

Perfluorinated and Sulfonated Proton Exchange Membranes: Effect of
Supercritical Fluid Processing on Ion Exchange Capacity and Proton
Conductivity

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PERFLUORINATED AND SULFONATED PROTON EXCHANGE MEMBRANES: EFFECT OF SUPERCRITICAL FLUID PROCESSING ON ION EXCHANGE CAPACITY AND PROTON CONDUCTIVITY

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Abstract

The present work has processed Nafion® and sulfonated polystyrene-isobutylene-styrene (SIBS) with supercritical fluid (SCF) carbon dioxide at a 40°C and 200 bar with the aid of ten co-solvents of different size and polarity. The goal of the investigation was to morphologically re-arrange the sulfonic acid groups to maintain the proton conductivity, while also re-arranging the CO₂-phillic perfluorinated groups to block the methanol for crossing over.

Measured ion exchange capacities (IEC) of the processed samples showed an increase, supporting our hypothesis, but very sensitive to the co-solvent selected. In addition, density results confirmed the membrane integrity. The last stage of this investigation has been studying the proton conductivity to have a better description of the orientation arrangement of the molecules. These results coupled with thermogravimetric, swelling, and dynamic mechanical analysis can provide a better picture of the structure property relation of these complex heterogeneous polymers.

MEMBRANAS DE INTERCAMBIO PROTÓNICO SULFONADAS Y PERFLUORINADAS: EFECTOS DEL PROCESAMIENTO CON FLUIDO SUPERCRÍTICO EN LA CAPACIDAD DE INTERCAMBIO DE IONES Y LA CONDUCTIVIDAD PROTÓNICA

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Resumen

Como parte de este trabajo se han procesado membranas de Nafion® y membranas sulfonadas de poliestireno- isobutileno-poliestireno con dióxido de carbono en estado supercrítico a una temperatura de 40C y una presión de 200 bar con la ayuda de 10 co-solventes de diferente tamaño y polaridad. La meta de esta investigación era el reorganizar morfológicamente los grupos sulfónicos manteniendo la conductividad protónica, a la vez que se reorganizaban los grupos compatibles al dióxido de carbono de forma que la permeabilidad de metanol fuera reducida.

Medidas de la capacidad de intercambio iónico de muestras de Nafion® procesadas mostraron aumento en el valor de dicha capacidad, apoyando nuestra hipótesis. Sin embargo estos resultados probaron ser sensitivos al co-solvente seleccionado. Además resultados de medidas de densidad de las muestras confirmaron que la integridad de la membrana se mantenía aun luego de esta ser procesada. La ultima fase de esta investigación ha estudiado la conductividad protónica de muestras seleccionadas en busca de obtener una mejor descripción de la orientación y arreglo de las moléculas en las membranas. Estos resultados junto con análisis termogravimétrico, mecánico-dinámico y de hinchamiento pueden proveer una mayor información de la relación entre la estructura y las propiedades de estos polímeros.

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To God for giving me the strength to accomplish my goals.

To my mom, dad, sister and brother for their continuous support and encouragement.

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I- Introduction

Throughout the years there has been a growing interest for finding better materials capable of improving the performance of fuel cells, chemical protective clothing and other protection and energy equipment. The search for new and effective ways to produce energy has been a matter of great research around the world since oil consumption has kept increasing through out the world. In 2005 an increase of 1.3% on global oil consumption was reported as the consumption of other fossil fuels such as coal presented a 5% growth. ^[1] In addition the environmental consequences of the use of gasoline and other petroleum-based fuels have generated worldwide preoccupation due to airborne emissions.

Various alternatives to the use of fossil fuels have been researched in modern technology. As part of those alternatives we can mention: solar power, hydroelectric power, wind power and fuel cells. Table 1.1 presents the general advantages and disadvantages related to these types of energy production technologies.

Table 1.1: Advantages and disadvantages of energy production alternatives^{[2],[3]}

Technology	Advantages	Disadvantages
Solar power	<ul style="list-style-type: none">▪ Inexhaustible fuel source▪ No pollution▪ Versatile	<ul style="list-style-type: none">▪ Low energy production▪ Only areas of the world with lots of sunlight are suitable for solar power generation▪ High investment cost
Hydroelectric	<ul style="list-style-type: none">▪ Inexhaustible fuel source▪ Minimal environmental impact▪ Viable source-▪ Can be used throughout the world	<ul style="list-style-type: none">▪ Smaller models depend on availability of fast flowing streams or rivers▪ Run-of-the-River plants can impact the mobility of fish and other river life.

Technology	Advantages	Disadvantages
Wind Energy	<ul style="list-style-type: none"> ▪ Inexhaustible fuel source ▪ No pollution ▪ Often an excellent supplement to other renewable sources 	<ul style="list-style-type: none"> ▪ Very diffuse source means low energy production- ▪ Only areas of the world with lots of wind are suitable for wind power generation ▪ Relatively expensive to maintain
Fuel Cell	<ul style="list-style-type: none"> ▪ Low temperature operation ▪ High power density ▪ Low emissions 	<ul style="list-style-type: none"> ▪ H₂ is difficult to store and distribute ▪ Higher cost compared to other technologies ▪ If other fuels are used (i.e. methanol), high permeability of fuel

From these alternatives fuel cells have been widely studied since various decades ago. A great deal of effort is being made to circumvent the disadvantages that are currently limiting the development and accessibility of this technology.

In summary, fuel cells have 3 basic components which are: the cathode, the anode and the electrolyte. The electrolyte is the section of the fuel cell technology that is demanding most attention, since the performance of the electrolyte greatly affects the overall performance of the fuel cell. The type of electrolyte serves as a way to classify the fuel cell. There are various types of fuel cells which are^[3] :1) polymer electrolyte fuel cell (PEFC), 2) alkaline fuel cell (AFC), 3) phosphoric acid fuel cell (PAFC), 4) molten carbonate fuel cell (MCFC), 5) intermediate temperature solid oxide fuel cell (ITSOFC), and 6) tubular solid oxide fuel cell (TSOFC).

This investigation focuses on the polymer electrolyte fuel cell, which uses a proton exchange membrane (PEM) in order to provide a separation between the anode and the cathode, and to serve as the proton conductor. The most common polymer electrolyte membrane is Nafion®, which is a perfluorosulfonated membrane. However, its high fuel permeability, poor mechanical properties, high cost and difficulty of disposal has led researchers in a quest for finding new alternatives to Nafion®. Also, the search for PEMs that could be used at higher temperatures is ongoing since operating at higher temperatures reduces electrode flooding and increases the kinetic rate of the fuel cell reactions.^[4,33]

Various approaches have been followed in the search for improved membranes. One approach has been the modification of Nafion® mostly by adding components that could stop the methanol permeation without affecting the proton conductivity.

Another highly studied alternative is the polybenzimidazole (PBI) membrane. Since 1974 this polymer has been proposed and studied as a possible electrolyte for fuel cells. Polymer modification such as, H₃PO₄ doped PBI/sulfonated polysulfone blends, and polymer doping presented promising results applicable to the fuel cell technology.

In addition to the previously mentioned alternatives sulfonated polymers, such as sulfonated poly(styrene-isobutylene-styrene)^[5], sulfonated polyphosphazene^[6], sulfonated polyphenylene oxide^[7], sulfonated polyarylene ether sulfone^[8], sulfonated polyether ether ketone^[9], and sulfonated polystyrene-ethylbutylene-styrene^[10] have been studied as potential candidates for PEMs. The presence of the sulfonic acid groups in

this kind of polymers allows them to conduct protons and help the polymers increase their water uptake.

The list of polymers mentioned above includes special kinds of polymers, called block copolymers. These block copolymers are converted to ionomers due to their sulfonation, thus giving these polymers characteristics that could be applied to the fuel cell technology. Several studies that will be discussed later, suggest a strong correlation between the morphology and the transport properties of membranes prepared with these polymers.

Processing the membranes could provoke morphological changes, rearranging the polymer structure in a form that could increase Nafion® and sulfonated polystyrene-isobutylene-styrene ion exchange capacity and proton conductivity. The alternative proposed here is processing the polymers with supercritical fluids, specifically supercritical CO₂. The major objective of this study is to modify the polymer structure in a way that could provide a proton exchange membrane with equal or higher proton conductivity while decreasing the methanol permeability (Figure 1.4).

Our hypothesis resided in the believe that processing the polymer with SCF CO₂ (specially with the use of chemical co-solvents) could morphologically re-arrange the sulfonic groups maintaining or increasing the ion exchange capacity.

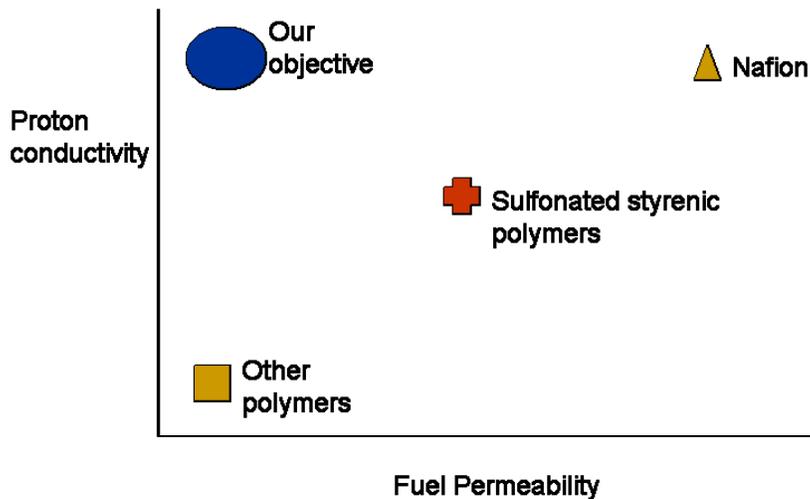


Figure 1.1 : Schematic representation of PEM objective.

Based on this idea this investigation focused on three primary objectives:

- Measure ion exchange capacity of various sulfonated and fluorinated membranes.
- Perform a physical characterization of the membranes to determine how integrity is affected due to SCF processing.
- Determine the relationship between the processing conditions (sulfonation level, co-solvent), structure and the ion exchange capacity of the membrane.
- Measure the proton conductivity of selected membranes after SCF processing

II- Literature Review

A. Improvement of Polymer Electrolyte Membranes

As mentioned earlier there is great interest on improving polymer electrolyte membranes in order to make the fuel cell technology more efficient and affordable. Various approaches have been followed in the search for improved membranes. One approach has been the modification of Nafion® mostly by adding components that could stop the methanol permeation without affecting the proton conductivity. For example palladinized Nafion® membranes were prepared and found to have less methanol permeability, and higher water uptake.^[11] These results were attributed to the Pd nanoparticles dispersed through the membranes. The Pd made the membrane more polar, thus retaining more water. In the other hand the Pd nanoparticles distributed in the membrane surface reduced methanol permeation. Changes in proton conductivity were also seen as shown in figure 2.1.^[11]

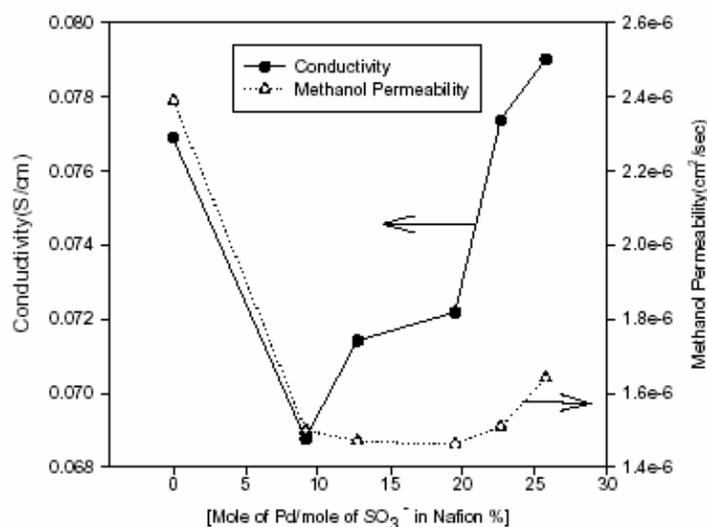


Figure 2.1: Proton conductivity and methanol permeability changes in palladinized Nafion.^[11]

Another alternative attracting lot of attention is the phosphoric acid doped PBI membranes due to its applicability to high temperature fuel cells and membranes giving conductivity results of 4.6×10^{-2} S/cm at 165°C at 80-85 % relative humidity (Nafion® 6.1×10^{-2} S/cm at 22°C) ^[12] . The doping of this polymer also has been linked to a better thermal stability ^[12]. In general, it has been found that the mechanism governing the proton transport on these membranes is the Grotthuss' mechanism. Excess acid acts as an acid pool retained on the polymer matrix thus resembling an acid solution. The basics of the Grothuss mechanism states that solvent molecules orientate in such way that hydrogen bonds can be formed, through which a proton jump can occur.

In addition to the previously mentioned alternatives sulfonated polymers have been studied as potential candidates for PEMs. The presence of the sulfonic acid groups in this kind of polymers allows them to conduct protons. In addition, these groups help the polymers increase their water uptake. Carreta et al.^[13] confirmed the increase in proton conductivity and water uptake by studying ionomeric membranes based on partially sulfonated polystyrene and Nafion® 117. In their study, membranes were solution casted from partially and homogeneously sulfonated polystyrene and characterized for proton conductivity and methanol permeability by the use of a four-probe DC technique and the use of a glass diffusion cell respectively. They found out an apparent Arrhenius dependency of proton conductivity with temperature as can be seen in Figure 2.2 The activation energies were the same for all membranes except for the membrane at 15% sulfonation that

showed a higher activation energy, being slightly superior even to the one for Nafion®.

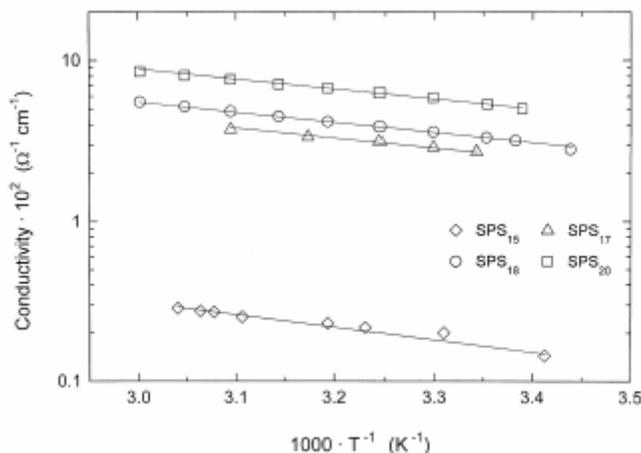


Figure 2.2 Arrhenius plot of proton conductivity vs. temperature results from partially sulfonated polystyrene membranes^[13]

In addition, they found out a higher conductivity at higher sulfonic group concentration, having a sudden increase after reaching the 15% sulfonation level leading to the conclusion of this being a percolation threshold for the membrane. The existence of this percolation threshold is also understood to be the reason of changes in the activation energies of this membrane. This theory about the existence of the percolation threshold will be discussed later.

The effect of the sulfonation level of poly(styrene-isobutylene-styrene) on proton conductivity and methanol permeability was studied by Elbad Y. et al.^[5] They reported that the 50% sulfonated poly(styrene-isobutylene-styrene) had a lower methanol permeability than Nafion® 117, a characteristic desirable for direct methanol fuel cells (DMFC). They also encountered that the selectivity, which they defined as the ratio of proton conductivity to methanol permeability, was higher for

all sulfonated samples than for the Nafion® membrane being the first one 5 to 10 times more selective. However proton conductivity results were not as promising since results for the SIBS membranes, were much lower than for Nafion® even at high sulfonation percents.

Studies with other sulfonated polymers have also given results worth of giving attention. For example, measurements of the conductivity of sulfonated polyphosphazene blends showed that there was a linear correlation between the swelling of the membrane and its conductivity. In addition membranes prepared by blending sulfonated poly[bis(3-methylphenoxy)]phosphazene (SPOP) with either Kynar® FLEX, PAN or PBI showed a higher conductivity at higher IEC, essentially because of better swelling of the membrane.^[14]

Most of the sulfonated polymers studied have in common that they are block copolymers converted to ionomers due to their sulfonation. Repulsion forces between the ionic and non – ionic components on the ionomers' structure allow processing them like thermoplastics, while having properties of elastomers. A consequence of this chemical dichotomy leads to the polymer segregating in phases. The phases will tend to separate but since they are linked by the polymer chains, the polymer acts as a crosslinked polymer, giving its elastomeric properties. However when the polymer is heated, the repulsion forces are reduced, the polymer chains are free to rearrange, and the polymer can be molded as any thermoplastic polymer.

Phase segregation of a sulfonated block copolymer was studied and confirmed by Weiss et al. using x-ray scattering on polystyrene-ethyl-co-butylene-styrene^[15]. According to their results, three phase morphology was found in this polymer in the

solid state. It is suggested that this three phase segregation occurs because different blocks in the polymer segregate as a result of thermodynamic incompatibilities and a second phase segregation occurs as a result of electrostatic interactions among ion pairs. ^[16]

This same phase segregation is understood to be related to the proton conduction inside the polymer. The percolation theory discussed by Mohanty et al. ^[17] and further studied by various researchers as it applies to ion containing polymers suggests that ion rich domains, when present at small concentrations, act as ion clusters inside the bigger polymer matrix (Figure 2.3a). As the volume fraction of these clusters increases, the clusters become interconnected, thus aiding the proton transport (Figure 2.3b). The point at which this occurs is typically called the percolation threshold.

Studies performed on Nafion® 117 using small angle X-ray analysis suggested that ion clusters interconnected by small narrow ionic channels approximately 5 nm in size were present in the membrane's morphology, possibly being this reason for the Nafion membrane good conductivity ^[18].

Other researches, such as the study of the phase segregation and the percolation theory in poly(phenyl oxide) matrices ^[7], have concluded that the results for the diffusion of protons through the membranes agree with the percolation theory. In overall the acceptance of this theory implies a correlation between the membranes morphology and its transport properties.

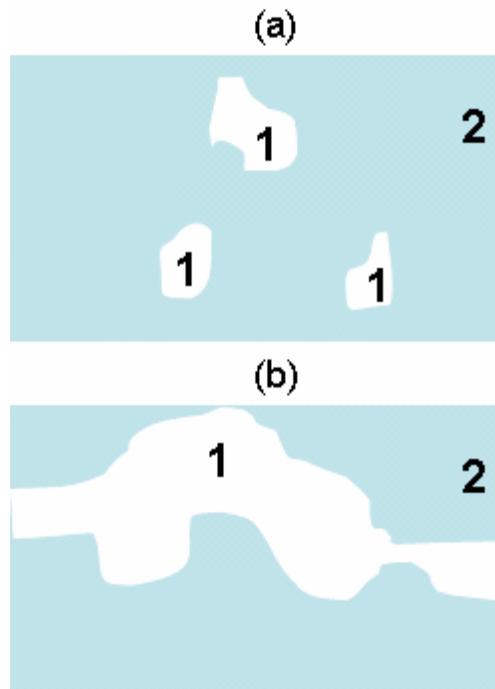


Figure 2.3: Percolation theory illustration.

The existence and importance of this correlation in polystyrene-isobutylene-styrene (SIBS) and Nafion was also studied by Elabd Y.A., et al^[5]. In their experiments, these researchers measured proton conductivity for the membranes using AC impedance spectroscopy with a two probe and a four probe techniques. In the first technique the proton conductivity was measured normal to the plane as proton conduction occurs on a typical fuel cell, and in the second technique proton conductivity was measured aligned with the plane of proton conduction. It is important to note that both techniques have been previously used to measured proton conductivity on Nafion membranes and considerably different proton conductivity values were found between both techniques. Figure 2.4 shows a schematic representation of the electrode assemblies as presented by the researchers.

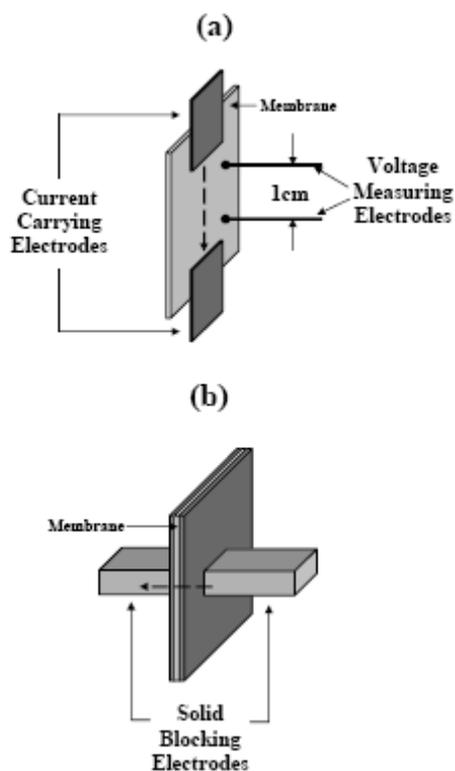


Figure 2.4: Schematic representation of the electrode assemblies used to measured proton conductivities, (a) in plane (b) normal to the plane^[5]

The SIBS membranes structures were characterized by the use of small angle x-ray scattering (SAXS), with the results suggesting an anisotropic structure on which the lamellar domains are highly oriented in the plane of the membrane. This result was used to analyze the values obtained for proton conductivity. For Nafion® 117 the values obtained confirmed previous findings reported in the literature; however, no characterization of the membrane is reported that could aid in the explanation of this phenomena.

In SIBS, a 9-12 times reduction, between the values measured in plane and normal to the plane were also found. This difference is attributed to the orientation of nanodomains inside the polymer matrix. After analyzing percolation studies,

researchers concluded that the transport in the direction of oriented lamellar domains provides less resistance in the membranes thus enhancing proton transport. In conclusion they demonstrated that structure- transport properties relationships exist in block copolymer ionomers.

Poly(styrene- isobutylene-styrene) membranes with various ion exchange capacities were synthesized and later characterized by Y.A. Elabd, et al. An increase ion exchange capacity resulted in an increase of density and water solubility. It was suggested that the increase in sulfonic acid groups produced a denser polymer with less free volume. In addition it was found that the proton conductivity and methanol permeability of the polymer increased as the IEC increased. Figure 2.5 and 2.6 show the results for this investigation compared to Nafion® values. Regressions to the percolation model described in chapter one are also presented in the figure.

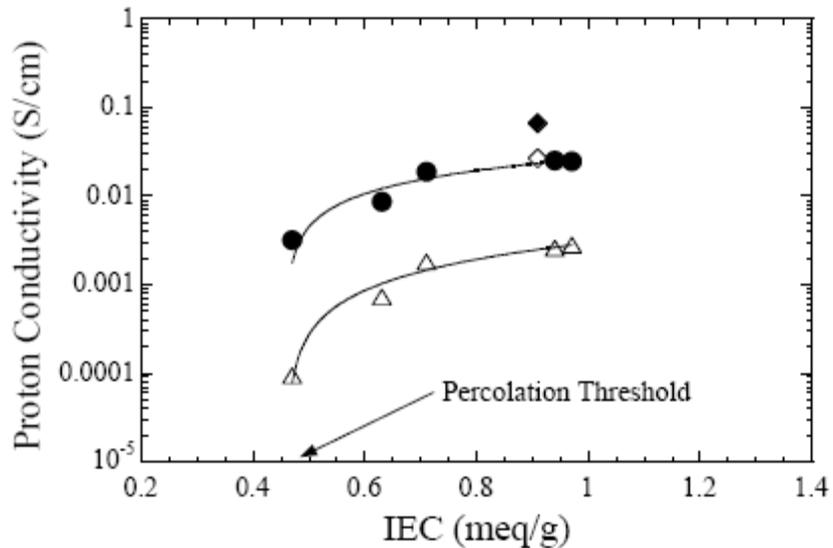


Figure 2.5: Proton conductivity measured in the plane and normal to the plane of the membrane versus IEC for Nafion 117 (♦,◇, respectively) and S-SIBS membranes (●,Δ, respectively).^[5]

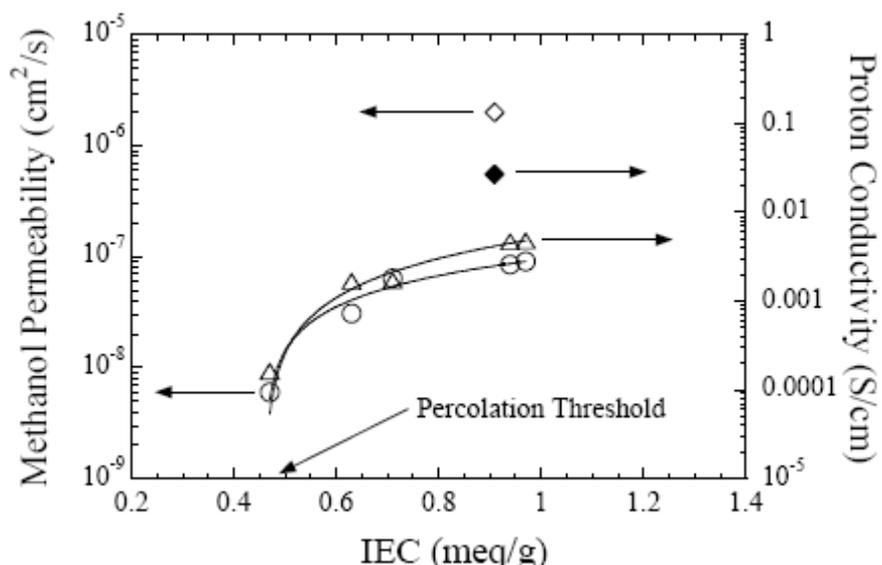


Figure 2.6: Methanol permeability and proton conductivity (normal to the plane) versus IEC for Nafion 117 (\blacklozenge, \diamond , respectively) and S-SIBS membranes (\circ, Δ , respectively).^[5]

B. Supercritical CO₂ processing of polymers

Processing of polymers with supercritical fluid CO₂ is a field that has been growing significantly due to the wide range of applications already found. A review presented by Tomasko, et al. presented several applications of the supercritical fluid technology such as particle formation, foaming, blending and injection molding^[19]. In addition, the use of CO₂ as a reaction solvent is being explored as a “green” alternative for solvents in chemical reactions and studies have shown improvement in selectivity, conversion and rates of various processes. Another important feature, is the known fact that the interaction between the carbon dioxide and a polymer lowers the glass transition temperature of the polymer and thus affects properties such as:

viscosity, permeability and interfacial tension. The process of lowering the glass transition temperature is called plasticization, due to an increase in the free volume inside the polymer caused by the gas sorption.^[20] This free volume increment increases the chain mobility.

Another polymer – SCF review by S.Yeo and E. Kiran^[21] emphasized as one of the important features of the use of SCF CO₂ in the formation of particles, that the supercritical CO₂ high diffusivity and moderate solubility in the polymer combined with the plasticization of the polymer provides the proper environment for guest materials to migrate into the polymer matrix to generate the active ingredient – loaded particles with reasonable loading.

C. Supercritical CO₂ processing of polymers membranes

Processing of poly(styrene-isobutylene-styrene) and poly(styrene- ethylene-butylene-styrene) with various sulfonation levels was performed using supercritical CO₂ at different temperatures and pressures in 2002.^[22] These polymers were thermally characterized using thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC). Also structure characterization was made by the use of atomic force microscopy (AFM) and scanning electron microscopy (SEM). It was found that working at higher pressures, thus densities, increased the CO₂ ability of changing the membranes structure. In addition it was found out that the use of polar co-solvents also increased this characteristic probably improving the CO₂ affinity to the polymer molecules.

Nafion® 117 and sulfonated poly(styrene-isobutylene-styrene) were processed with supercritical CO₂^[23] using a fixed temperature and pressure of 200

bar and 40°C, as suggested by Ramirez. She performed TGA studies after the SCF processing of the polymer with and without the aid of ten co-solvents. The solvents studied included: tetrahydrofuran, cyclohexanone, methanol, ethanol, isopropyl alcohol, toluene, acetone, acetonitrile, and water. Results showed a shift of the degradation temperature to lower temperatures suggesting a better orientation of the membrane chains. Swelling studies performed also suggested that morphological changes occurred on the membranes. However TGA results suggested cleavage of the external perfluorinated group in the Nafion® membrane, creating a concern about the membrane's integrity. This concern is addressed in our work and will be discussed on later chapters.

Based on the results obtained by these investigations it was decided to process Nafion® 117 and sulfonated poly(styrene-isobutylene-styrene) with supercritical CO₂ using a fixed temperature and pressure with the aid of the co-solvents, measuring changes on the ion exchange capacities, property that gives an indication of the membranes' proton conductivity.

III- Fundamentals

A. Fuel Cells

Fuel cells are chemical cells that convert chemical energy into electricity due to the controlled reaction between hydrogen and oxygen. One of the simplest fuel cells can be schematized as presented on figure 3.1. The proton exchange membrane (PEM) hydrogen fuel cell is basically composed of two electrodes and a polymer electrolyte membrane. Hydrogen is fed to the cell where it reacts in the anode passing to hydrogen cation thus releasing an electron. The electron flows through an outside circuit while the cation permeates through the membrane. When the cation reaches the cathode it reacts with oxygen that is also fed to the cell producing primarily water.

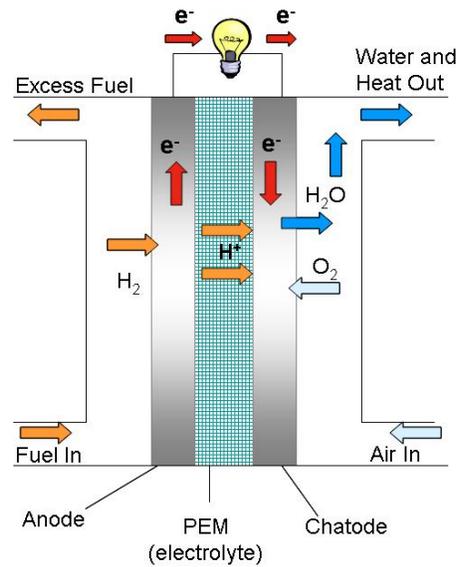


Figure 3.1: Schematic representation of the hydrogen fuel cell

Table 3.1 describes the different types of fuel cells and their approximate working temperatures.

Table 3.1: Summary of types of fuel cells^[3]

Type of fuel Cell	Working Temperature	Electrolyte	Other Description
Polymer electrolyte	< 120°C	ion exchange membrane	Water management in the membrane is critical for efficient performance, because the membrane must be hydrated. The operating temperature is limited by water saturation needs and polymer resistance.
Alkaline Fuel Cell	0° - ~250°C	concentrated KOH	The electrolyte is retained in a matrix . The fuel supply is limited to non-reactive constituents except for hydrogen. CO is a poison, and CO ₂ will react with the KOH to form K ₂ CO ₃ , thus altering the electrolyte.
Phosphoric Acid Fuel Cell	150°C – 250 °C	Phosphoric acid concentrated to 100%	Use of concentrated acid (100%) minimizes the water vapor pressure so water management in the cell is not difficult. The matrix universally used to retain the acid is silicon carbide.
Molten Carbonate Fuel Cell	600°C – 700 °C	Combination of alkali carbonates	The electrolyte is retained in a ceramic matrix of LiAlO ₂ . At the high operating temperatures in MCFCs, Ni (anode) and nickel oxide (cathode) are adequate to promote reaction. Noble metals are not required.
Tubular Solid Oxide Fuel Cell	1000 °C	Nonporous metal oxide	Typically, the anode is Co-ZrO ₂ or Ni-ZrO ₂ cermet, and the cathode is Sr-doped LaMnO ₃ .
Intermediate Temperature Solid Oxide Fuel Cell	600°C- 800 °C	nonporous metal oxide	Operates like the tubular solid oxide fuel cell but at lower temperature

B. Polymer- Solvent Interactions

The way a polymer interacts with any given solvent can have a significant influence on the characteristics this polymer will present. Knowing how a polymer gets dissolved can provide a preliminary understanding of the importance of the polymer – solvent interactions. As we know, polymers are composed of long chains that are either coiled within themselves or joined to other chains depending on the intermolecular or intramolecular forces acting within it. These forces can be dispersion forces, induction, dipole- dipole or hydrogen bonding just to mention some of them.

When a polymer is added to a solvent, if the polymer- solvent interactions are stronger than the polymer-polymer forces, the polymer starts absorbing solution, occurring swelling. The polymer chains start to loosen up and the chains are called to be solvated. This process continues until the chains disperse in the solvent thus dissolving. On the other hand, if the polymer solvent interactions are not strong enough, the polymer can swell but the chains do not disperse creating what is called a polymer gel.

In general the magnitude of the polymer solvent interactions is determined by factors such as the solvent polarity and chemical characteristics, and the solubility parameters. A deeper understanding of polymer–solvent interactions has been achieved considering thermodynamics factors. However thermodynamics of polymer solutions is special because since the 1940's it was found that these solutions deviated from the ideal solution behavior often used to work with most non- polymeric

solutions. The most important point is that the entropy calculated for polymer solutions are usually lower. In this same decade the Flory- Huggins Theory was developed in which a lattice model was used to formulate the equations for the thermodynamics of polymer solutions. A complete explanation of the derivations of the equations can be found on any polymer science textbook . The Flory- Huggins theory lead to the creation of the dimensionless Flory interaction parameter “ χ_{12} ” expressed as

$$\chi_{12} = \frac{zr_1\Delta\omega_{12}}{kT} \quad (\text{Eq.3.1})$$

where z is the lattice coordination number, r_1 represents the number of segments in a solvent molecule, $\Delta\omega_{12}$ is the change in internal energy for formation of an unlike molecular pair (solvent- polymer) . This parameter is used in the determination of the enthalpy of mixing of the polymer solution by the equation,

$$\Delta H_m = kT\chi_{12}n_1\phi_2 \quad (\text{Eq.3.2})$$

Since for an ideal solution the enthalpy of mixing is zero, the interaction parameter “ χ_{12} ” should be as small as possible in order to have a good polymer-solvent pair.^[24] The determination of this interaction parameter for a wide range of polymer - solvent system is still a subject of many studies due to the difficulty in the mathematical prediction of this parameter compared to measured values.

One approach for the determination of this parameter and the prediction of the solubility of a polymer on a given solvent is by the use solubility parameters, as per the equation

$$\chi_{12} = \frac{V_1}{RT} (\delta_1 - \delta_2)^2 \text{ (Eq.3.3)}$$

where V is the volume of the mixture, δ_1 and δ_2 are the solubility parameters for the solvent and the polymer. The solubility parameter of the solvent is related to its cohesive energy.

On the other hand the solubility parameter of a polymer is calculated by the use of group contributing methods or experimentally by swelling methods. However this approach can be used only for endothermic ($\Delta H_m \geq 0$) mixing. It has also been found inaccurate for polymers with a certain degree of crystallinity. In addition this method has been considered inaccurate for situations in which hydrogen bonding interactions occur. In order to deal with these limitations three-dimensional solubility parameters, such as the Hildebrand solubility parameter, are used which account for dispersive, polar and hydrogen bonding interactions^[24].

C. Block Copolymers

A copolymer is a polymer that contains chains composed of one or more monomer molecules, when these monomer molecules are arranged in a specific pattern they are called block copolymers. Block copolymers can be named according to the quantity of blocks contained in the molecule as di-block, tri-block, or multi-block for two, three, or more blocks respectively. The block quantity does not necessarily have to match the monomer quantity thus giving another classification based on the arrangement it has. Most common arrangements are pictured on figure 3.2.

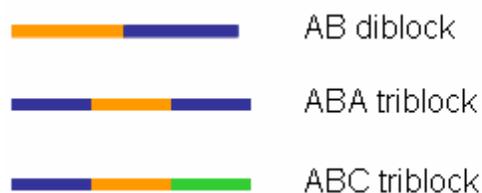


Figure 3.2 : Some common arrangements of block copolymers

A special kind of block copolymer being studied as possible alternatives to PEM are the styrenic block copolymers (SBC). SBC are thermoplastic elastomers, that means that they can be processed as thermoplastics but have the mechanical properties of rubbers. Common SBC consist of three blocks, two hard polystyrenic blocks and one elastomeric block. The two hard blocks give them their thermal stability while the elastomeric block gives them their processability. Commonly used elastomeric blocks include polybutadiene, polyisoprene, and poly(ethylene-butylene) to mention a few. Styrenic thermoplastics elastomers resist water, alcohols, and dilute alkalies and acids. They are soluble in, or are swelled by, strong acids, chlorinated solvents, esters, and ketones.^[25]

Most SBC have the special characteristic that they microphase separate in rubber like and harder segments. This separation is one of the characteristics believed to help membranes made from this kind of polymers conduct protons in a more effective way since channels with specific characteristics and attraction properties are created within the structure that influence the proton transport. The same thermodynamics applied to the solvent – polymer interaction can be applied in the monomer- monomer interactions where a value of “ χ_{12} ” is greater than 10.5 will imply that the polymer will microphase separate.^[24]

Major phase separation can be seen in thermoplastic ionomers. These are copolymer containing ionic groups that further increase the phase separation inside the polymer since ionic more polar segments separate from the non polar backbone of the polymer. Covalent bonds maintain the copolymer together and limit the extent of the phase separation. The importance of the phase separation for the proton transport has been extensively studied and several theories such as the percolation theory, explained earlier, have been proposed.

D. Supercritical Fluids

A supercritical fluid (SCF) is simply defined as a substance compressed above its critical pressure and heated past its critical temperature. They have been object of study since the 1880's. Their importance comes from their unique combination of solvent and transport properties. A fluid in its SCF state shows liquid like densities and gas-like transport properties. This means that as a liquid-like fluid it possesses the capacity to effectively extract and dissolve solutes, while as a gas-like fluid easily diffuses throughout solid matrices. This makes them ideal for uses as a specialty solvent for a wide variety of applications in today's chemical, pharmaceutical, food material and other industries.

An important physical property often studied in SCF is its solvent density. It is greatly affected by minor changes in pressure, thus affecting their solvent power and giving the capacity of fine tuning the fluid selectivity with a careful selection of temperature and pressure of the fluid. Throughout the years several studies have looked at the solubility of naphthalene in supercritical CO₂, being the first study performed by Büchner in 1906. Figure 3.3 shows how as the pressure is increased, the

solubility of naphthalene increases until it reaches a maximum value.

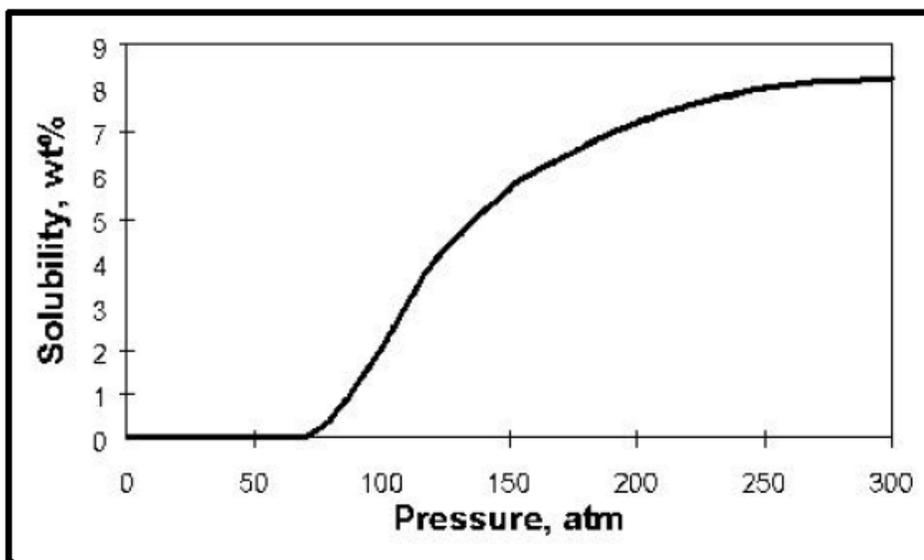


Figure 3.3 Solubility of Naphtalene in Supercritical Carbon Dioxide with Changes in pressure at 45°C.^[26]

This behavior has been found to be a general one for most solid solutes in supercritical fluids. At lower pressures (densities) the saturation pressure of the solute primarily influences its solubility. At higher pressures (densities) the solvent density dominates the solubility up to a maximum value.

This characteristic is one of the main reasons that the area most studied in SCF is supercritical extraction (SFE). Other fields of study within SCF include: reactions, polymer modifications, and dispersions.

Applications for the supercritical fluid technology have been increasing throughout the years including: reactions and polymerizations, coffee decaffeination and extraction of oils from seeds, fractionations, supercritical fluid chromatography and replacement of environmentally hazardous solvents in the pharmaceutical industry.

One of the most studied supercritical fluids has been supercritical carbon dioxide. The CO₂ supercritical fluid technology has been being studied as an alternative for the improvement of processes, especially those that require the use of solvents considered harmful to the human being or environment. The advantages of using supercritical CO₂ are various. First of all the supercritical conditions of CO₂ are easily obtained being its critical pressure 73.8 Bar and critical temperature 31.1 °C. Other advantages include that it is non-toxic, non-flammable, inexpensive and environmentally friendly. In addition, as previously explained, its density is adjustable by slight pressure variations and it's easily removed by depressurization.

The density changes in CO₂ have been confirmed by a large quantity of studies. Figure 3.4 shows the changes in density with varying pressure at different temperatures. From this figure it can be seen that the density increased as the pressure increased thus giving the supercritical fluid solvating properties similar to those of liquids. It can also be seen that at a temperature near the CO₂ critical temperature (T_c=304K) small changes in pressure provoke large changes in density.

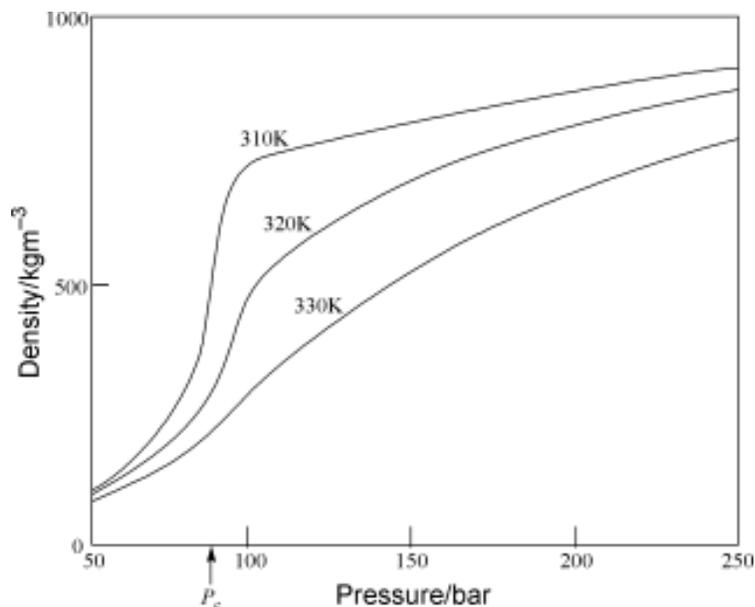


Figure 3.4: Density variations for CO₂ with temperature and pressure changes^[27]

Although most studies related to the CO₂ processing have been focused on supercritical extraction, this technology has been proved useful in applications such as polymer particle formation, foaming, blending, injection molding, and recently the modification of polymer membranes.

E. Fundamentals of Ion Exchange Capacity

Ion exchange is a process that was discovered and described as occurring in soils in the second half of the 40's and beginnings of the 50's. From those years to the present studies concerning this process have evolved and addressed the phenomena occurring in soils, zeolites and in polymeric ion exchangers.

An ion exchanger can be defined as a solid material that is able to absorb positively or negatively charged ions from an electrolyte solution and release an equivalent amount of opposite ions of equal charge sign to the solution. Inorganic ion

exchangers and organic ion exchangers exist. The organic ion exchangers are mostly polymer matrices with functional groups that are part of the monomer or introduced by processes such as doping. The major functional groups found in polymeric matrices are: SO_3^- , COOH , $[\text{N}(\text{CH}_3)_3]$ (type 1), $[\text{N}(\text{CH}_3)_2\text{C}_2\text{H}_4\text{OH}]$ (type 2), NH_2 , $-\text{NH}_2$, $-\text{NRH}_2$, $-\text{NR}_1\text{R}_2$, depending on the final application of the polymer.

Ion exchangers are characterized by their ion exchange capacity (IEC). The ion exchange capacity is measured in meq/g or meq/L, where one equivalent is defined as a mole of charge. For example if the following ion exchange reaction occurs $\text{RSO}_3\text{H} + \text{Na}^+ + \text{H}_2\text{O} \rightarrow (\text{RSO}_3^-)(\text{Na}^+) + \text{H}_3\text{O}^+$, where “R” represents the inert resin and RSO_3H represents the active resin, an equivalent will be equal to one mol of Na^+ . On the other hand if the following reaction occurs $2\text{RSO}_3\text{H} + \text{Mg}^{2+} + 2\text{H}_2\text{O} \rightarrow 2(\text{RSO}_3^-)(\text{Mg}^{2+}) + 2\text{H}_3\text{O}^+$, an equivalent will be equal to $\frac{1}{2}$ mol of Mg^{2+} . In summary 1 mole equivalent charge = 1 mole H^+ = 1 mole Na^+ = $\frac{1}{2}$ mole Mg^{2+} , and so on.

However various definitions exist for this property. The definition most used to characterize this property is the total or maximum ion exchange capacity. This capacity is fixed and is determined by the total number of ionic groups on a certain polymer weight or volume. This value is typically measured using elemental analysis.

On the other hand, the useful capacity of the membrane is the one obtained when the membrane has reach equilibrium in a certain amount of time. It depends on the ion exchange rate determined by the experimental conditions or polymer

structure. Any changes to the structure that could lead to a higher useful capacity or a reduction in the time a polymer needs to reach equilibrium would greatly affect the performance of the polymer, such as higher proton conductivity.

F. Proton Conductivity and measurement methods

The most common way to evaluate a proton exchange membrane's performance is its proton conductivity. Proton conductivity is typically measured in S/ cm. Proton conductivity depends on several factors such as: water content, temperature and membrane's structure. Several ways of measuring proton conductivity for membranes have been studied through the years, but the mostly used are the two- probe and four- probe methods by electrochemical impedance spectroscopy.

Impedance is defined as measure of the ability of a circuit to resist the flow of electrical current^[28]. It is used to analyze more complex circuit's behavior that does not comply with the ideal resistor characteristics, for which the resistance term is used. It is measured by applying a potential to an electrochemical cell and measuring the current response through the cell. A small excitation signal is preferred causing the cell response to be pseudo-linear; thus if a sinusoidal potential is applied a phase shifted sinusoid at the same frequency is obtained as a response. Impedance is mathematically expressed as

$$Z = \frac{E}{I} \quad (\text{Eq. 3.4})$$

on which E represents voltage and I represents current. After expressing the voltage and the current as a function of time and applying the Euler relationship a

complex number expression can be obtained for the impedance as a function of the radial frequency as,

$$Z(\omega) = Z_0 (\cos\phi + j\sin\phi) \quad (\text{Eq. 3.5})$$

where Z_0 is the ratio of the amplitude of the applied voltage to the amplitude of the current response and ϕ is the phase shift of the response.

Impedance data is analyzed by adjusting the data to an electrical circuit that represent the components of the electrochemical system. An electrolyte is often represented as a resistance in the circuit. In a bounded area with area “A” and length “L” carrying a uniform current the resistance is defined as

$$R = \rho \frac{L}{A} \quad (\text{Eq. 3.6})$$

where ρ is the electrolyte resistivity. The reciprocal of ρ is more commonly used and is called the conductivity, κ . So conductivity of an electrolyte is represented as

$$\kappa = \frac{L}{RA} \quad (\text{Eq. 3.7})$$

Mathematical representations such as the Bode plot and the Nyquist plot are used to determine the values for every component of a circuit, such as the resistance, in order to obtain complete information of an electrochemical cell.

IV- Materials and Methods

A. Materials

1. Polymers:

Nafion 117 was used as part of this investigation. Nafion is the most commonly used membrane in fuel cell technology. It is a perfluorinated sulfonated membrane as presented in the figure 4.1. The membrane was provided by Aldrich Chemicals and it had a thickness of 0.7 inches. Some of its most relevant properties are its ion exchange capacity of 0.91 meq/g and its ionic conductivity of 0.10 S/cm.

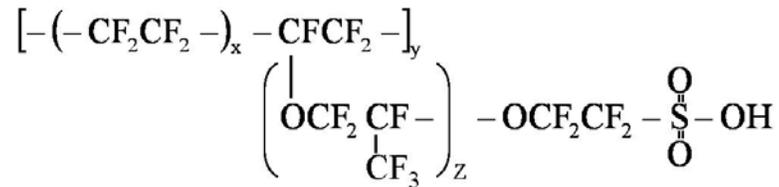


Figure 4.1: Structure of Nafion.

Also poly (styrene-isobutylene-styrene) was used. This block copolymer is classified as a thermoplastic elastomer. It consists of two hard polystyrene end blocks and one soft elastomeric isobutylene mid block as can be seen in figure 4.2. Sulfonated samples of this polymer were processed and characterized. As mentioned earlier the sulfonation level affects the degradation temperature of the polymer. Also the presence of the sulfonic groups is thought to enhance the proton transport in the copolymer.

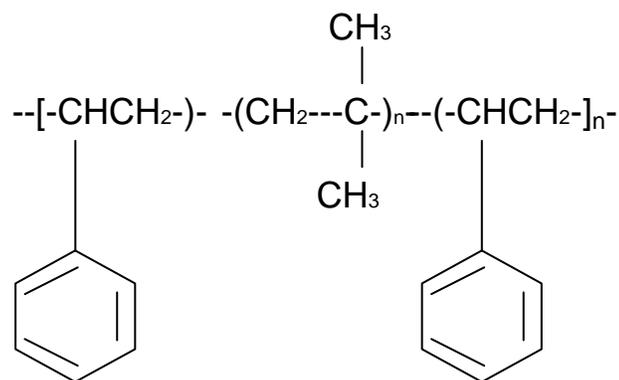


Figure 4.2: Poly (styrene-isobutylene-styrene) Structure

2. Carbon dioxide

The central material of this investigation is the carbon dioxide in its critical state. It has an increasing popularity between researchers due to its environmentally friendly nature and its easily obtained critical conditions among other characteristics. Carbon critical pressure is 72 bar and critical temperature is 31°C. At these conditions the carbon dioxide has liquid-like solvent properties and a gas-like transport properties making it useful for several applications mentioned in earlier chapters.

Although the CO₂ molecule is non polar, its large quadrupole moment helps increase its affinity with some polar molecules. Figure 4.3 shows its phase diagram. A feature found in supercritical CO₂ as well as in other supercritical fluids is that around the critical point relatively small changes in temperature and pressure can produce significant changes in density and solvating capacity.

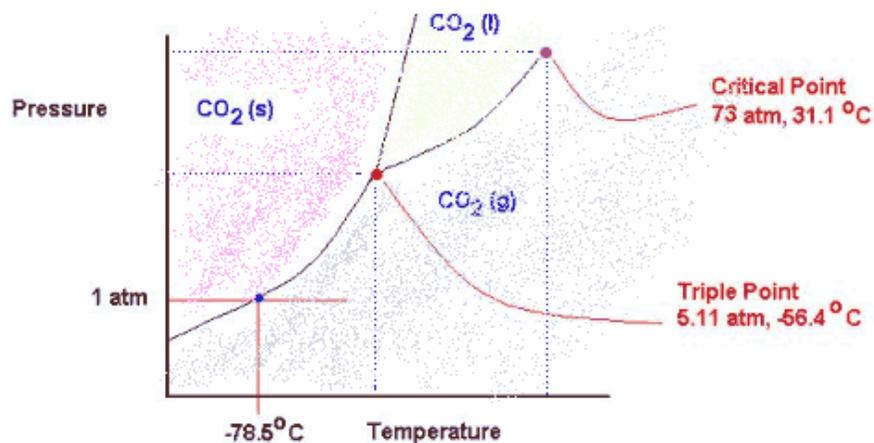


Figure 4.3: Carbon dioxide phase diagram^[29]

3. Co-solvents:

Co-solvents were used in order to enhance the interaction between the supercritical CO₂ and the polymer. Due to the non-polar nature of the carbon dioxide, solvents are usually needed in order to increase its affinity with more polar molecules. Solubility parameters and dielectric constants were used to determine the solvents that could be used during the procedure. Previous work performed in our laboratory processed styrenic block copolymers using CO₂ with the addition of several co-solvents.

These studies showed that the presence of polar co-solvents aided in provoking significant changes in the copolymers' morphology and thermal properties. Recent findings within our research group suggested that solvents with higher dielectric constants favored the interaction between the carbon dioxide and the processed materials. The table 4.1 shows all the

co-solvents utilized along with the values of dielectric constants and solubility parameters.

4. Solutions for Ion Exchange Capacity Determination

As part of the characterization procedures a 2M NaCl solution and a .01 M NaOH solution were utilized. Both solutions were prepared on the laboratory from primary material provided by Fisher Chemical. For the NaOH solution approximately 100 mg of NaOH (Fisher 40g/mol) were weighted and diluted in 250 ml of deionized water using a volumetric flask. The NaCl solution was prepared by dissolving 116.88 g of NaCl (Fisher, 58.44 g/mol) into 1000 ml of deionized water using a volumetric flask

Table 4.1: Solubility parameters and dielectric constant of solvents used

Solvent	Structure	Solubility Parameter (Cal/cm ³) ^{1/2} ^[30,31,32]	Dielectric Constant (ϵ) ^[30,31,32]
Isopropyl Alcohol	(CH ₃) ₂ CH-OH	8.8	20.1
Tetrahydrofuran (THF)	C ₄ H ₈ O	9.1	7.5
Methylene Chloride	CH ₂ Cl ₂	9.7	9.1
Ciclohexanone	C ₆ H ₁₀ O	9.9	18.2
Acetone	C ₃ H ₆ O	9.9	20.7
Acetic Acid	C ₂ H ₃ O-OH	10.1	6.2
Acetonitrile	C ₂ H ₃ N	11.9	36.6
Ethanol	CH ₃ CH ₂ -OH	12.7	24.3
Methanol	CH ₃ -OH	14.5	33.0
Water	H ₂ O	23.4	80.0

B. Methods

1. Supercritical Fluid Processing

The supercritical fluid extractor presented on figure 4.5 was used to provide contact between the polymer and the supercritical CO₂. This equipment enables us to provide contact between the polymer and CO₂ at an established temperature and pressure. In preparation for the processing an ISCO 260D syringe pump was filled with the liquid CO₂. After the pump was full, the carbon dioxide, now as a supercritical fluid (due to temperature and pressure changes), passed thru the extraction unit (ISCO SFX-210) where a cell was packed with the polymer of choice. Some samples were processed using supercritical CO₂ only while other samples were processed after adding 5 drops into the co-solvent of choice ensuring all the sample had contact with the co-solvent. The use of only 5 drops of the co-solvent was determined by previous work performed in the laboratory with the different co-solvents, in order to avoid dissolving the membrane. After passing thru the cell, the supercritical CO₂ was decompressed as it left the system thru a coaxially heated restrictor to overcome the Joule-Thompson effect of cooling upon expansion. The conditions used during the processing were 200 bars and 40°C.



Figure 4.5: Supercritical Fluid extraction unit

2. Density Measurement

A density kit connected to an analytical balanced was used to measure unprocessed and processed polymer sample densities. This technique requires the use of a solvent on which the polymer is insoluble. Hexane was solvent of choice for the measurement, since it does not dissolve or swells the membrane. Table 4.2 shows this solvent solubility parameters and structure.

Table 4.2: Solvent used for density measurement

Solvent	Structure	Solubility Parameter ^[34]
Heptane	$ \begin{array}{ccccccc} & \text{CH}_2 & & \text{CH}_2 & & \text{CH}_2 & \\ & / & & / & & / & \\ \text{CH}_3 & & \text{CH}_2 & & \text{CH}_2 & & \text{CH}_3 \\ & \backslash & & \backslash & & \backslash & \\ & \text{CH}_2 & & \text{CH}_2 & & \text{CH}_2 & \end{array} $	7.0

3. Ion exchange capacity measurements

The processed and weighted membrane samples were submerged for a total of 24 hrs in a 2M NaCl solution since at this time it was understood the membrane already reached equilibrium with the solution. After time completion membrane was removed and remaining NaCl solution was titrated using a .01M NaOH solution. The ion exchange capacity was calculated using the equation:

$$IEC = \frac{(V_{NaOH})(M_{NaOH})}{W_{sample}} \text{ (Eq. 4.1)}$$

4. Proton conductivity

Proton conductivity of each membrane was measured using AC impedance spectroscopy. Measurements were taken between 0.10 kHz and 1MHz using a Solartron AC Impedance system (1260 impedance analyzer, 1287 electrochemical interface, Zplot software). Proton conductivity was measured with a two-electrode cell comprised of 1.22 cm² stainless steel blocking electrodes. All membranes were prehydrated in RO water for at least 24 hrs and then quickly enclosed in a sealable cell to maintain hydration during impedance measurements. The real impedance was determined from the X-intercept of the regression of the imaginary versus real impedance data over a high frequency range (10 kHz–1 MHz).

IV- Results and Discussion

A – Membrane Integrity

Prior to presenting and discussing the results related to the IEC of the membranes it is important to address a concern that was discussed in the first chapters: the physical integrity of the membrane. The work performed by M. Ocasio suggested a cleavage of the external perfluorinated group of the Nafion® membrane after processing with SCF CO₂.^[23]

Measurement of the membranes' density with and without SCF CO₂ processing, including SCF CO₂ processing with the aid of several co-solvents, was performed. Densities were measured in duplicates for each processing condition. Results for Nafion showed no significant changes in the membrane density as can be seen in figure 5.1. Measurement was performed only in Nafion samples, since this was the only membrane that showed structural losses in results obtained by M. Ocasio in her previous work due to CO₂-philic behavior of perfluorinated groups. The significance of these results is that although a cleavage of the external perfluorinated group was observed for SCF CO₂ processing^[23], Nafion re-arranges its morphology, preserving its packing arrangement, and as will be discussed ahead its IEC. In other words, SCF CO₂ processing of Nafion is not detrimental to the physical stability of the membrane, or its chemical ability to transport ions.

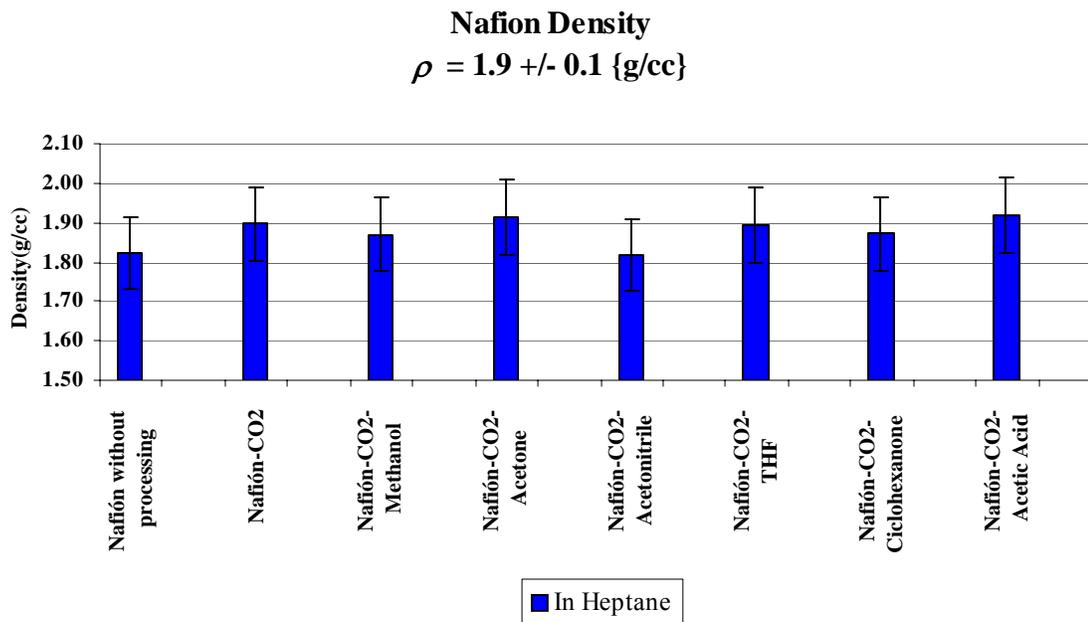


Fig. 5.1 Nafion density before and after processing with supercritical Carbon Dioxide with the aid of co-solvents.

B- Ion Exchange Capacity

Several studies were performed in order to address the membranes' IEC. First it was necessary to determine the conditions necessary to achieve reliable values for the ion exchange process of the membranes. Two conditions were studied which included the samples' weight and the sample immersion time on the NaCl solution. Nafion samples with weights of 20, 30, 40 and 50 mg were used and immersed for times equals to 2, 24 and 120 hrs with the objective of determining equilibrium conditions. Two runs of each combination were performed. Results showed that after a period of 24 hours of immersion time the IEC values reached a steady state as can be seen on figure 4.2.

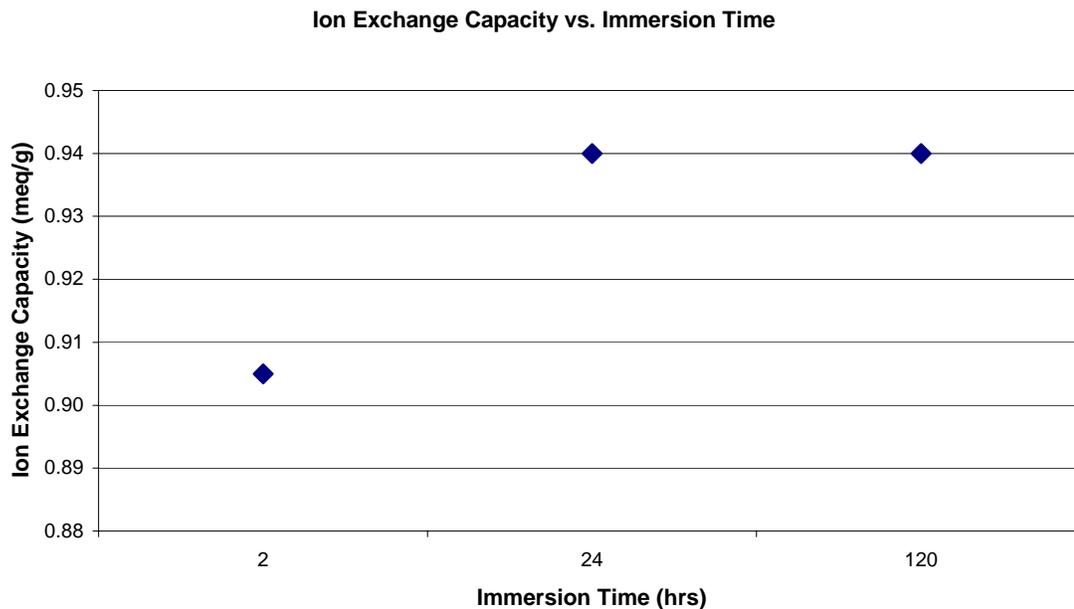


Figure 5.2 Ion exchange capacity behavior vs immersion time on NaCl solution for 50 mg samples.

This behavior was only observed for samples weighting at least 50 mg. At this sample weight, the values for IEC in most of the runs showed a significantly lower standard deviation than the other sample weights, independently of the immersion time as shown in figure 4.3.

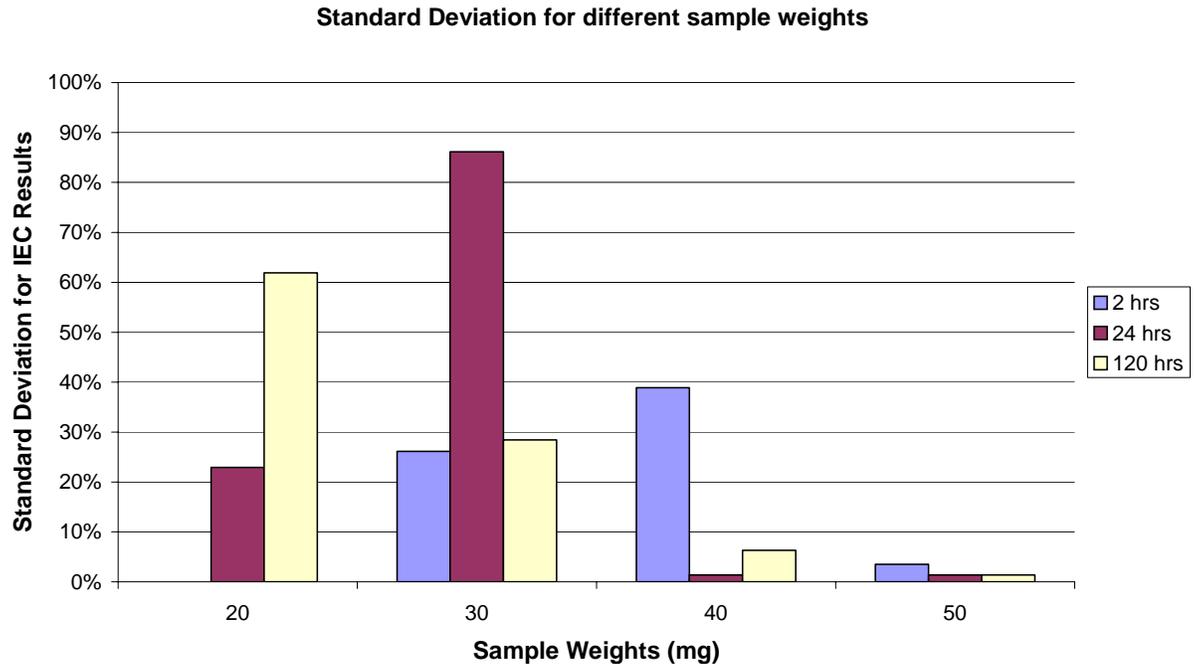


Figure 5.3 Standard deviation for IEC measurements at different sample weights and immersion times.

The minimum 24-hour immersion period could be attributed to the time required for the membrane to fully hydrate, thus aiding in the transport process of the ions until a steady state is reached.

Based on the previous results, several runs were made with Nafion membranes with and without SFC CO₂ and the aid of co-solvents. Results shown in figure 5.4 demonstrate that the IEC of the Nafion membranes was maintained or slightly increased with the aid of SCF CO₂ and some polar co-solvents. The significance of these results can be further validated considering that an experimental error analysis gives only a 0.05% error to the measurements. The most considerable changes on the ion exchange capacities were seen on the samples processed with the

aid of acetic acid, acetonitrile, THF and cyclohexanone. These solvents are highly polar; however, no specific co-solvent parameter (i.e., solubility parameter, dielectric constant, dipolar moment) was found to relate to this behavior. Perhaps the correlation must be done with the SCF modified solution (less than 5% co-solvent used, 95%+ CO₂). The study of solvent strength in SCFs has been carefully studied using spectroscopic techniques ^[38], and the resulting parameters (e.g., polarizability per volume) are a strong function of concentration. Due to the complexity of such study, we proceeded to conclude that the changes were not related to any measured co-solvent property, but perhaps SCF solvent properties such as polarizability per volume.

Comparing the experimentally measured IEC for the un-processed membrane with the theoretical results provided by the membrane's manufacturer one can conclude that treating the membrane with supercritical CO₂ aided with acetic acid increased its ion exchange capacity to a value much higher than the reported by the manufacturer of 1.01 meq/g obtained also by titration. These results should be presented considering that methanol permeability results^[33] show a significant reduction (2-3 orders of magnitude), while the IEC is maintained or slightly increased. One possible explanation for this behavior is that the polarizability per unit volume of CO₂ is very similar to the polarizability per unit volume of perfluorinated groups, therefore these groups are easily solvated by SCF CO₂, especially considering the high diffusivity of the SFC CO₂. The polar co-solvents of unique size and shape easily penetrate the

membranes perhaps aligning the sulfonic groups of the membrane to create easily accessible percolation channels.

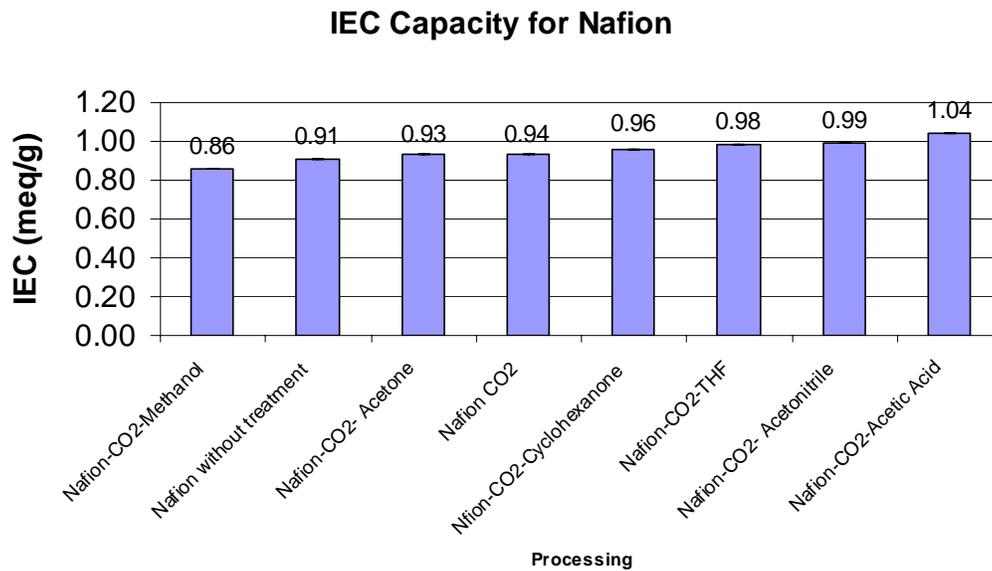


Figure 5.4 Ion exchange capacity results for Nafion samples at different processing conditions.

Calculations made considering the amount of SO_3^- in the Nafion samples gave values for the H^+ to SO_3^{-2} ratios around 1.0 showing that all sulfonic groups are interacting with one H^+ and that all of these protons are being transported out as part of the ion exchange process (Figure 5.5).

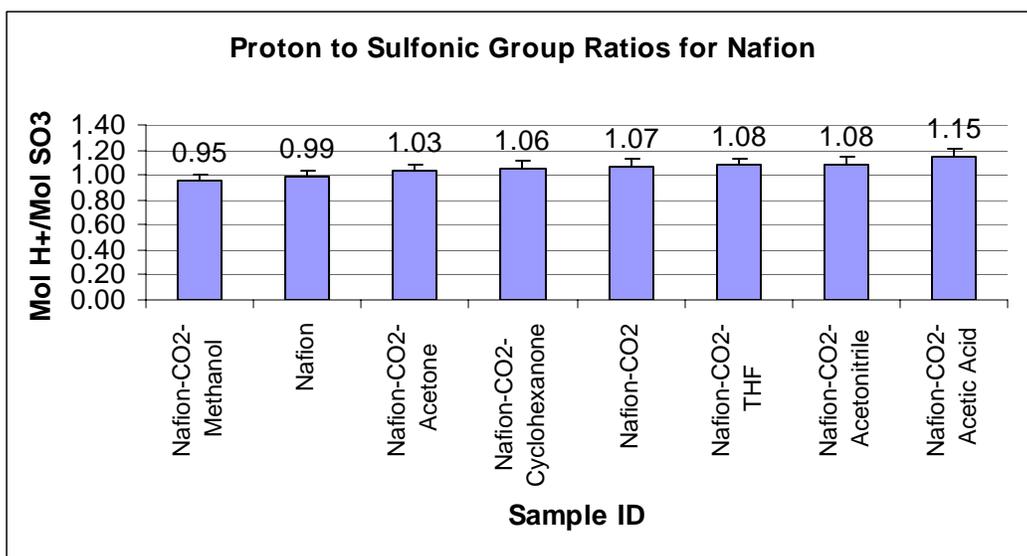


Fig 5.5 Proton to sulfonic group ratios for Nafion samples

Proton conductivity measurements were made to the samples with the most significant IEC results. For all the samples studied, a significant decrease compared to theoretical values given by the manufacturer was observed in the proton conductivity as can be seen on figure 5.6. After an analysis of the results, measurement conditions and previous studies it was concluded that the proton conductivity values were affected by the direction of the SFC processing. All the samples were processed at the supercritical fluid extractor in the direction in the plane to the membrane but the measurements were made normal to the plane of the membranes as represented in figure 5.7.

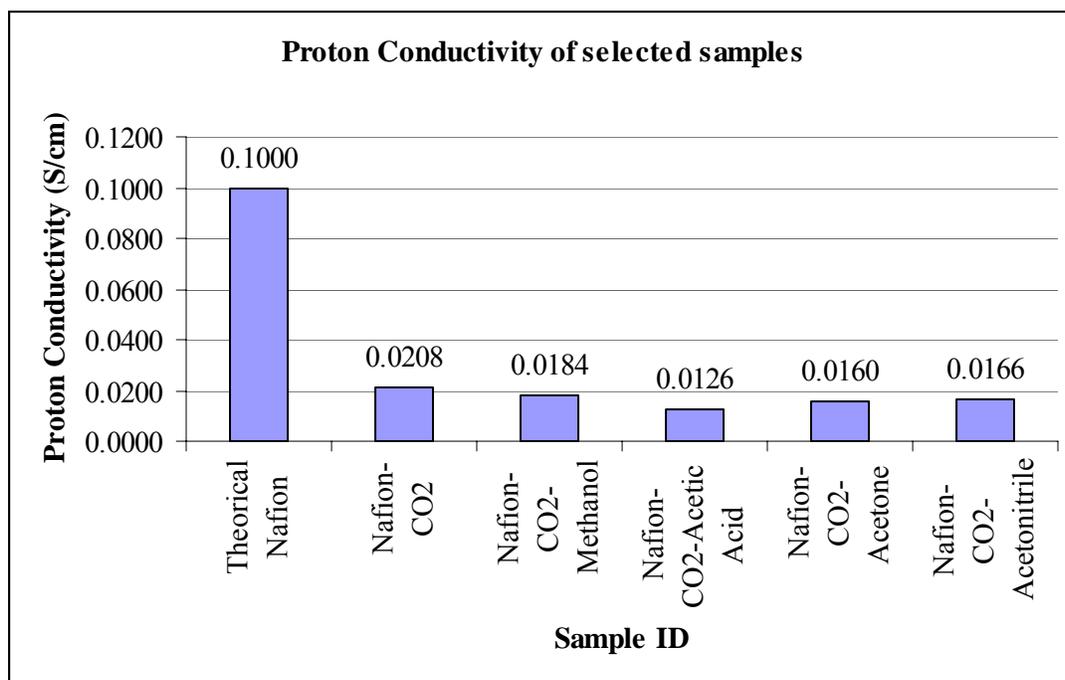


Figure 5.6 Proton conductivity values for Nafion samples treated with CO₂ aided with different co-solvents.

A previous study ^[5] showed a difference of a magnitude of 2.5 times between proton conductivity values obtained by measurements made normal and in the direction of the plane of the membrane. This characteristic has been used to study the anisotropy phenomena usually found in these types of membranes.

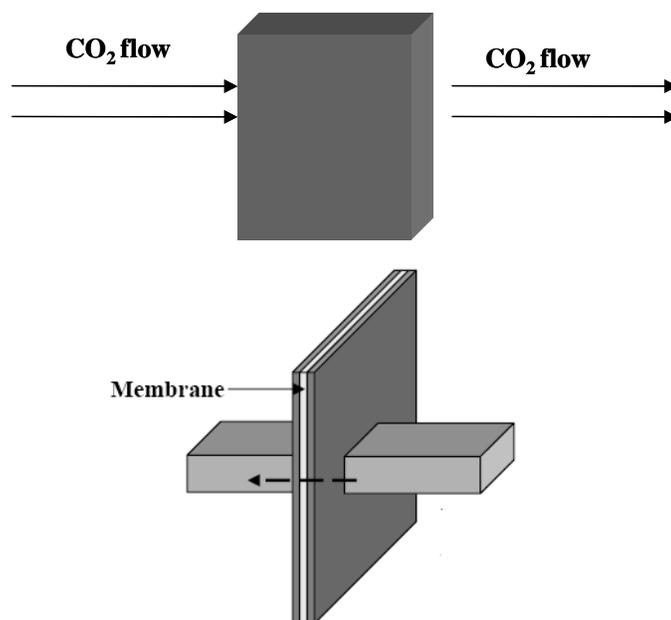


Figure 5.7 Upper: Schematic representation of CO₂ flow at supercritical equipment Bottom: Schematic representation of direction of proton conductivity measurements

Ion exchange capacity results for SIBS samples with two sulfonation levels showed no significant differences as seen in figures 5.8 and 5.9. First of all, the values obtained for the untreated sample for both levels were lower than theoretical results, suggesting that not all sulfonic groups were available for ion exchange, perhaps due to blockage by the polyisobutylene segments which usually provide barrier properties. For 97 % sulfonated SIBS samples processed with supercritical fluid gave ion exchange capacity values with no significant difference. The behavior could be attributed to the phase segregation common of the highly sulfonated samples resulting in lamellar structures with polyisobutylene in the external layer, which is not easily penetrated with SCF CO₂ (with and without co-solvents). For 53% sulfonated samples the IEC capacities were greatly reduced compared to the value obtained for the untreated membrane. Is important to mention that a higher error was associated

to the IEC measurements for SIBS since they had less reproducibility. This behavior could be attributed to the membranes being sulfonated in house, making the samples less homogeneous.

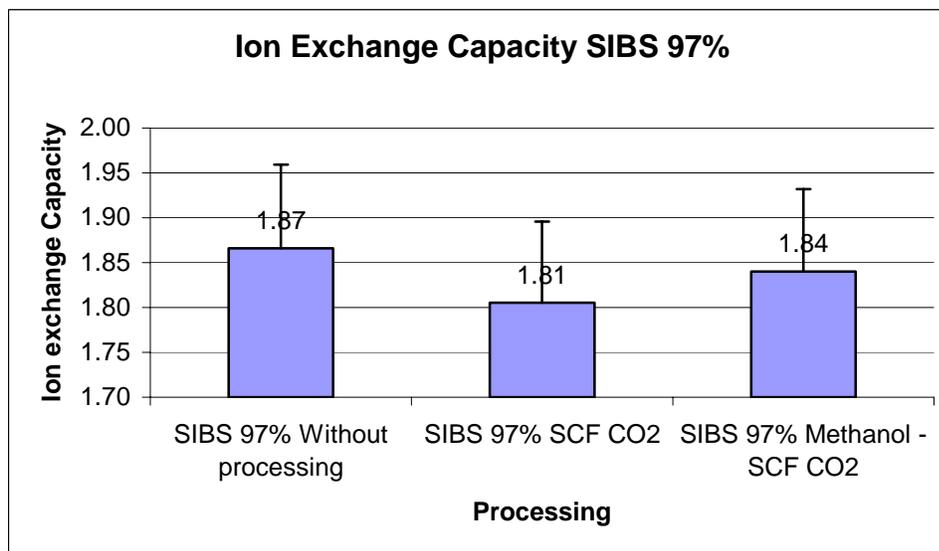


Fig 5.8 Ion exchange capacity results for SIBS samples with 97% sulfonation.

Calculations made considering the amount of SO_3^{-2} in the SIBS samples with 97% sulfonation provided values for the H^+ to SO_3^{-2} ratios in the range of .55 to .72 for treated and untreated samples (Figure 5.11). These results suggest one proton for every two sulfonic groups for SCF processed samples and 1:1.5 for the unprocessed membrane, thus suggesting that SCF processing is ineffective improving IEC for highly sulfonated SIBS.

For SIBS 53% sulfonated treated with SFC CO_2 with and without aid of co-solvent a significant decrease was observed in the H^+ to SO_3^{-2} ratios, obtaining values in the .20 to .25 range (from 1:4 to 1:5 proton:sulfonic group). This difference could imply a reduced proton transport after SFC CO_2 treatment due to the polymer

adopting a structure on which the SO_3^{-2} groups are more phase segregated (recall that unprocessed samples showed a ratio of 1:2). This is possible since the reduced sulfonation level has a different morphology (cylindrical as observed from SAXS data), which allows the SCF CO_2 to enter the membrane and further segregate the sulfonic groups.

Since IEC measurements for SIBS membranes gave no significant results it was decided not to perform proton conductivity measurements for this membrane.

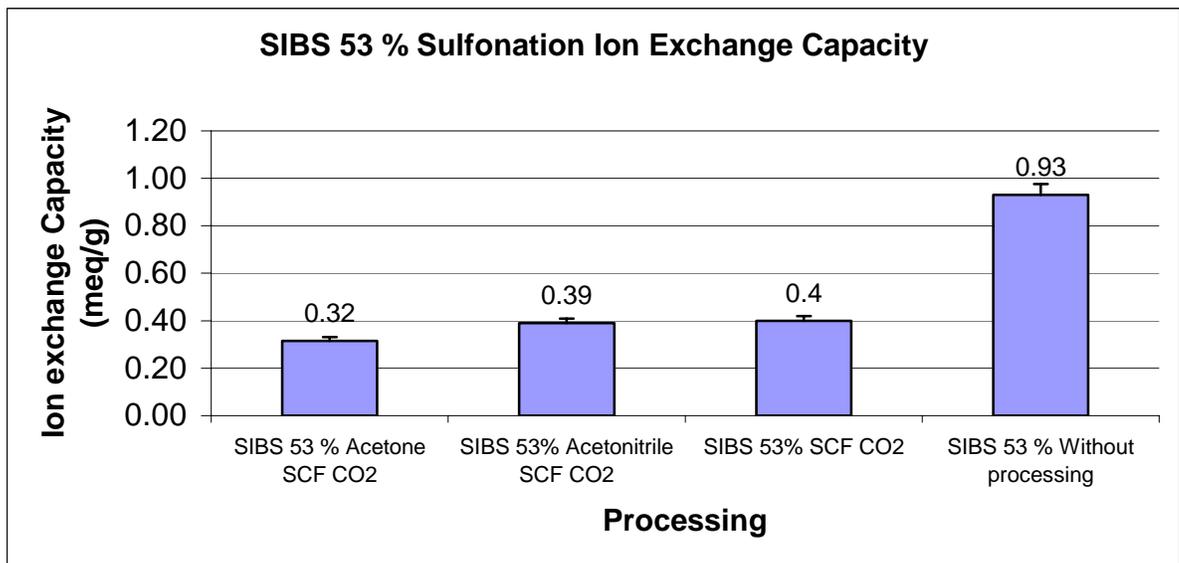


Fig 5.9 Ion exchange capacity results for SIBS samples with 53% sulfonation.

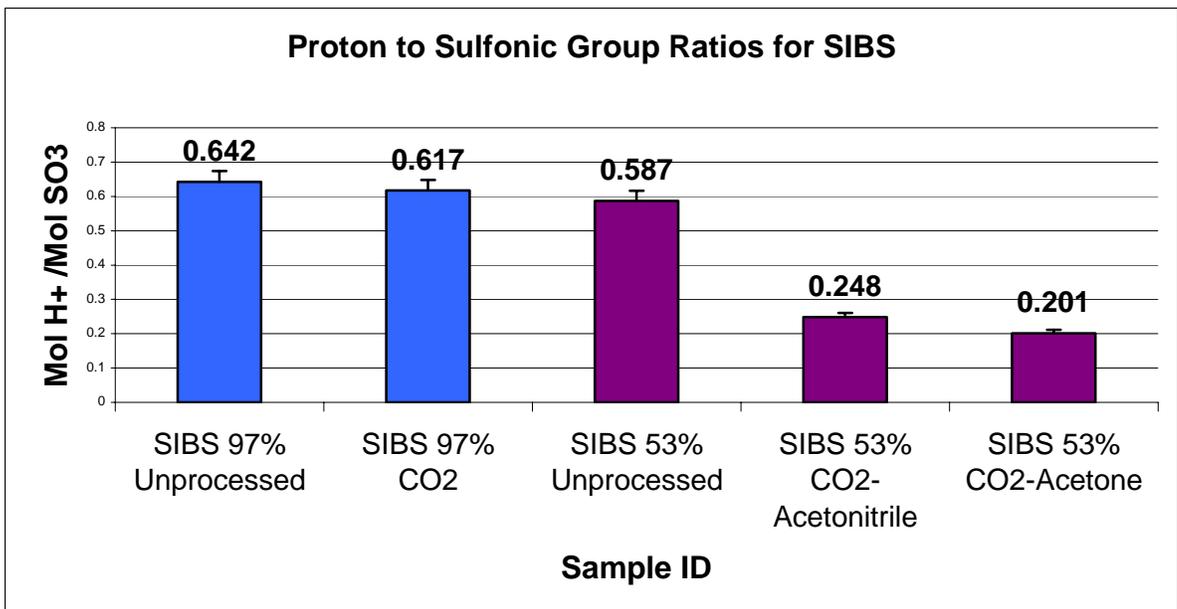


Fig 5.10 Proton to sulfonic group ratios for SIBS samples at 97% and 53% sulfonation

VI- Conclusions and Recommendations

Based on the results presented on the previous chapter we can conclude that processing the Nafion membranes using supercritical CO₂ preserves its density or packing arrangement, while maintaining or slightly increasing the IEC with the use of various polar modifiers. This is significant, since SCF processing also reduces the methanol permeability making SCF processing a very valuable alternative for processing Nafion for direct methanol fuel cells or other specialty separation applications.

It should be pointed out that no specific solvent parameter was not found to correlate the IEC results obtained. However, in SCF's a recent development for describing solvent properties is through the use of solvatochromic parameters (*e.g.*, α , β , π^*). This allows for a more indepth study of SCF solvent properties, which are complicated since they often require a spectroscopic transition at high pressures and tends to be very sensitive to co-solvent concentration.

On the other hand, no significant results are obtained when SIBS membranes were processed with supercritical CO₂ with or without co-solvents mainly due to structure restrictions (*e.g.*, difficulty of CO₂ to penetrate polyisobutylene domains). On the contrary, SIBS membranes seemed to be more phase-segregated (from the reduction in the proton to sulfonic acid group), especially for the lower sulfonation level. One should expect this condition to get worse, especially bellow the percolation threshold of 31% for SIBS ^[5].

Changes in proton conductivity were not fully evaluated, since processing direction was found to be extremely important for this property. However, from the parallel processing and perpendicular measurements one could conclude that SCF CO₂ was successful penetrating the membrane and creating new channels that disrupted the perpendicular channels where proton conductivity was normally measured. Therefore, it proved that SCF CO₂ is indeed an excellent solvent for Nafion membranes; however, processing direction has to be carefully considered for optimum results.

Based on the observations from this investigation we recommend to study other perfluorinated sulfonated membranes with the highly polar SCFs, to see whether one can have very selective membranes that could provide high IEC (and therefore high proton conductivity) and low methanol permeability.

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