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Ageing Effect of Proton Exchange Membrane Nafion 117 in Different Solutions

S. Seema[1], T. Thangesh[2], R. Anuradha[3], T.R. Rajasekaran[1,2], S. Nagarajan[4], V. Sabarinathan[1,2*]

[1]Department of Renewable Energy Science, Manonmaniam Sundaranar University, Tirunelveli-627012, Tamil Nadu, India
[2] Department of Physics, Manonmaniam Sundaranar University, Tirunelveli-627012,Tamil nadu, India
[3] Department of Chemistry, Annai Hajira Women's College, Melapalayam, Tirunelveli 627 005, Tamil nadu, India
[4] Department of Chemistry, Manonmaniam Sundaranar University, Tirunelveli-627012, Tamil Nadu, India
* **Corresponding Author Email**: sabarinathan.msu@gmail.com

Abstract

Membrane durability is one of the critical issues in the development of proton exchange membrane fuel cells (PEMFC). In this paper, the authors studied effects of aging on various solvents such as ethanol, isopropyl alcohol (IPA) and distilled water (DM) based on its proton conductivity using electrochemical impedance spectroscopy (EIS). Further, the swelling nature is reported along with its structural properties and transport mechanism. A facile non-conducting (medium) homemade setup under an aqueous environment used to study conductivity. Nafion 117 membrane is being a perfluoro sulfonated ionomer to be very sensitive under aging treatment when it was stored for very long period at 36 ºC (humid atmospheres). Moreover, the aging process inducing the condensation of sulfonic groups to form anhydrides as interpreted. Highest ionic conductivity of 0.069 x 10-1 S cm-1 was observed on first day in DM water which is higher than in that of ethanol and IPA solvents. This conductivity value in water occurs with respect to its pH level and seems to be strong evidence for better performance in PEM fuel cells.

Keywords: Nafion membrane, transport mechanism, Aging, water uptake, conductivity, structure.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs), hold great promise as sustainable energy sources, especially for its usage in electric cars and stationary equipment's[1]. Poly (Perflurosulfonic acid) membranes, like Nafion, are frequently used as the polymer electrolyte in fuel cells. Nafion is composed of a hydrophobic polytetrafluoroethylene (PTFE) backbone and pendant chains that are perfluorinated and terminated by hydrophilic sulfonic groups [2, 3].The mechanism underlying water sorption, which permits proton dissociation and consequently ionic conductivity, is hydration of these hydrophilic end groups. Because of the ionomer Nafion's dual nature, there is a nanophase separation in which the low dielectric polymer phase separates the ionic groups into distinct domains [4-6]. Nafion is alluring because of its high proton conductivity along with its combined mechanical, chemical, and thermal stabilities. Over the past ten years, there has been a significant reduction in membrane thickness to improve fuel cell performance, but at the expense of membrane stability [7, 8]. The durability of fuel cell components, particularly membrane failure, has been the subject of numerous studies. The estimation of the membrane lifetime in stationary fuel cell conditions has been done through in situ aging tests. The lifetime varies greatly depending on the operating conditions (temperature, power output, humidity of the gas, etc.) range from a few hundred to over 20,000 hours [7]. It is well known that the cycling conditions causing cycles of dehydration and swelling can promote serious physical harm that eventually results in membrane failure. The examination of the water generated by the cell also demonstrated the presence of sulfate and fluoride ions, indicating a considerable chemical breakdown of the membrane. This chemical degradation is ascribed to the in-situ generation of radicals from hydrogen peroxide, which is expected from the electrochemical reaction in a small scale. These durability studies are still phenomenological because it is only possible to describe the effects on the properties of the membranes, such as gas crossover, loss of conductivity, and embrittlement. In fact, a various degradation factors work in cluster, including the deterioration of other parts like the bipolar plates, seals, and electrodes [9-11]. Furthermore, it has been demonstrated that the performance loss can be somewhat recovered, indicating the possibility of a combination of various degradation mechanisms. Consequently, the authors are unable to propose a comprehensive degradation mechanism that would account for the aging-related effects on the properties[12]. These factors suggested that ex situ aging studies ought to be carried out in order to pinpoint the primary determinants of membrane degradation and ultimately to gain some insights into the mechanisms involved. In fuel cell conditions, Nafion membrane is generally regarded as thermally stable (typical operating conditions are between 50 and 80ºC in the presence of humidity). Consequently, ex situ aging of Nafion is carried out in the presence of H_2O_2, as this is thought to be the primary contributing factor to the chemical degradation of Nafion[13]. Frequently, cycles of swelling and dehydration are applied to the membranes, either with or without mechanical constraints, in order to assess the physical stability of the membranes [14]. As the field of study on proton exchange membrane fuel cells (PEMFCs) are growing as a sustainable energy source. Before its widespread commercialization, a number of issues must be resolved. The durability of membrane is one important factor in PEMFC development. Ex situ tests are typically carried out in the presence of H_2O_2 in order to comprehend the behaviour of the membrane while it is being used and, consequently, to clarify the aging mechanism. It is widely acknowledged that a radical attack that causes polymer chain scissions, which in turn causes the loss of mechanical properties and causes membrane failure, it’s the primary cause of chemical degradation during fuel cell operation. More recently, research has demonstrated that Nafion membranes exposed to high humidity and temperatures (80°C) for extended period of time are susceptible to hygrothermal aging, which dramatically alters the membrane's mechanical, ionic conductivity, ion-exchange, and other properties. Nafion is frequently used as a solid electrolyte in fuel cells, electrolysis cells, batteries, and other electrochemical devices due to its exceptional chemical stability and perfluorinated backbone [3]. When Nafion's sulfonic acid groups combine with water, they create an ionic cluster because they are highly flexible and hydrophilic. One significant element influencing the characteristics of Nafion membrane is its water content.

Water molecules interact with the ionic groups in the cluster to cause swelling of the membranes when it is introduced into Nafion membranes [15]. Nafion membranes have also been shown to swell more in a variety of organic solvents than in water. Because the sulfonic acid groups in alcohol solvents have a stronger acid strength than those in other solvents, alcoholic solvents like methanol, ethanol, and isopropanol have a particularly strong affinity for Nafion [15, 16]. Moreover, the kind of counterion shows a clear impact on the Nafion membrane's swelling. It has been observed that the ionic interaction between the sulfonate group and counterions increases with increasing atomic radius of the counterions, resulting in a decrease in the degree of swelling [17]. Due to its combination of high ionic conductivity and high thermal, chemical, and mechanical stabilities, it is used as the electrolyte in proton exchange membrane fuel cells (PEMFCs). Direct alcohol fuel cells (DAFCs), which are based on PEMFCs, use alcohol directly in a basic fuel cell design instead of reforming it into hydrogen gas. Alcohol that has been dissolved in water is used to feed the anodic compartment in DAFC. The mixture's alcohol component is meant to undergo oxidation at the anode and water component in order to hydrate Nafion and take part in the anode reaction. Alcohols do, however, cross the membrane from the anode to the cathode, changing the swelling conditions of the Nafion, although very few ionic conductivity measurements were performed in these conditions[18]. Numerous groups have studied the proton conductivity of Nafion in various aqueous environments and conditions. Slade[19] along with others compiled the data from the literature into a recent paper. As far as we are aware, very few researches have looked into Nafion's conductivity in non-aqueous solvents. Doyle[20] along with others determined Nafion's ionic conductivity in a variety of organic solvents and solvent mixtures. They found that the solvent viscosity, molar volume, donor characteristics, and the solvent uptake by the membrane are the key variables influencing the ionic conductivity in membranes swollen by polar non aqueous solvents[21]. In this paper, we have investigated the effects of Nafion in different solvents – Ethanol (EtOH), Isopropyl alcohol (IPA) and Distilled water (DM) on its conductivity measurements by Electrochemical Impedance Spectroscopy (EIS). Also, Nafion’s density, solubility and swelling changes are calculated using its general formula and reported. Conductivity measurements are listed with respect to its pH values.

2. Materials & Methods

Nafion117 perfluorinated membrane (DuPont) were used with an equivalent weight of 1100 g/mol and thickness of 178 μm. Alcoholic solvents of ethanol and isopropyl alcohol (Merck) and Demineralized water (DM) were used as ageing solvents. Initially, Nafion-117 membranes were cut in to several pieces with the size of 1x1 cm^2 and dried in an oven at 60^0C. Dried membranes were cleaned/pretreatment by sonicating with 0.5 M H_2SO_4 for 1 h, then it was boiled in deionized water for 1h at 80^0C, rinsed thoroughly with distilled water, and then dried in the oven. After dried the 1x1 cm^2 membranes were immersed in different solvents such as water, IPA, and ethanol for 120 days. Conductivity measurements were performed for all the cut-membranes with same immersion period for different solvents. The impedance test cell consists of a non-conducting (glass) medium as its bottom, holding the membrane with the solvent thereby maintaining its humidity as in Fig.1. The probes were directly dipped over the membrane and measurements were taken under ambient humidity and room temperature; all the measurements were performed in the frequency range between 100 mHz to 7 MHz using

Biologic's VSP-300 multichannel potentiostat. Density of wet Nafion117 membrane were determined using the hydrostatic weighing method. The sample is weighted in order to assume its mass, m. Initially, the weight is recorded by suspending and immersing the sample in a petri dish containing water to be as W_0. The Nafion sample is again rewetted and suspended in water without any distraction caused by the walls of the petri dish. Now, a new weight, W was recorded. Using the formula (1), the density of the Nafion membrane sample d_N is calculated [22, 23],

$$d_N = \frac{m}{(W - W_0)/\, d_w} + d_A \;\; .... \;\; (1)$$

Where; d_W and d_A are the density of water (0.9982 g/cm^3) and air (0.00129 g/cm^3) respectively at room temperature.

$$\text{Solubility (\%)} = \text{Initial weight / final weight} * 100 \;\ldots.\; (2)$$

The solubility was calculated from the ratio of the final weight divided by the initial weight of the Nafion sample, multiplied by 100.The solubility percentage of Nafion samples was calculated by Martin and Moore[24].

$$\text{Solvent uptake} = (W_w - W_d) / W_d * 100 \;\ldots.\; (3)$$

Solvent uptake is determined with the weights of dried and swollen Nafion membranes from the formula[25, 26].Where, W_w and W_d are the weights of the swollen and dried membranes. Nafion membranes were measured when dried and taken out from the immersion. The thickness of the Nafion samples is calculated using a digital screw gauge. The Nafion membrane has been immersed in three different solvents to continuously measure its conductivity under regular intervals of over 120 days.

The ionic conductivity (σ) of membranes was calculated using the well-known formula [26, 27]

$$\boldsymbol{\sigma} = \boldsymbol{l}/\boldsymbol{RS} \;\; .... \;\; (4)$$

Where; l = thickness, R= resistance, and S = sample area.

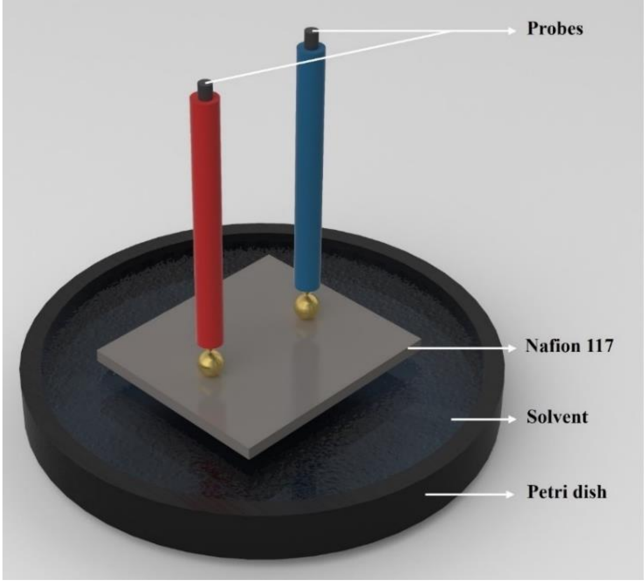

Fig 1: Schematic representation of the experimental setup for testing the Nafion 117 membrane.

3. Result and Discussion

Ageing effect on physical and chemical properties of samples submerged in various solvents are arranged from the least to greatest in table1. DM < EtOH < IPA is the density trend observed from Fig 4. IPA taking the lead compared to other solvents because of its ability to breakdown the nafion's polymer chains. The vacancy in the polymer chain can accommodate more solvent within its structure reflected by the water uptake of IPA in tandem with its density. Likewise, EtOH and DM solvents have a weaker tendency to breakdown the PSFA polymer chain compared to IPA confirmed by their density and water uptake results. The density of DM 1.4 g/cm^3 is comparable to the humidified films in water reported as 2 g/cm^3 by Striebel et al and colleagues [28]. Water uptake have a direct influence on physical properties of the membrane as DM (2.202mm) < EtOH (0.263mm) < IPA (0.280mm) shows thickness of the membrane increases with respect to water uptake shown in Fig 4. High water uptake causes the formation of water clusters in the PFSA polymer chain mostly hydronium ions along with solvents are present within those clusters. Proximity of the water cluster varies with the solvent. Alcoholic solvents are susceptible to have amphiphilic interaction (alkyl groups present in alcohols tend to interact with the hydrophobic regions and polar hydroxyl group interacts with hydrophilic region) with the polymer. Whereas, solvents like water have interaction with hydrophilic $^-SO_3H$ groups short chains alone. This disparity causes plenty of water cluster formation in organic solvents compared to water. These elemental water clusters shown in Fig 3(b) have a huge impact on formation of water channels shown in Fig 3(a) within the polymer membrane. PFSA membrane soaked in alcohol solvents have a complex water channel runs through both hydrophobic and hydrophilic region compared to the channels on water soaked PFSA membrane travels only through the hydrophilic region. A schematic representation of hydronium ions interaction with sulfonated polymer chain is shown in Fig 6. Initially, IPA and ethanol molecules bombard the hydrophilic domains shaded as blue during the swelling stage. However, as swelling progresses, they create new channels towards the hydrophobic domains shaded as red, impeding water flow and, consequently, proton transfer, leading to decreased conductivity. Water, on the other hand, exhibits lesser swelling changes compared to IPA and ethanol, suggesting its resistance to hydrophobic domains as water molecules predominantly travel between hydrophilic domains [16, 29-31]. Proton conductivity stands as the paramount property of Nafion membrane; hence, impedance measurements were measured for conductivity studies aimed at elucidating the aging properties of various solvents. Nafion aged in various solvents for 120 days underwent impedance measurements, resulting in a Nyquist plot depicting the relationship between the real part (Z') and imaginary part (Z'') of impedance. Figure 2 illustrates the Nyquist plot of Nafion117 membranes immersed in water (DM), ethanol (EtOH) and isopropyl alcohol (IPA) measured at 10 regular intervals over a continuous period of 120 days. Electrochemical impedance data is measured between the frequency window of 100 mHz to 7 MHz for all three samples throughout the 120 days. A modified Randle's circuit includes a solution resistance R_S, a double layer capacitor C, the charge transfer resistance R_{ct} and a Warburg element W, which contains information on the diffusion coefficient of the species. All the EIS data were fitted using the same modified Randle's circuit. Conductivity of the membrane calculated using equation 4 for 120 days were listed in table 2. A plot between conductivity and ageing period was shown in fig 3. Nafion 117 membrane soaked on water provides the highest conductivity of about 6.9×10^{-3} S/cm on the 1st day of its aging period. Conductivity of IPA (0.95×10^{-3}S/cm) < EtOH (0.48×10^{-3}S/cm) < DM (6.9×10^{-3} S/cm) on pilot day. Based on pH value on pilot day we can interpret the hydronium ions in the solvent sucked up into the membrane and trapped into the water clusters formed within the membrane as shown in fig 3(b) which results in the highest conductivity we achieved. As days progressed clusters became weak and gradually releases the trapped hydronium ions along with the weakly bonded sulfonate group into the solvent. H^+ ions hopping through the hydrophilic network of the PFSA polymer was impeded by rebound of hydronium ions along with the sulfonate group into the solvent causes damage to water channels in the hydrophilic region of the membrane which hinders the proton transfer mechanism. Sulfonate functional groups are the only hydrophilic short chain, which transfers the hydronium ions through the polymer chain. Loss of those sulfonated short chains have a negative impact in conductivity of the membrane as reflected in table 1. For every 30 - 40 days interval there is a huge slide of 10^{-1} S/cm on conductivity. At the end of ageing period all samples conductivity were in the order of 10^{-6} S/cm shows the huge loss of conductivity shown in Fig 3.

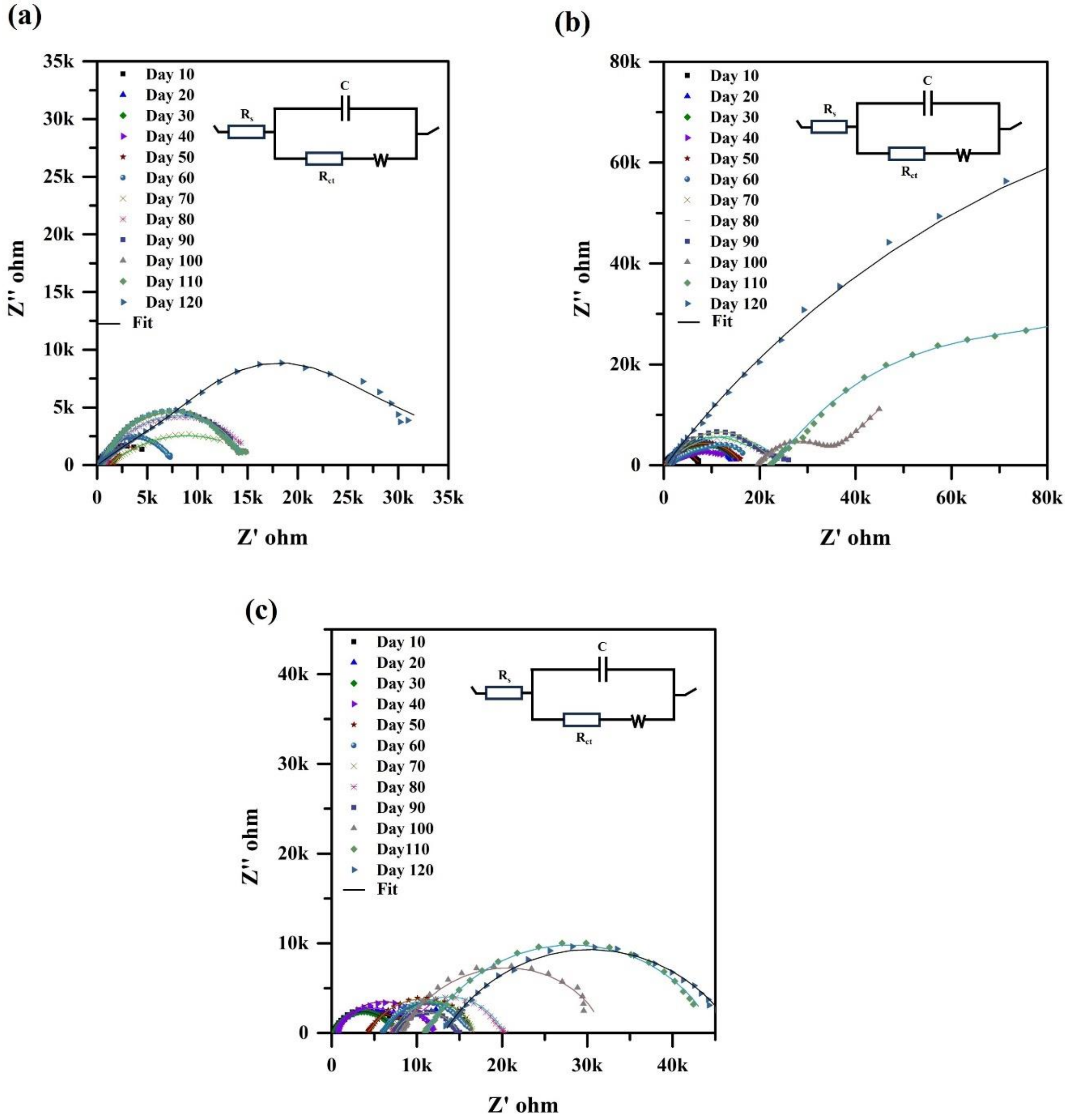

Fig 2: Nyquist plots of (a) Demineralised water (DM), (b) Isopropanol (IPA) and (c)Ethanol (EtOH).

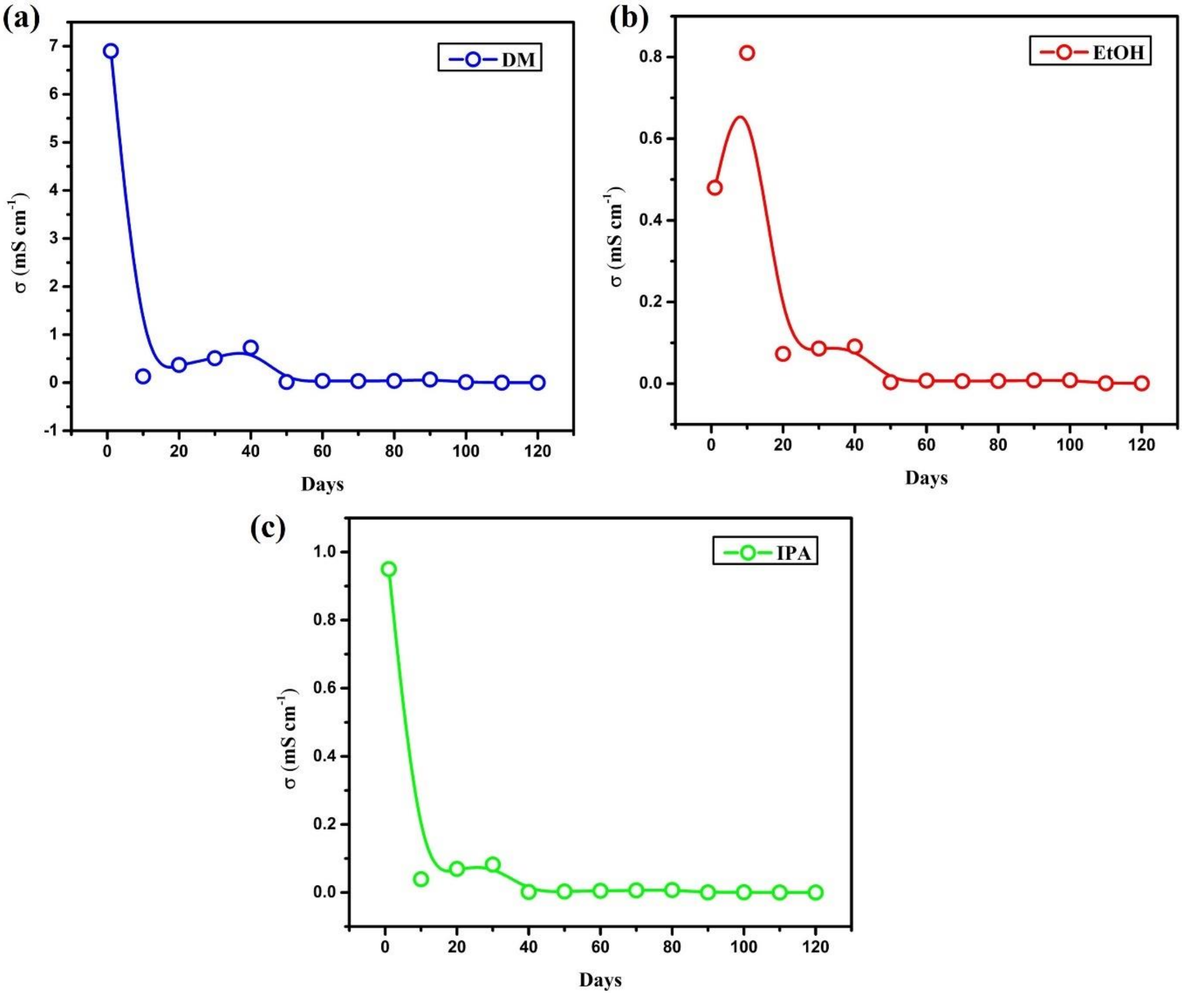

Fig 3: Time-dependent ionic conductivity (σ) of Nafion 117 membrane immersed in different solvents over 120 days: (a) Demineralised water (DM), (b) Ethanol (EtOH), and (c) Isopropanol (IPA).

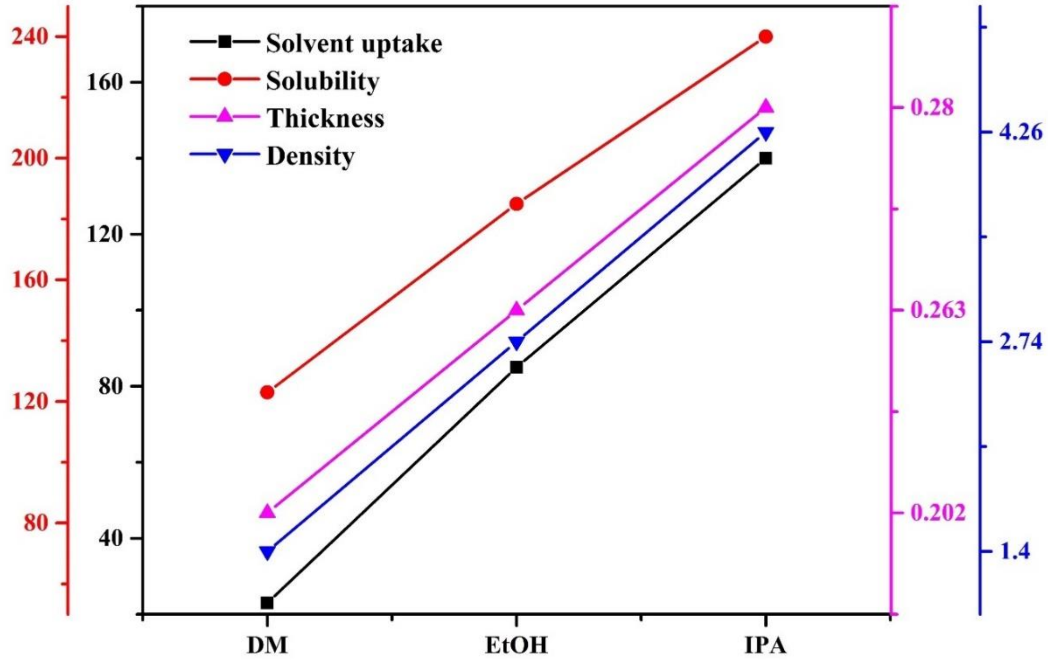

Fig 4: Comparative analysis of solvent uptake, solubility, thickness, and density of a polymer in three different solvents: Demineralized water (DM), Ethanol (EtOH), and Isopropanol (IPA).

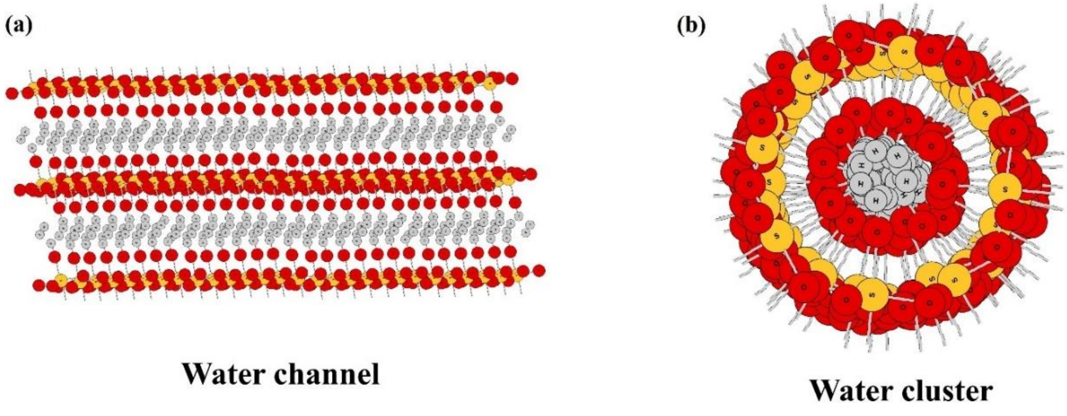

Fig 5: (a) Water channel of Nafion 117 membrane formed by elemental water cluster (b) Water cluster of Nafion membrane

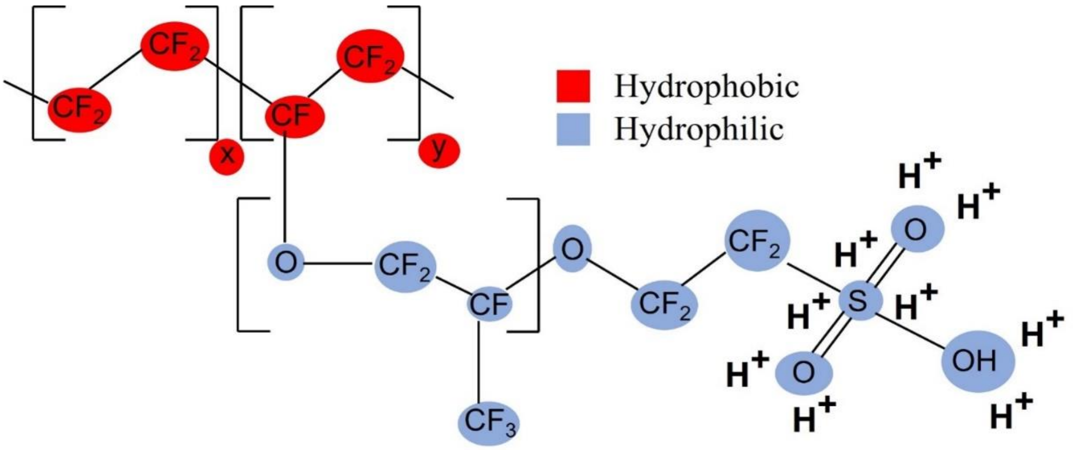

Fig 6: Schematic representation of the molecular structure of Nafion 117 copolymer.

Table 1: Physical properties of Nafion 117 membranes after 90 days of aging

Solvent	**Density (g/cm^3)**	**Calculated solubility (wt. %)**	**Solvent uptake (%)**	**Thickness (mm)**
DM	1.4	123	23	0.202
EtOH	2.72	185	85	0.263
IPA	4.26	240	140	0.280

*Dry Nafion 117 Density - 1.98 g/cm^3 *Dry Nafion 117 Thickness - 178 μm

Table 2: Time-dependent ionic conductivity (σ) of Nafion 117 membrane immersed in different solvents over 120 days

Days	**EtOH (Scm^{-1})**	**IPA (Scm^{-1})**	**DM (Scm^{-1})**
1	0.48×10^{-3}	0.95×10^{-3}	0.69×10^{-2}
10	0.81×10^{-3}	0.39×10^{-4}	0.13×10^{-3}
20	0.73×10^{-4}	0.69×10^{-4}	0.37×10^{-3}
30	0.86×10^{-4}	0.82×10^{-4}	0.51×10^{-3}
40	0.91×10^{-4}	0.15×10^{-5}	0.73×10^{-3}
50	0.34×10^{-5}	0.29×10^{-5}	0.14×10^{-4}
60	0.74×10^{-5}	0.48×10^{-5}	0.38×10^{-4}
70	0.61×10^{-5}	0.61×10^{-5}	0.34×10^{-4}

80	0.64 x 10^{-5}	0.73 x 10^{-5}	0.37 x 10^{-4}
90	0.78 x 10^{-5}	0.36 x 10^{-6}	0.66 x 10^{-4}
100	0.81 x 10^{-5}	0.67 x 10^{-6}	0.98 x 10^{-5}
110	0.72 x 10^{-6}	0.54 x 10^{-7}	0.35 x 10^{-6}
120	0.84 x 10^{-6}	0.79 x 10^{-7}	0.86 x 10^{-6}

4. Conclusion

The study examined the effects of aging on the physical and chemical properties of Nafion 117 membranes when submerged in different solvents. The findings indicate that the density trend of the membranes is DM < EtOH < IPA, with isopropyl alcohol (IPA) demonstrating the highest density due to its ability to break down the Nafion polymer chains more effectively. This breakdown increases water uptake and membrane thickness, particularly for IPA, followed by ethanol (EtOH), and then demineralised water (DM). The interaction between the solvents and the polymer chains influences water cluster formation, affecting the water channels and, consequently, proton conductivity. Impedance measurements over 120 days revealed that the initial ionic conductivity of membranes soaked in DM was the highest, followed by those in IPA and EtOH. However, the conductivity of all membranes decreased significantly over time, with final values dropping to 10^{-6} S/cm. This decline is attributed to the weakening and release of sulfonate groups and hydronium ions from water clusters, which hinders ion transfer. Ultimately, the study highlights the substantial impact of solvent type and aging on the structural and functional integrity of Nafion membranes, with IPA causing the most pronounced changes due to its interaction with both hydrophobic and hydrophilic regions of the polymer. Whereas DM causes the least structural and functional change and maintains a useable conductivity before completely saturates compared to the other alcohol solvents. Minimal sulfonate short chain breakage of membranes in DM is the major reason for a sustained conductivity whereas alcohol-based solvents deteriorate the sulfonated chains rapidly causes them to exhibits a lesser ionic conductivity for more than 100 days. This study concludes the Nafion 117 is prone to organic solvents saturates rapidly whereas it can retain a desirable ionic conductivity on water-based solvents.

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