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"Ion exchange membranes, based on SEBS, for application in fuel cells"

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Dedications

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RESUMEN

La sulfonación indirecta (vía clorometilación) del polímero copoli(estireno-(etileno-butileno)-estireno) (polySEBS), es una ruta alternativa al uso convencional del ácido clorosulfónico para dicho fin. La reacción de sulfonación indirecta es una vía efectiva para insertar grupos sulfónicos en los anillos aromáticos de los bloques estirénicos del polySEBS para conferirle capacidad de intercambio de protones.

En esta tesis, el polySEBS clorometilado fue modificado químicamente por el grupo isotiouronio, posteriormente hidrolizado y oxidado para generar grupos sulfónicos selectivamente en la porción aromática (poliestireno) del polySEBS. Las membranas poliméricas clorometiladas y sulfonadas fueron caracterizadas y comparadas por RMN, FT-IR, absorción de agua, TGA, capacidad de intercambio iónico (IEC) y conductividad iónica. Los resultados obtenidos muestran que, a medida que aumentó el tiempo de oxidación en ácido perfórmico, la absorción de agua alcanzaba hasta el 79.6% debido a la conversión de isotiouronio a los grupos sulfónicos en la estructura del polímero. Además, la muestra después de 7 horas de reacción de oxidación (sSEBS-7H) alcanzó el 59% de sulfonación, determinado por RMN, el cual tenía un valor de IEC de 1.46 meg/g y también un valor de conductividad iónica de 18.7 mS/cm a temperatura ambiente, que son valores 46% y 75% más altos que los del Nafion 117, un polímero comercial covencionalmente utilizado como PEM (Proton exchange membrane, por sus siglas en inglés). Por lo tanto, la membrana sSEBS-7H preparada, a través de la clorometilación, puede ser utilizada como una membrana intercambiadora de protones en celdas de poder, ya que exhibe una buena conductividad iónica y estabilidad estructural.

Palabras clave: PolySEBS, Sulfonación indirecta, Clorometilación, Conductividad iónica, Membrana Intercambiadora de Protones

ABSTRACT

The indirect sulfonation, via chloromethylation, of poly(styrene-(ethylenebutylene)-styrene) copolymer (polySEBS), under mild conditions, is here reported as an alternative route for the conventional use of chlorosulfonic acid. This indirect sulfonation reaction is an effective route to insert sulfonic groups in the aromatic rings of SEBS to impart it a proton exchange capability. The chloromethylated polySEBS was chemically modified by isothiouronium group, afterwards hydrolysed and oxidized to generate sulfonic acid groups selectively into the aromatic portion (polystyrene) of the polySEBS, at high extent.

In this thesis, the chloromethylated and sulfonated polymeric membranes were characterized and compared by NMR, FT-IR, water uptake, TGA, ion exchange capacity (IEC), and ion conductivity. The obtained results show that as the oxidation time increased, in performic acid, the water uptake achieved up to 79.6% due to the conversion of isothiouronium to the sulfonic acid groups into the polymer structure. Furthermore, the sample after 7 hours of oxidation reaction (sSEBS-7H) achieved 59% of sulfonation, determined by RMN, and had an IEC value of 1.46 meq/g and also an ion conductivity value of 18.7 mS/cm at RT, which are 46% and 75% higher than those values of Nafion 117, a commercial polymer conventionally used for proton exchange membranes (PEM). Thus, the as-prepared sSEBS-7H membrane, via chloromethylation, can be used for PEM in fuel cells since it exhibits good ionic conductivity and structural stability.

KEYWORDS: PolySEBS, Indirect Sulfonation, Chloromethylation, Ion conductivity, Proton Exchange Membrane

CHAPTER 1. INTRODUCTION

1.1 Motivation

The depletion of energy resources derived from fossil fuels, and the problem of climate change associated with these, have prompted the search for different alternatives for energy production. As a consequence, electrochemical systems related to hydrogen production, such as proton exchange polymeric membrane (PEM) fuel cells, have caused great attention, due to their zero-emission of pollutants into the environment during operation. However, there are high costs of these electrochemical systems which are related to platinum based-catalyst and commercial polymeric membranes based on perfluorosulfonated polymers such as Nafion [1], [2].

The main function of a PEM-type membrane is to act as a proton conductor, which is due to the presence of sulfonic acid groups into polymers, because their excellent dissociation in the presence of water molecules, which in turn promote the transport of protons within the membrane. The study on the chemical modification of aromatic polyether ketones, polyimides, polybenzimidazoles, polymers such as polyphenylenes, polysulfones, and other copolymers, have been considered as the main alternative to obtaining proton exchange membranes with similar chemical and thermal stability performance of Nafion but with lower cost [3], [4]. The sulfonic groups are attached to the aromatic moieties into the above-mentioned polymers. Thus, some investigations are focusing on sulfonation of copolymers with polystyrene, such as the poly(styrene-b-butadiene-b-styrene) (polySBS), poly (styrene-b-isoprene-b-styrene) (polySIS) and their corresponding hydrogenated versions, the poly(styrene-b-ethylene-co-butylene-b-styrene) (polySEBS) and poly(styrene-b-ethylene-alt-propylene-styrene) (polySEPS) [5]–[9]. The polySEBS, poly(styrene-b-ethylene-butylene-b-styrene) triblock copolymer is an interesting commercially available material for industrial and technological use due to its properties as ion-conducting and electroactive copolymer when it is selectively functionalized on the aromatic rings of the polystyrene blocks, especially with

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sulfonic groups. The elastomeric central segment of such copolymer has the advantage of high thermal resistance since it does not contain labile double liaisons, and its chemical constitution, as well as the aromatic groups in a telechelic position, impart an elastomeric thermoplastic characteristic not usual to find in a single polymer. Also, this polymer is expected to provide a significant cost reduction compared to Nafion as proton exchange membranes [10], [11]. The direct sulfonation is the conventional used method to introduce sulfonic groups in the aromatic groups to produce hydrophilic polymer membranes appropriate for fuel cell applications, where strong acids such as sulfuric or chlorosulfonic acid are used for, which in turn have the disadvantage of lack of the precise control over the degree of sulfonation, site-specificity, and the possibility of side reactions, or even degradation of the polymer by backbone scission that represent important drawbacks for the mechanical and chemical stability of the membranes [12]–[14].

However, an option to overcome such drawbacks is the use of alternative chemical modification. So far, it has not been proposed the direct chloromethylation of polySEBS as a possible sulfonation route, since the main approach that has been conferred on chloromethylation is to obtain anionic membranes by the reaction between the chloromethyl group and tertiary amines [15], [16]. The here proposed two-steps chemical modification strategy (chloromethylation followed by sulfonation) has been used in other polymers such as polyethersulfone, [17], [18] and polysulfone in search to graft firstly a functional group into the benzene ring, the method can be used to derivative different functionalized polymers [19] because the polymers that have been chloromethylated can be modified by nucleophilic substitution for the formation of new substituents [20], [21]. Also, radiation-induced grafting with vinyl-based monomers is another method to produce chloromethyl groups in polymers, which can be converting into sulfonic acid with a methylene spacer, via the formation of thiouronium salt with thiourea, base-catalyzed hydrolysis for the formation of thiol, and a final step of oxidation of thiol groups [22]–[24].

1.2. Hypothesis

The styrene block within polySEBS can be effectively functionalized with sulfonic acid groups, leading to the successful synthesis of proton exchange membranes with enhanced properties suitable for various applications in fuel cells and other electrochemical devices.

1.3. General objective

The aim of this work is to synthesize a sulfonated poly(styrene-ethylene-butylenestyrene) membrane, exploring various possible routes of synthesis to achieve optimal performance and properties like PEM. By analyzing different pathways of synthesis, this research seeks to determine the most efficient and effective method for preparing proton exchange membranes from polySEBS with enhanced characteristics suitable for diverse applications.

1.4. Specific objectives

- Exploring novel routes of synthesis of ion exchange membrane technology.
- Investigate and compare different routes for the preparation of sulfonated poly(styrene-ethylene-butylene-styrene) membranes for electrochemical applications.
- Synthesis and characterization of ion exchange membranes with different chemical structures and physical properties, and evaluation of ion conductivity and ion exchange capacity, which are parameters for their performance as fuel cell membranes.
- Research on the influence of the structure and chemical composition of ion exchange membranes on their proton transport properties, such as ionic conductivity, chemical resistance, and mechanical stability.

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CHAPTER 2. STATE OF THE ART

This chapter provides a comprehensive state-of-the-art review of ion exchange membranes (IEMs), focusing on their role in hydrogen fuel cells. It examines both proton exchange membranes (PEMs) or also called cation exchange membranes (CEMs) and anion exchange membranes (AEMs), discussing their chemical structure, ionic conductivity mechanisms, material composition, and performance factors. The chapter highlights the advantages and limitations of traditional materials like Nafion[™], and explores recent advances in alternative polymers membranes and strategies to enhance thermal and chemical stability. Comparative analysis of PEMs and AEMs is also presented, emphasizing their respective challenges and future perspectives in fuel cell technology.

2. Background

2.1 Energy Context and Climate Change

The global energy matrix is currently dominated by the use of fossil fuels such as oil, natural gas, and coal, which account for more than 80% of the world's energy consumption. This energy model has enabled economic and social development over recent decades but has also led to severe environmental consequences, including global warming, air pollution, and ecosystem degradation. The combustion of hydrocarbons is the main anthropogenic source of greenhouse gas emission (particularly carbon dioxide (CO₂), methane (CH₄), and nitrogen oxides (NO_x)), which contribute to the rise in global average temperature and the intensification of extreme climate events. Various international reports, such as those published by the Intergovernmental Panel on Climate Change (IPCC), warn that, unless GHG emissions are drastically reduced, the consequences for humanity will be irreversible [1], [2]. Moreover, oil price volatility and the progressive depletion of accessible reserves have triggered recurring energy crises, highlighting the urgent need to diversify energy sources and reduce dependency on fossil fuels [3].

In response to these challenges, international policies and agreements have been promoted to decarbonize the economy and foster the development of renewable energy sources such as solar, wind, hydroelectric, and biomass. However, the largescale integration of these sources into the energy matrix presents technical challenges, including intermittency and the need for efficient storage systems. In this context, the hydrogen fuel cell emerges as a key energy vector, capable of flexibly and cleanly storing and transporting energy [4][5].

2.2 Historical development of the fuel cell

The basic principles of a fuel cell were first described by Christian Friedrich Schönbein in 1838 through the reverse process of electrolysis. Shortly thereafter, in 1839, William Grove constructed the first working fuel cell based on Schönbein's ideas. Grove demonstrated that when the products of electrolysis (hydrogen and oxygen) are fed into platinum rods immersed in individual cells, separated by a liquid electrolyte (sulfuric acid, H₂SO₄), and externally connected in series (Figure 1), an electric current could be generated [6][7].



Figure 5. First demonstration of a fuel cell in 1839. Four individual cells were connected in series, and the generated electricity was used to decompose water by electrolysis [7].

Thus, during the electrochemical process inside the cell, the chemical energy (i.e., the Gibbs free energy change, $-\Delta G$) of the fed fuel (hydrogen, alcohols, etc.) is directly converted into direct current (DC) electricity. Electrons are released at the anode (the negative terminal) via the electro-oxidation of the fuel and flow through the external circuit (producing electrical energy equivalent to $-\Delta G$), reaching the cathode (positive terminal), where oxygen is reduced.

2.3 Fuel cells types

There are various types of fuel cells, primarily classified by the type of electrolyte they use: proton exchange membrane fuel cells (PEMFC), anion exchange membrane fuel cells (AEMFC), alkaline fuel cells (AFC), phosphoric acid fuel cells (PAFC), molten carbonate fuel cells (MCFC), and solid oxide fuel cells (SOFC), among others [8].

	AFC (Alkaline)	PEMFC (Polymer Electrolyte Membrane)	DMFC (Direct Methanol)	PAFC (Phosphoric Acid)	MCFC (Molten Carbonate)	SOFC (Solid Oxide)
Operating temperature (°C)	<100	60-120	60-120	160-220	600-800	800-1000
Anode reaction	H₂ + 2OH ⁻ → 2H₂O + 2e ⁻	H2 → 2H ⁺ + 2e ⁻	$CH_3OH + H_2O$ $\rightarrow CO_2 + 6H^+$ $+ 6e^-$	H₂ → 2H* + 2e ⁻	$H_2 + CO_3^{2-} \rightarrow$ $H_2O + CO_2 +$ $2e^{-}$	$H_2 + O^{2-}$ → 2 $H_2O + 2e^{-}$
Cathode Reaction	¹ ⁄ ₂ O ₂ + H ₂ O + 2e ⁻ → 2OH ⁻	$1/_{2}O_{2} + 2H^{+}$ $+ 2e^{-} \rightarrow H_{2}O$	$3/2 O2 + 6H^+$ + 6e- → $3H_2O$	$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$	$\frac{1}{2}O_2 + CO^2 + CO^2 + 2e^- \rightarrow CO_3^2 - CO_$	¹ ⁄ ₂ O ₂ + 2e ⁻ → O ²⁻
Applications	Transport Aerospace Military			Stationary cogeneration.	Stationary cogeneration and transport (trains, boats, etc.)	
Mobile ion	OH ⁻	H⁺	H⁺	H⁺	CO32-	O ²⁻

Table 1. General overview of fuel cell types [0].	Table 1.	General	overview	of fuel	cell types	[8].
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Fuel cells are primarily classified based on the type of electrolyte they use, which in turn determines their operating temperature, efficiency, type of fuel, and application. Below is a brief description of the main types of fuel cells:

- Proton Exchange Membrane Fuel Cells (PEMFC): they use a solid polymer membrane as the electrolyte, which allows protons (H⁺) to pass from the anode to the cathode. They operate at low temperatures (60-80 °C), enabling rapid start-up, making them suitable for transportation and portable applications. They require pure hydrogen as fuel and are sensitive to carbon monoxide (CO) contamination [8], [9].
- Anion Exchange Membrane Fuel Cells (AEMFC): similar to PEMFCs, but they use a membrane that allows hydroxide ions (OH⁻) to pass from the cathode

to the anode. They also operate at low temperatures (60-90 °C) and have the advantage of using non-noble metal catalysts and less pure fuels, which reduces system cost. However, they face challenges in terms of membrane stability in alkaline environments [6].

- Alkaline Fuel Cells (AFC): they use an aqueous solution of potassium hydroxide (KOH) as the electrolyte. They operate at moderate temperatures (100-250 °C) and can achieve high efficiencies, but are highly sensitive to CO₂ contamination. This limits their use to space and military applications, where pure fuel and oxidant supplies can be guaranteed [6].
- Phosphoric Acid Fuel Cells (PAFC): They use liquid phosphoric acid as the electrolyte. They operate at higher temperatures (150-200 °C) and are less sensitive to CO contamination than AFCs. They are mainly used in stationary applications for combined heat and power generation [8].
- Molten Carbonate Fuel Cells (MCFC): They use a mixture of molten alkaline carbonates as the electrolyte. These cells operate at high temperatures (600-700 °C) and can use various fuels, including natural gas and biogas. They are suitable for large-scale stationary power generation, such as power plants [10].
- Solid Oxide Fuel Cells (SOFC): They use a solid ceramic oxide as the electrolyte. These operate at very high temperatures (800-1000 °C) and can utilize a wide range of fuels, including hydrogen, natural gas, and propane. They offer high efficiency and low emissions, but the high temperature creates durability challenges for the materials involved [8].

The selection of the fuel cell type depends on the specific application, factors such as efficiency, cost, fuel availability, operating temperature, and durability must be considered. In the context of the hydrogen economy, PEMFCs and AEMFCs are the most promising technologies for transportation and portable applications, due to their low operating temperatures and high power density.

2.4 Fuel cell operation

Fuel cell operation is based on electrochemical principles that allow the direct conversion of the chemical energy contained in a fuel into electrical energy, with high efficiency and low pollutant emissions. To understand the role of ion exchange membranes and their impact on the overall performance of the system, it is essential to analyze the basic principles of a hydrogen fuel cell.

2.4.1 Fundamental principles of hydrogen fuel cell

A fuel cell is an electrochemical device that converts the chemical energy of a fuel (usually hydrogen) and an oxidant (usually oxygen from air) into electricity, water, and heat through oxidation and reduction reactions occurring at electrodes separated by an electrolyte [11], [12]. Unlike internal combustion engines, energy conversion in a fuel cell is not limited by the Carnot cycle, allowing for higher efficiencies.

The basic principle can be illustrated using a hydrogen–oxygen fuel cell, where the global reactions are as follows:

- Anode: $H_2 \rightarrow 2H^+ + 2e^-$
- Catode: $\frac{1}{2}O_2 + 2H^+ + 2e^- \to H_2O$
- General reaction: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O \operatorname{con} \Delta G = -237.34 \, kJ/mol$

The maximum amount of electrical energy in a PEMFC corresponds to the Gibbs free energy (ΔG) of the above reaction:

$$W_{el} = -\Delta G$$

The theoretical voltage of a fuel cell is given by Equation (1):

$$E = \frac{-\Delta G}{nF} \quad (1)$$

Where n is the number of electrons involved in the reaction, and F is Faraday's constant (96,485 C/mol). Therefore, substituting into equation (1):

$$E = \frac{-\Delta G}{nF} = \frac{-237,340 \, J/mol}{2 \cdot 96,485 \, As/mol} = 1.23 \, V$$

At a temperature of 25°C and atmospheric pressure, the theoretical potential of a PEMFC is 1.23 V, which in real conditions is reduced due to various internal system losses [13].

2.4.2 Components of a hydrogen fuel cell

Once the operation of a fuel cell is defined, it is important to understand the components that make it up. A fuel cell system consists of a stack of multiple individual cells and auxiliary equipment, which together produce electric power (and heat) directly from the electrochemical oxidation of the fuel (Figure 2) [14].

The essential component is known as the MEA (Membrane Electrode Assembly), and it represents the highest cost component of a fuel cell. It is composed of a polymeric membrane and catalytic plates, commonly made of platinum supported on carbon [15].



Figure 6. General view of the components in a PEMFC stack (two individual cells connected in series) [15].

The polymeric proton exchange membrane is the essential part of the PEMFC. It is typically made of the commercial polymer Nafion^M, and its function is to transport hydrogen ions across the membrane, acting as the electrolyte thanks to the presence of acidic groups.

Just like the membrane, the electrodes or gas diffusion layers (GDLs) are critical to the system. They serve both the anode and cathode sides, where the redox reactions (catalytic layer Pt/C) take place. The efficiency of the fuel cell is also influenced by the porosity of the electrodes, which are typically composed of platinum catalyst layers supported on carbon (Figure 3), in direct contact with both the electronic and ionic conductors [16].



Figure 7. Pt/C catalytic layer present in the MEA [16].

The supplied hydrogen comes into contact with the diffusion plates, allowing it to spread toward the catalytic layer, where it is transformed into H⁺. Through the diffusion plates, electrons flow from the anode to the cathode, generating direct electric current; these plates also remove excess water produced at the cathode [16].

Additionally, the system includes bipolar plates, which provide the mechanical strength to the stack. These plates contain flow channels for hydrogen circulation under high pressure.

The materials typically used for bipolar plates are metal, ceramics, or in some cases plastic. There are different flow channel designs (serpentine, parallel, parallel– serpentine, discontinuous, and spiral), as shown in Figure 4, which are selected depending on the system's performance [17].



Figure 8. Bipolar plates: (a) serpentine, (b) parallel, (c) parallel–serpentine, (d) discontinuous, and (e) spiral [17].

2.4.3 Ion exchange membranes: a key component in hydrogen fuel cells.

Ion exchange membranes (IEMs) are the central component of PEMFC and AEMFC-type fuel cells, as they determine the efficiency, durability, and cost of the

system. Their main function is to enable the selective transport of ions (protons or hydroxide ions) between the anode and the cathode, while acting as a barrier to prevent the passage of electrons, gases, and fuels [18].

An ideal IEM must meet the following requirements:

- High ionic conductivity: For minimizing ohmic losses and maximize cell efficiency.
- Low permeability to gases and fuels: To prevent reactant crossover and reduce efficiency loss.
- High chemical and mechanical stability: To withstand the operating conditions of the cell (temperature, humidity, pH, etc.) and ensure long service life.
- Low cost: Making the technology competitive with other energy alternatives.

IEMs are typically fabricated from polymers containing charged functional groups, which are responsible for ion transport. In the case of PEMs, the most widely used polymer is Nafion[™], a perfluorosulfonic copolymer that offers high proton conductivity and chemical stability. However, Nafion[™] is expensive and shows performance issues at high temperatures and low humidity [19].

For AEMs, polymers containing quaternary ammonium groups are used to enable hydroxide ion transport. These polymers are generally less stable than Nafion[™] in alkaline environments, which poses a major challenge for their development [6].

Research and development of new IEMs with improved properties is currently a highly active area of scientific and technological interest. Various strategies are being explored, including the synthesis of new polymers, modification of existing polymers, incorporation of additives, and the fabrication of composite membranes.

2.4.4 Transport mechanisms in ion exchange membranes.

Efficient proton transport through the proton exchange membrane (PEM) is essential for the operation of the hydrogen fuel cells. This process occurs due to the presence of acidic groups (mainly sulfonic acid groups, -SO₃H) in the polymer matrix, which dissociate in the presence of water, releasing protons (H⁺) that can migrate across the membrane.

There are three main proton transport mechanisms in PEMs, Figure 5 [20]:

- Grotthuss mechanism (or proton hopping): In this mechanism, the proton is rapidly transferred from one water molecule to another through a hydrogen bond network, without the hydronium ion (H₃O⁺) itself physically moving along the membrane. The proton "hops" from one molecule to another, enabling fast and efficient transport, especially under high hydration conditions. This mechanism dominates in well-hydrated membranes and is responsible for the high proton mobility observed in Nafion[™] and other sulfonated polymers.
- 2. Vehicle mechanism: In this case, the proton is transported as part of a hydronium ion (H₃O⁺) or larger complexes (such as H₅O_{2⁺}, H₉O_{4⁺}), which physically move through the aqueous channels of the membrane. This mechanism is more relevant under low hydration conditions, where ion mobility depends on the diffusion of the hydrated species.
- 3. Surface mechanism: This occurs when protons move along the surface of the hydrophilic domains of the membrane, interacting with the acidic functional groups. This mechanism may be significant in membranes with a high density of acid groups and under low relative humidity.



Figure 5. Schematic of the different transport mechanisms occurring in a solid polymer electrolyte for proton conduction. A = Grotthuss, B = Vehicle, C = Surface mechanism [20].

The efficiency of proton transport strongly depends on the microstructure of the membrane, the amount and distribution of acid groups, and the degree of hydration. In Nafion[™], for example, the so-called "cluster-channel" morphology facilitates the formation of continuous water pathways that favor the Grotthuss mechanism [21].

The proton conductivity (σ) of a PEM is generally expressed in Siemens per centimeter (S/cm) and depends on temperature, relative humidity, and the concentration of acid groups. Typical values for NafionTM under optimal conditions are on the order of 0.1 S/cm [22].

2.5 Ion exchange membranes (IEM)

Ion exchange membranes (IEMs) are critical components in hydrogen fuel cell technology, as they enable the selective transport of ions between the anode and cathode, while acting as a barrier to prevent reactant crossover and electronic short-circuiting. IEMs must possess a series of key properties to ensure high performance and durability in fuel cells, including high ionic conductivity, low gas permeability, chemical and mechanical stability [23].

IEMs are mainly classified into two categories: proton exchange membranes (PEM) and anion exchange membranes (AEM), depending on the type of ion they transport. PEMs are widely used in low-temperature fuel cells, while AEMs have gained growing interest in recent years due to their potential to operate with non-noble metal catalysts and less pure fuels [24].

2.5.1 Proton exchange membranes (PEM)

Proton exchange membranes (PEMs) are solid polymers that contain acidic groups (typically sulfonic acid groups, -SO₃H) attached to the polymer backbone. These acidic groups allow the dissociation of protons (H⁺), which are transported across the membrane via specific transport mechanisms. PEMs are widely used in low-temperature fuel cells (PEMFCs) due to their high proton conductivity, good chemical and mechanical stability, and ease of processing.

The main function of a PEM is to enable the efficient transport of protons from the anode to the cathode, while acting as an impermeable barrier to gases (hydrogen

and oxygen) and electrons. An ideal PEM must exhibit the same characteristics mentioned above for IEM.

2.5.2 Anion exchange membranes (AEM)

Las Anion exchange membranes (AEMs) represent an innovative and promising alternative to traditional proton exchange membranes (PEMs) in fuel cells. Their primary function is to enable the selective transport of anions, typically hydroxide ions (OH⁻), from the cathode to the anode, while blocking the passage of electrons and gases. The development of AEMs has made it possible to operate fuel cells under alkaline conditions, allowing the use of non-noble metal catalysts, less pure fuels, and greater tolerance to contaminants such as CO [6].

However, the design of efficient and durable AEMs presents significant challenges, mainly related to the chemical stability of the cationic functional groups in highly alkaline environments, and the optimization of anion conductivity. The following subsections describe the materials, transport mechanisms, and factors that affect the performance of AEMs.

AEMs consist of a polymeric matrix functionalized with cationic groups, generally quaternary ammonium, which are responsible for the dissociation and transport of anions. Commonly used polymer backbones include polysulfones, polyetherketones, polyethylene, polystyrene, and polyarylenes, selected for their thermal stability and ease of chemical modification [25].

The quaternary ammonium group (-NR₃⁺) or cationic functional groups: is the most widely used, although other groups such as imidazolium, piperidinium, and phosphonium have also been explored in efforts to improve chemical stability in alkaline media. These groups are introduced through cloroalkylation followed by amination, or via direct quaternization.

2.5.3 Nafion[™]: Commercial Membrane for Fuel Cells

The most widely used material in the fabrication of PEMs is Nafion[™], a perfluorosulfonic copolymer developed by DuPont. Nafion[™] consists of a polytetrafluoroethylene (PTFE) backbone with side chains containing sulfonic acid groups (Figure 6). Its chemical structure gives Nafion[™] a set of unique properties,

including high proton conductivity, excellent chemical and mechanical stability, and good hydration capacity [19], [26].



Figure 6. Structural formula of Nafion[™] by DuPont [18].

The proton conductivity of Nafion[™] depends on the amount of water present in the membrane. As the membrane becomes hydrated, the sulfonic groups dissociate, and the protons move across the membrane via specific transport mechanisms (see section 3.1.2). Nafion[™] can reach proton conductivity values of up to 0.1 S/cm at room temperature and high humidity [22].

However, Nafion[™] presents some limitations, including its high cost, low stability at high temperatures and low humidity, and methanol permeability, which limits its use in direct methanol fuel cells (DMFCs).

In recent years, a variety of alternative materials have been developed for PEMs, including non-perfluorinated sulfonated polymers, composite membranes, and nanoparticle-reinforced membranes. These materials aim to overcome the limitations of Nafion[™] and improve the performance and durability of PEMs [20], [27].

Some examples of non-perfluorinated sulfonated polymers include:

- Poly(styrene sulfonate) (PSS): A low-cost polymer that is easy to synthesize, but has poor chemical and mechanical stability.

- Sulfonated poly(ether ether ketone) (SPEEK): A polymer with good thermal and chemical stability, but lower proton conductivity than Nafion[™].

- Sulfonated polysulfone (SPS): A polymer with high mechanical and chemical stability, and good proton conductivity.

Composite membranes are produced by combining two or more materials with different properties, with the aim of obtaining a membrane with superior

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performance. For example, a sulfonated polymer can be combined with an inorganic material (such as silica or titanium dioxide) to enhance mechanical stability and proton conductivity.

Nanoparticle-reinforced membranes are fabricated by incorporating nanoparticles (such as graphene oxide or carbon nanotubes) into the polymer matrix, with the goal of improving proton conductivity, mechanical stability, and gas permeability.

The choice of PEM material depends on the specific application and the required performance and durability parameters.

2.5.4 Factors affecting PEM efficiency and durability

The performance of a proton exchange membrane (PEM) in a fuel cell is determined by a combination of structural, physicochemical, and operational factors. The main factors that affect the efficiency and durability of PEMs are:

- a) Water uptake: Water is essential for proton transport, as it facilitates both the Grotthuss mechanism and the vehicle mechanism. Insufficient hydration drastically reduces proton conductivity, while excess water can lead to membrane swelling, loss of mechanical integrity, and gas crossover. Therefore, controlling the relative humidity inside the cell is critical for optimal performance [19].
- b) Operating temperature: Increasing the temperature generally enhances ionic mobility and proton conductivity, but it can also accelerate the chemical degradation of the membrane and reduce its water retention capacity. Conventional PEMs like Nafion[™] typically operate between 60 and 80 °C, although alternative materials have been developed for operation at higher temperatures [22].
- c) Density and distribution of acid groups: A higher concentration of sulfonic acid groups increases the degree of dissociation and, consequently, the proton conductivity. However, excessive density can compromise mechanical stability and increase the membrane's solubility in water [20].
- d) Microstructure and morphology: The organization of hydrophilic and hydrophobic domains within the polymer matrix determines the formation of water channels and, therefore, the efficiency of proton transport. The cluster-

channel model in Nafion[™] is a well-known example of how morphology affects membrane performance [21].

- e) Contamination and chemical degradation: Exposure to free radicals, contaminants (such as metal ions or peroxides), and extreme pH conditions can degrade the membrane's functional groups, reducing its lifespan and performance. Chemical stability is thus a key design criterion for the development of new PEMs [19].
- f) Membrane thickness: Thinner membranes offer lower ohmic resistance and thus higher efficiency, but they may be more susceptible to gas crossover and mechanical degradation. The optimal thickness depends on balancing conductivity, selectivity, and durability.

2.5.5 Synthesis and modification of ion exchange membranes (IEMs)

The development of ion exchange membranes (IEMs) with optimized properties requires not only the appropriate selection of base materials but also the implementation of synthesis and modification strategies that enable control over the microstructure, functionalization, and stability of the membranes. The synthesis and modification of IEMs is a multidisciplinary field that encompasses polymer chemistry, materials engineering, and surface science.

The main objective of these strategies is to maximize ionic conductivity, selectivity, and durability of the membranes, while minimizing costs and facilitating the scalability of manufacturing processes. Below, the main synthesis methods for IEMs are described, along with the modification techniques used to enhance their properties.

2.5.7 Synthesis methods for ion exchange membranes

The development of ion exchange membranes (IEMs) with optimized properties requires not only the appropriate selection of base materials, but also the implementation of synthesis and modification strategies that allow control over the microstructure, functionalization, and stability of the membranes. The synthesis and modification of IEMs is a multidisciplinary field that includes polymer chemistry, materials engineering, and surface science.

The synthesis of ion exchange membranes can be approached through various routes, depending on the type of membrane (PEM or AEM), the base polymer, and the desired functionalization. The most common methods include:

- a) Direct polymerization of functionalized monomers: This method involves polymerizing monomers that already contain the desired ionic functional groups (sulfonic groups for PEMs, cationic groups for AEMs). It allows precise control over the density and distribution of functional groups but may require strict synthesis conditions and specialized monomers [25].
- b) Post-synthetic modification of base polymers: In this approach, a base polymer (e.g., polysulfone, polyetherketone, polystyrene) is used and subsequently functionalized through specific chemical reactions. For PEMs, sulfonation is the most common reaction, while AEMs use bromoalkylation and quaternization reactions.
- c) Sulfonation (CEM): The introduction of sulfonic acid groups is carried out via electrophilic aromatic substitution, using sulfonating agents such as chlorosulfonic acid or fuming sulfuric acid. The degree of sulfonation controls the ion exchange capacity and proton conductivity of the membrane [25], [28].
- d) Quaternization (AEM): Cationic functionalization is achieved through the introduction of quaternary ammonium, imidazolium, piperidinium, etc., via bromoalkylation followed by amination, or through direct Menshutkin reaction [29].
- e) Synthesis of composite membranes: Incorporating inorganic materials (e.g., graphene oxide, silica, zirconia) or nanoparticles into the polymer matrix allows the production of composite membranes with enhanced properties such as conductivity, mechanical stability, and chemical resistance. These materials can be physically dispersed or chemically bonded to the polymer matrix [30], [31].

2.6 References

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3 EXPERIMENTAL METHODOLOGY

This chapter details the experimental methods used to modify and characterize polySEBS membranes. The global approach involves polymer synthesis, chemical modification to introduce ionic groups, membrane preparation, and comprehensive characterization of the physical, chemical, and electrochemical properties of such synthesized membranes.

The following sections describe the materials, modification procedures, membrane fabrication techniques, and characterization methods used in this work. The goal is to develop membranes with high proton conductivity, good mechanical properties, and suitable water uptake for their potential application in fuel cell.

3.1 Materials

The following materials were used in this study:

Polymers:

- Poly(styrene-b-ethylene-butylene-b-styrene) (polySEBS) with 30 wt.% styrene content and average molecular weight of 118,000 g/mol (determined by GPC), provided by Dynasol (CALPRENE H 6110)

Reagents for polymer modification:

- 1,2-Dimethoxymethane (DMOM) (>99%), Sigma-Aldrich

- Silicon tetrachloride (SiCl₄) (>99%), Sigma-Aldrich

- Anhydrous zinc chloride (ZnCl₂) (>99%), Lachema
- Thiourea (>98%), Lachema
- Sodium hydroxide (>99%), PENTA
- Hydrogen peroxide (30%), Lach-Ner
- Formic acid (>95%), Sigma-Aldrich
- 1,4-diazabicyclo[2.2.2]octane (DABCO) (>99%), Sigma-Aldrich

Solvents:

- Chloroform (>99%), Lach-Ner
- Toluene (>99%), Lach-Ner
- Ethanol (technical grade)

3.2 Polymer chemical modification

The poly(styrene-b-ethylene-butylene-b-styrene) (polySEBS) copolymer was chemically modified to introduce functional groups (sulfonic and quaternized ones) suitable for proton exchange membrane applications. Three main modification routes were explored:

- 1. Chloromethylation
- 2. Indirect sulfonation
- 3. Quaternization

These modifications were primarily targeted at the styrene blocks of the polySEBS copolymer, as the aromatic rings provide suitable sites for functionalization.

The chemical modifications were carried out sequentially, with chloromethylation serving as the initial step for both indirect sulfonation and quaternization. This approach allows the controlled functionalization and the ability to tailor the membrane properties for specific applications.

3.2.1 Chloromethylation and membrane preparation

Chloromethylation of polySEBS was carried out to introduce -CH₂Cl groups onto the aromatic rings of the styrene blocks. This reaction serves as a crucial first step for further functionalization of the polymer.

Procedure:

- 1. In a three-neck round bottom flask, 12.5 g of polySEBS was dissolved in chloroform under stirring.
- 2. The methylation agent, 1,2-dimethoxymethane (DMOM) (0.27 mol), and the catalyst zinc chloride (ZnCl₂) (0.032 mol) were added to the solution and stirred for approximately 1 hour.
- 3. The chlorinating agent, silicon tetrachloride (SiCl₄) (0.032 mol), was then added to promote the chloromethylation reaction.
- 4. The reaction mixture was stirred continuously at room temperature for 30 hours. During this time, the color of the solution gradually changed from colorless to brown.
- 5. After the reaction, the solution was diluted with additional chloroform and precipitated in ethanol.
- 6. The precipitated polymer was filtered and dissolved in toluene to form a 5% (w/w) solution for membrane preparation.

Membrane preparation. The 5% (w / w) solution of the chloromethylated polymer in toluene was poured onto a Teflon plate to obtain the membrane by the solvent evaporation method, inside a flow box at room temperature to maintain constant evaporation of the solvent, and the membrane was obtained after 24 hours. Once the membranes were obtained, different reactions were subsequently carried out.

3.2.2 Sulfonation of chloromethylated polySEBS membranes

The indirect sulfonation of chloromethylated polySEBS (CM-SEBS) was performed to introduce sulfonic acid groups (-SO₃H) into the polymer structure. This multi-step process involves the conversion of chloromethyl groups to sulfonic acid groups via intermediate reactions.

Procedure:

- 1. S-alkylation (Thiouronium salt formation):
 - a) CM-SEBS membranes (10x10 cm) were immersed in a 10% (w/w) thiourea solution in ethanol.
 - b) The reaction was carried out at 60°C for 48 hours.
 - c) After reaction, membranes were washed thoroughly with distilled water and dried at room temperature.
- 2. Hydrolysis:
 - a) The membranes from step 1 were immersed in a 10% (w/w) NaOH solution in ethanol.
 - b) The hydrolysis reaction was conducted at 60°C for 48 hours.
 - c) Membranes were washed several times with distilled water and dried at room temperature.
- 3. Oxidation:

A performic acid solution was prepared by mixing 88% formic acid and 30% hydrogen peroxide in a 7:3 volume ratio. This mixture was allowed to react for 1 hour before use.

- a) The membranes from step 2 were immersed in the performic acid solution.
- b) Oxidation was carried out at room temperature for various durations (1, 3, 5, and 7 hours) to study the effect of reaction time on the degree of sulfonation.

c) After oxidation, membranes were washed thoroughly with distilled water.

3.2.3 Quaternization of chloromethylated PolySEBS membranes

The quaternization of chloromethylated polySEBS (CM-SEBS) was performed to introduce quaternary ammonium groups, transforming the polymer into an anion exchange membrane precursor. This process involves the reaction of the chloromethyl groups with tertiary amine.

Procedure:

- 1. CM-SEBS membranes were cut to appropriate sizes for the reaction.
- 2. A 10 wt.% solution of 1,4-diazabicyclo[2.2.2]octane (DABCO) amine was and CM-SEBS membrane was immersed in this solution for quaternization.
- 4. The reaction was carried out at room temperature for 72 hours.
- 5. After reaction, the membrane was washed several times with ethanol to remove excess amine.
- 6. The quaternized membrane was dried at room temperature and characterized.

3.3 Characterization

Prior to characterization, the membranes were treated according to the next described methodology for better reproducibility in the results, the steps are shown below [1][2]:

- a) Immersion of the membrane in deionized water for 24 hours.
- b) Immersion of the membrane in HCl 1.0 N for 24 hours. Then, washing with deionized water for 10 minutes.
- c) Immersion of the membrane in NaOH 1.0 N for 24 hours. Then, it was washed with deionized water for 10 minutes.
- d) Immersion of the membrane in HCl 1.0 N for 24 hours. Then, it was washed with deionized water for 10 minutes.
- e) Immersion of the membrane in deionized water for 24 hours.

3.3.1 Nuclear magnetic resonance

Solid-state NMR (ssNMR) spectra were recorded at 11.7 T using a Bruker AVANCE III HD spectrometer. The 4-mm cross-polarization magic-angle spinning (CP/MAS) probe was used for ¹H and ¹³C ssNMR experiments at Larmor frequencies of $v(^{1}H) = 500.181$ MHz and $v(^{13}C) = 125.783$ MHz, respectively. ¹³C and ¹H NMR chemical shifts were calibrated using α -glycine (¹³C: 176.03 ppm; carbonyl signal) and adamantane (¹H: 1.85 ppm), respectively, as external standards. All ssNMR spectra were acquired at the speed of the sample spinning of 11 kHz. The ¹H MAS NMR spectra were recorded with 2 s recycle delay. The ¹³C MAS and CP/MAS NMR experiments were recorded with 15 s and 2 s recycle delays, respectively. A cross-polarization (CP) contact time of 1.5 ms was used in both ¹³C CP/MAS NMR experiments. High-power ¹H decoupling (SPINAL64) was used for the removal of heteronuclear coupling.

Samples were packed into ZrO₂ rotors and subsequently kept at room temperature. All NMR experiments were conducted under active cooling in order to compensate for frictional heating caused by the rotation of the samples [3]. All experiments were carried out at 298 K temperature. Bruker TopSpin 3.2 pl5 software package was used for the processing of the spectra.

3.3.2 FTIR spectroscopy

FTIR spectroscopy was used to identify the functional groups present in the different samples. This analysis was performed at room temperature on the Nicolet 6700 IR spectrometer ThermoScientific equipment, using the Attenuated Total Reflectance (ATR) technique in the range 400-4000 cm⁻¹, 64 scans with a resolution of 4 cm⁻¹.

3.3.3 Elemental analysis

The Elemental analysis (Perkin Elmer 2400 Series II Instrument Elemental Analysis of CHNS/O) measurements were carried out to determine C, N, S and H of the samples. 10 mg of sample were burned under oxygen atmosphere in a combustion tube. The determination of elementals is for the gaseous combustion products which pass through the combustion catalysts and absorption agents.

3.3.4 Scanning electronic microscopy

SEM, which has been carried out using a FEI Quanta 250 scanning electron microscope (ThermoFisher Scientific, Waltham, MA, USA). The chloromethylated membrane (CM-SEBS) and the sulfonated SEBS after 7 hours of oxidation membrane (sSEBS-7H) samples were freeze-fractured in liquid nitrogen to investigate the cross-section of them. Images were recorded, and EDX mapping was performed to identify the element distribution across the membranes.

3.3.5 Thermogravimetric analysis

Thermogravimetric analysis was used to observe the thermal stability of the membranes subjected to a programmed increase in temperature, measuring the loss of weight of the sample as a function of temperature. For this test, 10 ± 0.5 mg of each sample to be evaluated were weighed. The Q500 TA Instrument equipment was used, in the range of 25 to 600 ° C and with a heating rate of 10 °C/min, in an atmosphere of Nitrogen with a flow of 20 mL/min thereof.

3.3.6 Water uptake

The water uptake property is a significant characteristic, which indirectly confirms the incorporation of the hydrophilic groups within the membrane. For this, a certain amount of membrane was dried at 35°C under vacuum for 24 hours, and then its dry mass was recorded. Subsequently, the membrane was immersed in deionized water for 24 hours at RT and after that the excess water was removed to determine its wet weight. The water absorption capacity was calculated by the weight (*w*) of the wet and dry samples, as indicated in equation 1.

$$w[\%] = \frac{w_{wet} - w_{dry}}{w_{dry}} x100 \quad \text{eq. 1}$$

3.3.7 Contact angle

Optical tensiometer (Theta Lite, Attension) was used to determinate the contact angle (°). A drop of deionized water (3 μ L) was deposited on the surface of the membranes to analyze their hydrophilic behavior, and the contact angle average was calculated using OneAttention software.

3.3.8 Atomic force microscopy

Topography and phase image of the membranes were analyzed using atomic force microscopy (NaioAFM, Nanosurf, Switzerland) under tapping mode. The AFM images were obtained with a maximum scan range of 48.7 × 48.7 μ m². The resonance frequency was adjusted around 150 kHz.

3.3.9 Mechanical evaluation

The mechanical properties of the membranes were measured using the Universal testing machine model 3369 (Instron, Norwood, MA, USA) at room temperature. At least five specimens per sample were tested. The size of the specimens was 30 mm×10 mm (test area), and they were tested in tensile mode with a strain rate of 10 mm/min.

3.3.10 Ion exchange capacity

Ion exchange capacity (IEC) is a fundamental characteristic of ion exchange membranes. The IEC of the membrane was determined by the back titration method [4]. For this, 0.25 grams of the membrane was weighed with a previous vacuum drying at a temperature of 35 °C for 24 hours, the membrane was immersed in 25 mL of a 0.1 N sodium hydroxide solution for 24 hours with constant stirring. Then, 7 mL aliquots were drawn and titrated with a 0.1N HCl solution in an automatic titrator. The IEC was determined using equation 2.

$$IEC = \left(\frac{(C_{NaOH} - (C_{HCl} * V_{HCl}))}{V_{sample}}\right) \left(\frac{V_{NaOH}}{m}\right) \text{ eq. } 2$$

 C_{NaOH} = NaOH concentration 0.1 N C_{HCl} = HCl concentration 0.1 N V_{HCl} = volume of HCl 0.1 N used on the titration V_{sample} = sampling volume (7 mL) V_{NaOH} = volume of 0.1 N NaOH used to immerse the membrane (25 mL) m = dry membrane weight

3.3.11 Ion conductivity measurements

The resistance (R, Ω) of the membranes were measured by impedance spectroscopy in a four-electrode configuration using a potentiostat/galvanostat Metrohm Autolab PGSTAT302N and by applying platinum working and Ag/AgCl reference electrodes, respectively. The equilibrated membrane sample was placed at 25 °C between two 25 mL chambers filled with 0.5 M KCl. The frequency range and current applied were 8 × 105 – 1 Hz and 1 mA, respectively. Considering the surface area (A, cm²) and thickness (L, cm) of the membranes, their area resistance ($R_A = R \cdot A$, Ωcm^2), specific resistance ($R_S = \frac{R_A}{L}$, Ωcm) and finally ionic conductivity ($\sigma = \frac{1}{R_S}$, $mS cm^{-1}$) were computed[2][5].

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CHAPTER 4. Sulfonated polySEBS membrane

This chapter describes the experimental results by indirect sulfonation reaction as an effective route to insert sulfonic groups in the aromatic rings of polySEBS to impart it both cation exchange capability and ion conductivity. The polymeric membranes were characterized by ¹H and ¹³C NMR, FT-IR, elemental analysis, water uptake, TGA, ion exchange capacity (IEC), and ion conductivity.

4.1 Characterization

4.1.1 Polymer modification

The chloromethylation of polySEBS was carried out as shown in Figure 7, where the chloromethyl group was introduced into the styrene blocks of the polymer by an aromatic electrophilic substitution.



Figure 7. PolySEBS chloromethylation.

PolySEBS chloromethylation was achieved for obtaining membranes, as described in the methodology section, which was chemically modified at different stages. The mechanism description is as follows. Firstly, thiourea in ethanol was

used to displace chlorine by sulfur through the formation of thiouronium salts, and then the hydrolysis and oxidation of the membranes were carried out to form the sulfonic acid groups, shows that Figure 8. Sulfonic acid groups on the membranes were bound to the aromatic ring with the methylene, as spacer [1].



Figure 8. Membrane sulfonation steps.

4.1.2 Nuclear magnetic resonance

The ¹H and ¹³C ssNMR spectroscopy was used for investigation of neat and 7HsSEBS-7H membranes, Figure 9 and Figure 10, respectively. Firstly, the ¹³C CP/MAS NMR spectra (Figure 9, left-hand column) of neat and sSEBS-7H membranes were analyzed. The peak at 11 ppm was assigned to methyl groups (-CH₃) and peaks between 25 - 50 ppm were assigned to aliphatic (methylene -CH₂and/or methine >CH-) groups, respectively. Moreover, the signals at 126 ppm and 145 ppm corresponding to the aromatic carbons (=CHAr- and =CAr<) were detected. As evident from Figure 9b left-hand column, a new peak at 57 ppm appeared which confirms the presence of -CH₂- group(s) on aromatic ring(s). This indicates successful sulfo-methylation reaction in *para* position of benzene ring(s). The presence of sulfonic acid was confirmed using ¹H MAS NMR spectroscopy (Figure 9, right-hand column), where a new peak at 8.3 ppm was detected and attributed to -SO₃H group(s) [2].

Secondly, the extent of the sulfo-methylation reaction was calculated by the following equation, using peak intensities of corresponding signals in ¹³C MAS NMR spectrum of sSEBS-7H membrane, see Figure 9.

% degree of sulfo-methylation =
$$\frac{I(Ar-CH_2-)}{\frac{I(=C_{Ar}<)+I(=CH_{Ar}-)}{6}} \cdot 100$$
 eq. 1

The extent of sulfo-methylation reaction of the SEBS-7H membrane was calculated to 59%. In comparison of literature, a radiation-grafted anion exchange membrane exhibited a degree of grafting of 65.6% [3]. Despite the differences in functionalization methods, chemical sulfo-methylation in the case of sSEBS-7H and gamma radiation grafting, the degree of grafting observed in both results falls within a similar range. Finally, from comparison of ¹³C MAS NMR and ¹³C CP/MAS NMR spectra it can be defined that the prepared sSEBS-7H membrane is a two-phase system containing rigid polystyrene and flexible polyethylene-polybutylene domains.







Figure 9. Experimental ¹³C CP/MAS NMR spectra (left-hand column) and ¹H MAS NMR spectra (right-hand column) with magnified inset (dashed box) of neat (a) and sSEBS-7H (b) membranes, respectively.



Figure 10. Experimental ¹³C MAS NMR spectrum of sSEBS-7H membrane, used for calculation of % degree of sulfo-methylation reaction.

4.1.3 FTIR spectroscopy

The incorporation of the functional groups into the polymer chains was confirmed by FT-IR, whose spectra are shown in Figure 11. In this figure, the spectra for the polySEBS, chloromethylated SEBS (CM-SEBS), and sulfonated SEBS after 7 h of oxidation (sSEBS-7H) samples are observed, which exhibit various bands that correspond to the different functional groups present in the different samples. In the case of polySEBS, the bands at 2915 and 2848 cm⁻¹ correspond to the asymmetric and symmetric stretching of the C-H bond of the methylene group, respectively. While the other bands at 1455, 1372, and 698 cm⁻¹, correspond to the asymmetric stretching of the C-H bond of -CH₃ of the elastomeric portion (butylene-ethylene), to the deformation of the C-H bond of -CH₂-, and the aromatic groups of styrene, respectively.



Figure 11. FT-IR spectra for different prepared membranes.

Once SEBS was (chloro)methylated, changes in its spectrum were observed, especially with the appearance of a new band at 1263 cm⁻¹, due to the presence of the CH₂-Cl chloromethylated groups [4]. Furthermore, the wide band located between 800 and 850 cm⁻¹ is due to the substitution of chloromethyl which occur in the aromatic rings of the styrene blocks shifting from the original position (698 cm⁻¹) [5][6][7]. The bands at 2915 and 2848 cm⁻¹ are maintained, which is indicative of the selectivity of the chloromethylation reaction towards the electron-rich π system of the styrene aromatic ring.

Regarding to the sulfonated sample after 7 hours of oxidation (sSEBS-7H), its spectrum shows clear changes. For instance, the bands at 1032 and 1006 cm⁻¹ are related to the stretching of the S-O bond due to the formation of the groups sulfonic acid, and in turn, it is possible to identify between 1100 and 1247 cm⁻¹ the bands associated with the symmetrical and asymmetric vibration of the double ligature S=O of said group. Furthermore, the wide band observed between 3200 and 3600 cm⁻¹ corresponds to the vibration of the O-H bond associated with the absorption of water molecules [5], [8]. The substitution of chloromethylated groups allowed a high content of sulfonic groups during the last stage of the oxidation reaction.

4.1.4 Elemental analysis

The elemental analysis, using the Perkin Elmer 2400 Series II Instrument Elemental Analysis of CHNS/O, were carried out to determine C, N, S and H of the samples. For this, 10 mg of sample were burned under oxygen atmosphere in a combustion tube. The determination of elementals is for the gaseous combustion products which pass through the combustion catalysts and absorption agents.

The polySEBS material was analyzed after the chloromethylation reaction and in its sulfonated form, to know the elemental content of chlorine and sulfur, respectively. Table 2 summarizes the carbon, hydrogen, chloride, and sulfur content for each of the samples. These values indicate that chloromethylation was carried out successfully, as well as the substitution of chlorine by sulfur for the formation of sulfonic groups.

Table 2. Elemental analysis results.				
Sample	C, %	H, %	CI, %	S, %
polySEBS	87.4	12.3	-	-
CM-SEBS	83.2	11.4	3.2	-
sSEBS-7H	74.4	10.8	-	3.9

It is important to point out that the 3.2% chlorine in the chloromethylated polymer demonstrates a greater substitution of the chloromethyl groups compared to another study of chloromethylation of the polySEBS where a percentage of elemental

chlorine content of 1.75% was achieved [4]. Furthermore, the sulfur content confirms that the chlorine substitution was complete.

4.1.5 Scanning electronic microscopy

The SEM images for the CM-SEBS sample are presented in Figure 12. As it can be observed in Figure 12a, the image confirms a well-compacted dense and uniform membrane without the existence of big pores. Figure 12b shown in green color the EDX element mapping giving chlorine presence all along the membrane, which confirms that chloromethylation of polySEBS was successful.



Figure 12. SEM image and EDX mapping of the chlorine element of CM-SEBS membrane crosssection.

Regarding the used treatment for the chemical modification of the chloromethylated membrane, it did not affect the uniformity and continuity of such membrane, according to Figure 13. The SEM-EDX mapping image (Figure 13b) is shown in yellow that sulfur is distributed uniformly in the polymer matrix, which implies the effective preparation of the sulfonated membrane after 7 hours of oxidation in performic acid treatment. This result revealed that the chlorine was replaced perfectly by sulfur during the sulfonic acid functionalization of polySEBS.



Figure 13. SEM image and EDX mapping of the sulfur element 7H-sSEBS membrane crosssection.

4.1.6 Thermogravimetric analysis

The pristine polySEBS thermogram (Figure 14) shows that the initial degradation temperature of the polymer chain is 377 °C. In the case of CM-SEBS sample, there was a first weight loss (7.56%) between 150 °C and 377 °C related to the decomposition of the chloromethylated groups that are present in the polymer matrix.



Figure 14. Thermogravimetric analysis of prepared membranes.

In the case of sSEBS-7H, an initial weight loss of 6.3% is observed in the range of 30 - 150°C, which is associated with the evaporation of water, mainly, and eventually organic solvents [9]. The second weight loss occurs between 150 °C and 377 °C corresponding to a weight loss of 7.94%, that is associated with the loss of the sulfonic groups from the polymer [10]. The percentage of loss for the sulfonated sample is according to the percentage of loss for the chlorinated sample, which corroborates that the oxidation reaction is effective to completely replace chlorine with sulfur to generate the sulfonic groups. Also, the residual values are according to the sample type, being the lowest value for the polySEBS, then the CM-SEBS and the highest value for the sulfonated sample because the carbon content was reduced. Finally, the decomposition temperature of the functionalized and pristine polymers occurred around 400 °C. It should be noted that the sulfonated membrane is thermally stable up to 150 °C, which is sufficient for application in fuel cells, since they usually operate between 20 and 80 °C [11].

4.1.7 Water uptake

The water content within an ion exchange membrane is a crucial parameter during the operation of a fuel cell because the dimensional stability of the membrane is affected by water, if there is an excess of it the membrane suffers an important dimension change [12]. According to Table 3, the water uptake of the membranes increased related to the oxidation time in performic acid, due to the chemical conversion from tiol (-SH) group into sulfonic acid group (-SO₃H).

Sample	Water uptake (%)
sSEBS-1H	61.5 <u>+</u> 1.9
sSEBS-2H	63.3 <u>+</u> 2.1
sSEBS-3H	68.8 <u>+</u> 3.1
sSEBS-7H	79.69 <u>+</u> 2.7

Table 3. Water uptake of sulfonated membranes.

The sSEBS-7H membrane had the highest average water uptake (79.7%), and the other sulfonated samples showed a gradual increase in such parameter as the reaction time elapsed. Although the sulfonic groups in the membrane favor the water uptake due to the easy ionic interaction with the water molecules, high water uptake by the membrane can promote a reduction of mechanical properties or even the fracture of the membranes [13]. The formation of ionic sites is important since they help the absorption of water molecules, favoring their mobility through the membranes according to the Grotthuss mechanism, which results in a better proton conductivity through the membrane of ion exchange [14]. Thus, there must be an adequate balance between water uptake and the mechanical integrity of the membrane to be functional for PEM.

4.1.8 Atomic force microscopy

Atomic force microscopy was used to investigate the topology of the membranes. Figure 15 shows the unmodified (pristine polySEBS) and sulfonated polymer membrane (S-SEBS-7H), which were prepared by solvent evaporation as described in the methodology.



Figure 15. Atomic force microscopy images of a) Pristine SEBS and b) modified polymer sSEBS-7H

The image of pristine SEBS membrane doesn't have a specific topology or homogeneous texture without obvious changes in the membrane's surface. In the case of the image of S-SEBS-7H membrane, the surface has revealed roughness due to the phase interaction of hydrophilic (–SO3H, polar group) and hydrophobic (polymer backbone, nonpolar structure) domains dependent of the chemical

structure[15]–[17]. There are relevant investigations that associate this topological change as a result of interaction between sulfonated styrene block and ethylene-buthylene block in the polymer backbone, which suggest an alternating hard and soft regions [18], [19].

4.1.9 Mechanical evaluation

The mechanical evaluation was essential to know the tensile properties of the sulfonated membranes in comparison with the pristine polymer membrane. The typical tensile curves are shown in Figure 16. The Young's modulus, tensile, strength, and elongation at break values for the different evaluated samples are summarized in Table 4.



Figure 16. Representative stress-strain behavior of pristine polySEBS membrane and sulfomethylated membranes with different oxidation times

The sulfonic acid group into the polymer matrix enhances the ion conductivities of the cation membranes but also increases the rigidity (see Young's modulus in Table 3) due to the sulfonic groups (-SO₃H), which are voluminous, reducing the chain mobility [20]. It can be inferred that the space between the aromatic ring and sulfonic

acid group, promoted by the methyl, could benefit the chain mobility of the sulfonated membranes, but it is not the case.

Sample	Young's	Tensile	Elongation at	Energy at break,
	modulus,	strength,	break, $\varepsilon_{\scriptscriptstyle b}$ (%)	toughness(mJ · mm ⁻
	<i>E</i> (MPa)	$\sigma_{\scriptscriptstyle b}$		³)
polySEBS	5.4 ± 0.2	17.6 ± 1.4	685.8 ± 10.5	54.4 ±1.4
sSEBS-1H	144.8 ± 3.4	16.8 ± 0.5	201.1 ± 8.7	23.9 ±1.0
sSEBS-3H	139.2 ± 8.3	16.5 ± 0.5	185.5 ± 11.8	21.6 ±1.4
sSEBS-5H	161.04 ± 4.9	14.27 ± 0.3	151.3 ± 8.9	16.2 ±1.2
sSEBS-7H	147.74 ± 8.7	12.37 ± 0.4	136.1 ± 7.2	13.4 ±0.9

Table 4. Tensile characteristics of pristine polySEBS membrane and sulfomethylated membranes

As shown in Table 3, the Young's modulus trends to increase as a function of the functionalization time of polySEBS. Hoewever, in the SSEBS-7H, such value was slightly lower than the sample with less reaction time but there is not a significant statistical change between them. On the other hand, there is a certain trend to reduce the elongation at break, tensile strength, and toughness as functionalization time increases, especially for the sSEBS-7H membrane, which is related to its chemical structure, due to the sulfonic acid group's formation. The introduction of sulfonic acid groups can be caused some loss of elastomeric character of the membranes, reducing the chain mobility [11], [20].

4.1.10 Ion exchange capacity and ion conductivity measurements

lonic conductivity (σ) is a fundamental parameter in ion-exchange membranes that reflect the efficiency of fuel cells. This parameter is affected by the temperature, the content of ionic groups, and the membrane thickness. Therefore, the evaluation was made at 25 °C. The values obtained for the ionic conductivity, specific resistance, ion exchange capacity and thickness of the sulfonated membranes at different times of immersion in formic acid (PFA), as well as of the corresponding values for NafionTM 117, which is a material widely used in ion-exchange membranes [21], are presented in Table 5.

Table 5. Results of specific resistance and ionic conductivity for sulfonated membranes.				
	Specific	lon	Ionic Exchange	Membrane
Sample	resistance	conductivity	capacity [meq/g]	thickness
	[Ω]	[mS cm ⁻¹]		[µm]
sSEBS-1H	83.5 ± 5.4	12.2 ± 0.8	1.39	216
sSEBS-3H	68.8 ± 4.0	14.8 ± 0.9	1.43	211
sSEBS-5H	58.8 ± 2.9	17.1 ± 0.8	1.46	204
sSEBS-7H	55.5 ± 2.1	18.2 ± 0.7	1.47	213
Nafion™ 117	161.6 [21]	6.19	0.91	127

As can be seen from Table 5, the increment of ionic conductivity of the hydrated membranes depends on the content of sulfonic acid groups formed at the different oxidation times (1, 3, 5, and 7h) in performic acid. Likewise, the variation of the specific resistance is inversely proportional to the content of sulfonic groups, which is consistent with the ionic conductivity values.

The specific resistance difference percentage between the samples with the shortest and longest reaction times was 66.5%, while the difference in ionic conductivity between them was 49.2%, which is indicative of ion transport is also affected by the effect of diffusion (membrane thickness), although the transport efficiency for these membranes was relatively high (75%), as a consequence of the insertion of sulfonic groups.

In other works, it has been reported that the ionic conductivity of NafionTM 117 was 6.19 mS/cm at the same measurement conditions to which the results of this work were obtained [21]. In comparison, the values for NafionTM of conductivity is just 34 % and, in terms of specific resistance is 191 % higher than the best values obtained in the work, despite having a lower membrane thickness. Likewise, the value of the ion exchange capacity for the membrane with the highest sulfonation sSEBS-7H was 60 % greater than the value of the commercial polymer NafionTM 117 (IEC = 0.91 meq/g). The results of both ionic conductivity and IEC are indicative

that the alternative sulfonation pathway is promising in the fabrication of fuel cell membranes.

4.2 Conclusions

In conclusion, indirect sulfonation of polySEBS by chloromethylation route is an alternative method to the direct sulfonation by using strong acids, allowing to obtain efficient, structural stable and resistant membranes. Sulfonic acid groups were generated during oxidation of thiol groups in the membranes, where water uptake, ion exchange capacity and ion conductivity increased with the conversion time of the reaction. Surface roughness was identified for high sulfonated membrane by AFM, the topology was generated for hydrophilic (-SO₃H) and hydrophobic parts (polymer backbone) on the membrane. The prepared membrane sSEBS-7H showed an IEC value of 1.46 meq/g and high ionic conductivity (18.7 mS/cm⁻¹ at 25°C) in comparison with reported values for commercial membranes, such as Nafion [™] 117. According to TGA, acid groups of sulfonated membranes prepared by indirect sulfonation were thermally stable up to 150°C, and Young's modulus (147.74 MPa) measure showed a good mechanical stability, offering a great potential for its use in fuel cells. In addition, ion conductivity and IEC, thermal and mechanical stability are important parameters of the membrane, which can affect the performance a fuel cell operation.

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CHAPTER 5. Quaternized polySEBS membrane

This chapter describes an experimental quaternizated membranes, as an alternative to introduce cationic pendant groups to the aromatic rings of polySEBS, imparting anion exchange capacity and ion conductivity. Anion exchange membranes based on polySEBS were synthesized through two steps involving chloromethylation followed by quaternization in ethanol solution. As described previously in chapter 4, the chloromethylated membrane was prepared by solvent evaporation.

5.1 Background

5.1.1 Anion exchange membrane (AEM)

Recently, considerable attention has been paid to anion exchange membrane (AEM) because of their numerous advantages in comparison with PEMs, such as mechanical properties and good chemical stability under high pH condition [1]. Therein, the AEMs play an inherently significant role in improving fuel cell performance, thus it attracts special research interests. AEMs are usually composed of polymer matrix and cationic charged groups. The most frequently used reactions to fabricate AEMs are chloromethylation and quaternization. Chloromethylation introduces chloromethyl groups onto the phenyl ring via electrophilic substitution reaction between chloromethylation reagents and polymers and quaternization process introduces to the polymer quaternary ammonium groups by using tertiary amines [2].

The chemical modification of aromatic polymers such as polyether ketones, polyimides, polybenzimidazoles, polyphenylenes, polysulfones, and other copolymers has been widely studied as a main alternative for developing ion exchange membranes with performance comparable to Nafion[™], but at a lower cost and with good chemical and thermal stability. [3]–[6].

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5.1.2 Chloromethylation and quaternization

Commonly, the introduction of halomethyl groups serves as an intermediate for a wide range of polymer chemical modification. It enables nucleophilic elaborations such as quaternization, phosphination, and esterification. This versatility makes the halomethyl group a valuable functional group in the modification of polymer backbones and the design of anionic membranes. Similarly, the chloromethylation of aromatic polymers, followed by quaternization of the resulting benzyl chloride moieties with tertiary amines, yields quaternary ammonium cationic groups, providing the membranes with anion exchange capacity [5], [7].

5.2 Characterization

5.2.1 Polymer modification

As part of this work, anionic membranes from polySEBS were synthetized by using chloromethylated membranes, which was used previously to fabricate sulfomethylated membranes. The quaternization reaction was carried out by reacting to the chloromethylated polySEBS with 1,4-diazabicyclo[2.2.2]octane (DABCO) in ethanol solution, leading to the incorporation of quaternary ammonium pendant groups to the polymer backbone, as shown in Figure 17.



Figure 17. Quaternization of chloromethylated group pendant of polymeric chain.

5.2.3 FTIR spectroscopy

Figure 18 shows a comparison FTIR spectra for the pristine polySEBS, chloromethylated polySEBS membrane (CM-SEBS) and quaternized polySEBS membrane.



Figure 18. FTIR spectra of AEMs from polySEBS.

In comparison to the pristine polymer, the chloromethylation of the aromatic rings in polySEBS shows the formation of CM-SEBS, as confirmed by the stretching vibration at 1266 cm⁻¹, which is attributed to the presence of chloromethyl groups. In the spectrum of DABCO-SEBS, the disappearance of this absorption band indicates the displacement of the chlorine atom and the successful incorporation of ammonium pendant groups. Additionally, two characteristic peaks at 3369 cm⁻¹ and 1620 cm⁻¹ are observed, corresponding to the O–H stretching vibration and the C–N bond vibration, respectively [8], [9]. These observations suggest the quaternary ammonium groups had been successfully introduced into the polySEBS.

5.2.4 Thermogravimetric analysis

The thermal stability of the membrane samples were evaluated using a thermogravimetric analysis (TGA) as shown in Figure 19. Firstly, the pristine polySEBS membrane thermogram takes place the initial degradation temperature of the polymer chain is 377 °C, which is similar in all samples.



Figure 19. Thermogravimetric analysis of prepared membranes.

On the other hand, sSEBS-7H shows an initial weight loss of 6.3% is observed in the range of 30 - 150°C, which is associated with the evaporation of water, mainly, and eventually organic solvents. The second weight loss occurs between 150 ° C and 377 ° C corresponding to a weight loss of 7.94%, that is associated with the loss of the sulfonic groups from the polymer. Similarly, DABCO-SEBS shows an initial weight loss of 8.2 % is observed in the range of 30 - 147 °C, which is associated with the evaporation of water and organic solvents. The second weight loss of 14.64%, that is associated with the loss of the sulfonic groups from the polymer. Similarly, DABCO-SEBS shows an initial weight loss of 8.2 % is observed in the range of 30 - 147 °C, which is associated with the evaporation of water and organic solvents. The second weight loss of 14.64%, that is associated with the loss of the ammoniun groups from the polymer. Finally, the decomposition temperature of functionalized polySEBS backbone in both membranes occurs around 400 ° C [10]–[12].

5.2.5 Atomic force microscopy

Atomic force microscopy was used to investigate the topology of the membranes. Figure 20 shows the unmodified (pristine polySEBS) and quaternized polymer membrane DABCO-SEBS, which were prepared by solvent evaporation as described in the methodology.



Figure 20. AFM images of a) Pristine membrane and b) DABCO-SEBS membrane.

The AFM image of the pristine polySEBS membrane exhibits a homogeneous texture without significant surface features. In contrast, the DABCO-SEBS membrane presents a rougher surface morphology, which is attributed to the phase separation between hydrophilic domains (polar, quaternary ammonium pendant groups) and hydrophobic regions (non-polar polymer backbone). This morphological contrast with the hydrophilic property after functionalization. There are relevant investigations that associate this topological change as a result of interaction between functionalized styrene block and ethylene-buthylene block in the polymer backbone, which suggest an alternating hard and soft regions [13]–[17].

5.2.6 Mechanical evaluation

The mechanical evaluation through tensile testing was essential to understand the physical behavior of the anion-exchange (DABCO-SEBS) and cation-exchange (sSEBS-7H) membranes in comparison with the pristine polySEBS membrane.



Figure 21. Stress-strain curves of pristine, cation and anion exchange membranes.

As shown in Table 6, the functionalization of polySEBS modifies its mechanical properties. The Young's modulus notably increased upon functionalization, reaching 147.7 MPa for sSEBS-7H and 103.5 MPa for DABCO-SEBS, compared to only 5.4 MPa for the pristine polySEBS. This increase in stiffness is attributed to the introduction of sulfonic acid and quaternary groups, which restrict the mobility of the polymer chains.

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Sample	Young's	Tensile	Elongation at	Energy at break,
	modulus,	strength,	break, $\varepsilon_{\scriptscriptstyle b}$ (%)	toughness(mJ · mm ⁻
	<i>E</i> (MPa)	σ_b (MPa)		3)
polySEBS	5.4 ± 0.2	17.6 ± 1.4	685.8 ± 10.5	54.4 ± 1.4
sSEBS-7H	147.74 ± 8.7	12.37 ± 0.4	136.1 ± 7.2	13.4 ± 0.9
DABCO-SEBS	103.56 ± 7.3	18.1 ± 0.6	102.1 ± 8.7	12.8 ± 1.1
sSBS		17.3		

Table 6. Tensile characteristics of pristine, sulfonated and quaternized polySEBS membranes.

SEBS	23.6 ± 0.5	520 ± 10	
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In contrast, a significant reduction in elongation at break was observed upon functionalization. While the pristine polySEBS membrane exhibited a high elongation at break of 685.8 %, this value decreased to 136.1 % for sSEBS-7H and further to 102.1 % for DABCO-SEBS, indicating a loss of elastic behavior. Similarly, toughness decreased from 54.4 mJ·mm⁻³ in the pristine membrane to 13.4 and 12.8 mJ·mm⁻³ for sSEBS-7H and DABCO-SEBS samples, respectively. These results suggest that chemical modification of the polymer increase stiffness and energy absorption capacity. These structural changes imparted by sulfonic acid and DABCO groups pendants, which reduce chain flexibility and elastomeric property of the polySEBS matrix [18], [19].

In Table 6, the tensile strength values of prepared membranes were significantly lower than membranes reported in the literature. However, DABCO-SEBS exhibited a tensile strength of 18.1 MPa, which can still be considered good value in comparison with other membranes [20][21]. Exploring chemical modification by other routes can affect the mechanical properties, depending on the functional groups attached to the polymer backbone.

5.2.7 Water uptake and contact angle

Water uptake and contact angle measurements are essential parameters for assessing the surface properties of functionalized polymeric membranes. As shows in Figure 22, pristine polySEBS membrane exhibits a high contact angle of 94.28°, which indicate a hydrophobic surface. In relation with sulfonated membrane described in the chapter 4, demonstrates a significantly increased water uptake of 79.7%, accompanied by a reduced contact angle of 83.17°, reflecting enhanced surface hydrophilicity due to the presence of sulfonic acid groups interaction with water. In other hand, the membrane functionalized with DABCO, shows water uptake of 54.2% and an contact angle of 89.2°, which describes a less interaction with water. This comparison suggests that the cation exchange membrane exhibits a greater affinity for water than the anion exchange membrane, likely attributable to the

stronger hydrophilic character of sulfonic groups compared to the quaternary ammonium groups derived from DABCO [22], [23].



Figure 22. Water uptake and contact angle of pristine, sulfonated and quaternized membranes.

This comparison suggests that the cation exchange membrane exhibits a greater affinity for water than the anion exchange membrane, likely attributable to the stronger hydrophilic character of sulfonic groups compared to the quaternary ammonium functionalities derived from DABCO.

5.2.8 Ion exchange capacity and ion conductivity measurements

The synthesized anion exchange membranes (AEMs) functionalized with DABCO exhibited a high ionic conductivity, reaching a value of 13.5 mS·cm⁻¹, as shown in Table 7. This result is comparable to that of the sulfonated membrane (sSEBS-7H), which showed also a high conductivity of 18.2 mS·cm⁻¹ compared with the commercial membrane Nafion $^{\text{M}}$ 117 (6.19 mS·cm⁻¹). In terms of comparison of the ion exchange capacity of DABCO-SEBS (1.32 meq/g) and sSEBS-7H (1.47 meq/g)

membranes. Both membranes demonstrated an effective of ion transport related to the incorporation sulfonic and quaternary ammonium pendant groups.

quaternized membranes.					
	Specific	lon	Ionic Exchange	Membrane	
Sample	resistance	conductivity	capacity [meq/g]	thickness	
	[Ω]	[mS cm ⁻¹]		[µm]	
DABCO-SEBS	74.5 ± 5.6	13.5 ± 0.9	1.32	195	
sSEBS-7H	55.5 ± 2.1	18.2 ± 0.7	1.47	213	
Nafion™ 117	161.6 [24]	6.19	0.91	127	

Table 7. Results of specific resistance and ionic conductivity for sulfonated and quaternized membranes.

The values of an ion conductivity of sSEBS-7H and DABCO-SEBS have a correlation with the ion exchange capacity value according to Table 7. This suggests that a higher ion exchange capacity tends to enhance the ion transport within the membrane.

5.3 Conclusion

In comparison with sulfonated membranes, an anion exchange membrane can operate in a fuel cell with alternative catalyzers different to platinum. For this reason, the functionalization of polySEBS via chloromethylation followed by quaternization with DABCO was successfully achieved to develop anion exchange membranes. FTIR analysis technique confirmed the incorporation of quaternary ammonium groups, as evidenced by the disappearance of the chloromethyl band and the appearance of characteristic peaks associated with the insertion functional groups. Moreover, thermogravimetric analysis demonstrated that the functionalized membranes exhibit good thermal stability, with degradation of ammonium groups occurring above 350 °C. AFM images revealed an increase in surface roughness after functionalization, attributed to phase separation between hydrophilic and hydrophobic domains. Mechanical testing showed a significant increase in Young's modulus, accompanied by reduced elongation at break, indicating lower elasticity due to restricted polymeric chain mobility.

Water uptake and contact angle measurements showed lower hydrophilicity of the quaternized membranes compared to their sulfonated counterparts, reflecting the less polar nature of quaternary ammonium groups. Finally, the DABCO-SEBS membrane demonstrated promising ion exchange capacity (1.32 meq/g) and ion conductivity (13.5 mS·cm⁻¹), compared with commercial Nafion[™] 117, suggesting its potential application as an anion exchange membrane for alkaline fuel cells.

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5. APPENDIX

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Research article

Indirect sulfonation of telechelic poly(styrene-ethylene-butylene-styrene) *via* chloromethylation for preparation of sulfonated membranes as proton exchange membranes

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Abstract. The indirect sulfonation, via chloromethylation, of poly(styrene-(ethylene-butylene)-styrene) (polySEBS), under mild conditions, is here reported as an alternative route for the conventional use of chlorosulfonic acid. This indirect sulfonation reaction is an effective route to insert sulfonic groups in the aromatic rings of SEBS to impart a proton exchange capability. The chloromethylated polySEBS was chemically modified by the isothiouronium grouP, afterward hydrolyzed and oxidized to generate sulfonic acid groups selectively into the aromatic portion (polyStyrene) of the polySEBS, to a great extent. The chloromethylated and sulfonated polymeric membranes were characterized by NMR, FT-IR, water uptake, TGA, ion exchange capacity (IEC), and ion conductivity. The obtained results show that as the oxidation time increased in performic acid, the water uptake achieved up to 79.6% due to the conversion of isothiouronium grouPs of sulfonation, determined by RMN, and had an IEC value of 1.46 meq/g and also an ion conductivity value of 18.7 mS/cm at *RT*, which are 46 and 75% higher than those of Nafion 115, a commercial polymer conventionally used for proton exchange membranes (PEM). Thus, the as-prepared sSEBS-TH membranes, via chloromethylation, can be used for PEM since it exhibits good ionic conductivity and structural stability.