# Electrospun Fe-N-C Based Electrodes for PEM Fuel Cells

by

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# ABSTRACT

# **Electrospun Fe-N-C Based Electrodes for PEM Fuel Cells**

#### FAEZEH RAHBARSHENDI

# MATERIALS SCIENCE AND NANO ENGINEERING M.Sc. THESIS, JULY 2024

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Keywords: PGM-Free catalyst layer, Durability test, Fe-N-C, Cerium oxide, Core-shell electrospinning

The main objective of this thesis is to fabricate catalyst layers using electrospun single and core-shell nanofibers by utilizing Fe-N-C catalyst and PVDF/Nafion<sup>®</sup>, and examining the effect of cerium oxide (CeO<sub>2</sub>).

The initial section of this research focused on the development of hollow fiber carbonbased Fe-N-C catalyst and PVDF/Nafion<sup>®</sup> fiber-based catalyst layers The findings indicated that utilizing core-shell electrospinning ceria included to produce hollow fiberbased electrodes holds the great potential for enhancing the efficiency and longevity of fuel cells. This innovative hollow fiber structure is being presented for the first time in literature on PEM fuel cell. It establishes the higher standard by greatly improving the maximum power densities and operating stability.

The MEAs with the cathode catalyst loading of 3 mg cm<sup>-2</sup> utilizing core-shell fibers withceria obtained the maximum power density of 84 mW cm<sup>-2</sup> during the initial testing phase known as beginning-of-life (BOL). As the main findings of the end-of-test (EOT)

examination, the power density of 96 mW cm<sup>-2</sup> was achieved. The perfect increase in power demonstrates the exceptional long-term durability and stability. The MEAs also exhibited higher current densities during the EOT testing, indicating enhanced performance during extended operational circumstances. Ceria has a pivotal role on preventing the hydrogen peroxide production during ORR, improving the performance and durability of PEM fuel cell.

The second section of the thesis emphasized on the production of electrospun catalyst layer utilizing Fe-N-C catalysts based using nano graphene and PVDF/Nafion<sup>®</sup>. This part aims to investigate the effect of carbon support in the Fe-N-C structure and the resulting nanofiber-based catalyst layer structure and PEM fuel cell performance. Comprehensive characterizations confirm the presence of graphitic domains and the excellent dispersion of the catalyst within the fibrous matrix. This electrospun mat has been produced for additional exploration of its operational performance, based on the results obtained during the initial phase.

The thesis showcases a novel method to enhance the efficiency of PEM fuel cells by integrating state-of-the-art methods for material processing with inventive catalyst architectures. The results emphasize the ability of core-shell structures and ceria's effect to establish higher benchmarks in both efficiency and durability of PEM fuel cells.

# ÖZET

# PEM Yakıt Hücreleri için Elektro Eğrilmiş Fe-N-C Bazlı Elektrotlar

# FAEZEH RAHBARSHENDI

# MALZEME BİLİMİ VE NANO MÜHENDİSLİĞİ YÜKSEK LİSANS TEZİ, TEMMUZ 2024

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Anahtar Kelimeler: PGM içermeyen katalizör katmanı, Dayanıklılık testi, Fe-N-C, Seramik oksit, Çekirdek-kabuk elektro eğirme

Bu tez, Fe-N-C katalizörleri ve PVDF/Nafion<sup>®</sup> kullanarak elektrospun tek ve çekirdekkabuk nanofiber katalizör katmanları geliştirmeyi ve seryum oksit (CeO<sub>2</sub>) eklenmesini araştırmayı amaçlamaktadır.

Tezin ilk bölümünde, boşluklu fiber ticari Fe-N-C katalizörleri ve PVDF/Nafion<sup>®</sup> fiber bazlı katalizör tabakaları üretilmiş ve karakterize edilmiştir. Sonuçlar, çekirdek-kabuk elektro-eğirme tekniği kullanılarak üretilen boşluklu fiber bazlı elektrotların, yakıt hücresi performansını ve dayanıklılığını artırmak için umut verici bir yaklaşım olduğunu göstermiştir. Çekirdek-kabuk elektro-eğirmesi ile üretilen yenilikçi boşluklu fiber yapısı, PEM yakıt hücreleri literatüründe ilk kez gösterilmiştir. Elde edilen maksimum güç yoğunlukları ve dayanıklılık testleri sonunda büyük ölçüde iyileşmiştir ve bu da yeni bir ölçüt oluşturmaktadır. Çekirdek-kabuk liflerden elde edilen MEA'lar, başlangıç testi aşaması olarak bilinen başlangıç ömrü (BOL) sırasında 84 mW cm<sup>-2</sup> maksimum güç yoğunluğuna ulaşılmıştır. Ömür sonu testlerinin (EOT) incelenmesi sonucunda, 96 mW cm<sup>-2</sup> güç yoğunluğuna ulaşılmıştır. Bu güç artışı, uzun vadeli dayanıklılığı ve kararlılığı göstermektedir. MEA'lar ayrıca, EOT testleri sırasında daha yüksek akım yoğunlukları sergilemiş ve uzun süreli çalışma koşullarında iyileştirilmiş performans sağlamıştır.

Tezin ikinci bölümü, nano grafen bazlı Fe-N-C katalizörleri ve PVDF/Nafion<sup>®</sup> kullanarak elektro-eğirilmiş katalizör tabakaları üretilmesi üzerine çalışmalar yapılmıştır. Bu bölümde, Fe-N-C yapısında karbon desteğinin etkisini ve sonuçta oluşan nanofiber bazlı katalizör tabakalarının yapısını ve PEM yakıt hücresi performanslarını incelemek amaçlanmıştır. Kapsamlı karakterizasyonlar, grafitik alanların varlığını ve katalizörün lifli matris içinde mükemmel dağılımını doğrulamaktadır. Bu elektro-eğirilmiş mat, başlangıç aşamasında elde edilen sonuçlara dayanılaak yakıt hücresi performansının ek değerlendirmeleri için üretilmiştir.

Bu tez çalışmasıileri düzey yöntemleri yenilikçi katalizör mimarileri ile entegre ederek PEM yakıt hücrelerinin verimliliğini artırma yaklaşımını sunmaktadır. Burada elde edilen sonuçlar temiz enerji teknolojilerinin ilerlemesini kolaylaştıracaktır. Özellikle çekirdek-kabuk yapıların PEM yakıt hücrelerinin hem verimlilik hem de dayanıklılık açısından daha yüksek ölçütlere uygulanabilirliğini vurgulamaktadır.

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#### **1 INTRODUCTION**

# 1.1. Clean Energy Demand and PEM Fuel Cells

The increasing demand for energy due to the expanding global economy exposes the severe constraints of our current energy systems, which rely heavily on fossil fuels. [1] It is becoming more and more obvious that fossil fuel reserves, notwithstanding important discoveries, are not enough to supply the world's long-term energy needs. [2] There are major dangers to global energy security because of this impending scarcity, which threatens to upset the equilibrium between energy supply and demand. [3] As such, it is now imperative to explore other energy sources. [4]

Among these challenges, specifically fuel cells, Proton Exchange Membrane (PEM) fuel cells appear like an appealing alternative. [5] PEM fuel cells work by the electrochemical mechanism which transforms the chemical energy of hydrogen to electricity without burning, in contrast to conventional power generating systems that include combustion. [6] This results in power that is more efficient and emits less carbon emissions. Thus, fuel cells are considered as the essential tool in the transition towards more environmentally friendly energy sources. [7]

PEM fuel cells are highly appealing because of their ability to run at lower temperatures. In addition, they possess rapid initialization periods. Moreover, they exhibit versatility, performing admirably across a wide spectrum of sizes, spanning from industrial applications to portable devices.[8] They possess versatility, rendering them valuable in diverse environments. They can be in automobiles, portable energy systems, and emergency power supplies. These applications enhance energy sustainability and mitigate carbon footprints.[9, 10]

PEM fuel cells are increasingly recognized as crucial for the global transition to the sustainable energy alternatives. [11] As the global shift away from fossil fuels progresses, PEM fuel cells are not merely an alternative but are increasingly becoming a vital element of strategic, long-term energy planning. [12] They represent a vital step forward in the search for sustainable energy sources since they provide a solution to both greatly reduce environmental effects and stabilize the energy supply. [13, 14]

# 1.2. PEM Fuel Cells Components and Principles

PEM fuel cells consider as the state-of-the-art energy conversion systems that effectively generate electrical power via electrochemical reactions between airborne oxygen and hydrogen fuel.[15] The MEA is the crucial component of the PEM fuel cell. [16] The structure comprises a membrane positioned between an anode and one cathode. Gas diffusion layers surrounding membranes facilitate the uniform distribution of reactants over the catalyst layers. [17] Various environmental and operational parameters, including temperature, humidity, and pressure, have an impact on efficiency of the PEM fuel cell. [18, 19] For the PEMs, which is frequently composed of Nafion<sup>®</sup>, to retain its ionic conductivity, a particular humidity level is needed. In most cases, the smooth passage of protons from the anode to the cathode requires hydration of the membrane. [20] Majority of PEM fuel cells operate best at 60°C to 80°C, but it is mandatory to perform this range because higher temperatures can cause membrane dehydration, while lower temperatures can decrease catalytic activity and raise the possibility of water condensation in colder climates. [21, 22]

MEA's anode side gets the hydrogen fuel, which is catalytically sectioned into protons and the electrons. [23] While electrons move via the external circuit to produce the electric current, protons move via the hydrated membrane to cathode. [24] Only consequence of this procedure is water, which is obtained at cathode when oxygen from the air mixes with protons traveling around the membrane and electrons returning from external circuit. [25] In addition, producing electricity, this reaction also produces heat and water vapor, which need to be controlled to preserve the system's longevity and efficiency. [26, 27]

Managing the water in the cell effectively is essential because too little water will dehydrated membrane and reduce the conductivity, while too much water can flood the catalyst and obstruct reactant gases. [28] Optimizing the hydration levels without flooding the cell requires sophisticated water management techniques, such as the creation of novel gas diffusion layers and flow channels. [29]

Both the fuels are normally compressed, increasing the PEM fuel cell's overall efficiency and flow rate. [30] To maximize the reaction rates and guarantee uniform distribution throughout the catalyst surfaces, the pressure needs to be carefully managed. [31]

The important parts of a fuel cell are depicted in (Figure1.1), along with the equations of the oxygen reduction reaction (ORR) and hydrogen oxidation reaction (HOR). [32] These mentioned reactions, which turn hydrogen and oxygen into electricity and water, are essential to the fuel cell's performance and are well to improve comprehension of the electrochemical processes involved. [33] The reactions occurring on both of the electrodes can be described like below:

$$HOR: 2H_2 \rightarrow 4H^+ + 4e^- \tag{1}$$

$$ORR: O_2 + 4H^+ + 4e^- \to 2H_2O$$
 (2)



Figure 1.1. Components of the PEM fuel cells [34]

# 1.2.1 Membrane

Nafion<sup>®</sup>, commonly employed in the PEM fuel cell, has a crucial act in the cell's operational conditions. [35] The objective of this is facilitating the movement of protons from the anode to cathode while impeding flow of the electron. [36] The efficiency of the membrane is significantly impacted by its amount of hydration. Adequate hydration is crucial for preserving its ionic conductivity.[37] When protons pass these channels, they encounter oxygen and electrons at the cathode. Fuel cell process exclusively generates water as its by product. [38]

#### **1.2.2 Electrode**

The components of electrodes in the PEM fuel cells is included as GDL and the catalyst layer.[39] GDL, often made of the carbon paper, ensures consistent gas transportation and controls moisture levels to maintain the membrane's efficiency. [40] Catalyst layer, typically consists of platinum nanoparticles, is linked to the gas diffusion layer (GDL) and has an essential role in enabling two significant reactions: HOR at the anode and ORR at the cathode. [41] Optimizing a design of these components is essential for increasing the transfer of electrons and protons. [42]

# 1.2.2.1 PEM fuel Cells Catalyst Layers

Platinum group metals (PGMs), namely platinum (Pt), are mainly utilized in catalyst layers of the anode and the cathode electrodes of PEM fuel cells to enhance the electrochemical processes which is necessary for the power generation. [43] The cathode side ORR is quite slow, which greatly reduces the fuel cell's total efficiency. [44] The kinetics of ORR have been improved through extensive research to increase PEM fuel cells' performance and efficiency. [45, 46]

Notwithstanding these technological developments and the intrinsic advantages of PEM fuel cell such as its high efficiency their commercial adoption still faces significant obstacles, chiefly because of the high expenses related to the extensive use of pricy materials like Pt and Nafion<sup>®</sup>, an ionomer that is frequently used. [47] However, those materials have high cost.[15, 48]

The U.S. Department of Energy (DOE) started initiatives lessening fuel cell dependency on PGMs in recognition of these difficulties. [49] It encourages the creation of substitute electrode materials and catalysts that are not costly PGMs. [50] A goal of this thesis is to develop novel materials that can perform as well as or better than current PGM-based catalysts while reducing the PEM fuel cell production costs dramatically. [51] This will increase using PEM fuel cells for broader commercial applications. [52-54]

#### **1.3.** M-N-C Catalysts

Catalysts containing transition metals like Fe, Co, or Ni along with nitrogen, carbon, known as M-N-C catalysts, are important in the development of PEM fuel cell technologies, particularly in improving the ORR. [55] Fe-N-C's are assuming potential in this category because of their exceptional catalytic activity and stability during operation. [56] Taking advantage of this process is mainly due to the perfect coordination of iron with nitrogen and carbon, resulting in the creation of active sites which efficiently facilitate ORR. [57] Moreover, these catalysts have a low price, greater availability compared to expensive metal catalysts.[58]

#### 1.3.1 Fe-N-C Catalysts

PEM fuel cells have noticed increasing acceptance of iron-nitrogen-carbon (Fe-N-C) catalysts as feasible substitute for Pt-based ones. These type of catalysts help the oxygen ORR at the cathode. [59] Typically, they are made of a carbon matrix with iron and nitrogen atoms incorporated in it. [60] Fe atoms added to a nitrogen-doped carbon framework increase the electrocatalytic activity required for the ORR, a crucial reaction for the PEM fuel cells' current density production. [61, 62]

Complex coordination environments are frequently present the structure of Fe-N-C, where iron centers coordinate with nitrogen groups bonded to the carbon backbone. [63] Effective electron transfer mechanisms are encouraged by this configuration, which is crucial for the ORR. To increase these catalysts' performance, researchers have concentrated on improving their microstructure. [64] The distribution and oxidation state of iron, the kind and location of nitrogen in the matrix, and shape and porosity of the carbon support are important structural characteristics. [65] These elements have a major impact on the catalysts' durability, ORR efficiency, and catalytic activity. [66, 67]

Fe-N-C's are good for having a strong ORR activity in acidic environments that PEM fuel cells typically operate in. [68, 69] Moreover, they are economically appealing because of their comparatively cheaper price and the plentiful availability of iron. Long-term stability and performance that is like Pt are still difficult to achieve, especially given the demanding operating conditions of PEM fuel cells. [70-72]

Demetallation and carbon corrosion are two common processes involved in the degrading mechanisms of them, and these processes are focus of much research. [73] To improve the stability and catalytic efficacy of these materials, post-treatment procedures along with sophisticated synthesis techniques such high-temperature pyrolysis have been used. [74]

A comprehensive schematic representation of them (carbon-based) structure is demonstrated in (Figure 1.2), which illustrates the precise integration of iron and nitrogen atoms into a carbon matrix. This illustration emphasizes the arrangement and bonding of the atoms, which is important to comprehend the catalytic activity required for the ORR.



Figure 1.2. Fe-N-C structure

Red: Iron

Blue: Nitrogen

Black: Carbon

#### 1.3.1.1 Fe-N-C's Instability

Fe-N-C catalysts, however, have potential and are less expensive than Pt-based catalysts; yet these catalysts have some stability problems that seriously hinder their commercial implementation.[75]

The primary cause of the instability observed in Fe-N-C's is the degrading mechanisms which take place during fuel cell operation. [76] An important element causing this instability is the generation of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), an ORR's intermediate stage. Fe-N-C catalysts typically reduce oxygen in two steps, despite of Pt-based catalysts that efficiently reduce oxygen to water directly. [77] This mechanism reduces oxygen to hydrogen peroxide, which is subsequently reduced to water. [78] Not all generated hydrogen peroxide, though, proceeds through this second reduction stage; part of it breaks down into reactive oxygen species (ROS), which can attack the carbon support and catalyst and cause structural deterioration and activity loss.[79]

The degradation of carbon support is another factor of these catalysts' instability. Incomplete reduction of  $H_2O_2$  can produce reactive oxygen species that damage the carbon matrix, resulting in catalyst loss and detachment. [80] Moreover, severe operating conditions of the fuel cell, like high potentials and acidic environments, the iron centers within the Fe-N-C structure, which are active sites for ORR, may leach or change into less active forms.[81, 82]

Another important problem is the demetallation of Fe from the catalyst structure. PEM fuel cells' acidic environment can hasten iron leaching, which lowers the active sites for ORR and reduces the catalyst's overall effectiveness.[83, 84]

To overcome these obstacles, new materials and synthesis techniques that improve the stability catalysts must be developed, as well as a thorough understanding of structure of the catalyst and the mechanisms of degradation. [85] The creation of more corrosion-resistant carbon supports, the stabilization of iron sites through improved coordination

with nitrogen, and the improvement of the catalyst's structural integrity through improved microstructure control during synthesis are examples of innovative approaches.[86]

#### 1.4. Enhancing PEM Fuel Cells Durability and Stability with CeO<sub>2</sub>

Stability and durability are essential for PEM fuel cells. Hence, it is crucial to tackle instability of these catalysts. [87] These catalysts show high efficiency but may degrade over the time, particularly when exposed to the severe environments.[88] To improve the durability and efficacy of product while minimizing presence of dangerous molecules such as hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), it is essential to make modifications or incorporate the additional components.[89] CeO<sub>2</sub> has been recognized in the literature as one of the most promising choices for this purpose. [90] CeO<sub>2</sub> exhibits the exceptional redox characteristics, enabling it to mitigate oxidative stress and improve the catalyst's stability through its role as the oxygen buffer. [91] CeO<sub>2</sub> possesses distinctive characteristics that render it the essential constituent in the PEM fuel cells, augmenting resilience and amplifying the overall efficiency.[92]

#### 1.4.1 CeO<sub>2</sub> and Its Characteristic to Improving the PEM fuel cell stability

CeO<sub>2</sub> is practical for the durability of the PEM fuel cells. It hinders production of  $H_2O_2$ , a harmful byproduct that can cause significant damage to cellular components.[93] The unique redox properties of the CeO<sub>2</sub> allow it to effectively interact with reactive oxygen species, converting them into water instead of  $H_2O_2$ , so protecting the integrity of the cell. [94] Because of these qualities, CeO<sub>2</sub> is a material that shows the promise for enhancing the longevity and performance of fuel cell systems. [95, 96]

Moreover, CeO<sub>2</sub> possesses the capability to increase the overall performance of PEM fuel cells beyond its function as a protective agent. [97] CeO<sub>2</sub> enhances the efficiency of

reactant usage and preserves the catalyst's active sites by reducing the production of  $H_2O_2$ . which results in enhanced electrical output and operational efficiency.[98]

It is renowned for its capacity to increase fuel cell component durability. [99] It can improve the resistance of other catalytic materials to carbon monoxide (CO) poisoning, which is a prevalent problem in fuel cells that can seriously impair efficiency. [100] CeO<sub>2</sub> contributes to the lifetime and activity of the major catalysts utilized in fuel cells by promoting the oxidation of CO into carbon dioxide (CO<sub>2</sub>).[101, 102]

To improve CeO<sub>2</sub>'s catalytic capabilities and suitability for fuel cell settings, recent research has investigated doping on it with additional elements. [103] The material's electrical conductivity and mechanical strength have been demonstrated to enhance with doping with elements like zirconium or yttrium, making it even more appropriate for ORR applications.[95]

Here are the Ceria's reactions which helps the oxygen to be stored, enhancing water production by Fe-N-C catalyst:

$$Ce^{3+} + .0H + H^+ \to Ce^{4+} + H_20$$
 (3)

$$Ce^{4+} + .00H \rightarrow Ce^{3+} + H^+ + O_2$$
 (4)

### **1.5.** Electrode Fabrication Methods

Various conventional methods are often used in the production of PEM fuel cells. [104] These methods consist of decal transfer, which entails applying the catalyst layer to a temporary substrate and then transferring it to the membrane; brushing, which involves manually applying the catalyst paste directly onto the electrode surface; and spraying, which is used to evenly coat the electrode surface with atomized particles. [105-107] Additionally, electrospinning, though a relatively new development, has emerged as a significant technology in this field. Each of these technologies has played a crucial role in the advancement of PEM fuel cell technology, offering different approaches for building electrodes. [108]

#### 1.5.1 Electrode Fabrication via Electrospinning

Electrospinning is one of the most versatile and efficient production methods for creating ultrafine fibers ranging in size from nanometers to micrometers. [109] Using electrical pressures, this technique melts polymer solutions into thin fibers or draws charged threads of the solution. [110] The process commences by exposing the polymer solution to the high voltage. Subsequently, the solution is discharged via a minuscule aperture. As it approaches the collector that is connected to the ground, it undergoes solidification. The electrical force causes the solution to elongate into a slender filament.[111]

Electrospinning has significantly altered the manufacturing of the materials that possess a high ratio of surface area to volume. These materials are highly sought after for a wide range of applications, such as filtration, tissue engineering, sensors, and energy storage.[112] An underlying benefit of electrospinning is its simplicity and adaptability. This technique can be utilized on a wide range of materials, including polymers, composites, and ceramics.[113] Process variables can be manipulated to regulate both the diameter of the fiber and the porosity. The factors that are involved in this are solution viscosity, electric field intensity, and collector distance. [114, 115]

When compared to the materials made by other fiber-forming techniques, electrospun materials are particularly the renowned for their improved mechanical qualities, such as the tensile strength and flexibility. [116] This is a result of the fibers' meticulous arrangement and compact arrangement. These qualities are modifiable throughout the electrospinning process.[117]

Recently, researchers have begun studying electrospinning as the possible technique for manufacturing nanostructured fuel cells. Furthermore, it has been investigated for the purpose of developing battery membranes and electrodes. [118] The high porosity and nano-scale fiber diameter of these electrospun materials significantly increase the active surface area for reactions, resulting in improved ion exchange and catalytic properties.[119]

The electrospinning set up schematic is displayed in (Figure 1.3).[120]



Figure 1.3. Electrospinning setup

#### 1.5.1.1 Core-Shell Electrospinning

To produce nanofibers with unique core and shell structures, a specialized method known as core-shell electrospinning is employed within the larger field of electrospinning. In order to create fibers with a core substance encased in a shell material, this method uses a coaxial arrangement where two distinct solutions are rapidly spun. [121, 122] Enhancing functionality and application potential, this unique structure enables the combination of various qualities from the core and shell materials. [123]

## 1.5.1.2 Core-Shell Electrospinning Mechanism

The first step in the core-shell electrospinning process involves creating two polymer solutions: one for the core and another for the shell, with one being a hydrophobic polymer and the other a hydrophilic polymer. [124] A coaxial spinneret is attached to individual syringes that contain these solutions. [125] An electrostatic force created by a high voltage pulls the polymer solutions out of the spinneret and forms a Taylor cone at the tip. [126] A continuous core-shell fiber is created and collected on a grounded collector as the solvent evaporates, encasing the core solution inside the shell solution. [127, 128]

The applied voltage, the polymer solution flow rates, the distance between the needle tip and the collector, and the viscosity and surface tension of the polymer solutions are important parameters affecting the electrospinning process.[129] The fiber shape and diameter can be precisely controlled by varying these parameters (Figure 1.4).[130]



Figure 1.4. Core-shell electrospinning setup

# 1.5.1.3 Core-Shell Electrospinning Applications in Energy Storage and Conversion Applications

Because of its multifunctionality, controlled release capabilities, and improved mechanical qualities, core-shell nanofibers made by electrospinning have several uses. [131] Core-shell nanofibers are used in the creation of supercapacitors and high-performance batteries. Because of its special construction, materials that improve electrical conductivity and energy storage capacity can be included. One of its advantages is increasing the electrochemical performance. By removing the core material and boosting stability and active sites, core-shell systems offer better electrochemical qualities. For example, silicon nanoparticle-based lithium-ion battery anodes have used

electrospun core-shell fibers, which, because of their sturdy structure, offer high capacity and long cycle life. [83]

#### 1.6. Electrospun Microfiber-Based Electrodes for PEM Fuel Cells

Several studies on the application of electrospinning techniques with this commercially available catalyst can be found in the literature. Sadia et al. showed that by producing nanofiber mats with a large surface area, enhanced macro-porosity, and decreased gas transport resistances, electrospinning can get around transport constraints in thicker PGM-free electrodes. [132] The uniform ionomer covering on the electrospun nanofibers, which had an average diameter of 450–700 nm, increased water management and active site accessibility, which in turn improved H<sub>2</sub>/Air fuel cell efficiency. Through the optimization of electrode layout and transport parameters, this novel technique demonstrates the possible integration of PGM-free catalysts into next-generation fuel cells and other catalytic applications. [132]



Figure 1.5. a) SEM of Fe-N-C/ Nafion<sup>®</sup>/PVDF mat and b) PEM fuel cell performance of the fiber-based catalyst layer [132]

In another work, Slack et al. fabricated electrospun nanofiber cathode mats that were integrated into H<sub>2</sub>/air fuel cell MEAs by employing a Fe-N-C catalyst generated from MOF based Fe-N-C and a PVDF and Nafion<sup>®</sup> binder combination. Comparing these nanofiber cathodes to traditional sprayed-cathode MEAs, the former demonstrated better performance and durability. [133] When electrodes with the Nafion<sup>®</sup> binder were sprayed, there was a 63% decrease in power. However, when hydrophobic PVDF was added to the

binder, the power generation remained stable for 300 hours. A maximum power density of 154 mW/cm<sup>2</sup> was attained by the PGM-free nanofiber-cathode MEA with a 1:1 Nafion<sup>®</sup>: PVDF binder at 80°C and 1 atm. Through carbon-corrosion accelerated stress testing (AST), the nanofiber cathodes also maintained power generation; after 500 cycles, the maximum power density increased initially before progressively decreasing. [133]



Figure 1.6. SEM micrograph of the uniform fiber composition of MOF-based Fe-N-C/ Nafion<sup>®</sup>/PVDF [133]



Figure 1.7. a) PEM fuel cell performance and b) durability test result of Nafion<sup>®</sup>: PVDF sprayed and electrospun electrodes [133]

Recently, Xiaomin et al. on Fe-based PGM-free (Platinum metal free (PMF) type) catalysts that are utilized in various membrane-electrode assemblies (MEAs) for fuel cells cathodes. [134] They experimented with a range of cathode configurations for MEA testing, including conventional powder, fiber mats with varying binders, and Nafion<sup>®</sup> mixed with either polyethylene oxide (PEO) or PVDF. Their research revealed that

because PVDF can remove peroxide and water from the cathode, MEAs with cathodes made of a Nafion<sup>®</sup>-PVDF blend demonstrated reduced power loss and increased endurance. The MEA with a Nafion<sup>®</sup> : PVDF ratio of 75:25 exhibited the most favorable combination of catalyst stability and power efficiency, as it was able to consistently generate power even in prolonged running conditions. [134]



Figure 1.8. Fuel Cell durability tests for both Nafion<sup>®</sup> fiber and PVDF/ Nafion<sup>®</sup> fibers [134]



Figure 1.9 (a) End of time polarization curve for fibers and (b) end of time polarization curve for sprayed-based electrodes [134]

# 1.7. Objectives of The Thesis

The main objective of this thesis is to improve the durability and efficiency of Fe-N-C (PGM-free)- based PEM fuel cells by including ceria as an additive. [135] This study investigates the innovative approach of using both spraying and electrospinning techniques to evaluate CeO<sub>2</sub>'s effect. The thesis specifically focuses on the no explored field of core-shell electrospinning in the context of fuel cells. The aim of this thesis is to create and produce catalyst layers for PEM fuel cells using electrospun Fe-N-C fibers, both single and hollow, with the addition of CeO<sub>2</sub>. The focus of this thesis will be exploring the use of core-shell electrospinning, a technology that has not been discussed in earlier work on fuel cells. [134]

This research also aims to assess the influence of ceria additives on the performance and durability of PEM fuel cells. It will evaluate parameters such as power output and operational stability. Additionally, it will examine the long-term durability of PEM fuel cells with ceria-enhanced catalyst layers, specifically focusing on their resistance to degradation and overall lifespan. Another significant objective of the thesis is to set a higher benchmark for improving the effectiveness of catalysts, with the purpose of making PEM fuel cells more commercially viable by enhancing their performance and lifespan.

# 2 CHARACTERIZATION METHODS

This chapter provides a summary of the operating concepts behind the characterization tools used in the study.

#### 2.1. Physicochemical Characterization

#### 2.1.1 Scanning Electron Microscopy (SEM)

The morphology of electrospun electrodes were investigated with using SEM. Highresolution micrographs of surfaces and materials can be obtained using the potent analytical method known as Field Emission Scanning Electron Microscopy (FE-SEM). A field emission gun (FEG) is used in FE-SEM instead of SEM to produce a sharper electron beam. As a result, precise imaging at nanoscale scales is possible and spatial resolution is enhanced. [136]

A concentrated electron beam uses a raster pattern to scan the specimen surface in FE-SEM. Secondary electrons, backscattered electrons, and distinctive X-rays are among the signals produced by the electrons' interactions with the sample's atoms. An image is created by detecting and processing these signals. Higher brightness and a smaller beam diameter—two benefits that are essential for high-resolution imaging—come from using a FEG. [137]The primary benefit of the FE-SEM is its capacity to generate images with a very high resolution, usually between one and two nanometers. The images appear three-dimensional because it has a deeper depth of field than optical microscopy. [138]

Using a Zeiss LEO-Supra 35 VP FESEM, SEM images were taken for this study. The morphology of the materials was examined in both top and cross-sectional views using the secondary electron mode. Consequently, a low bias voltage of 5 kV was used to obtain SEM micrographs of fabricated fiber-based catalyst layers.

#### 2.1.2 Transmission Electron Microscopy (TEM)

Using the high-energy electron beam passing through an extremely thin material, Transmission Electron Microscopy (TEM) is a technique that makes it possible to see the interior structure at the atomic level. With this technique, an image is created by detecting the transmitted electrons and employing electromagnetic lenses to focus the electron stream. TEM is extensively used in materials science, nanotechnology, and biology to investigate the fine details of crystalline structures, nanoparticles, and biological samples. It offers the exceptional resolution and is often combined with the analytical techniques like EELS and EDX for comprehensive material analysis.[139]

This dissertation focused on the identification of Fe-N-C, Ceria, and the core-shell structures, as well as the visualization of electrospun fibers using TEM. The utilization of the pictures facilitated the precise quantification of average fiber diameters and the examination of intra-fibrous porosities. TEM-EDS was employed to assess the uniformity of particle dispersion by generating distribution pictures of different particles on the fibers. The scientific instrument employed for this experiment was the JEOL JEM-ARM200CF, 200 kilovolts and equipped with a probe size of approximately 1 angstrom. The JEOL Centurio system, which was mounted on the STEM, was utilized to do the EDS study.

#### 2.1.3 Energy-Dispersive X-ray Spectroscopy (EDS)

On the microscopic scale, Energy-Dispersive X-ray Spectroscopy (EDS) is an effective technique for determining the material's elemental composition. EDS works in conjunction with electron microscopy methods like Transmission Electron Microscopy (TEM) or Scanning Electron Microscopy (SEM). It detects characteristic X-rays emitted from the material when exposed to a focused electron beam, allowing for the identification and quantification of the elements present. EDS is particularly valuable for mapping the distribution of elements in a sample, providing insights into the material's composition, uniformity, and potential contaminants. TEM analysis plays a crucial role in characterizing the complex materials and optimizing their properties for various applications in chemistry, materials science, and nanotechnology. [140]

# 2.1.4 Diffraction Spectroscopy using X-Rays (XRD)

XRD is a strong analytical technique used to ascertain and elucidate the composition, physical properties, and the crystalline arrangement of a material. The process involves the measurement of the angles and intensities of the diffracted beams resulting from the exposure of a sample to X-rays. This method provides accurate data regarding the organization of atoms within the crystal lattice. This method is frequently employed to examine metals, polymers, and ceramics in the domains of materials science, chemistry, and geology. The capability of XRD to ascertain the composition of materials, quantify the size of crystalline particles, and identify deformations is highly advantageous. [141]

In this study, we aim to evaluate the consistency of the electrospun mats and detect the unique peaks of ceria and Fe-N-C. We examined the different samples: one with Fe-N-C and Nafion<sup>®</sup> applied to GDL, another with Fe-N-C and Nafion<sup>®</sup> combined with ceria on GDL, a third featuring Fe-N-C, PVDF, and Nafion<sup>®</sup> within a single electrospun fiber structure, a fourth incorporating Fe-N-C, PVDF, Nafion<sup>®</sup>, and ceria in a separate electrospun fiber, and finally, the core-shell fiber with a PEO core and a shell similar to

the single mat. The aim of analyzing these samples is to identify and map the distribution of Fe-N-C and ceria within the fibers.

#### 2.1.5 Brunauer-Emmett-Teller (BET)

This method is commonly employed to quantify the precise surface area of diverse materials and electrospun fibers. The method utilizes nitrogen gas adsorption to measure the surface area. The procedure entails quantifying the amount of nitrogen gas that is absorbed onto the surface of the material at various relative pressures. The acquired data is utilized to compute the precise surface area, hence offering valuable information regarding the material's porosity and surface attributes. The measurement of BET is essential for assessing materials in which surface area has a significant impact on performance, particularly in surface reactions, adsorption, and catalysis. The technique is based on the initial formation of a single layer of gas molecules on the surface of a solid, which is then followed by the adsorption of many layers. [142]

The surface area of the electrospun mats was measured using BET characterization in this study. An in-depth analysis of the electrospun mats' surface area can provide valuable insights into the porosity and surface qualities. This information is crucial for evaluating the mats' performance in the fuel cell studies.

#### 2.1.6 Thermogravimetric Analysis (TGA)

TGA is a method used to study the material's composition and the thermal stability by tracking changes in mass as it is heated. The sample is heated gradually in a controlled setting, and any weight changes are recorded based on temperature. This method reveals key information about a material's volatile content, oxidation resistance, and decomposition temperatures. TGA is widely applied in materials science, chemical engineering, and polymer analysis to understand thermal properties and how substances
decompose. It helps assess material composition, thermal stability, and the performance of coatings or additives.[143]

### 2.2. Electrochemical Tests

#### 2.2.1 Fuel Cell Performance and Durability Tests

A polarization graph is a crucial instrument for evaluating the efficiency of the fuel cell. The relationship between current density and the voltage output is demonstrated. This graph illustrates the efficiency of fuel cells and how it varies with different loads. The "beginning-of-life" (BOL) phase denotes the early stage of a fuel cell's operation, during which it exhibits its highest performance characteristics without any notable degradation. On the other hand, "End-of-Test" (EOT) indicates the fuel cell's performance after prolonged usage and aging. Analyzing the BOL and EOT data on the polarization graph enables researchers to gain insights into the long-term stability and endurance of the fuel cell. Temporal variations in the graph can serve as indicators of the problems such as the gradual decrease in membrane thickness, the loss of catalyst material, and the diminishing of the active surface area. The image is most likely depicting the microstructure of the material that is linked with these stages.[144]

PEM fuel cells require durability testing to assess their dependability and the long-term efficiency in actual operating settings. These tests replicate real-world usage conditions to detect any possible deterioration that may impact the lifespan and efficiency of the fuel cell. During durability testing, key criteria that are evaluated include the occurrence of gas crossing, the thinning of the membrane, the deterioration of the catalyst, and any mechanical failures of components. The catalyst layer experiences irreversible damage due to the deterioration of the catalyst, ionomer, and carbon support, resulting in a reduction in the electrochemical surface area (ECSA) and overall performance. Gaining insight into the degradation mechanisms is essential for enhancing the catalyst layer and prolonging the lifespan of the fuel cell. Accelerated stress testing (AST) and continuous operation evaluations yield valuable data regarding the durability of materials in the MEA

structure. This understanding facilitates the development of more resilient materials and improved fuel cell designs, which is crucial for the progress of PEM fuel cells towards commercialization.[145]

# 3 Development of Fe-N-C/PVDF Single and Hollow Microfiber-Based Catalyst Layers for PEM Fuel Cells

#### 3.1. Motivation

The development of Fe-N-C-based single and hollow fiber catalyst layers for PEM fuel cells is driven by the urgent demand for energy solutions that are more efficient, durable, and cost-effective. [146] Fe-N-C catalysts present a favorable substitute for precious metal catalysts, resulting in substantial reduction in material expenses while maintaining exceptional catalytic efficiency. By including PVDF as a binder, the mechanical stability of the catalyst layers is improved leads to long-lasting performance even in challenging operational settings. [147] Our research aims to develop hollow nanofibers, with the objective of optimizing the surface area for catalytic reactions using PVDF: Nafion<sup>®</sup> binder and improving the overall performance and durability of PEM fuel cells.

Besides, the effect of the CeO<sub>2</sub> addition on the performance and the durability of PEM fuel cell investigated.

#### 3.2. Materials

From Pajarito Powders LLC, Fe-N-C powder was received. PVDF (polyvinylidene fluoride; Solvay, MW: 380 000) was acquired from PolyK technologies and Solvay. Acetone, isopropanol, and dimethylformamide, also known as DMF, were procured from

Sigma-Aldrich. The source of HiSPEC 40% Pt on carbon (HiSPEC 4000) was Fuel Cell Earth LCC. Nafion<sup>®</sup> 20% solution was purchased from Ion Power. Poly (ethylene oxide) (PEO, MW: 1000000) obtained fron Sigma-Aldrich. CeO<sub>2</sub> is purchased from Sigma-Aldrich. Nafion membrane was achieved from Ion power company

#### **3.3.** Experimental Procedure

### 3.3.1 Preparation of the Single Electrospun Mat

An electrospinning ink was prepared with a catalyst:Nafion<sup>®</sup>:PVDF weight ratio of 70:15:15 for the electrospun fiber cathodes. The solvent was a 7:3 (w/w) mixture of dimethylformamide (DMF) and acetone. The PGM-free catalyst powder was first dispersed using ultrasonic bath in a 7:3 (w/w) DMF:acetone mixed solvent. Next, a Nafion<sup>®</sup>/solvent dispersion was added to the catalyst solution. Finally, a PVDF (12wt%) solution was added to the ink mixture. To ensure homogeneity, the mixture was mechanically stirred for 6 hours. The electrospinning process was run at a voltage of 15 kv, a flow rate of 1 ml/h, a needle distance of 12 cm from the collector, a humidity of 70%, and a drum rpm of 400.

Table 3.1 Ink composition

INK	Fe-N-C/ Nafion <sup>®</sup> /PVDF Ratio (wt. %)	Solvent	Solid Ratio (%)
1	70:15:15	DMF/Acetone	17



Figure 3.1. Single needle electrospun mat

# 3.3.2 Preparation of the Core-Shell Fibers

For the shell component, the previously described recipe is used. For the core component, PEO at 5 wt% is dissolved in a mixture of IPA and water at a 2:1 ratio. Electrospinning was conducted using a core-shell needle at a voltage of 15 kV, with a core flow rate of 0.2 ml/h and a shell flow rate of 1 ml/h. The needle was positioned 10 cm from the collector, which has a rotation speed of 400 rpm.



Figure 3.2. Core-shell electrospun mat

Fe-N- C/Nafion <sup>®</sup> /PVDF	PEO Concentrat ion (Core)	Flow Rate of the shell	Flow Rate of the Core	Applied Voltage	Speed of the collector	Humidity
70:15:15	5 wt%	1 ml/hr	0.2 ml/hr	15 KV	400 rpm	65%

Table 3.2 Ink composition and electrospinning parameters

#### 3.3.3 Optimization of Electrospinning Parameters

#### 3.3.3.1 Processing Map

The electrospinning processing map is essential for optimizing the production of fibers. The electrospun mats in this investigation consisted of PVDF, Nafion<sup>®</sup>, and Fe-N-C catalyst in a ratio of 70:15:15. The optimal conditions for producing high-quality fibers were found by conducting tests on different solid content ratios ranging from 15% to 19%.

The findings revealed that fibers with ideal diameters and consistent forms were obtained when the solid concentration ranged from 16% to 18%. At these proportions, the fibers exhibited low thorough distribution, which are crucial for improving the effectiveness of electrospun mats. These findings indicate that achieving a proper equilibrium between solid components and liquids is crucial to produce fibers of superior quality.

The electrospun mats also indicated that increasing the solid content generally results in improved powder coverage and greater fiber diameters. However, it can also give rise to problems such as particle agglomeration. By keeping the solid content within the optimal range, one can prevent the issues and achieve the required fiber characteristics.

In summary, the processing map (Figure 3.3) highlights the importance of accurately regulating the solid content ratio in order to enhance the quality of electrospun mats produced from Nafion®, PVDF, and Fe-N-C catalyst. Effective management of these

factors guarantees the manufacture of fibers with exceptional functional and structural characteristics.



Figure 3.3 Processing map of the optimized electrospun mat

### 3.3.4 Characterizations

The SEM analysis of the fibers' surface morphology was conducted using Jeol JSM 6010 LV and Supra 35VP Leo instruments. Prior to analysis, an Au/Pd coating was applied to the fibers using a Cressington 108 sputter coater at a current of 40 mA for a duration of 120 seconds. SEM images were obtained using a voltage of 5 kilovolts and a working distance of 8-10 millimeters. Fiber sizes were quantified using ImageJ software. The core-shell structure was validated using TEM and EDS analysis conducted on a JEOL JEM 2000FX microscope operating at 200 kV. The homogeneity of the material and the existence of its components were evaluated by the XRD analysis. The analysis was performed using a Bruker D8 Advance instrument with Cu K $\alpha$  radiation. The scanning range of 2 $\theta$  was from 5° to 90°, with intervals of 0.02°. The BET tests involved measuring the surface areas of both single fibers and core-shell fibers. This was done using a Surface Area and Porosity Analyzer, after the samples were degassed at a temperature of 130°C

for a duration of 24 hours. The nitrogen adsorption-desorption isotherms were measured at a temperature of -196°C. The BET surface area was calculated based on the linear section of the isotherm.

### 3.3.5 MEA Preparation Procedure

#### **3.3.5.1 Anode Preparation Procedure**

Gas diffusion electrodes (GDE) for the anode of all three CCL's were created by airspraying with a Pt load that was consistently 0.3 mg cm<sup>-2</sup>. 8 mL of IPA was added to the 0.15 g of 20% Nafion<sup>®</sup> solution and 0.1 g of 30% Pt/C catalyst that were combined to create the inks in a vial. After an hour of sonication, this mixture was air-sprayed on a Sigracet 39BC gas-diffusion-layer (GDL). while being stirred. Until the target Pt load was reached, spraying was continued. After every spray phase, 10 minutes of drying at 60°C were conducted. This anode is used for both fibers and sprayed catalyst layers.



Figure 3.4. Air-sprayed Pt/C-based anode

#### **3.3.5.2 MEA Preparation**

First, the electrospun fiber mat was cut into 5 cm<sup>2</sup> squares with precision. These squares were layered with a Sigracet 39BC GDL, a Nafion<sup>®</sup> 212 membrane, and a single PGM-free catalyst fiber mat. A Pt/C anode, made of Pt/C catalyst ink that had previously been sprayed onto another GDL, was added to this layered assembly. After that, the entire stack was heated to 140°C and compressed to 15 MPa of pressure. The pressing procedure was keeping the assembly heated for ten minutes without applying any pressure, then for five more minutes under pressure. This process successfully merged the parts together to create a cohesive functional MEA.

Initially, the core-shell fiber mat was hot-pressed onto a Nafion<sup>®</sup> 212 membrane for 10 minutes without pressure, then for 5 minutes with pressure of 15 MPa. This assembly was then immersed in hot water at 80°C for two hours to remove the PEO carrier polymer. Following this preparation, the construct was again hot-pressed at 140°C and the pressure of 15 MPa, first 10 minutes without pressure and 5 minutes with pressure while using a Pt/C anode-GDL and a cathode Sigracet 39BC GDL.



Figure 3.5 a) MEA-based on core-shell fiber hot-pressed on Nafion<sup>®</sup> and b) MEA based on core-shell fiber soaked in water

### 3.3.6 PEM Fuel Cell Testing

The fuel cell testing experiments are conducted under the following operating conditions:  $H_2/air$  PEM fuel cell tests conducted using Standard litre per minute (SLPM) gass flows which are 0.125 for hydrogen and 0.5 for air, backpressure of 200 kPa, 100%

humidity, and a temperature of 80°C. There is no pre-testing conditioning done. The OCV requires roughly 1 hour to attain a stable state after reaching a temperature of 80°C and applying backpressure. The testing technique commences with implementing the BOL test, starting at 0.2 V and extending up to the Open Circuit Voltage (OCV). Subsequently, a durability test is performed under a consistent voltage of 0.5 V for a duration of 50 hours. Ultimately, the EOT test is utilized to evaluate the performance at the end of a given period.

#### 3.4. Preparation of Sprayed Electrodes based Fe-N-C

To prepare the cathode catalyst layer of Fe-N-C, 40 mg of ball milled PGM-free catalyst (Pajarito PMF Material) was first wetted with 0.728 g of deionized water. 1.46 g of IPA was then added to the mixture. Following complete wetting of the catalyst, 0.244 g of a 20% Nafion<sup>®</sup> ionomer dispersion was added to the solvent mixture. Following that, the mixture was sonicated for two hours in an ice ultrasonic bath. Using the airbrush, the resultant ink was sprayed onto a 5 cm<sup>2</sup> Sigracet 39BC GDL to achieve a catalyst loading of 3 mg cm<sup>-2</sup>.



Figure 3.6. Air-Sprayed Fe-N-C catalyst layer

#### 3.4.1 MEA Preparation Procedure

Sigracet 39BC carbon paper GDLs were manually air-sprayed with cathode inks, until a dry cathode catalyst loading of 3.0 mg cm<sup>-2</sup> was reached. After that, the cathode was mixed and hot-pressed with a Pt/C powder anode-GDL and a Nafion<sup>®</sup> 212 membrane at 140°C for 10 minutes without pressure and five minutes under pressure of 15 MPa.

#### 3.4.2 Characterization

The SEM (Jeol JSM 6010 LV with Supra 35VP Leo) was used to analyze the surface morphology of the sprayed catalyst layers. The samples underwent a coating process with Au/Pd using a Cressington 108 sputter coater at a current of 40 mA for a duration of 120 seconds. Subsequently, pictures were taken at an electron beam voltage of 5 kV, with a working distance of 8-10 mm. Particle sizes were determined by employing ImageJ software. XRD examination was conducted using a Bruker D8 Advance diffractometer, operating at 40 kV and 40 mA, with Cu K $\alpha$  radiation. The samples were scanned from 5° to 90° in 0.02° increments, yielding information on the crystalline phases, uniformity, and composition of the material.

#### 3.4.3 PEM Fuel Cell Testing

The fuel cell testing experiments are carried out according to the specified operating conditions: The H<sub>2</sub>/air PEM fuel cell tests were performed with gaseous fluxes of 0.125 standard liter per minute (SLPM) for H<sub>2</sub> and 0.5 SLPM for air, a backpressure of 200 kPa, 100% humidity, and a temperature of 80°C. No pre-testing conditioning is performed. It takes approximately 1 hour for the OCV to stabilize after achieving a temperature of 80°C and applying backpressure. The testing procedure begins by doing the BOL test, starting at a voltage of 0.2 V and gradually increasing it until reaching the OCV. Following that, a durability test is conducted at a constant voltage of 0.5 V for a period of 50 hours. The

EOT test is ultimately employed to assess performance at the conclusion of a specific timeframe.



Figure 3.7. Graphical abstract of the experimental procedure



Figure 3.8. Flow chart of the experimental procedure

#### 3.5. Result and Discussion

# 3.5.1 SEM

The sprayed powders on the GDL of PEM fuel cells are shown in SEM pictures, with and without the addition of CeO<sub>2</sub> in (Figure 3.9 a and b), respectively, the particle distribution of both is very uniform. Figure b, which contains CeO<sub>2</sub>, exhibits slightly different particle distribution. A uniform single-layer structure is indicated by the consistent diameter across the length of the fiber in images (c) and (g), which show the single fiber without ceria. The top view of the core-shell fiber containing ceria, and images d and h show a significantly larger average diameter than the single fibers. The core-shell configuration is confirmed by further inspection of the core-shell fibers by cross-sectional views in images (e) and (f), respectively, before and after PEO removal. The postextraction image reveals more distinct shell boundaries, and the cross-sections clearly distinguish between the core which is like a hole and the shell.

The distribution of sizes by showing an increase in fiber diameter when comparing single fibers to core-shell fibers, evidence from ImageJ software strongly supports the validity of the core-shell structure. The single fiber mat has an average diameter of 1.804 micrometers and an exact error margin of  $\pm 0.068$  micrometers. This constancy is a result of the single-layer fibers controlled and homogeneous production process. On the other hand, an increased average diameter of 2.79 micrometers with an error bar of  $\pm 0.13$  micrometers are displayed by the core-shell fiber mat. One of the key features of the core-shell design is the noticeable increase in diameter for the core-shell fibers, which indicates the presence of extra shell material surrounding the core.



Figure 3.9 . SEM micrograph of a) Sprayed powder without CeO<sub>2</sub> b) Sprayed powder with CeO<sub>2</sub> c) Single fiber without CeO<sub>2</sub> d) Core-shell fiber with CeO<sub>2</sub> e) Cross section of core-shell fiber before PEO removal f) Cross section of core-shell fiber after PEO removal g) Top view of single fiber and h) Top view of core-shell fiber



Figure 3.10. The effect of structure on the fibers average diameter a) single fiber and b) core-shell fiber

# 3.5.2 TEM and EDX

The TEM image of the single fiber (Figure 3.10 a) displays a uniform structure without clearly defined layers. The regularity observed suggests that the fiber is made up of a homogeneous composition while TEM image of the core-shell fiber (Figure 3.10 b) clearly shows a distinct differentiation between the core and the shell. The central part of the fiber, consisting mainly of PEO, is observed as a darker area, while the outside layer, formed of Fe-N-C, PVDF, and Nafion<sup>®</sup>, is lighter. The core-shell architecture exhibits a clearly defined interface between the core and the shell, indicating good fabrication. [148]

The EDS mapping, depicted in (Figure 3.11), demonstrates the spatial distribution of elements in both individual fibers and core-shell fibers. Fe, N, and C are evenly dispersed throughout the structure of both entities, suggesting a homogenous composition.



Figure 3.11. TEM images of a) single fiber and b) core-shell fiber



Figure 3.12. EDS mapping of a,b,c,d) single fiber and e,f,g,h) core-shell fiber

### 3.5.3 XRD

The sprayed powders devoid of  $CeO_2$  show prominent peaks at about 30°, suggesting a highly crystalline structure that mostly corresponds to certain planes in nitrides or iron carbides. Broader peaks when ceria is added, with a significant increase observed at around 28.5° and 47.5°. The broader peaks indicate lattice distortions or the formation of

a composite phase with the Fe-N-C matrix, indicating the presence of  $CeO_2$  on crystallographic planes such as the (111) and (220) planes of cerium oxide. [135] [149]

The existence of PVDF and Nafion<sup>®</sup> in the fibers lead both single and core-shell kinds to primarily display flat XRD patterns and around 19° plane of (100) can attributed to them, which represent their amorphous structure. The inclusion of PEO in the core during the fiber production process is responsible for these making the sharp peaks more smooth. [150]



Figure 3.13. XRD pattern of the samples

#### 3.5.4 BET

The surface area of the both single and core-shell electrospun fibers, examined by means of BET, Notable have distinctions between the single and core-shell fibers are obtained. The Fe-N-C particles with PVDF and Nafion<sup>®</sup> that made up the single fibers had a greater surface area of 204.16 m<sup>2</sup>/g. Conversely, the core-shell fibers had a reduced

surface area of 161 m2/g which is a similar composition to the single fiber in the shell, but with a PEO core.

These disparities are further explained by the BET isotherms. At higher relative pressures ( $p/P_0$  close to 1), the isotherm for the single fibers exhibits a steep increase in adsorption, which suggests considerable capillary condensation within mesopores or inter-fiber voids. This implies that the structure is more porous or open, which is characteristic of homogenous materials such as the single fiber. Conversely, the core-shell fibers show a less noticeable rise at high pressures, which suggests a decrease in porosity. Since the PEO core is non-porous, its presence probably helps achieve this effect by taking up space inside the fiber where porosity could otherwise grow and increase surface area. [151, 152]

Understanding the influence of fiber design on material qualities requires an awareness of this structural difference. The total surface area accessible for nitrogen adsorption is reduced because the PEO core in the core-shell fibers prevents porosity development. This matches theoretical predictions, according to which the porosity properties of fibers can be strongly impacted by a dense, non-porous core material like PEO, which in turn affects surface area measurements. [153]

Further research involving post-extraction analysis of the core-shell fibers examined by advanced microscopic techniques, like SEM or TEM, utilized to directly observe the enhancement of porosity after the removal of the PEO core and to visually confirm the morphological changes for a deeper understanding of how the core-shell structure influences fiber properties.



Figure 3.14. BET characterization of single and core-shell fibers

# 3.6. Fuel Cell Testing Results

#### 3.6.1 Fiber Catalyst Layer-Based Electrodes

# 3.6.1.1 BOL

The BOL test results reveal that core-shell fiber-based catalyst layer combinations outperform single fiber-based catalyst layer in PEM fuel cells, as seen by their enhanced power production and voltage stability. At a current density of 150 mA cm<sup>-2</sup>, the core-shell fiber lacking CeO<sub>2</sub> retains a voltage of roughly 0.5 V, which is notably greater than the single fibers with and without CeO<sub>2</sub>, which decrease to around 0.3 V and 0.2 V, respectively (Figure 3.15 a).

Figure 3.18. b demonstrates that the core-shell fiber ceria included has a maximum power density of approximately 84 mW cm<sup>-2</sup>, whereas the single fiber with CeO<sub>2</sub> reaches a peak of around 35 mW cm<sup>-2</sup>, and the single fiber without CeO<sub>2</sub> reaches a peak of about 20 mW cm<sup>-2</sup> in terms of power density. The unusual structure of the core-shell fibers enables them to significantly improve electrochemical processes and enhance fuel cell performance.

Incorporating  $CeO_2$  into individual fibers enhances the catalytic characteristics of the electrocatalyst, leading to improved stability and increased lifespan through the reduction of degradation. When PVDF is present in the fibers, hydration concerns usually lead to a decrease in performance. However, the core-shell configuration enhances gas flow and speeds up hydration, resulting in an additional improvement in performance.[134]



Figure 3.15. a) I -V plots and b) Current density vs. Power density graphs of the fiber catalyst layer-based electrodes in the

# 3.6.1.2 Durability

The durability test results showed that core-shell fiber-based catalyst with ceria layers's are better than single fibers in terms of durability since core-shell based ones exhibited

higher current and power densities. When assessing the performance of various catalyst configurations under prolonged operating circumstances, this distinction is essential.

Despite an initial performance drop, likely caused by membrane pre-hydration, coreshell fibers quickly recover and surpass the performance of single fibers. For the coreshell fiber with ceria, this drop cannot be seen Interestingly, and the power is increasing during the time. power densities in core-shell fibers increased and remained roughly 40 mW cm<sup>-2</sup> for without ceria and for ceria based it increased from 70 to 80 mW cm<sup>-2</sup>, which is significantly greater than in single fibers without CeO<sub>2</sub>, which was stabilized at about 20 mW cm<sup>-2</sup>. This suggests that the hydrophobic polymer, PVDF, poses hydration issues that the core-shell arrangement successfully addresses. Single fiber without ceria however, exhibited lower power density at 0.5 V but maintained a consistent level, and Single fiber with CeO<sub>2</sub> shows a stabilized power density around 32 mW cm<sup>-2</sup>. All the core-shell based MEA's' core part are removed by washing.



Figure 3.16. Durability test of the fiber catalyst layer-based electrodes

#### 3.6.1.3 EOT

The EOT test results for various fiber types provide a good understanding of the efficiency of different catalyst designs. The graphs depict the voltage and power density profiles obtained from measuring various current densities for single fiber-based electrodes with and without CeO<sub>2</sub>, as well as core-shell fiber-based electrodes lacking CeO<sub>2</sub>.

The superior electrical efficiency and stability of the CeO<sub>2</sub>-free core-shell fiber-based electrodes are evidenced by their ability to sustain the highest voltage across a wide range of current densities, as depicted in the voltage profile graph. When subjected to a current density of 150 mA cm<sup>-2</sup>, the core-shell fiber without CeO<sub>2</sub> retains a voltage of roughly 0.5 V. In contrast, the single fibers with and without CeO<sub>2</sub> experience a decrease in voltage to around 0.4 V and 0.3 V, respectively. The core-shell construction effectively regulates the PEM fuel cell's internal conditions, such as gas diffusion and electrolyte hydration, to enhance performance, even without the presence of CeO<sub>2</sub>. When comparing single fibers with and without CeO<sub>2</sub> show improved voltage retention, highlighting the beneficial effect of CeO<sub>2</sub> in facilitating the electrochemical processes.

The power density profiles (Figure 3.17 b) provide additional evidence that the coreshell fibers with CeO<sub>2</sub> have the highest power density, reaching a peak of approximately 96 mW cm<sup>-2</sup>. The peak power output of the single fiber with CeO<sub>2</sub> is approximately 50 mW cm<sup>-2</sup>, while the single fiber without CeO<sub>2</sub> reaches a peak of roughly 35 mW cm<sup>-2</sup>. This refers to the proper management of internal resistance and the promotion of catalytic activity, both of which contribute to increasing overall efficiency. Although single fibers with CeO<sub>2</sub> exhibit better performance compared to those without CeO<sub>2</sub>, their power densities nevertheless remain lower than that of core-shell fibers. This supports the idea that while CeO<sub>2</sub> improves performance, the structure benefits of the core-shell architecture have a greater impact on power generation.



Figure 3.17. I -V plots and b) Current density vs. Power density graphs of the fiber catalyst layer-based electrodes in the EOT

### **3.7.** Air-Sprayed Electrodes

#### 3.7.1.1 BOL

Different voltage and power density profiles as a function of current density reflect the electrochemical performance seen in the BOL experiments for sprayed powders with and without ceria in proton exchange membrane fuel cells. For evaluating the catalyst layers' initial capacities and efficiencies under operating settings, these BOL tests are essential.

The addition of ceria demonstrates a demonstrated ability to sustain greater voltage over a wide range of current densities in the BOL voltage versus current density graph. This response suggests a strong ability to support electrical loads from the beginning, which is indicative of lower overpotential losses and improved electrochemical stability. These characteristics underline the positive effect of ceria in enhancing initial operational metrics and are necessary for effective fuel cell operation. [154, 155]

The power density graph provides additional evidence supporting ceria's beneficial effects at the BOL stage. Compared to the ceria-free powder, the Ceria-containing powder

not only reaches a greater peak in power density but also exhibits improved performance over the whole measured range. This ongoing improvement in performance implies that ceria supports initial operational stability and efficiency on a larger scale.

The capacity of ceria to support efficient ORR and stable the electrocatalyst structure under operating stresses is largely responsible for these advancements. Furthermore, the presence of CeO<sub>2</sub> improves the catalysts' resistance to deterioration and by extending their chemical durability. [93] Crucially,  $H_2O_2$  production is inhibited by CeO<sub>2</sub>, a vital function that also prevents additional catalyst degradation and cell efficiency loss. CeO<sub>2</sub> helps reduce  $H_2O_2$  production by enabling a more thorough reduction of oxygen molecules directly to water, safeguarding the catalyst and extending the fuel cell's operating life. [156]

In conclusion, the BOL test findings verify that adding CeO<sub>2</sub> greatly improves the power density and voltage stability of sprayed electrodes in PEM fuel cells. These results highlight the significance of ceria in creating reliable and effective catalyst systems that function well from the start of their operational lives. This promising beginning suggests the possibility of long-term durability and performance, which will encourage further research into the application of ceria in cutting-edge clean energy systems.



Figure 3.18. a) I-V plots and b) Current density vs. Power density graphs of the sprayed electrodes in the BOL

### 3.7.1.2 Durability Test

The durability test findings indicate that the catalyst layers containing ceria additive powder retain a consistent power density of around 120 mW cm<sup>-2</sup> during the entire test. The continuous performance of ceria highlights its crucial function in improving the structure of the electrocatalyst and safeguarding it from degradation processes, such as catalyst particle breakage or poisoning by hydrogen peroxide. Ceria enhances the longevity of the catalyst by promoting a more effective conversion of oxygen molecules into water, hence reducing the production of detrimental byproducts that may destroy the catalyst.

On the other hand, the power density of the formulation without ceria consistently decreases and eventually levels off at approximately 60 mW cm<sup>-2</sup>. The drop is probably attributable to catalyst agglomeration, active material loss, or heightened internal resistance in the fuel cell. The results underscore the crucial significance of ceria in preserving catalytic activity over a period.



Figure 3.19. Fuel cell durability test results of the conventional sprayed electrodes

# 3.7.1.3 EOT

The sprayed powder containing CeO2 consistently exhibited higher voltage across the whole range of current density during the EOT experiments. Significantly, it sustained a voltage level exceeding 0.2 V even when subjected to greater current densities of 700 mA cm<sup>2</sup>. Conversely, the powder without CeO2 exhibited inferior performance. CeO<sub>2</sub> showed a noticeable voltage drop below this level, suggesting faster deterioration and higher overpotential losses. The prolonged voltage performance demonstrates how CeO<sub>2</sub> improves electrochemical stability and lessens the effects of degradation over time.

The ceria-based sprayed powder, as shown in (Figure 3.20 b), reached a peak power density at the EOT of roughly 175 mW cm<sup>-2</sup>, which is impressively near to its original peak of about 180 mW cm<sup>-2</sup> during the BOL testing. The ceria-doped catalyst's resilience is demonstrated by this slight reduction, which remained close to beginning power production throughout the entirety of the test. On the other hand, during the BOL testing, the ceria-free powder peaked at about 160 mW cm<sup>-2</sup>; but, by the EOT, it had decreased to about 140 mW cm<sup>-2</sup>. This decline is more noticeable and shows how vulnerable the catalyst is to operational pressures; that is to say, it degrades more quickly without the protective effects of ceria.

In conclusion, the performance of PEM fuel cells is significantly improved both immediately and over time by the addition of  $CeO_2$  to the catalyst composition. These results demonstrate the benefit of using ceria in catalyst designs and encourage additional research into this material to create fuel cell systems that are more dependable and efficient. The strategic integration of ceria in modern PEM fuel cell applications is justified by the sustained performance and durability found with ceria-doped catalysts, which render them extremely appropriate for applications where long-term dependability and efficiency are critical.



Figure 3.20. a) I-V plot and b) Current density vs. power density graphs of the sprayed electrodes in the EOT

#### **3.7.1.4 EOT: BOL Histogram**

The performance of PEM fuel cell catalyst is greatly influenced by  $CeO_2$ , as demonstrated by the power density ratios (EOT: BOL) graphed for sprayed powders with and without  $CeO_2$  at various voltages. At a voltage of 0.3 V, the power density ratio of the ceriacontaining powder is roughly 0.9, while the ceria-free powder has a ratio of 0.6, indicating a 50% enhancement. At a voltage of 0.5 V, the powder containing ceria maintains a ratio of approximately 0.8, whereas the powder without ceria decreases to 0.4, showing a doubled improvement. The ceria-containing powder demonstrates a significant influence, especially at 0.7 V, where it achieves a power density ratio of around 1.9, nearly twice the ratio of 1.0 observed with the ceria-free powder. These data demonstrate that the addition of  $CeO_2$  greatly enhances performance stability and increases operating stability under stress. Nevertheless, deterioration can be detected with time in both the powders without ceria and the powders with ceria at 0.3 V and 0.5 V. The results emphasize the importance of including CeO<sub>2</sub> into catalyst formulations to enhance durability and assure more stability in performance over an extended period.

Voltage	EOT without Ceria (mW cm <sup>-2</sup> )	BOL without Ceria (mW cm <sup>-2</sup> )	EOT with Ceria (mW cm <sup>-2</sup> )	BOL with Ceria (mW cm <sup>-2</sup> )
0.3	90.28	122.36	164.29	157.57
0.5	64	200.75	150.59	224.6
0.7	18.77	34.8	71.37	36.26

Table 3.3. Power density values at the voltages of 0.3, 0.5 and 0.7 V  $\,$ 



Figure 3.21. EOT: BOL histogram of the sprayed electrodes

### 4 Development of the graphene-based Fe-N-C

# 4.1. Our Initial Work on Nano-sized Fe-N-C catalysts

In our previous study, nano-sized Fe-N-C catalysts for fuel cells were investigated with a focus of the influence of iron precursors and CeO<sub>2</sub> addition. with a focus on the synthesis techniques, the effects of different iron precursors, and CeO<sub>2</sub> integration. FeCl<sub>2</sub>, FeCl<sub>3</sub>, and FeSO<sub>4</sub> were used to decorate nitrogen-doped reduced graphene oxides with iron, and CeO<sub>2</sub> was used to enhance these structures to create the catalysts. Using this method, it was demonstrated that FeCl<sub>3</sub> was the most efficient precursor, greatly increasing the efficiency and performance of the catalyst. CeO<sub>2</sub> inclusion led to an additional roughly 20% boost in peak power densities, indicating these materials' potential for use in real-world fuel cell applications. Building on that initial research, in this thesis, we are now exploring the potential of these materials as fibers produced through the electrospinning technique, with the goal of further enhancing the physical properties and performance of the catalysts. [135]

### 4.2. Electrospun Mat Preparation Procedure

Fe-N-C, Nafion<sup>®</sup>, and PVDF are carefully blended in ratios of 50/35/15 to create an ink that is ideal for electrospinning. Several careful processes are involved in the preparation process to guarantee that the electrospinning ink forms properly. First, a Nafion<sup>®</sup> solution is spread out over a petri dish after being dissolved in a mixture of ethanol and water. After allowing this solution to dry, a thin layer of Nafion<sup>®</sup> is produced. After drying, 0.077 grams of this Nafion<sup>®</sup> film are put in a vial with 0.2 grams of acetone and 0.4 grams of dimethylformamide (DMF). For a full day, this mixture is continuously swirled to guarantee complete mixing. Meanwhile, PVDF solution with a Wt. %14 concentration is made with acetone and DMF in a 7:3 solvent ratio. Next, for an equal dispersion, 110 mg of the catalyst is added to the Nafion<sup>®</sup> solution and sonicated for an hour. Lastly, the catalyst-containing Nafion<sup>®</sup> solution is mixed with 0.18 grams of the PVDF solution. The completed mixture is agitated for five more hours to complete the electrospinning ink preparation. FeNC/Nafion<sup>®</sup>/PVDF in various ratios were also experimented with for the electrospin mat preparation. Nevertheless, the RGO flakes were likely to jam the needle.



Figure 4.1. Ink preparation steps

PVDF Solution wt.%	Wt.% of FeNC	Wt.% of Nafion <sup>®</sup>	Wt.% of PVDF	PVDF Solution	Solid solution Ratio (%)
14	64	24	12	0.13	27
14	64	18	18	0.20	24
14	50	25	25	0.27	18
14	60	25	15	0.16	12
14	50	35	15	0.18	21
14	60	25	15	0.09	19
14	55	30	15	0.092	18
14	55	25	20	0.12	19
14	55	30	15	0.16	19
14	55	25	20	0.12	19
14	50	35	15	0.18	22

Table 4.1. Optimization of electrospinning ink

Table 4.2. Electrospinning setup operation parameters

Electrospinning Parameters					
Voltage	Humidity	dity Flow rate Distance		Speed rate of the collector	
18KV	68%	0,8mL/h	10 cm	450 rpm	



Figure 4.2. Electrospun mat of Fe-N-C/ Nafion®/PVDF with the ratio of 50:35:15

# 4.3. Characterization

### 4.3.1 SEM

Fe-N-C nanoparticles are clearly visible on the surfaces of the PVDF and Nafion<sup>®</sup> fibers in the scanning electron microscope (SEM) image which indicates that the catalyst has been successfully integrated into the fiber matrix, either by adhering to the fibers or by coating them efficiently. Furthermore, discrete Reduced Graphene Oxide (RGO) flakes are seen in the SEM picture. The existence of compounds based on graphene is confirmed by these discernible flakes.

Additionally, the SEM study demonstrates that the ionomer is more evenly distributed throughout the catalyst layers. The fibers' porous nature, which promotes a more even distribution, is responsible for this improved dispersion. [157]



Figure 4.3. Morphology of nanofibers including Fe-N-C/Nafion/PVDF by SEM a) including graphene flakes and b) single fiber

### 4.3.2 TEM

TEM images can provide further details on the distribution of Fe-N-C nanoparticles and RGO flakes in the sample. The electrospinning procedure involves the collection of materials for TEM. The images show the uniform dispersion of Fe-N-C nanoparticles, indicating a continuous dispersion across the electrospun polymer surface. In addition, it is clear that RGO flakes are present, demonstrating their incorporation into the material (Fig a, b and c). At higher magnifications, every fiber is clearly covered by the nanoparticles (Figs. d, e, and f), indicating full adhesion or coating. The TEM images also show the size dispersion of the nanoparticles, which range in size from two to three nanometers.

From TEM images, more details on the distribution of Fe-N-C nanoparticles and RGO flakes in the sample can be found. During the electrospinning procedure, samples are gathered for TEM analysis. The images show that the Fe-N-C nanoparticles are dispersed uniformly, indicating a consistent dispersion across the electrospun polymer surface. Additionally, RGO flakes demonstrate that how well the particles has attached to the fibers (Fig a, b and c). Increased magnifications clearly show that the nanoparticles completely cover each fiber (Figs. d, e, and f), indicating full adhesion or coating. The TEM photographs also show the size distribution of the nanoparticles, which have particle sizes ranging from 2-3 nm. [157]



Figure 4.4. TEM of a,b,c) graphene flakes on the fiber and d,e,f) fiber including nanoparticles



Figure 4.5. TEM image showing the nanoparticles diameter

#### 4.3.3 EDS

Energy-dispersive X-ray spectroscopy (EDS) analysis of the FeNC nanoparticles dispersed throughout the fibers revealed that the elements in the sample are distributed uniformly. Spectra obtained from different points on the sample surface confirm the presence of iron (Fe), nitrogen (N), and carbon (C); which is consistent with the composition expected for FeNC nanoparticles. Furthermore, the elemental mapping shows a homogenous distribution of these elements, indicating a homogeneous dispersion of the nanoparticles on the fibers.





Figure 4.6. EDS mapping of a,b,c,d and e) electrospun mat including Fe-N-C/ Nafion<sup>®</sup>/PVDF and f) EDS analysis of the fiber

#### 4.3.4 XRD

The Fe-N-C, PVDF, and Nafion<sup>®</sup> electrospun mat exhibits a clear XRD pattern, which provides insight into the crystalline structure of the materials. The dominant peak, denoted as (002), is observed at an angle of approximately 26° in the 2-theta scale. This peak is characteristic of substances containing graphite or graphene. There is evidence to imply that there is still some crystalline graphite structures present in the reduced graphene oxide (RGO) within the composite. This indicates that there are places in the sample that contain graphite.

The presence of a distinct and strong (002) peak indicates a significant degree of graphitization, leading to improved structural strength and electrical conductivity of the mat. The lack of further identifiable peaks suggests that Fe-N-C and PVDF are either well dispersed or amorphous inside the Nafion<sup>®</sup> matrix. Typically, the Nafion<sup>®</sup> matrix does not exhibit clear crystalline peaks in XRD analysis.

The XRD pattern provides evidence that Fe-N-C and PVDF are effectively incorporated into the fibrous Nafion<sup>®</sup> structure during electrospinning. Furthermore, it indicates that the RGO component has a role in enhancing the conductivity and mechanical stability of the mat. The XRD analysis identifies the graphitic domains that are crucial for the performance of the mat in applications such as fuel cells. [158]


Figure 4.7. XRD pattern of the electrospun mat

## 4.3.5 TGA

The electrospun mat containing FeNC has unique thermal characteristics obtained by thermogravimetric analysis (TGA), that are comparable to those seen in carbon-based catalyst samples. Significant weight loss happens after 350°C, which is a symptom of the breakdown of organic and carbonic materials and is probably caused by the polymers in the electrospun mat. There is a remnant that indicates the presence of iron despite the drastic drop in mass. In contrast to the powder form, the lower temperature breakdown indicates a polymer matrix susceptibility. Overall, the TGA data show that the carbonaceous components in the electrospun mat have broken down, and the mass that remains after this breakdown is suggestive of the existence of iron oxide.



Figure 4.8. TGA of the electrospun mat based on Fe-N-C/ Nafion<sup>®</sup>/PVDF

## 4.4. Future Perspective

In the next step, assessing the performance and durability of the Fe-N-C fiber-base catalyst layer will be investigated. The cathode catalyst layer will be prepared via core-shell electrospinning also. In addition, MEAs and a short fuel cell stack will be fabricated, and their fuel cell performance will be assessed.

## 5 CONCLUSION

In this dissertation, the main focus was the development of Fe-N-C catalysts that were incorporated into unique core-shell fiber architectures to be utilized in a fuel cell electrode structure as a novel approach for PEM fuel cells. The ultimate goal was to improve the performance, efficiency, and longevity of PEM fuel cells.

In this regard, Chapter 1 introduced the concept of clean energy demand and discussed the principles and components of PEM fuel cells with an emphasis on the significance of M-N-C catalysts, specifically Fe-N-C type, for enhancing fuel cell performance. In addition, the function of ceria in improving the long-lastingness and steadfastness of PEM fuel cells was depicted. Furthermore, different methods for the fabrication of electrodes, with a particular focus on electrospinning, notably core-shell electrospinning, which was done for the first time in the literature for PEM fuel cell applications, were presented.

Chapter 2 provided an overview of the characterization techniques employed in this study, such as SEM, TEM, EDS, XRD, BET, and TGA. Additionally, electrochemical experiments were conducted to assess the performance before and after the durability of PEM fuel cells (BOL and EOT).

Chapter 3 focused on Fe-N-C/PVDF single and hollow microfiber-based catalyst layers with an overview of the experimental procedures involved in the production of single and core-shell fibers. Optimization parameters for various analyses such as morphological analysis, XRD, BET, and PEM fuel cell testing were shown as well. The traditional technique of creating the CCL through the process of air-spraying was also investigated.

The results obtained from the electrode made of the core-shell fibers were revealed the unique features and potential advantages of the core-shell architecture. The performance of core-shell fiber-based electrodes in PEM fuel cells was exceptional, as they demonstrated higher voltage and power density in comparison to single fibers. More precisely, when the current density was set at 150 mA cm<sup>-2</sup>, the core-shell fibers without CeO<sub>2</sub> maintained a voltage of roughly 0.5 V. This voltage was greater compared to both the single fibers with CeO<sub>2</sub>. The core-shell fiber-based electrode had the maximum power density of around 70 mW cm<sup>-2</sup>. However, for the core-shell based MEA with ceria the power density of the MEA increased to 80 mW cm<sup>-2</sup> which was the best performance of the fibers. The single fiber with CeO<sub>2</sub> achieved the maximum power density of around 20 mW cm<sup>-2</sup>, whereas the fiber without CeO<sub>2</sub> produced a peak power density of around 20 mW cm<sup>-2</sup>. The results demonstrate that the core-shell design greatly improves performance by effectively controlling important parameters such as mass transport and electrolyte hydration.

The durability tests have verified the robustness of the core-shell fiber electrode, as it consistently exhibited better current and power densities when compared to single fibers for prolonged durations. The power density of the core-shell based electrode remained consistently at around 40 mW cm<sup>-2</sup>. For core-shell base MEA with CeO<sub>2</sub> the power density increased to 84 mW cm<sup>-2</sup>. It is significantly greater than the measured power density of 20 mW cm<sup>-2</sup> in single fibers lacking CeO<sub>2</sub>. This suggests that the core-shell structure enhances the hydration of the electrolyte, preserves the structural integrity, and facilitates efficient gas diffusion, resulting in superior overall performance. The results of the EOT test demonstrated that core-shell fibers-based electrodes maintained higher voltage and power density throughout various current levels in comparison to single fibers. The coreshell fibers lacking CeO<sub>2</sub> demonstrated a peak power density of around 66 mW cm<sup>-2</sup>, coreshell fiber with ceria increased to 94 mW cm<sup>-2</sup> while single fibers with CeO<sub>2</sub> had a power density of 50 mW cm<sup>-2</sup> and those without CeO<sub>2</sub> had a maximum power density of 35 mW cm<sup>-2</sup>. These results confirmed the enhanced fuel cell efficiency.

The electrodes that were air-sprayed, especially CeO<sub>2</sub> included, showed significant improvements in performance. Incorporating ceria into the sprayed catalyst layers resulted in a substantial enhancement in both voltage and power density across various current densities. At a voltage of 0.3 V, the power density ratio of the air-sprayed with ceria was roughly 0.9, whereas the air-sprayed MEA without ceria had a ratio of 0.6, demonstrating a 50% increase. At a voltage of 0.5 V, the powder containing ceria maintained a ratio of roughly 0.8, whereas the powder without ceria declined to 0.4,

indicating a doubled improvement. The powder with ceria showed a notable impact, particularly at 0.7 V, where it obtained a power density ratio of around 1.9, nearly double the ratio of 1.0 observed with the powder without ceria. The data clearly demonstrated that the inclusion of  $CeO_2$  significantly improved performance stability and promoted operating stability under stress.

Chapter 4 focused on the advancement of the produced Fe-N-C catalysts and their incorporation into electrospun mats. The successful synthesis and dispersion of Fe-N-C catalysts within the fibers were confirmed by the characterization findings of SEM, TEM, EDS, XRD, and TGA. PEM fuel cell performance tests were carried out for this ongoing work.

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