



Article Enhancing Water Retention, Transport, and Conductivity Performance in Fuel Cell Applications: Nafion-Based Nanocomposite Membranes with Organomodified Graphene Oxide Nanoplatelets

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Abstract: The synergistic combination of Nafion and sulfonated graphene oxide (GOsulf) in nanocomposite membranes emerged as a promising strategy for advancing proton exchange membrane fuel cell (PEMFC) technology. In the pursuit of elucidating the effect of GOsulf introduction on transport properties and electrochemical performance of Nafion, this work provides a systematic study combining swelling tests, water release tests, ¹H NMR characterization, and Electrochemical Impedance Spectroscopy (EIS) investigation. The incorporation of organomodified GO nanolayers alters the distribution of water molecules within the hydrophilic domains of Nafion and produces a considerable increase in the "bound-water" fraction. This increases its water retention capability while ensuring very high diffusivity even under high temperatures, i.e., 1.5×10^{-5} cm² s⁻¹ at 130 °C. These peculiar features enable Naf-GOsulf to successfully operate under a dehydrating environment, yielding a proton conductivity of 44.9 mS cm⁻¹ at 30% RH.



1. Introduction

With every passing year, the need for countermeasures to mitigate heavy dependence on fossil fuels (coal, natural gas, and oil), which are the main contributors to environmental pollution and climate change, is increasing [1]. Amongst different renewable energy strategies (solar, wind, and hydro), fuel cells are being considered an attractive energy conversion approach that has minimum pollutants emissions, high energy efficiency, and applicable to both vehicular and stationary usage [2–4]. Different types of fuel cell technologies have been introduced in the energy market, while some are in the research and development phase. Proton exchange membrane fuel cells (PEMFCs) have emerged as next-generation power sources due to their higher power densities, higher efficiencies, and effortless scaling up [5–7]. Nowadays, the PEM fuel cell is a commercially available technology and has been applied in the transportation sector by Toyota (Toyota Mirai 2017), Honda (Honda Clarity), and Hyundai (Hyundai Tucson FCV) [8].

Among different components, the proton exchange membrane represents the key core of the device, responsible for the conduction of protons from one electrode to another while restricting electrons and fuel cross-over [9]. Nafion[®], based on perfluoro sulfonic acid (PFSA), is a widely used and commercially available proton exchanging membrane [10,11], consisting of a perfluorinated backbone, giving it mechanical and thermal stability, while hydrophilic sulfonic side chains are responsible for proton conduction, giving it a clear phase separation [12]. Although the Nafion membrane exhibits good proton conductivity and good chemical stability and can be used for a long period of time (60,000 h) in a PEM



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). fuel cell [13], it carries some limitations, including low proton conductivity in low water content conditions and deterioration of thermal stability above 90 °C, and it is also prone to methanol crossover when used in direct methanol fuel cell (DMFC) [14]. Many studies have been made to enhance the proton conductivity and thermal stability of Nafion membranes, i.e., pore size tuning via UV [15], coating the Nafion membrane with another sulfonated polymer [16,17], and incorporating inorganic fillers like TiO_2 , CeO_2 , ZrO_2 to synthesize a composite membrane [18–21]. The latter strategy has progressively emerged as one of the most promising since the presence of inorganic nanofillers inside the polymer matrix increases the mechanical stability of the membrane while simultaneously enhancing its water-retaining capability and thus the proton conductivity [22,23]. For instance, Choi et al. prepared a composite membrane based on Nafion/TiO₂-ZrO₂ with varying ratios of Ti/Zr and tested it at high temperatures and low relative humidity [24]. They reported an enhanced performance of the composite membranes, with a TiO₂-ZrO₂ content of up to 30% of w/w. Cai et al. incorporated silica nanoparticles into the Nation membrane via the swelling method without destroying the original phase separation [25]. They tested this composite membrane in a high-temperature fuel cell and noticed an improved performance of about 37% at 110 °C and very low relative humidity (20%).

Lately, graphene oxide, the oxidized derivative of graphene [26], has gained a lot of attention as a filler to improve the performance of the Nafion membrane due to its large surface area, high physical stability, and easy surface functionalization [27]. Although GO demonstrates minimal ionic or electronic conductivity [28], it can be easily converted into a high proton conductor by incorporating organic molecules either within its interlayer space or on its surface, resulting in the development of innovative hybrid organomodified and nanosized fillers with exceptional proton conductivity [29]. As a result, the chemical grafting of organic molecules bringing hydrophilic sulfonic acid groups (-SO₃H) has rapidly emerged as a very promising approach, being able to improve the conductive performance of the resulting nanocomposite membranes by many folds while also significantly increasing its mechanical, thermal, and chemical resistance due to an increased compatibility between the nanomaterial and the hosting polymer matrix. Consequently, several Nafion nanocomposite PEMs with GOsulf-based fillers were explored, demonstrating outstanding electrochemical performance in both hydrogen- and methanol-feed PEMFCs [29–34]. Despite the very vast literature on Nafion-GOsulf electrolytes, the effects of such nanomaterial on internal distribution and mobility of water molecules confined in ionic channels of Nafion have been rarely investigated.

This systematic study aims to fill the lack of information on the structure/performance relationship in the Nafion-GOsulf electrolyte via the clarification of molecular phenomena occurring between the polymer matrix, sulfonated graphene oxide platelets, and water molecules in the nanocomposite electrolyte. Consequently, GOsulf was synthesized via chemical grafting of sulfonic functional groups on the GO surface [35] and then incorporated inside the Nafion matrix via simple solution intercalation. Based on previous studies [36,37], membranes at 3 wt% of filler loading with respect to the Nafion matrix were prepared. This filler content ensures the maximum improvement in terms of thermomechanical resistance and proton transport features. The nanocomposite membranes were characterized using a combination of swelling tests, water release tests, and Electrochemical Impedance Spectroscopy (EIS). ¹H NMR spectroscopy, via spectral analysis and investigation of the self-diffusion coefficient, was carried out to elucidate the molecular distribution and mobility of water molecules in the ionic channels of Nafion.

2. Materials and Methods

2.1. Materials

Nafion (20 wt% dispersion in water and lower aliphatic alcohols), 3-amino-1 propanesulfonic acid (acronym: SULF) used for organomodification of GO, Nitric Acid (65%), Hydrogen peroxide (30 w/w in H₂O), Sulfuric acid (95–98 wt%), and N,N-Dimethylformamide (DMF) were all purchased from Aldrich (Sigma-Aldrich, Milan, Italy).

2.2. Synthesis of Graphene Oxide and Its Organoderivative (GOsulf)

Graphene oxide (GO) was synthesized from graphite powder using a modified Staudenmaier's method, as detailed elsewhere [36,38]. In a typical synthesis process, 10 g of powdered graphite was placed in a round-bottom flask containing a mixture of concentrated sulfuric acid (400 mL) and nitric acid (200 mL). The reaction mixture was then cooled to 0 °C using an ice bath. Gradually, 200 g of potassium chlorate powder was added to the suspension while continuously stirring and maintaining a low temperature. After 18 h, the reaction was terminated by carefully pouring the mixture into distilled water. The resulting oxidation product was thoroughly washed until the pH reached 6.0 and finally dried at room temperature.

For the preparation of GOsulf, 100 milligrams of GO were dispersed in 100 milliliters of water. Subsequently, an aqueous solution of the aforementioned amine derivative (300 milligrams of SULF dissolved in 40 milliliters of water) was added. After 24 h of stirring, the product was separated via centrifugation, washed with water, and air-dried by spreading it on a glass plate.

2.3. Preparation of Nanocomposite Membrane

The Nafion filler-free membrane was prepared using a 20 wt% Nafion solution via standard procedure: 1 g of the Nafion solution was completely dried at approximately 60 °C to remove all solvents and then redissolved in 15 mL of DMF until it became a clear solution. The latter was then cast onto a Petri dish and left at around 60 °C overnight until all of the self-standing membrane was obtained. Nafion nanocomposite membranes were instead obtained using solvent casting procedure [39] via direct dispersion of the filler in the alcoholic Nafion solution (as purchased). The dispersion was ultrasonicated for 1 day, stirred for another day at room temperature until a clear solution was obtained, cast on a Petri dish, and then placed in the oven at about 40 °C until dried. Nanocomposite membranes at 3 wt% of loading with respect to the polymer were prepared on the basis of previous studies [36,40]. All Nafion-based membranes were subjected to mechanical reinforcement and chemical activation, as sketched in Scheme 1. Mechanical reinforcement was achieved by sandwiching and pressing the membrane between two Teflon plates, and the sandwich was placed in an oven at $150 \,^{\circ}$ C for approximately 15 min. Thereafter, the membranes were acid activated to convert them into their acid form. This involved rinsing in (i) boiling HNO_3 solution (1 M) for 1 h, (ii) boiling H_2O_2 (3 vol%) for 1 h, (iii) boiling H₂SO₄ (1 M) for 1 h min, and again washing with boiling deionized H₂O after each step. The final thickness of the membranes was approximately 50 µm.



Scheme 1. Schematic representation of the thermal and chemical activation process for preparing the Nafion membrane.

2.4. Characterization Techniques

Ion Exchange Capacity (IEC), measured in milliequivalents per gram of dry polymer, was determined using the acid-base titration method [41]. The samples, in their acid-activated form, were immersed in a 2M NaCl solution at room temperature for 24 h

to facilitate the complete release of H⁺ ions via exchange with Na⁺. Subsequently, the amount of released H⁺ ions was titrated using a standard 0.1M NaOH solution, with phenolphthalein serving as the indicator. IEC values (meq g^{-1}) were calculated with Equation (1):

$$IEC\left(meq \cdot g^{-1}\right) = \frac{M_{(NaOH)}V_{(NaOH)}}{W_{dry}}$$
(1)

Here, V represents the volume (in mL), and M denotes the concentration (in mol/L) of the NaOH solution required to neutralize the H^+ ions. W_{dry} corresponds to the dry weight of the sample.

Water uptake (wu%), expressed as a weight percentage, was determined by immersing the dried membranes (with a weight of w_{dry}) in deionized water at room temperature for 24 h. Each sample was promptly dried with tissue paper to remove surface water droplets and then reweighed (w_{wet}). Water uptake was calculated using Equation (2), and the reported values represent the average of at least three independent measurements.

wu (wt%) =
$$\frac{w_{wet} - w_{dry}}{w_{dry}} * 100$$
 (2)

NMR measurements were conducted on a Bruker AVANCE 300 wide bore spectrometer operating at 300 MHz for 1H. The probe employed was a Diff30 Z-diffusion 30 G/cm/A multinuclear with substitutable RF inserts. ¹H NMR was acquired via 90-FID sequence, using a 90° radio-frequency (rf) pulse length of 9.8 μ s. The self-diffusion coefficients (D) of water confined within the membranes were determined using the pulsed field gradient stimulated echo (PFG-STE) technique [42]. The experimental parameters included a diffusion time (Δ) of 8 ms, a pulse length (δ) of 0.8 ms, and a gradient amplitude ranging from 100 to 900 G/cm, with 8 scans performed. Due to the high precision of the fitting curve and the repeatability of the measurements, the uncertainties in D values were below 3%. Measurements were conducted by incrementally increasing the temperature from 20 °C to 130 °C, at intervals of 20 °C, allowing the sample to equilibrate at each temperature for approximately 15 min [43].

Through-plane proton conductivity (σ) was investigated via Electrochemical Impedance Spectroscopy (EIS) using a homemade two-electrode cell [44]. The cell was connected with a fuel cell test hardware (850C, Scribner Associates, Inc., Southern Pines, NC, USA) for temperature and humidity control and σ measured at 90 °C under humidity ranging between 30% and 90%. The AC impedance response of the cell was measured in the frequency range between 1 Hz and 1 MHz using a PGSTAT 30 potentiostat/galvanostat (Methrom Autolab) equipped with an FRA module, with an AC voltage amplitude of 10 mV. The analysis of the resulting Nyquist plot allowed us to determine the membrane resistance (R) as the high-frequency intersection of the impedance arc with the real axis [45]. Thereafter, proton conductivity was calculated using Equation (3).

$$\sigma\left(\mathrm{S\,cm}^{-1}\right) = \frac{\mathrm{l}}{\mathrm{R}_{\mathrm{el}} * \mathrm{A}} \tag{3}$$

where "l" is the membrane thickness, and "A" is the active area of the cell.

3. Results and Discussion

The Ion Exchange Capacity (IEC) of a Proton Exchange Membrane (PEM), which denotes the number of functional groups available for ion exchange, is widely acknowledged as a crucial parameter. It plays a pivotal role in determining the membrane's hydrophilicity, subsequently influencing its proton conductivity. Table 1 provides a comprehensive overview of IEC and water uptake values for all Nafion-based membranes. The reconfigured Nafion exhibits an IEC and water uptake of 0.94 meq g⁻¹ and 24.3 wt%, respectively. Notably, there is a nearly 13% decrease in the IEC following the incorporation of graphene oxide (Naf-GO), resulting in an IEC of 0.82 meq g⁻¹. Under acidic conditions, the epoxide

functionalities on the GO surface undergo ring-opening reactions with the -SO₃H groups of Nafion, leading to a reduction in the number of free exchangeable functional groups [46]. Despite this, the water uptake value for Naf-GO is marginally higher than that of Nafion, suggesting that the GO nanoplatelets alter the local distribution of water molecules within the hydrophilic domains of the nanocomposite. Conversely, both the IEC and water uptake experience a significant increase upon the incorporation of sulfonated GO, reaching 1.03 meq g⁻¹ and 49.2 wt%, respectively. This can be ascribed to the abundance of highly hydrophilic sulfonic acid functionalities on GOsulf platelets [37].

Table 1. Ion Exchange Capacity (IEC), water uptake, and proton conductivity of the Nafion-based membranes.

Sample	IEC [meq g ⁻¹] -	Water Uptake [wt%]		Conductivity [mS cm ⁻¹]	
		@25 °C	@80 °C	@30% RH	@90% RH
Nafion recast Naf-GO Naf-GOsulf	0.94 0.82 1.03	24.3 27.6 49.2	46.9 78.8 63.5	8.0 1.1 44.0	127.9 77.0 231.9

The membrane's performance is widely acknowledged to be closely linked to its water content. Water molecules play a direct role in proton conduction via both the vehicular and Grotthuss mechanisms. Consequently, a high water adsorption capacity is desirable, but an excessive swelling of the membrane can lead to dimensional discrepancies during MEA operation or, in more severe cases, mechanical failure. In this study, hydrolytic stability was assessed by examining the temperature dependence of water uptake under varying temperature conditions. The results, depicted in Figure 1 for the temperature range of 20–80 °C, reveal that the membranes' absorption capacity increases with higher temperatures. This can be attributed to the softening of the polymer chains due to thermal energy, resulting in a larger free volume and consequently, higher water content. However, while the water uptake variation for Naf-GO is substantial, both Nafion and Nafion-GOsulf demonstrate only a moderate dimensional shift during heating. This indicates that the temperature does not significantly alter the microstructure of their hydrophilic clusters, such as their size and shape. This feature is a reliable indicator of superior hydrolytic stability compared to the Naf-GO nanocomposite.



Figure 1. Water uptake vs. temperature for Nafion and nanocomposite membranes.

A systematic investigation via ¹H NMR spectroscopy was conducted to elucidate the spatial distribution and molecular dynamics of water molecules within the ionic clusters of the prepared PEMs [47]. Figure 2 presents the temperature-dependent evolution of the proton spectra for Nafion, Nafion-GO, and Nafion-GOsulf within the range of 20–130 °C. Typically, within the hydrophilic domains of a PEM, at least two distinct water populations coexist: water interacting with functional groups of the polymer and/or filler (bound water), and water molecules in a bulk state. During NMR measurements, these two populations undergo rapid exchange, resulting in a broad and asymmetric proton signal. It is noteworthy that the linewidth for both recast Nafion and Naf-GO is approximately 200 kHz, whereas it increases to 1560 kHz in the case of Naf-GOsulf. This observation suggests a larger fraction of bound water in the latter membrane. To further substantiate this observation, the variation in the signal area with temperature is depicted in Figure 2d. Recast Nafion and Naf-GO exhibit a sharp decrease in signal intensity with heating, retaining only 19% and 7%, respectively, of their initial water content at 100 °C. This is attributed to significant water evaporation from the membrane, which reasonably affects the bulk water due to its reduced electrostatic interactions. It is worth noting that the signal for Naf-GOsulf still retains 33.8% of its original area at 130 °C.



Figure 2. Temperature evolution of the ¹H-NMR spectra for (**a**) Nafion, (**b**) Naf-GO, and (**c**) Naf-GOsulf for the range of 20–130 °C. (**d**) Normalized area of the proton spectra vs. temperature for the various PEMs.

The water retention capability of the Nafion-based membranes was further scrutinized by assessing their water release under harsh conditions—specifically, subjecting them to 90 min at 80 °C and 30% relative humidity (RH). The findings are depicted in Figure 3. In its pristine form, Nafion displays inadequate retention capability, with water loss occurring very swiftly, resulting in a mere 4% residual water content after 90 min at 80 °C. The dehydration rate accelerates even further with the incorporation of GO platelets, leading to complete water evaporation in just 20 min. Conversely, Naf-GOsulf exhibits a more gradual dehydration rate coupled with a higher residual water content of 24.6%. This can be attributed to the robust hydrogen-bond interactions between the sulfonic acid groups of the organomodified GO nanolayer and water molecules, effectively impeding water evaporation from the nanocomposite PEM. This intriguing feature positions Naf-GOsulf as a promising candidate for successful deployment in high-temperature PEMFCs.



Figure 3. Water release behaviors of the Nafion and nanocomposite membranes as a function of time under 80 °C and 30% RH.

The self-diffusion coefficients (D) of water within the hydrophilic domains of the different PEMs were determined using the pulsed field gradient (PFG) NMR technique. These results are visually presented in Figure 4, covering a temperature range of 20–130 °C. It is evident that, at relatively low temperatures, the self-diffusion coefficient is significantly influenced by both the water uptake value and the relative distribution of water molecules between bulk and bound states. Notably, although Naf-GOsulf exhibits remarkably higher water uptake (49.2% compared to 24.3%), its diffusivity is comparable to that of Nafion, at least within the range of 20–80 °C. This can be attributed to the aforementioned higher fraction of less mobile-bound water within the nanocomposite membrane. Conversely, the incorporation of unmodified GO has an adverse effect on water diffusivity. Furthermore, above 60 °C, a majority of the mobile water is lost from this nanocomposite, rendering it impossible to detect any PFG-NMR signal beyond this temperature. Similarly, a nonnegligible amount of water evaporation above 80 °C also contributes to the reduction in D for pristine Nafion. In this context, the advantageous impact resulting from the introduction of sulfonated GO nanoplatelets becomes even more pronounced in the high-temperature range, i.e., 80-130 °C. Thanks to its superior retention capacity, the water self-diffusion coefficient for Naf-GOsulf increases linearly up to 100 °C and then remains nearly constant up to 130 °C, exhibiting a value of 1.5×10^{-5} cm² s⁻¹—nearly two orders of magnitude higher than the benchmark.

As a key parameter of PEMs, the proton conductivity (σ) of the various membranes was finally measured using EIS to elucidate the impact of filler incorporation on membrane performance. Proton conductivity was examined as a function of relative humidity (RH) at a temperature of 90 °C, as illustrated in Figure 5. For Nafion, proton conductivity ranges from 127.9 mS cm⁻¹ at 90% RH and 8.0 mS cm⁻¹ at 30% RH, indicating a decrease in σ by a factor of at least 15 between the highest and lowest RH values. Operating at high and low temperatures evidently leads to the removal of water molecules from the membrane, resulting in a substantial reduction in proton conductivity. This conductivity decline is a common observation in many literature membranes under similar operating conditions [29,48,49]. The introduction of unmodified GO leads to a clear decrease in proton conductivity, which is likely due to a disruption of the ionic channels. From one side, unmodified GO might not be properly dispersed in the Nafion matrix, thus producing an "obstruction effect" that hinders the free mobility of both the polymer chains and of the water molecules in ionic domains. On the other one, by taking into account the IEC results, we can hypothesize the unmodified GO nanoplatelets also interact with acidic groups of Nafion, which results in a reduced number of polar sites available for proton conductivity. In contrast, the conductivity of Naf-GOsulf consistently surpasses that of pure Nafion, aligning well with the results for water uptake, Ion Exchange Capacity (IEC), and diffusivity. This nanocomposite membrane achieves the highest σ of 231.9 mS cm⁻¹ at 90% RH, representing an 81% enhancement compared to the benchmark. Furthermore, the nanocomposite membrane-incorporating organomodified GO also exhibits a minor reduction in conductivity at lower RH, still yielding a σ of 44.9 mS cm⁻¹ at 30% RH and 90 °C. The retention of reasonable proton conductivity in the case of the Naf-GOsulf membrane is attributed to both its superior water retention capability and the direct involvement of GOsulf nanoplatelets in proton hopping along hydrogen bonding networks via the Grotthuss mechanism. Additionally, the interfacial hydrogen bonds between various oxygen-related functional groups on GOsulf and the polymer play a pivotal role in creating an extended network of proton-conducting pathways. This network, in turn, greatly enhances the efficiency of proton diffusion. The development of membranes capable of maintaining reasonable σ under low RH conditions is highly sought after for PEM fuel cells operating at high temperatures.



Figure 4. Temperature variation of self-diffusion coefficients of water confined in Nafion nanocomposite membranes and filler-free Nafion for comparison, from 20 °C up to 130 °C.



Figure 5. Proton conductivity vs. relative humidity for Nafion, Naf-GO, and Naf-GOsulf membranes.

4. Conclusions

The effect of the introduction of sulfonated graphene oxide (GOsulf) nanoparticles on water distribution, diffusion properties, and conductivity performance of the Nafion matrix has been investigated. GO functionalization was achieved via a reaction with an amino derivative having sulfonic acid pendant groups, and the resulting GOsulf was incorporated in Nafion via simple solution intercalation. Both the IEC and the water uptake increase remarkably upon the addition of GOsulf indicating an increase in membrane hydrophilicity. Yet, water retention capability was also enhanced with Naf-GOsulf preserving more than 26% of its original water content during water release tests. According to the ¹H-NMR results, the latter feature can be ascribed to a larger fraction of bound water, i.e., water molecules experiencing strong interactions with sulfonic acid groups of both the polymer and the filler particles. The feature enabled Naf-GOsulf to retain a considerable amount of "still mobile water" at very high temperatures, which resulted in a diffusivity value of 1.5×10^{-5} cm² s⁻¹ at 130 °C, namely two orders of magnitude higher than the Nafion benchmark. Due to these features, the nanocomposite membranes incorporating sulfonated GO nanoplatelets yielded outstanding proton conductivity even under very harsh operating conditions, i.e., 44.9 mS cm⁻¹ at 30% RH and 90 °C, owing to a prompt proton-conducting behavior of the sulfonic acid group.

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