







Implementation of molecular modeling to investigate ion transportation in proton exchange membranes comprising graphene oxide and polyacrylate nanocomposites

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Proton exchange membranes (PEMs) play a critical role in various energy conversion devices, such as fuel cells. Developing advanced PEMs with improved hydronium ion transportation and chemical stability is essential for enhancing the performance and durability of these devices. In this research project, we focus on the development and molecular modeling study of a novel composite material based on poly(acrylic acid) and graphene oxide for application as a high-performance proton exchange membrane. The need for better PEMs has led us to explore the potential of combining poly(acrylic acid) and graphene oxide, as both materials offer unique advantages in terms of proton conductivity and mechanical strength. Our goal is to investigate how these two components interact and synergize to enhance the overall performance of the PEM, particularly in challenging operating conditions. To achieve this, classical all-atom Molecular Dynamics (MD) simulations using Gromacs software were employed. The simulations allowed us to study the formation mechanism of the poly(acrylic acid) and graphene oxide composite material and its application in facilitating hydronium ion transportation within the PEM. Our simulation results revealed fascinating insights into the composite material's behavior. Notably, we observed the emergence of new interactions between poly(acrylate) oligomers and graphene oxide layers, evident from the analysis of interaction energy values. These interactions contribute to the material's enhanced transport properties, making it promising for PEM applications. Moreover, we assessed the mobility of hydronium ions in the graphene oxide and polyacrylate nanocomposite-based PEM and found it comparable to the mobility in traditional poly(acrylate)-based PEMs.

Key words: Poly(acrylate), Graphene Oxide, Hydronium Ion Transportation, Proton Exchange Membrane Fuel Cells, Molecular Modeling, Classical all-atom Molecular Dynamics.

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1 Introduction

The modern challenges in 21st century are related to ecological problems, and energy sources. In this regards, the development of new energy sources such as solar, wind, hydrogen, biofuel and others are increasing rapidly in the world [1]. Herein, the major problem for hydrogen fuel development is related to the high cost of hydrogen fuel cells. Hydrogen fuel cells are electrochemical devices, which are consisting of membranes that sandwiched between anode and cathode [2-4]. Moreover, high ionic conductivity of electrolyte in membrane materials is another challenge nowadays. In this regard there

are different membrane types including solid oxide fuel cells, molten oxide fuel cells, alkaline fuel cells, phosphoric acid fuel cells, and proton exchange membrane fuel cells [4-6]. The electrical generation energy for hydrogen fuel cell is higher than that of conventional power plants and can reach to ~ 60%. Herein, hydrogen fuel and oxygen from air are generating electrical energy in fuel cell via chemical reaction. The process takes place at the anode is oxidation of water, and reduction of oxygen or air is happened at the cathode. At the anode, the catalyst accelerates the oxidation of hydrogen molecules into electrons and hydrogen ions. Further, hydrogen ions (protons) move through the membrane to the cathode,

where the cathode catalyst promotes the formation of water from the combination protons, electrons and oxygen. Used by various consumers electric current generated by the flow of electrons through an external circuit [6-10].

The membrane electrode assembly is the most important part of any fuel cells. At proton exchange membrane fuel cells, it is usually a proton-conducting membrane. The role of the polymer membrane of membrane electrode assembly part is the related to: i) the effective separating the electrodes, ii) direct electrical contact of the electrodes, and iii) enable proton transport from the anode to the cathode. Therefore, the membrane must have maximum conductivity. For use in fuel cell specific conductivity at the level of 10^{-1} – 10^{-3} cm/cm is required [5-15]. In recent years, a small number of new polymers have been received a great attention, for instance, per (fluorinated) membranes of the type Nafion is developed for completely proton exchange membrane fuel cell and commercialized. Another special attention is belonging to the composite materials. Change properties of composites are primarily due to phenomena occurring at the interface phase, and to the properties of materials. At this point, polymer and graphene oxide related composite materials are developed for various applications such as gas-barrier materials, conductive thermoelectric materials, electronic devices, fabrication of fuel cell membranes, sensors, and others.

The use of graphene oxide and poly(acrylic acid) is promising in proton exchange membranes, allowing us to look at the ability of graphene oxide, due to its high surface activity, to increase the conductivity of protons through the membrane, to optimize proton and mass transfer processes. The promise of GO is ensured by the high rate of dispersion, the possibility of modification through polymerization and phosphorylation, the combination of inorganic nanoparticles or their integration as a mixture together with the parent material [16].

Herein, the combination of graphene oxide and poly(acrylic acid) as a composite material will be investigated in our present work for the proton exchange membrane applications. The optimization of transportation process of hydronium ion in proton exchange membrane is important at the molecular level at the different time scale and length- scale. Hereinafter, study of formation mechanism of poly(acrylic acid) and graphene oxide-based composite materials and its application for hydronium ion transportation for proton exchange membrane at the molecular level can be mapped with macroscopic properties of this material [13-21].

To this end, the molecular formation mechanism of poly(acrylic acid) and graphene oxide as a composite material, and then the diffusion of hydronium ion of proton exchange membrane will be investigated by the classical all-atom Molecular Dynamics (MD) simulations. In this regard, the molecular modeling methodology was explained next, and then followed by analysis of formation mechanism of poly(acrylic acid)/graphene oxide-based composite material and transportation mechanism of hydronium ion via this composite material were studied in details.

2 Materials and Methods

A combination of poly(acrylic acid)/graphene oxide was taken as a representative model of composite material, while poly(acrylic acid)/graphene oxide, water and hydronium ion were taken as a representative model of PEM as can be seen in Figure 1. The parameters and coordinates for poly(acrylic acid), graphene oxide, hydronium ion, and water were obtained from the gromos54a7 force field, including the optimized Lennard-Jones parameters and optimized force field parameters [22].

An initial simulation box with a force limit of 500 kJ/volume/nm was created and energy minimized at 298 K and 1 bar. The system was then equilibrated using NPT and NVT at 298 K and 1 bar for 1 ns each. After equilibration, MD simulations were run for 10 ns at a temperature and pressure of 298 K and 1 bar, using periodic boundary conditions in all directions [23]. Additional information about the MD simulations was taken from our published work [24].

Herein, the combination of 8 oligomer of poly(acrylic acid) and two graphene oxide sheet was simulated to study the formation of composite materials via classical all-tom molecular dynamics simulations. Next, classical all-atom classical MD simulations were performed on the 8 oligomer of poly(acrylic acid) in the presence of 40 hydronium ions and 120 water molecules to describe hydration level 3. Next, the diffusion of 40 hydronium ions with 8 oligomer of poly(acrylic acid)/graphene oxide sheet based proton exchange membrane in the presence of 120 water molecules was simulated to study the performance of composite material as an membrane electrode assembly material. Basically, a classical all-atom molecular dynamics (MD) simulation analysis was conducted using snapshots of the simulation box, interaction energies, and diffusion coefficients. The Gromacs and VMD packages were used to perform and analyze the classical all-atom MD simulations [25,26].

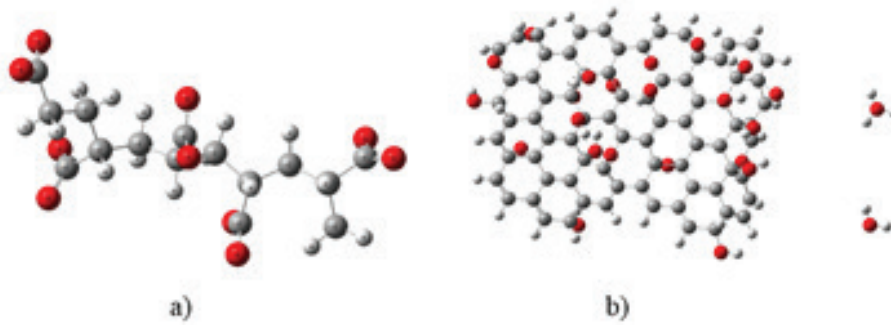


Figure 1 – 3D structures of a) poly(acrylic acid), and b) graphene oxide in the presence of hydronium ion and water molecule

3 Results and Discussions

A poly(acrylate) based proton exchange membrane

Figure 2 displays a representation of 8 poly(acrylic acid) in the presence of water and hydronium ion. It is noteworthy that poly(acrylate) oligomers were enveloped by water molecules, which formed water clusters, facilitating the transportation of hydronium ion. Additionally, the formation of more water clusters around poly(acrylate) could enhance the transportation of hydronium ion. In this regard, the classical all-atom MD simulations were performed to get the results related to the interaction energies, and diffusion coefficients at the different hydrations.

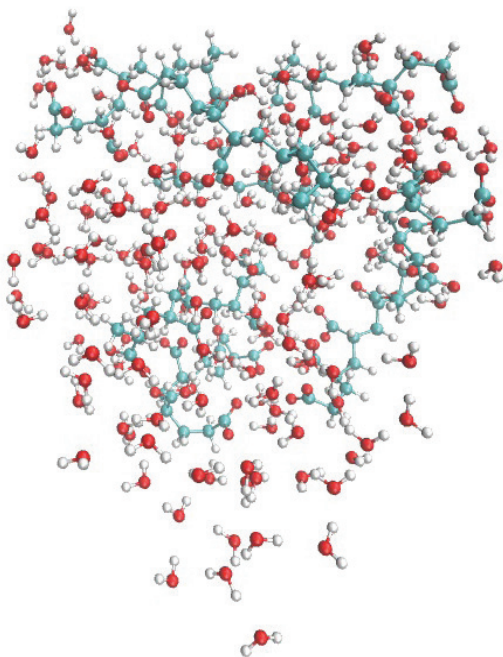


Figure 2 – Representation of designed system for poly(acrylate) based PEM at the hydration 3

In addition, the PAA/PAA, PAA/H₃O, PAA/Water, H₃O/H₃O, H₃O/Water, and Water/Water interaction energies for PAA based PEM at the hydration level 3 were illustrated in Table 1.

Table 1 – Interaction energies for poly(acrylate) based PEM at the hydration 3

Interactions	Interaction Energies (kJ/volume)
Between PAA and PAA	-17077.29
Between PAA and H ₃ O	-3240.43
Between PAA and Water	-556.712
Between H ₃ O and H ₃ O	-15873.08
Between H ₃ O and Water	-699.30
Between Water and Water	-4893.74

From the analysis of interaction energy values from Table 1, the interaction energy between PAA oligomers were -17077.29 kJ/volume at hydration 3. However, the interaction energy between PAA and hydronium ion was -3240.43 kJ/volume at hydration 3. Similarly, the value of interaction energy was noted between PAA and water around -556.712 kJ/volume for hydration 3. Moreover, the interaction energy between hydronium ions was reached to values of -15873.08 kJ/volume for hydration 3. At the same time, the interaction energy between water and hydronium ion was -699.30 kJ/volume for hydration 3. Then, the interaction energy between water molecules was around -4893.74 kJ/volume for hydration 3. In this regard, it can be highlighted that the strength interactions of PAA/water, water/hydronium ion, water/water were noted during the analysis.

After analysis of interaction energies, the diffusion coefficients were obtained for poly(acrylate) based PEM at the hydration 3, in order to study the diffusion mechanism of hydronium ion. The values of diffusion coefficients for hydronium ion and water were listed in Table 2.

Table 2 – Diffusion coefficients of H₃O and Water in PAA based PEM

For	Diffusion (10 ⁻⁵ cm ² /s)
H ₃ O	0.0110
Water	1.1992

From the results of table 2, it can be found that the mobility value of hydronium ion was around 0.0110×10^{-5} cm²/s, while the mobility value of water was around 1.1992×10^{-5} cm²/s at the hydration 3 for PAA based PEM. By comparing the diffusion coefficient value of water and hydronium ion, it can be noted that the diffusion coefficient value of water is higher than the hydronium ion. These findings could mean that Grotthuss mechanism was a dominant transportation mechanism of hydronium ion in PAA based PEM.

A poly(acrylate)/graphene oxide-based proton exchange membrane

The composite PEM model structure, containing 8 units of poly(acrylic acid) and 2 units of graphene oxide-based, was demonstrated in the presence of water and hydronium ions in Figure 3. It was noted that the poly(acrylate) oligomers were interacted with graphene oxide (GO) layers. In addition, the composite of poly(acrylate) oligomers and graphene oxide was covered by water molecules to allow the hydronium ion movement. Next, larger water channels were obtained around poly(acrylate) oligomer and graphene oxide layer. Herein, the classical all-atom MD simulations were employed to obtain the results about the interaction energies, and diffusion coefficients at the hydration 3.

In addition, the GO/GO, GO/PAA, GO/H₃O, GO/Water, PAA/PAA, PAA/H₃O, PAA/Water, H₃O/H₃O, H₃O/Water, and Water/Water interaction energies for PAA based PEM at the hydration level 3 was illustrated in Table 3.

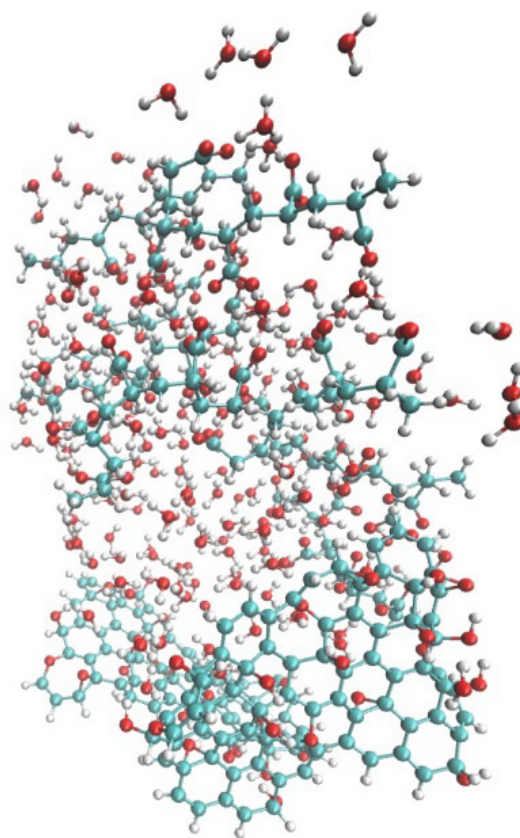


Figure 3 – Representation of designed system for poly(acrylate) and graphene oxide-based composite PEM at the hydration 3

Table 3 – Interaction energies for poly(acrylate) based PEM at the hydration 3

Interactions	Interaction Energies (kJ/volume)
Between GO and GO	-1001.21
Between GO and PAA	-39.25
Between GO and H ₃ O	-6.96
Between GO and Water	-44.31
Between PAA and PAA	-17130.78
Between PAA and H ₃ O	-3362.68
Between PAA and Water	-428.06
Between H ₃ O and H ₃ O	-15855.44
Between H ₃ O and Water	-601.61
Between Water and Water	-4881.01

The analysis of the interaction energy values from Table 3 showed that the interaction energies between the GO layers were around -1001.21 kJ/volume for hydration 3. The interaction energy between GO and PAA was -39.25 kJ/volume at hydration 3. The interaction energy between GO and the hydronium ion was around -6.96 kJ/volume for hydration 3. Additionally, the interaction energy between the PAA oligomers was -17130.78 kJ/volume at hydration 3. However, the interaction energy between PAA and the hydronium ion was -3362.68 kJ/volume at hydration 3. Similarly, the interaction energy between PAA and water was -428.06 kJ/volume for hydration 3. The interaction energy between the hydronium ions was similar around -15855.44 kJ/volume for hydration 3. At the same time, the interaction energy between water and the hydronium ion was -601.61 kJ/volume for hydration 3. The interaction energy between water molecules was 4881.01 kJ/volume for hydration 3.

Table 4 – Diffusion coefficients of H₃O and Water in PAA/GO based PEM

For	Diffusion (10 ⁻⁵ cm ² /s)
H ₃ O	0.0110
Water	1.0500

The table 4 results show that the mobility of the hydronium ion was about 0.0110×10^{-5} cm²/s, while the mobility of water was around 1.0500×10^{-5} cm²/s for the PAA/GO based composite PEM at hydration 3. The diffusion coefficient of water is higher than that of the hydronium ion. This suggests that the Grotthuss mechanism is the dominant transportation mechanism for the hydronium ion in the PAA/GO based composite PEM.

4 Conclusions

In the present study, our primary focus was on investigating the formation mechanism and properties of a composite material composed of poly(acrylic acid) and graphene oxide. Moreover, we explored its potential application as a proton exchange membrane to facilitate the transportation of hydronium ions. To gain insights into the intricate details of this system, we employed all-atom molecular dynamics simulations, which provided a detailed and compre-

hensive understanding of its behavior. One of the key findings of our research was the identification of new and intriguing interactions that occur between the poly(acrylate) oligomers and the graphene oxide layers. The thorough analysis of interaction energy values substantiated the formation of these novel interactions, suggesting that the composite material possesses distinct and advantageous properties. This discovery represents a significant step forward in the domain of composite materials, as it sheds light on the underlying forces that drive the formation of such composites and highlights their potential for various applications. In addition to investigating the formation mechanism, we were keen on evaluating the transport properties of the hydronium ions within the graphene oxide and polyacrylate nanocomposite-based proton exchange membrane. Our results could have practical applications in the widely-used poly(acrylate)-based proton exchange membranes due to our observation of enhanced hydronium ion mobility within this composite membrane. This aspect is of paramount importance, as efficient ion transport is a crucial factor in determining the performance of proton exchange membranes. The implications of our findings are profound and extend to the domain of membrane technology, particularly in the context of proton exchange membrane applications. The knowledge gained from this research provides a solid foundation for the rational design of future composite membranes that are based on graphene oxide. By leveraging the newfound understanding of the interactions between poly(acrylic acid) and graphene oxide, researchers and engineers can tailor composite membranes to suit specific applications, such as fuel cells, electrolyzers, and other electrochemical devices. This advancement can potentially lead to enhanced performance, improved efficiency, and cost-effectiveness of such devices. In conclusion, this study has contributed significantly to our understanding of the formation mechanism and transport properties of poly(acrylic acid)/graphene oxide composite materials for proton exchange membranes.

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