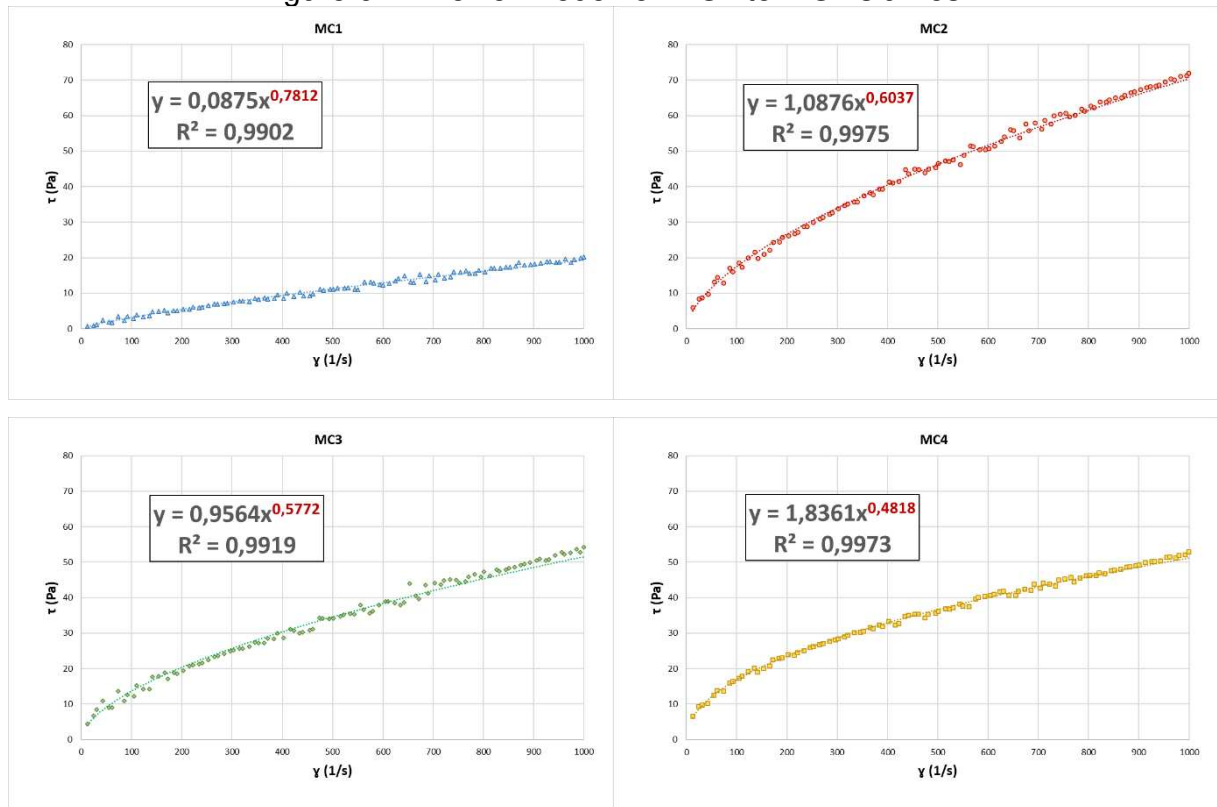


Source: Author.

It is possible to see that the first suspension MC1, was indeed very aqueous since its rheological behavior approaches a Newtonian fluid. When solids were increased, MC2, the viscosity also went up, showing a pseudoplastic behavior. Now, by adding surfactant, MC3, the viscosity slightly decreases. When adding more surfactant, MC4, the viscosity increases in the way that, for lower shear rates the behavior seems to be the same as MC2, only being different for higher shear rates, when its behavior gets close to MC3. By plotting the graphics of each behavior based on Ostwald de Waele model, Figure 61, it is possible to see that MC4 has the lowest “n” parameter, indicating that this slurry has the highest pseudoplastic behavior.

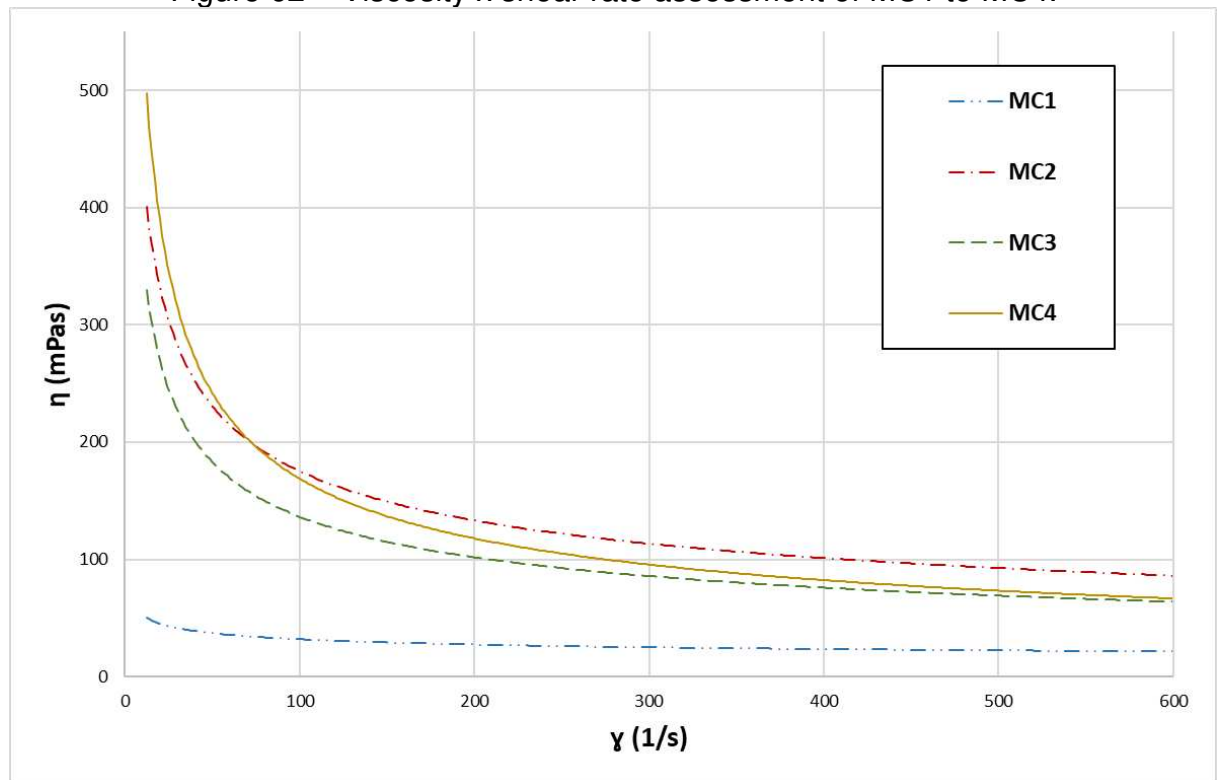
Figure 62 shows the viscosity of the suspensions as a function of shear rate.

Figure 61 – Power model for MC1 to MC4 slurries.



Source: Author.

Figure 62 – Viscosity x shear rate assessment of MC1 to MC4.



Source: Author.

4.3 ANODE TAPE MANUFACTURING

4.3.1 Functional anode

For functional anode manufacturing, 2 attempts were necessary to achieve a perfect tape. The compositions are shown in Table 15. A NiO/YSZ ratio of 3:2 was used, i.e., 60% NiO and 40% YSZ with respect to powder loadings.

Table 15 – Compositions tested for manual tape casting of functional anode.

Component		FA1 wt%	FA2 wt%
Powder	T-YSZ/NiO	44.53	54.31
Water	Distilled water	23.67	17.74
Dispersant	Ammonium polymethacrylate	1.78	1.34
Binder	Mowilith	27.83	24.97
Surfactant	Diethanolamine	1.63	1.22
Defoamer	Y-30	0.56	0.42
TOTAL	-	100	100

Source: Author.

The first composition FA1, was based on electrolyte MT4 composition, which was the best electrolyte result for tetragonal YSZ powder. The tape was cast over a stearic acid-coated film, which proved to show high efficiency in facilitating film removal. The doctor blade aperture was set as 0.2 mm. Figure 63 shows the high efficiency of the defoamer used while representing less than 1% of the suspension composition.

Figure 63 – Foam elimination by using defoamer, before and after addition.



Source: Author.

In Figure 64, it is possible to see that the suspension did not have a good interaction with the carrier film, since contractions appeared while wet, causing holes in the tape.

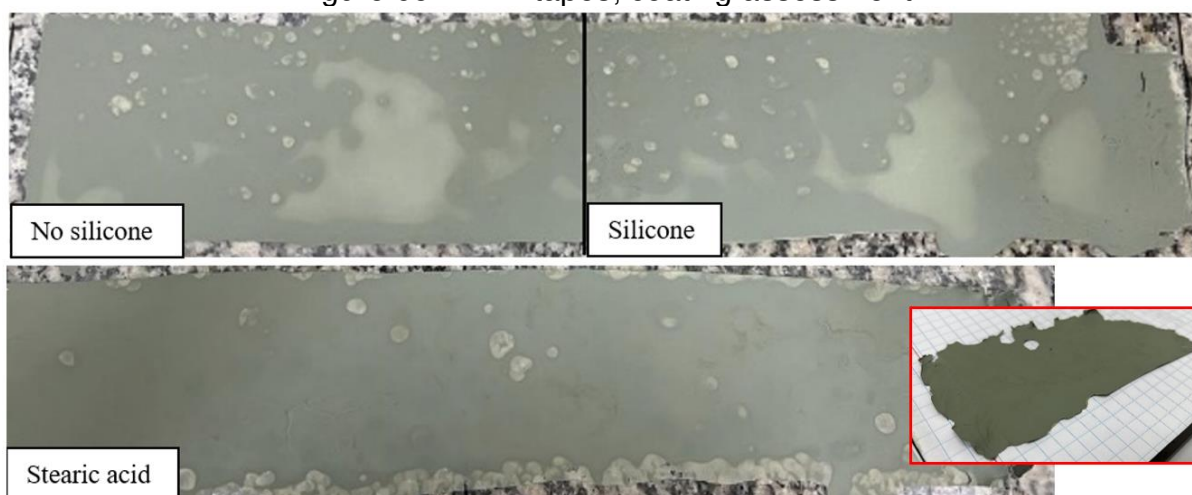
Figure 64 – Functional anode attempt of composition FA1.



Source: Author.

The stearic acid coating was suspected to be responsible for this undesirable effect. Hence, another tape was manufactured, with the same composition, over a film with and without a silicone coating. Figure 65 shows that no improvement was observed, thus, inducing that the problem could be the high surface tension of the suspension. Figure 65 also shows a piece of the FA1 tape delaminated from the stearic acid film, showing that even having holes in it, shows a good plasticity.

Figure 65 – FA1 tapes; coating assessment.



Source: Author.

Trying to solve the problem of holes, a new composition was tested, and this time, it was tried to solve hole problems by increasing suspension viscosity instead of reducing the surface tension. Therefore, FA2 composition has higher solids content. Now, with a higher viscosity, the tape keeps the shape after being cast, hindering contractions while wet. Figure 66 shows that the problem was solved, generating a defect-free tape. Figure 67 shows the delaminated electrolyte and functional anode side by side.

Figure 66 – Functional anode of composition FA2.



Source: Author.

Figure 67 – Electrolyte and functional anode.



Source: Author.

4.3.2 Structural anode

For structural anode manufacturing, 3 compositions were performed based on functional anode FA2 composition. The first composition (SA1), has the same solid ratio 3:2 of NiO/YSZ, no pore former, and it was prepared to be freeze dried. The second composition (SA2), has pore former into solids content, following the composition of Table 17, and it was also prepared to be freeze dried. Finally, the third composition (SA3), should be equal to SA2 but had dispersant content slightly increased (1,3% $\rightarrow$ 1,8%), because SA2 got relatively viscous during the dispersing step, which could compromise the dispersion of particles. After binding addition, the viscosity turned back to be suitable for tape casting. While increasing the dispersant, binder was chosen to be decreased (25,3% $\rightarrow$ 24,8%), to maintain all other constituents with the same content. SA3 tape was prepared to be directly debinded. Table 16 brings all compositions, while Table 17 brings solids composition with additional information.

Table 16 – Compositions for manual tape casting of structural anodes.

Component	SA1 wt%	SA2 wt%	SA3 wt%
Powder	54.7	54.7	54.7
Water	17.1	17.1	17.1
Dispersant	1.3	1.3	1.8
Binder	25.3	25.3	24.8
Surfactant	1.2	1.2	1.2
Antifoam	0.4	0.4	0.4
TOTAL	100	100	100

Source: Author.

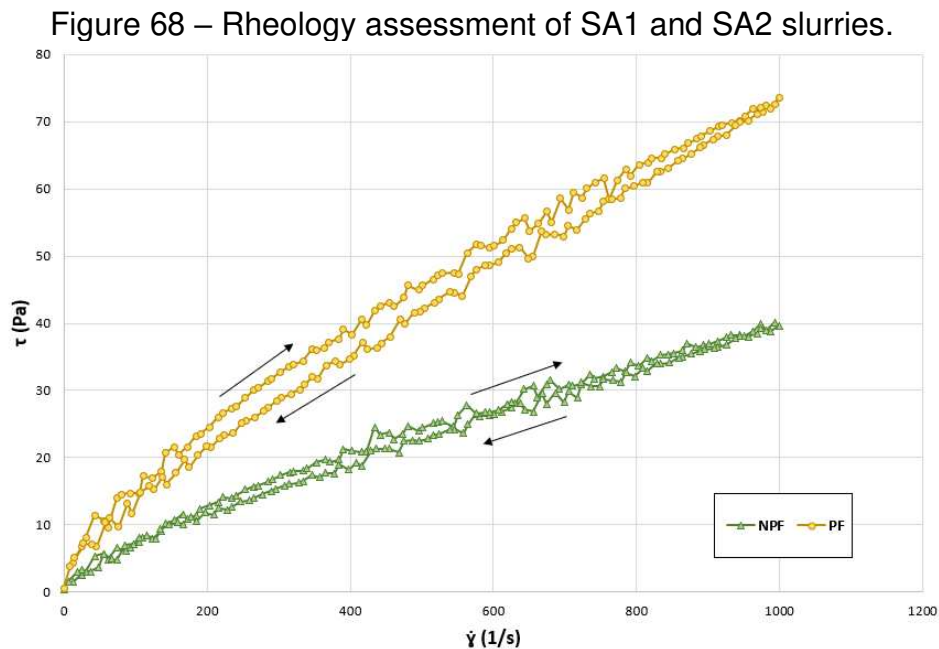
Table 17 – Solids composition of structural anode suspensions.

Component	SA1 wt%	SA2 wt%	SA3 wt%
YSZ	40	32.7	32.7
NiO	60	49.1	49.1
Corn Starch	-	18.2	18.2
Objective	Freeze Drying	N ₂ + Freeze Drying	Debinding
Doctor blade gap (mm)	1	0.5	0.8

Source: Author.

During the suspension preparation of SA2, which has pretty much the same composition as SA1, a significant increase in viscosity was noticed. It is important to note that both of them have the same solids content (54.7%), only differing by the presence of pore former (corn starch). Thus, only adding the pore former to the composition was enough to modify meaningfully the suspension rheology. Although SA3 composition had dispersant content increased, the problem of high viscosity during the dispersing step remains. Therefore, for corn starch uses as pore former, it is recommended to slightly reduce solids content, to get a better dispersion during the dispersing step. This would need to be carefully tested, because an excessive reduction of solids content can lead to other problems such as defects (cracks and holes), during the drying step. An alternative to control the viscosity is by using pore formers with smaller average particle sizes.

For assessing the effect of adding corn starch to the suspension, a rheological test was performed with suspensions SA1 and SA2. Figure 68 shows the shear stress versus shear rate curve of both suspensions, where NPF means “no pore former” (SA1), while PF means “pore former” (SA2).

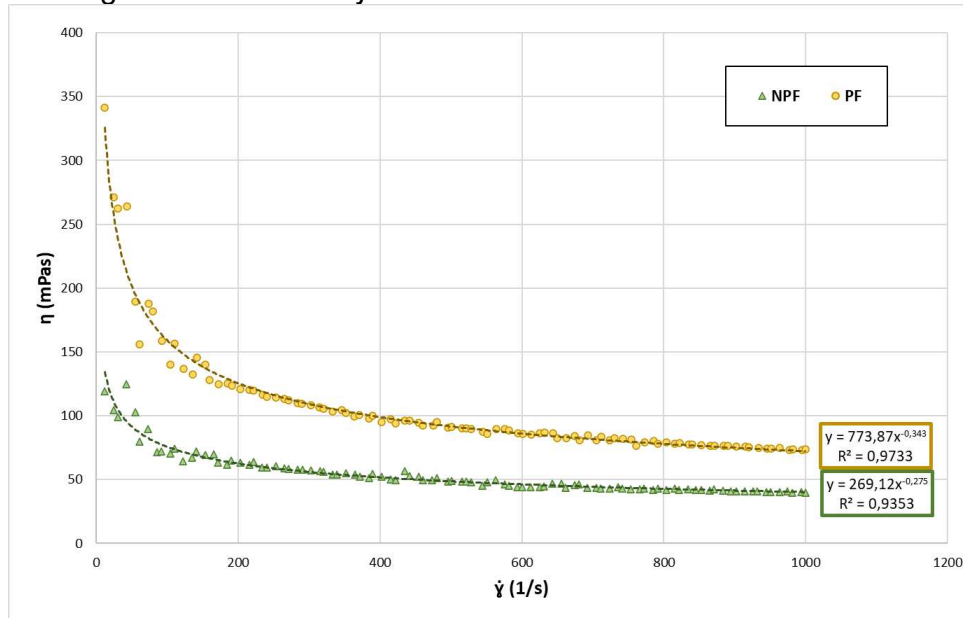


Source: Author.

A high increase in viscosity is shown when adding corn starch. Both suspensions showed pseudoplastic behavior, which is desirable for tape casting. Both suspensions showed a small thixotropic behavior, with the PF curve having a greater

thixotropy of 3660 Pa/s, while NPF exhibited 1550 Pa/s. Figure 69 shows the viscosity of the suspensions as a function of the shear rate, together with the power law fit curve generated by Excel.

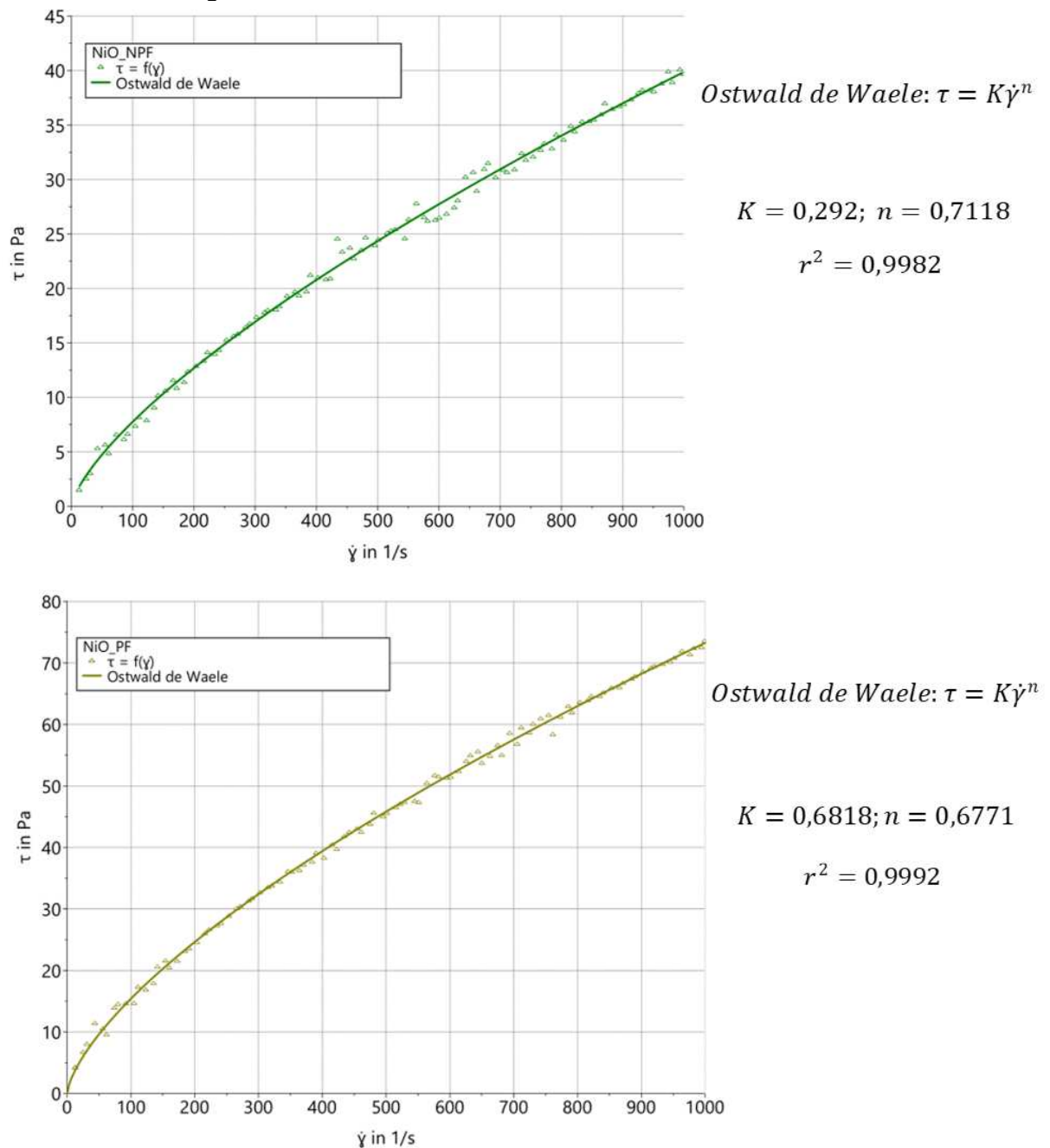
Figure 69 – Viscosity assessment of SA1 and SA2 slurries.



Source: Author.

By using the software HAAKE RheoWin Data Manager (from the equipment manufacturer), is possible to simulate different rheological models and check their accuracy, thus, identifying the correct model for the suspension rheology. For NPF and PF suspensions, the Ostwald de Waele model showed the highest r^2 values, thus being the best-fit result, Figure 70. The thixotropy was also calculated by the software.

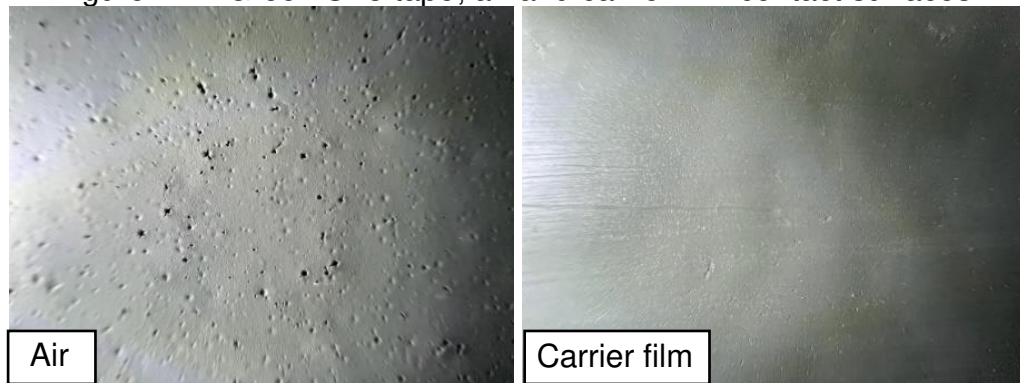
Figure 70 – Software fit model for SA1 and SA2 slurries.



Source: Author.

Since SA3 tape was manufactured to be directly debinded, the tape was cast and left to dry at room temperature over a day. Figure 71 shows both surfaces of SA3 tape after drying and being delaminated.

Figure 71 – Green SA3 tape; air and carrier film contact surfaces.



Source: Author.

It is possible to see that SA3 tape generated bubble holes and some “chicken feet” cracks, but when looking at the other surface of the tape (which was in contact with the carrier film), no defects can be seen. The bubbles are, again, a problem caused by the relatively high viscosity of the suspension, hindering bubble removal. Since the composition of SA3 virtually differs from FA2 only by having pore former in its composition, it is possible to state that the presence of corn starch increased the viscosity of the tape, enough to hinder bubble removal.

The horizontal stripe marks on the surface of SA3 tape, which was in contact with the carrier film, are stearic acid that is attached to the tape surface. Not a problem, since it is organic and will be removed during debinding. Figure 72 shows a zoomed view of a crack, a defect-free region, and a cross-section view of the tape.

Figure 72 – Green SA3 tape, zoom view.



Source: Author.

The SA3 tape was cast with a 0,8 mm doctor blade aperture, i.e., 800 μm . After drying, the tape was 430 μm thick, representing a drying shrinkage of 46.25%. In Figure 72, in the defect-free region, is possible to see white and darker green dots, which are expected to be corn starch and nickel oxide particles, respectively.

The debinding step was performed at 600 °C for 1h, with a heating rate of 1 °C/min, to prevent cracks caused by high internal stresses, while organic additives were being removed. Figure 73 shows the debinded tape cracked after an attempt to handle it, showing that after debinding, the ceramic is in its most fragile state. Thus, if is desired to handle it before sintering, is recommended to perform a pre-sintering step.

Figure 73 – SA3 debinded tape.



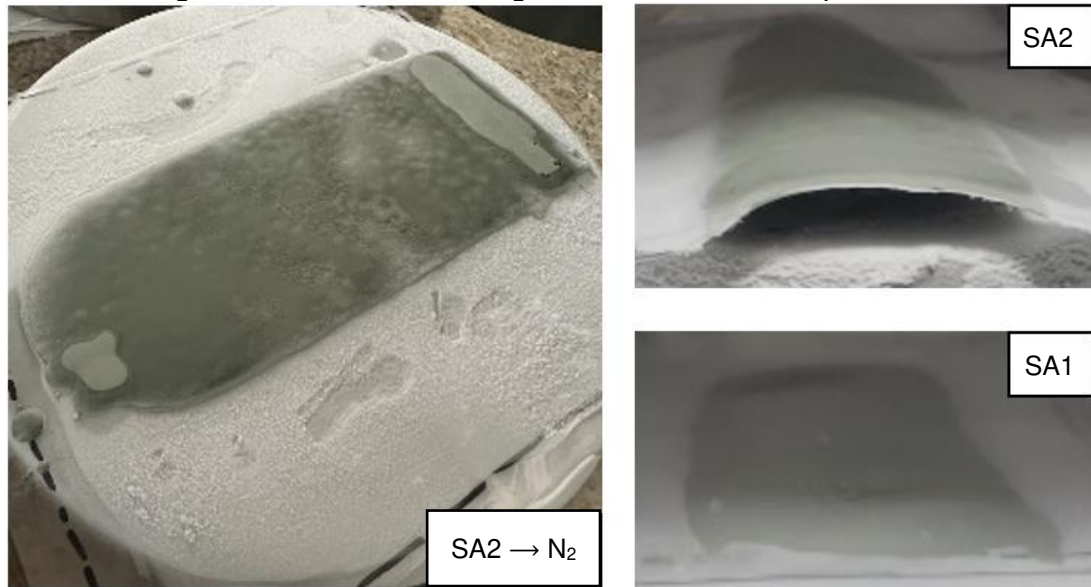
Source: Author.

4.3.2.1 *Freeze drying*

As mentioned before, the freeze-drying step was performed for 2 structural anode suspension compositions, SA1 and SA2. Both of them have the same composition, only differing by SA2 having pore former into solids composition, while SA1 does not. Both tapes were cast over a stearic acid-coated film with a doctor blade aperture of 1 mm and 0,5 mm respectively.

It is possible to see anode SA2, Figure 74, being fast-frozen by a pre-cooled surface with liquid nitrogen, right after being cast. This step was performed to induce the generation of highly directional ice crystals. The figure also shows SA2 tape after 7h inside the -80 °C freezer, right before being taken to the freeze-drying step. SA1 tape, at the same condition, is also shown.

Figure 74 – Freeze casting of SA1 and SA2 suspensions.

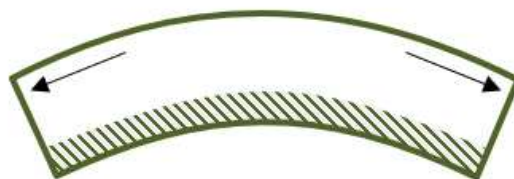


Source: Author.

It is possible to see that, tape SA2 bent inside the freezer, while SA1 did not. This can be explained because this tape was previously frozen at a much lower temperature ($-195\text{ }^{\circ}\text{C}$), solidifying it, and when it was taken to the freezer at a higher temperature ($-80\text{ }^{\circ}\text{C}$), the density slightly decreased, making the volume to increase, i.e., expansion. Since the tape is attached to the carrier film the upper surface has the freedom to expand while the attached surface does not, making the tape bend, Figure 75.

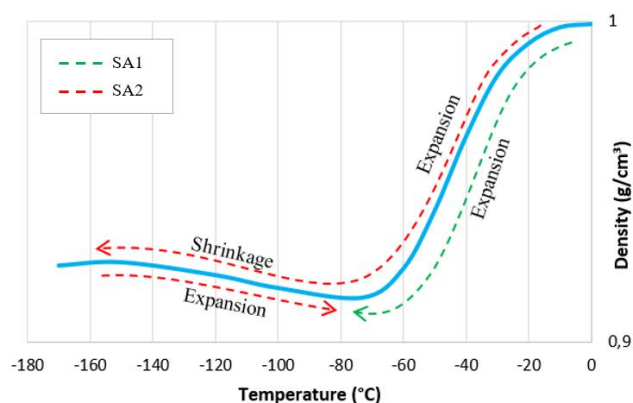
Since SA1 tape was cast and placed directly into the freezer, over an acrylic base, its freezing was slower and homogeneous. Therefore, we can conclude that both tapes suffered volume expansion from $0\text{ }^{\circ}\text{C}$ to approximately $-73\text{ }^{\circ}\text{C}$, but only SA2 suffered a shrinkage, followed by a second expansion when placed into the freezer, from $-195\text{ }^{\circ}\text{C}$ to $-80\text{ }^{\circ}\text{C}$. Figure 76 shows this process as a representative graphic based elsewhere (LIU et al., 2013).

Figure 75 – Bending representation of a tape.



Source: Author.

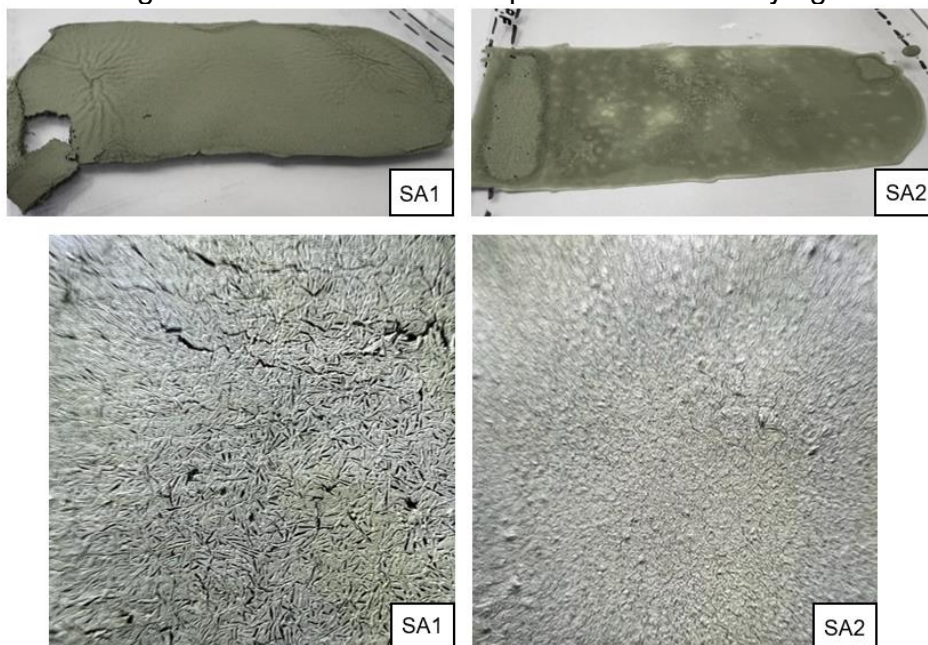
Figure 76 – Representative curve of tape density during freeze casting.



Source: Author.

Figure 77, shows both tapes after being removed from the freeze dryer, with a zoomed view of their surface. Now, since they are at room temperature, and there is no more water content in them, the curvature of the SA2 tape disappeared. Since they are still green, binder is present, keeping them flexible. However, they are very delicate to handle, due to their extremely high porosity. It is possible to see that the SA1 tape wrinkled in some regions. These wrinkles were already present when the tape was removed from the freezer, meaning that it occurred during freezing. On the other hand, SA2 does not have wrinkles but has some stains indicating a non-uniform freezing.

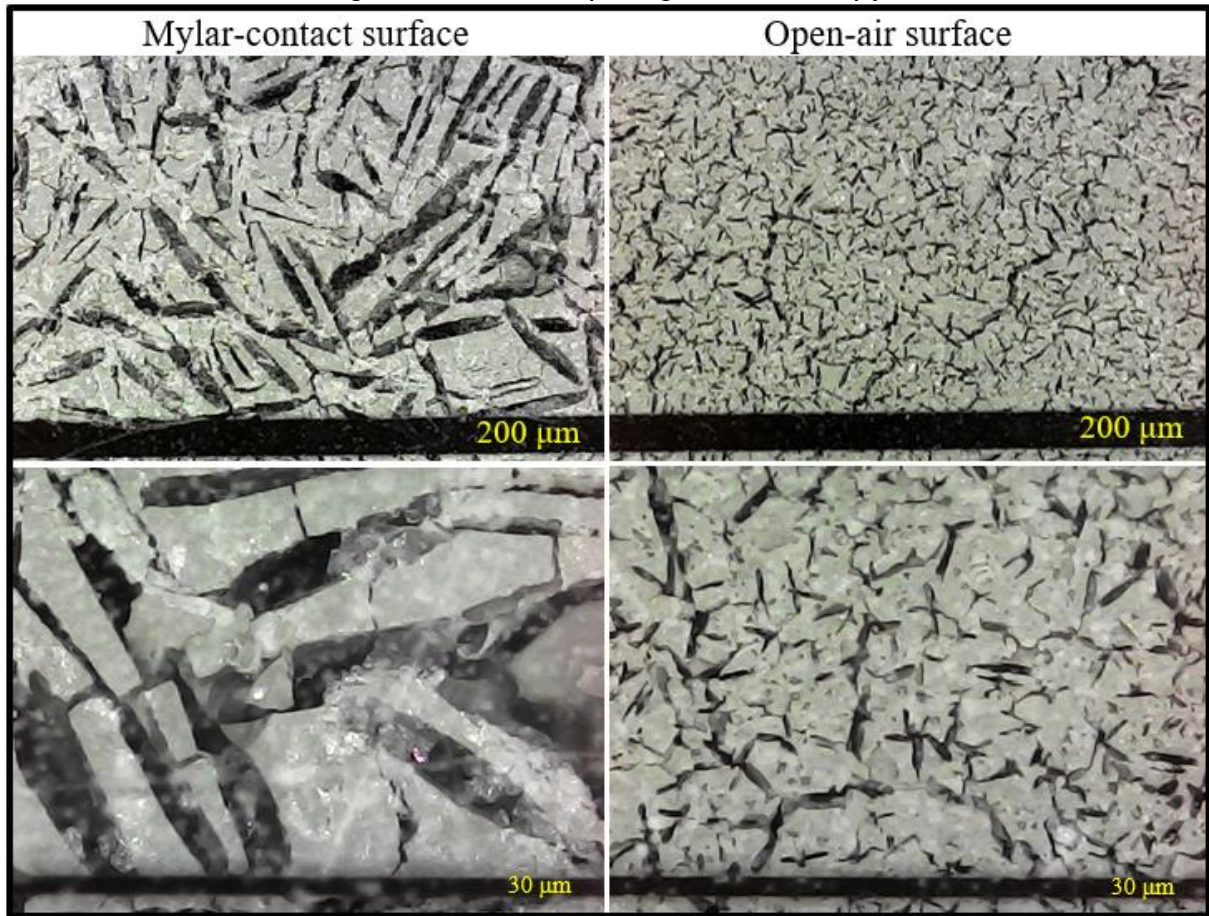
Figure 77 – SA1 and SA2 tapes after freeze drying.



Source: Author.

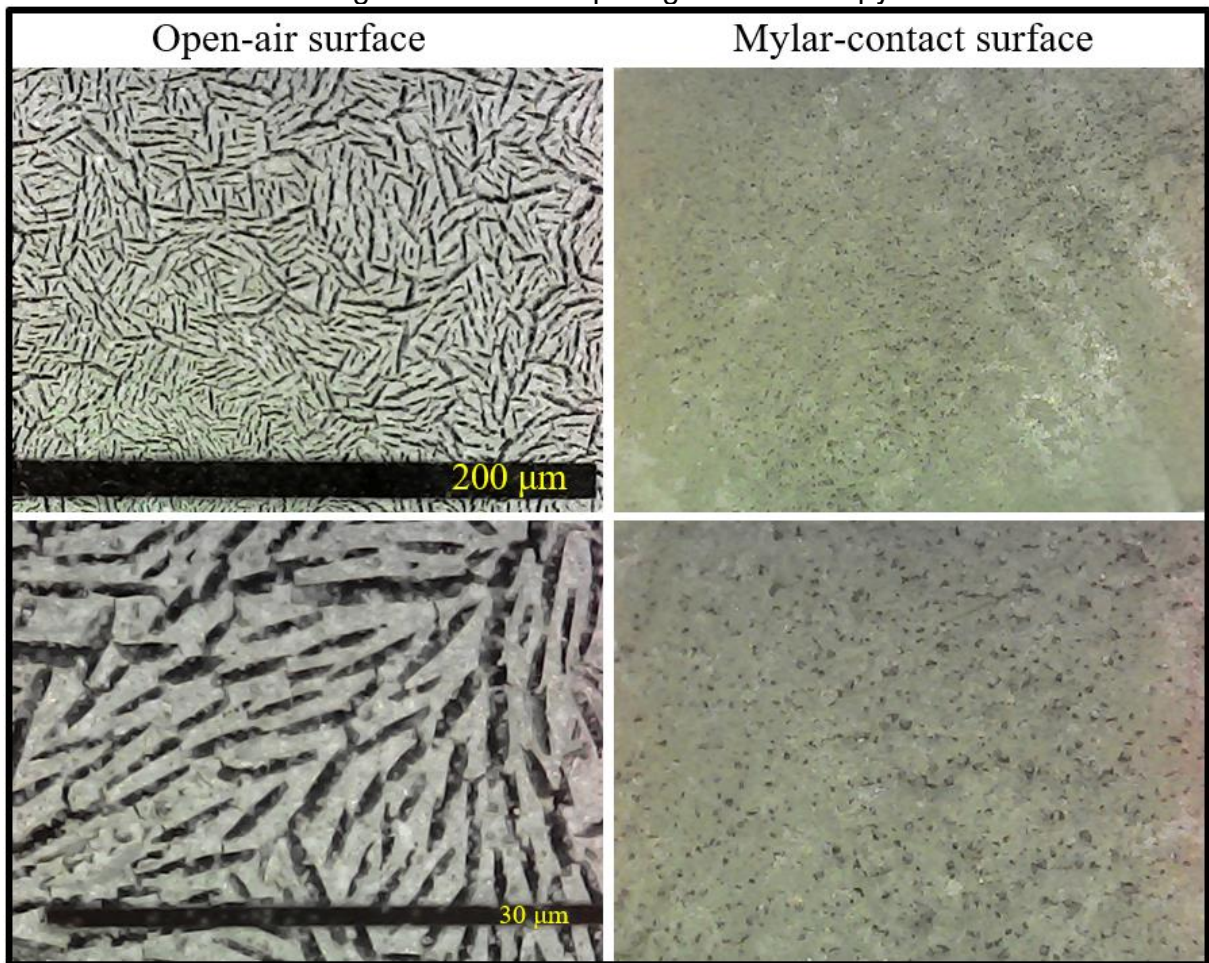
A digital microscope was used to see the surfaces of the tapes with greater magnification. The images for green tapes SA1 and SA2 are shown in Figure 78 and Figure 79 respectively, distinguishing the surface which were in contact with the carrier film from the open-air surface. Black stripes on the images are scales, where the thickest is 200 μm thick, while the finest is 30 μm .

Figure 78 – SA1 tape digital microscopy.



Source: Author.

Figure 79 – SA2 tape digital microscopy



Source: Author.

It is possible to see in Figure 78 that, for SA1 tape the Mylar-contact surface generated much bigger pores, while the open-air surface generated smaller ones. On the other hand, Figure 79 shows an inverted trend for SA2 tape, with bigger pores being generated in the open-air surface of the tape. Curiously, the Mylar-contact surface of SA2 tape didn't have blade-shaped pores, instead, they have circular shapes and are much smaller. This may be explained by two factors: freezing front velocity, and the curvature of the tape while freeze drying was occurring.

Since SA2 tape was frozen much faster, the freezing rate has possibly passed the critical freezing front speed, causing the undesirable effect of particle entrapment. Without time for arranging themselves between the crystals, particles are “swallowed” by it, being trapped. Without particle orientation, directional pores are inexistent in the final structure.

The other reason could be associated with the fact that this region was suffering compression forces during freeze drying, due to the curvature of the tape, while the open-air surface was suffering tension forces. However, since the curvature only appeared after leaving the tape inside the -80 °C freezer, and the ice crystals were already previously formed during freezing with liquid N₂ (without curvature), this justification does not fit well, unless the ice crystals change their shape after forming.

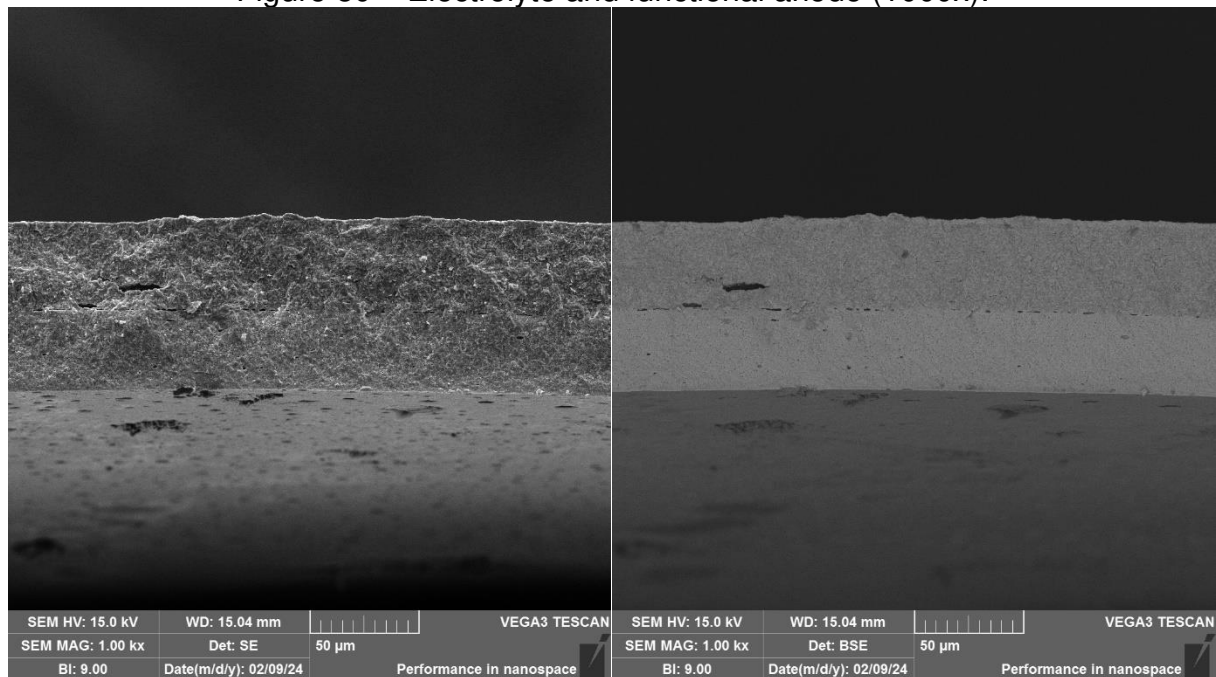
4.4 MICROSTRUCTURAL CHARACTERIZATION

This section is reserved for scanning electron microscopy (SEM), results, and discussions. After vacuum assembling the tapes were debinded and co-sintered to obtain the final assembled set for SEM images. The images were made in a VEGA3 TESCAN.

Secondary electron (SE), and backscattered electron (BSE), images were performed, to better comprehend the topography and to distinguish the elements in the samples, respectively. Typically, heavier elements appear brighter, while lighter elements appear darker.

4.4.1 Electrolyte and functional anode

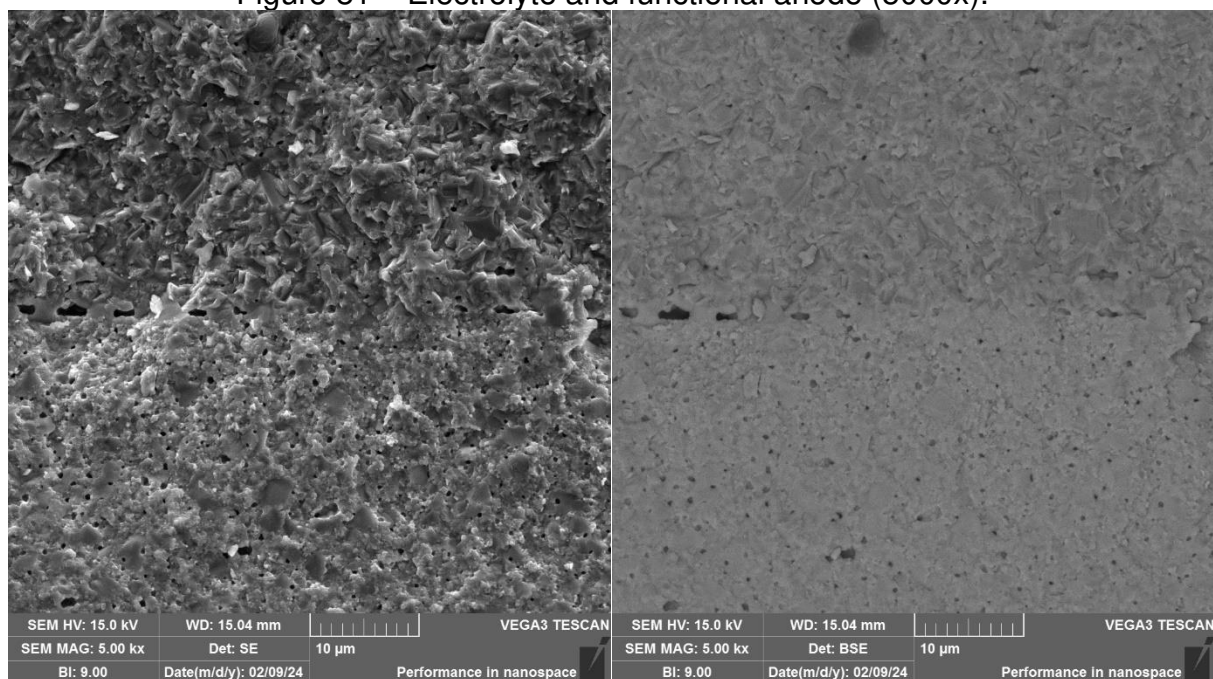
Figure 80 – Electrolyte and functional anode (1000x).



Source: Author.

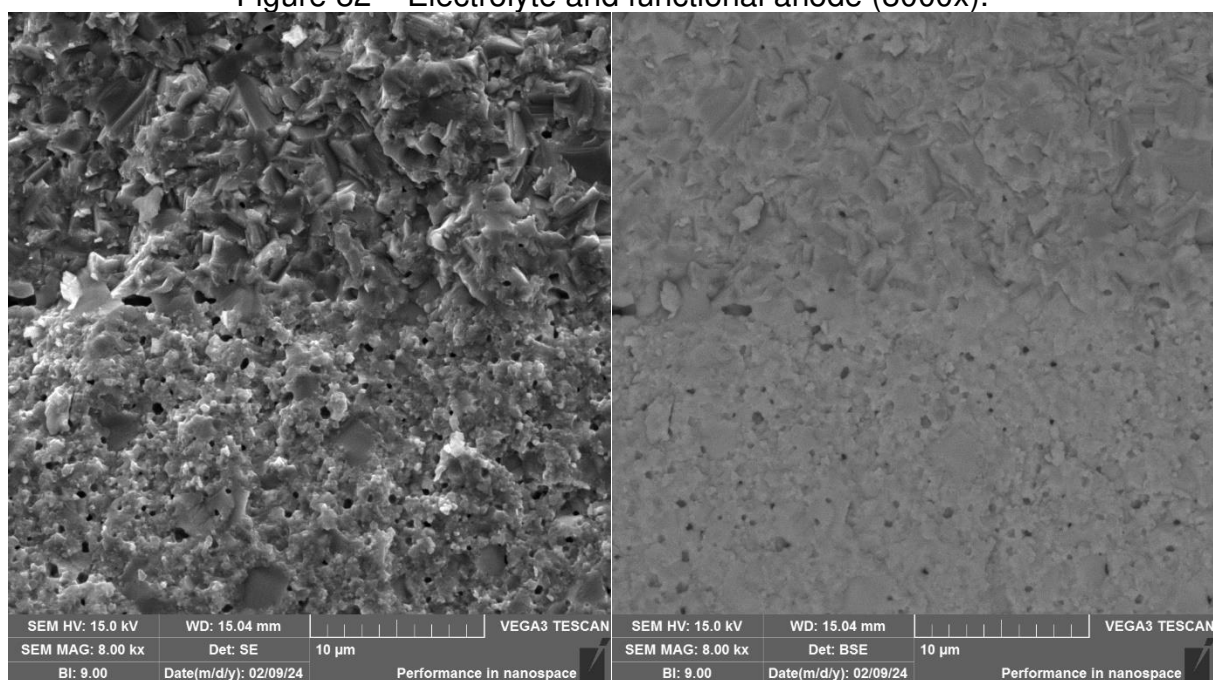
In Figure 80, it is possible to see both tapes assembled, with little voids between the interface, with less than 1 μm . The bottom tape, which is brighter, is the electrolyte, while the tape on top is the functional anode. The electrolyte is 37 μm thick, while the functional anode is 41 μm thick.

Figure 81 – Electrolyte and functional anode (5000x).



Source: Author.

Figure 82 – Electrolyte and functional anode (8000x).

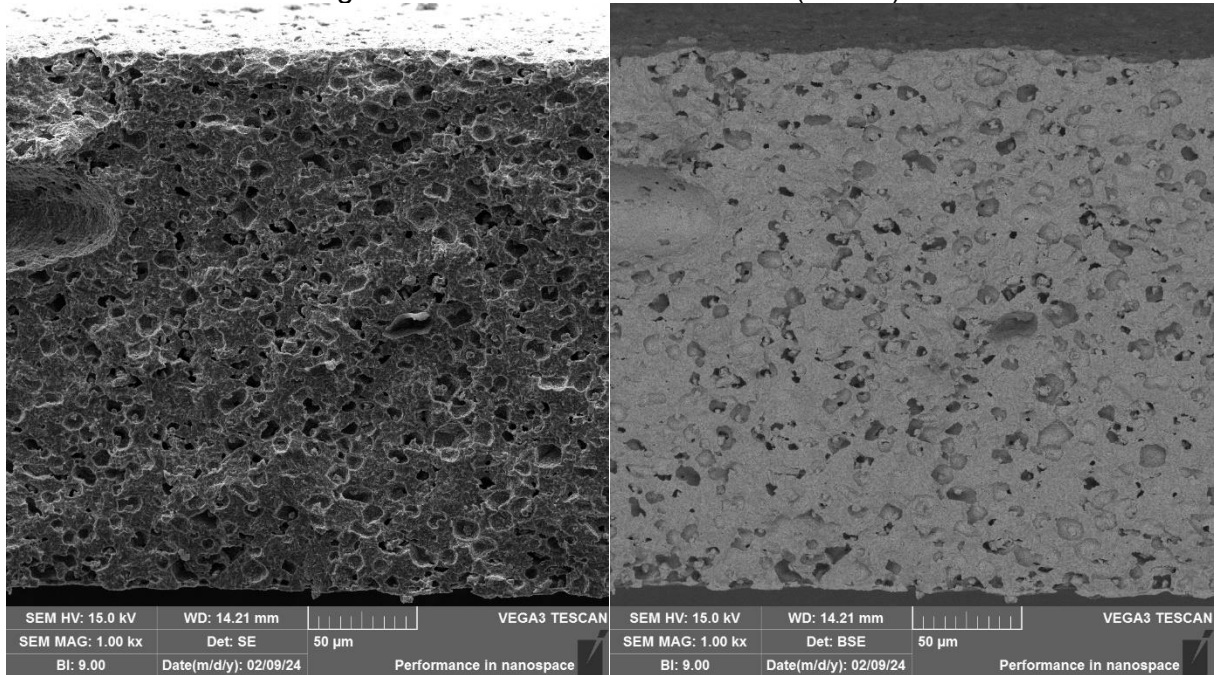


Source: Author.

In Figure 81 and Figure 82, it is possible to see that the electrolyte (bottom tape) has become more porous than the anode. This favors a suspicion that will be discussed further.

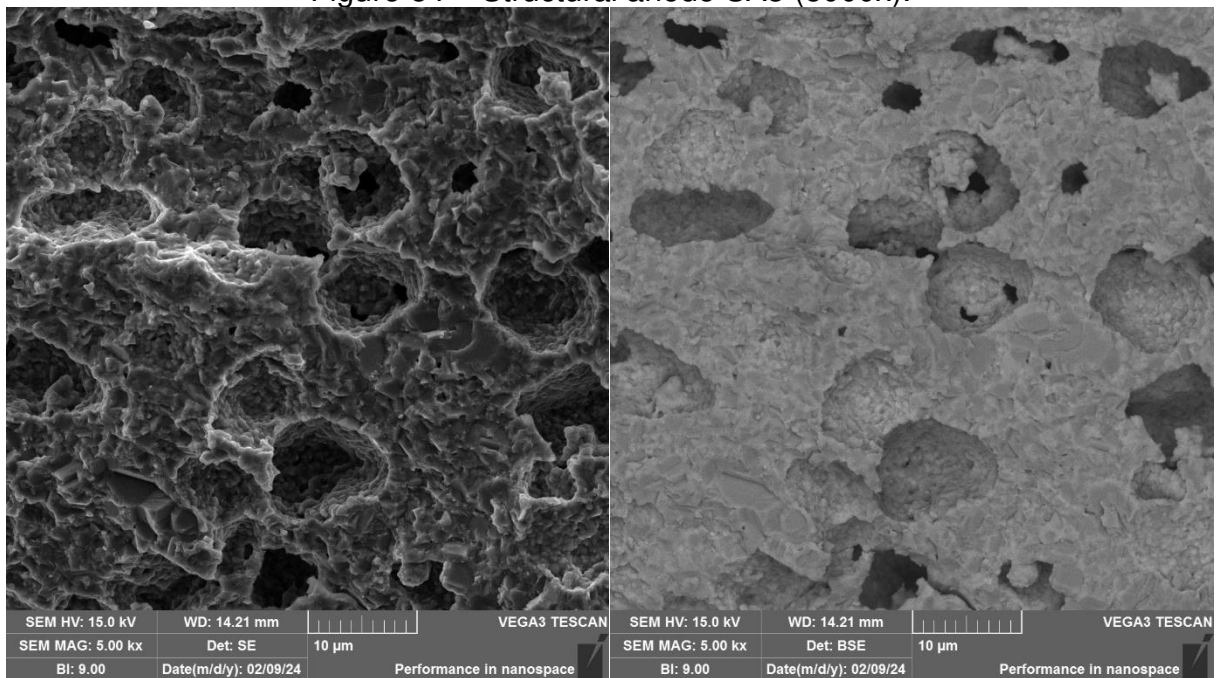
4.4.2 Structural anode SA3

Figure 83 – Structural anode SA3 (1000x).



Source: Author.

Figure 84 – Structural anode SA3 (5000x).

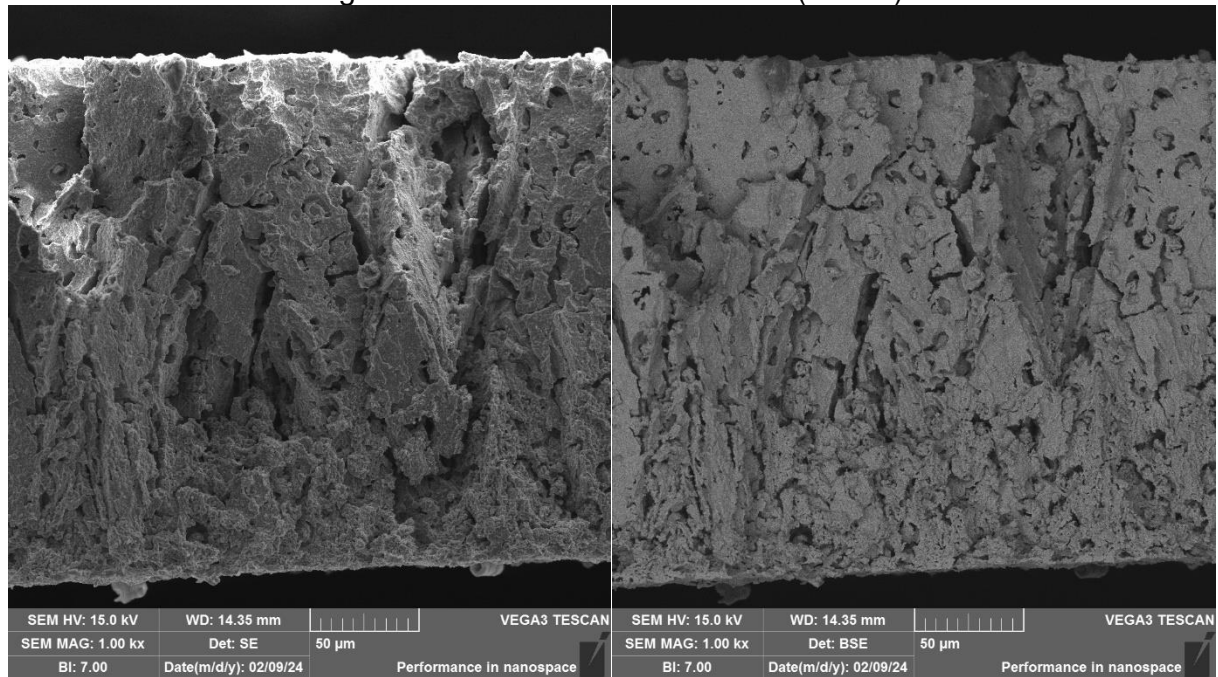


Source: Author.

Figure 83 and Figure 84 show a highly porous structural anode with 310 µm thickness. Pore size distribution is from 5 to 10 µm, with a majority of 10 µm.

4.4.3 Structural anode SA2

Figure 85 – Structural anode SA2 (1000x).

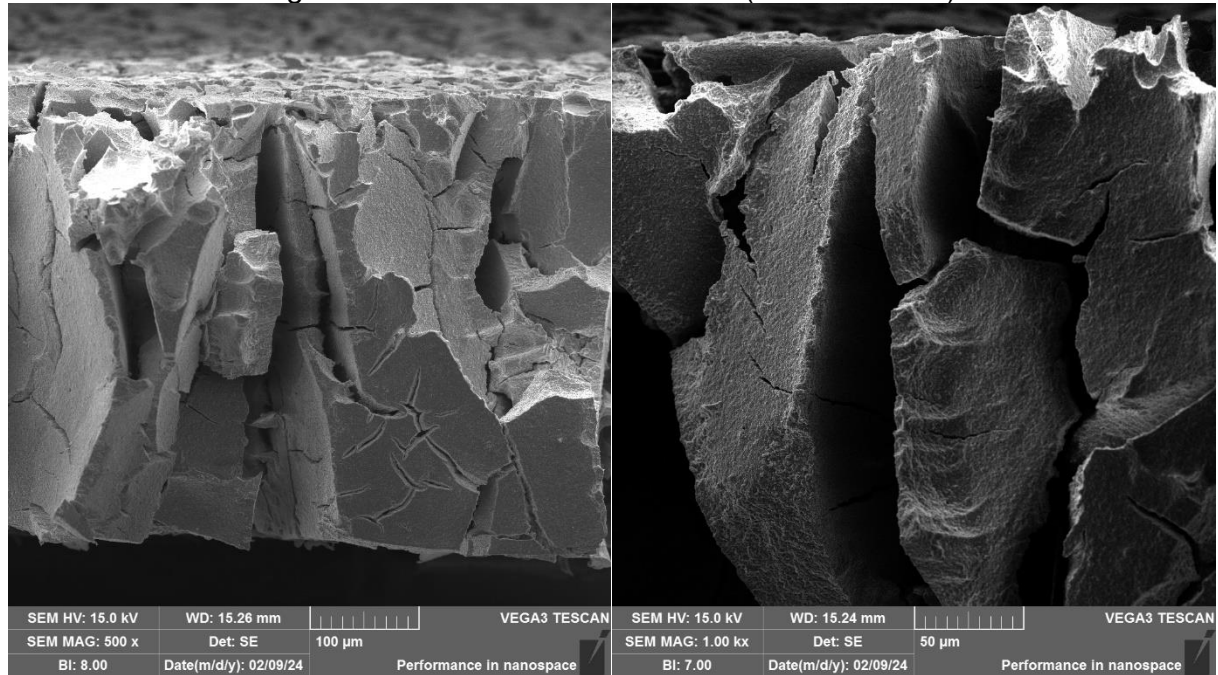


Source: Author.

It is possible to see in Figure 85 that there is a gradient of pore size/morphology, increasing from the bottom to the top. Knowing that the bottom surface was in contact with the carrier film, it was the origin of the freezing. Since this surface was fast frozen with the help of liquid nitrogen, the front freezing velocity was too high, entrapping particles during freezing, thus hindering the generation of “blade-shape” pores. Thereby, in this region, there are still rounded pores, because of the presence of pore former. While we go up, the blade shapes start to appear, and this is explained because at this point (far enough from the freezing surface), the temperature was sufficiently high to slow the freezing front velocity, thus giving enough time for particles to organize themselves between the ice crystals. It is possible to see rounded pores along the entire tape. The average thickness of the tape was measured to be 235 μm .

4.4.4 Structural anode SA1

Figure 86 – Structural anode SA1 (500x – 1000x).



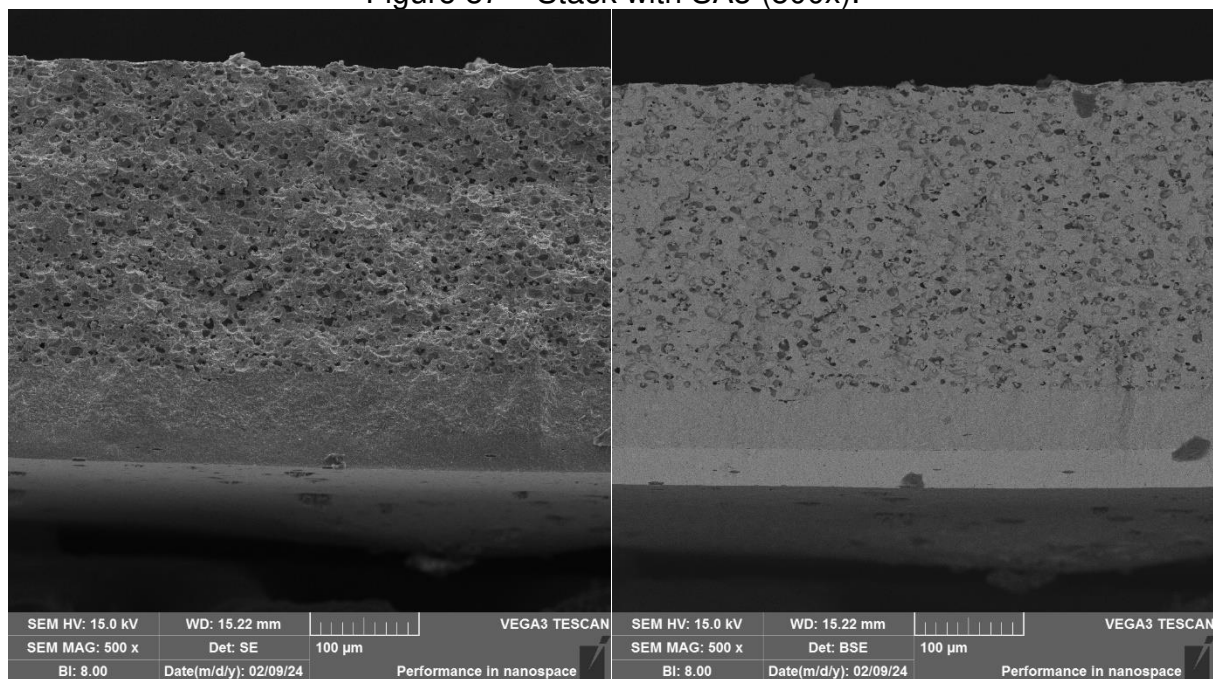
Source: Author.

It is possible to see that the blade-shaped pores cross the tape from one side to the other since the SA1 tape was frozen slowly. However, the freezing front velocity is also related to the thickness of the crystals, so slower freezing rates result in thicker crystals. Thereby, the size of the pores was excessively wide, with an average width of 34 μm . The tape presents an average thickness of 410 μm .

It is also visible that the width of the pores decreases in the bottom to the top direction. This was expected since the underside surface, which was in contact with the carrier film, is where the ice crystals are formed. During freeze casting, the base of the crystals is larger, while the top, is thinner.

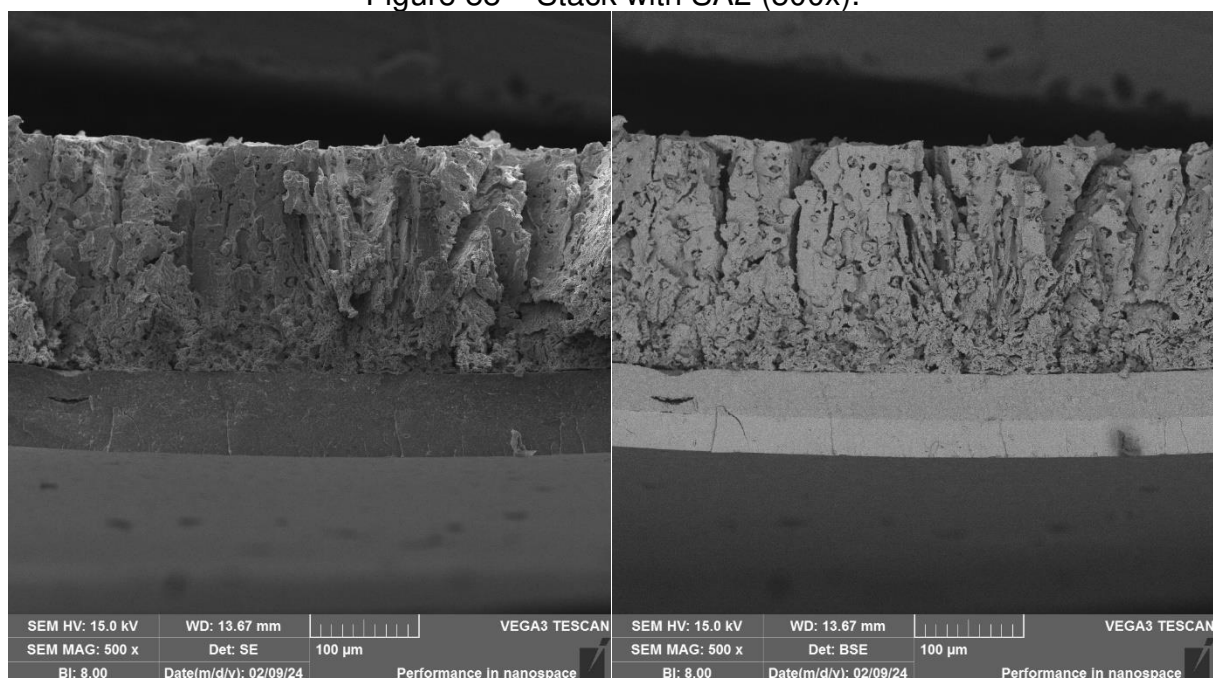
4.4.5 Anode-supported stacks

Figure 87 – Stack with SA3 (500x).



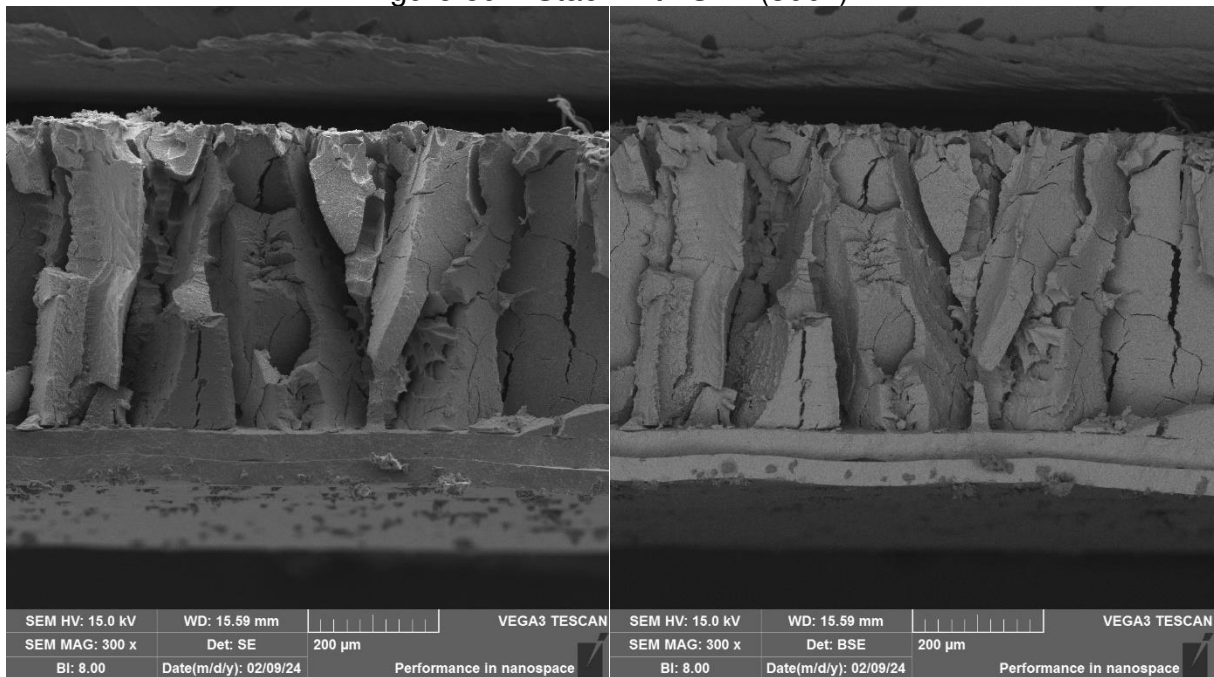
Source: Author.

Figure 88 – Stack with SA2 (500x).



Source: Author.

Figure 89 – Stack with SA1 (300x).



Source: Author.

For the stacks manufacture, constrained debinding and sintering were performed. Although constrained sintering is quite well known, constrained debinding was an error. After debinding the ceramic is in its most fragile state, therefore, a weight load on top of the tape may cause the stacks to completely break into many pieces. Another likely reason is the difference between thermal expansion coefficients, in the way that during debinding or sintering the tapes would break apart regardless of being constrained.

Therefore, SEM images of stacks are actually from fragments where the tapes remained assembled. Nevertheless, it is possible to see that the tapes are very well assembled, meaning that the technique used to assemble them was a success. Table 18 presents an assessment of shrinking during the process, where the sintered values presented are from the individual tapes.

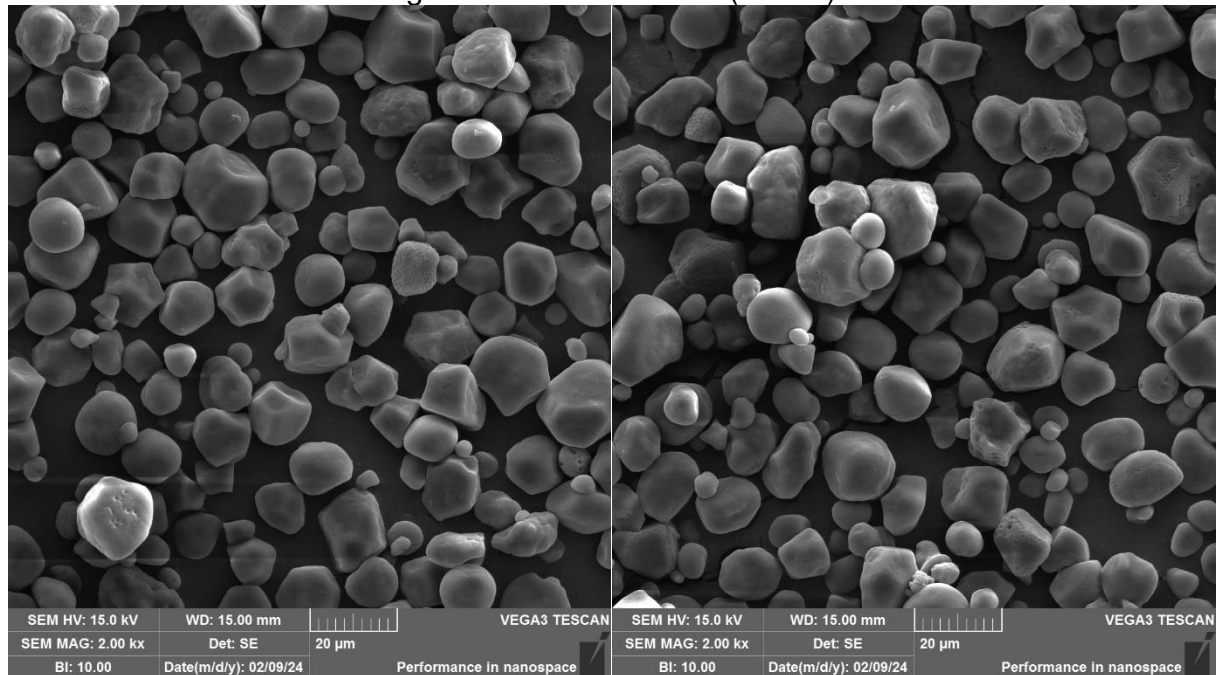
Table 18 – Shrinkage throughout the process.

Membrane	Thickness (μm)		Total shrinkage (%)	Final stack thickness (μm)
	Gap	Sintered		
SA1	1000	410	59	546
SA2	500	235	53	285
SA3	800	310	61	370
FA2	200	41	80	—
MT4	200	37	82	—

Source: Author.

4.4.6 Pore former

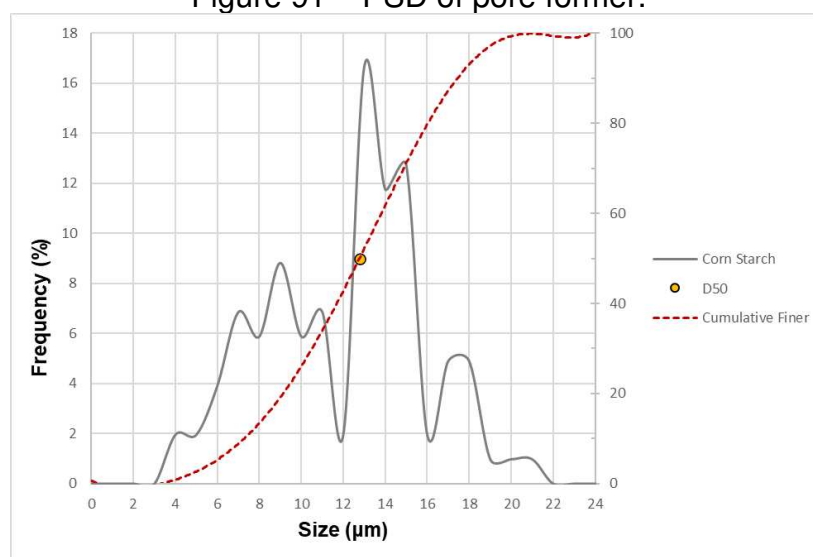
Figure 90 – Pore former (2000x).



Source: Author.

The particle size distribution of the pore former was manually measured by randomly selecting a group of around 100 particles in Figure 88. The distribution can be seen in Figure 91. The average particle size was estimated to be around 12 μm .

Figure 91 – PSD of pore former.



Source: Author.

5 CONCLUSIONS

The study of additives content in ceramic slurries, such as binders, plasticizers, and surfactants must be experimentally accompanied by the casting, since only by having the formed tape will be possible to state if that composition was good. Differently, dispersants can be optimized by rheological tests, without requiring casting.

Highly viscous slurries may often encounter problems with remaining bubbles, with typical methods for removing them not being so effective. It is recommended to give preference to moderate viscosity suspensions. In the case of not being able to solve the remaining bubbles issue, lamination can be performed to cover the holes with adjacent tapes, resulting in a multilayer tape. However, it must be taken into account that this will increase the thickness of the final set.

The holes that appear in wet tapes right after being cast are likely associated with high surface tension. This problem proved to be solved by either reducing the surface tension using surfactants or increasing the viscosity by increasing solids loading.

The use of stearic acid as a lubricant coating on the carrier film was a success. The new technique was demonstrated to be very effective in facilitating tape removal from the carrier film. Further analyses are required to check how the stearic acid coating affects the roughness and texture of the final tape.

Using liquid nitrogen as an aid for fast freezing can be excessively fast, leading to the entrapment of solid particles within the ice crystals. It is important to assess how fast it is possible to freeze while preserving highly directional pores generation. Nevertheless, an excessively slow freezing can also lead to undesirable wide pores.

While green, highly porous tapes must not be handled, since they can cause cracks within internal walls, thus reducing tape strength. Constrained debinding is not suitable for ceramic tapes, since they become extremely brittle, and loadings may cause them to break. Lamination (thermo-pressing), was not necessary to assemble the tapes, since vacuum assembly was quite effective.

The rheology of a suspension can be greatly changed by using powders with different average particle sizes. In addition, tetragonal powder used in this work is suspected to be spray-dry agglomerated with binder, since tetragonal powders are commonly used for pressing purposes. Another strong piece of evidence is that SEM

images of electrolytes show the presence of many rounded pores, which could be voids left by additives for agglomerating the powder.

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APPENDIX A – YSZ XRD Data

Powder	(hkl)	Diffraction angle 2 θ	Intensity
C_Sigma	(111) _m	28.48	618
	(111) _c	30.39	5150
	(111) _m	31.44	664
	(200) _c	35.24	1113
	(220) _c	50.48	2322
	(311) _c	60.09	1313
	(222) _c	62.97	475
	(004) _t	73.58	314
	(400) _t	74.36	380
	c	81.92	545
	c+t	84.42	406
T_Innov	(111) _m	28.12	468
	(111) _t	30.23	5114
	(002) _t + (200) _t	35.15	1088
	t + t	50.34	2352
	t + t	59.96	1507
	t	62.82	527
	(004) _t	73.33	307
	(400) _t	74.25	433
	t	81.74	613
	t + t	84.75	432
C_Innov	(111) _c	30.50	4913
	(200) _c	35.28	1272
	(220) _c	50.53	2647
	(311) _c	59.98	1745
	(222) _c	63.02	477
	(400) _c	74.02	433
	c	81.88	627
	c	84.51	471

*c – cubic; t – tetragonal; m – monoclinic.

Source: Author.