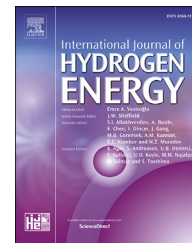




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# Atomistic simulation study of the hydrated structure and transport dynamics of a novel multi acid side chain polyelectrolyte membrane

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## ABSTRACT

Perfluoroimide acid (PFIA) belongs to a new class of Multi Acid Side Chain (MASC) polyelectrolyte membranes. Classical molecular dynamics simulations were carried out to study the hydrated nanostructure of PFIA and transport of water molecules and hydronium ions at  $T = 300$  K and  $T = 353$  K for a range of hydration levels. The radial distribution functions showed negligible change with temperature. The PFIA chain radius of gyration was minimally influenced by hydration and temperature which makes it suitable for fuel cells. Our simulations showed the formation of a large continuous water phase cluster in PFIA at high hydration levels which has also been observed in conductive probe atomic force microscopy experiments. These large continuous clusters lead to significantly higher vehicular diffusion rates for water molecules and hydronium ions at higher hydration levels. The vehicular diffusivity constants for water molecules and hydronium ions for PFIA were comparable to those for Nafion at both  $T = 300$  K and  $T = 353$  K. The vehicular proton conductivity values for PFIA were observed to be higher than those for Nafion at both  $T = 300$  K and  $T = 353$  K which agrees qualitatively with the experimental trends.

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## Introduction

Fuel cells are seen as a promising source of energy especially in the transportation sector. Hydrogen is an energy-dense fuel [1] which helps in increasing the range of fuel cell powered vehicles. Large-scale energy storage is necessary for energy

produced from sustainable but intermittent sources of energy like wind and solar. These sources will, in turn, promote a hydrogen based economy because of the low cost of producing energy needed to generate hydrogen by techniques like water splitting [2–4]. For a hydrogen based economy, energy storage solutions play a key role. Flow batteries [5] are one of the solutions proposed for energy storage.

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Polyelectrolyte membrane (PEM) is a key component in polyelectrolyte membrane fuel cells (PEMFC) and flow batteries. In a PEMFC, the polyelectrolyte membrane separates the hydrogen and oxygen streams and also allows the passage of protons. In organic and inorganic flow batteries, the polyelectrolyte membrane separates the catholyte and anolyte and allows the passage of protons [6–8]. Crossover of electrolytes in a battery results in higher charging and shorter discharging times [9] and this crossover is also prevented by the presence of polyelectrolyte membrane. Efficiency of PEMFCs and flow batteries are affected by the proton conductivity of PEMs [10]. In addition, the PEMs need to retain proton conductivity at temperatures near or above the operating temperature (353 K) of PEMFCs.

Nafion is a widely used membrane material for flow batteries [7] and PEMFCs [11]. A standard variety of Nafion (Nafion-117)<sup>1</sup> has good proton conductivity (0.01 S/cm for 50% Relative Humidity (RH)) [12] and good mechanical stability at room temperature, but loses water upon increase of temperature. Due to this loss of water, the proton conductivity of Nafion degrades [11,13]. There are other perfluorosulfonic acid (PFSA) membranes with lower EW (Equivalent Weight-weight of ionomer per mole of acid) than Nafion which display higher proton conductivity than that of Nafion [14]. Unfortunately, these membranes also lose their proton conductivity at low hydration levels. In addition, the low EW also causes a loss of mechanical integrity due to lesser number of tetrafluoroethylene (TFE) units in the polymer backbone [14]. Alternative aromatic backbone membrane materials like SPEEK (Sulfonated Poly Ether Ketone) [15], PEEK (Poly Ether Ketone) [16] have also been used primarily because of their low cost. However, these materials have lower proton conductivities than that of PFSA membranes [17]. Alternative membranes which have high proton conductivity at both low and high hydration levels, which corresponds to high and low temperatures respectively, and high mechanical integrity are needed to work effectively in both PEMFCs and flow batteries.

Multiple acid side chain (MASC) PEMs, which have multiple protogenic groups, like *ortho bis acid* [18], *meta bis acid* [19] and perfluoroimide acid (PFIA) (Fig. 1(a)) [18] have been developed to serve this purpose. There have been experiments [20] which have shown that the average current through a PFIA membrane is significantly higher than that in a Nafion™ 212 membrane,<sup>2</sup> which has an EW of 1100 [21], at 300 K. It has also been observed in experiments [22] that PFIA has significantly higher proton conductivity than NAFION™ NR211,<sup>3</sup> which has an EW of 990–1050 [23], across a wide range of hydration levels at 353 K. For instance, PFIA and Nafion have a proton conductivity of 0.1 S/cm [22] and 0.05 S/cm [22] for 50% RH at 353 K respectively.

According to DFT (Density Functional Theory) simulations [19], the number of water molecules required for dissociating both the side chain protogenic groups among these three MASC membranes was the least for PFIA. This was due to larger separation of the protogenic groups in PFIA which allowed for more hydrogen bonding in between the protogenic

groups and greater charge distribution along the chain [19]. An experimental [18] study showed that aromatic side chain MASC membranes like *ortho bis acid* displayed higher proton conductivity than PFSA membranes at high hydration levels but their proton conductivities dropped below those for PFSA membranes at low hydration levels. PFIA, on the other hand, displayed higher proton conductivity than PFSA membranes at both low and high hydration levels [18]. An added advantage of the PFIA MASC membrane is the high level of crystallinity it displays due to which its mechanical integrity is preserved at high temperatures. For example, a common variety of PFIA has an EW of 625 but has the crystallinity comparable to ionomers of EW~1000 [24]. This is due to the comparable number of TFE units in the PFIA monomer to that in EW~1000 PFSA membrane monomer.

The PFIA side chain has two protogenic groups whereas side chains of conventional PFSA membranes like Nafion (Fig. 1(b)), Aciplex and Hyflon have only one protogenic group. The protogenic groups makes the side chain hydrophilic which leads to phase separation and formation of water phase clusters [25]. Therefore, it is important to study an MASC PEM like PFIA and better understand the effects of the extra side chain protogenic group. This is the main goal of the present study.

There have been some recent FTIR (Fourier Transform Infrared Spectroscopy) experiments [22] which have shown that both the protogenic groups in PFIA dissociate at different hydration levels. The surface morphology of the PFIA membrane has been compared with other PFSA membranes in another recent conductive probe atomic force microscopy experiment [20]. A molecular simulation study of PFIA will help in further understanding of the hydrated membrane morphology and transport dynamics. Classical Molecular Dynamics (MD) simulations, which use a non-reactive and non-polarizable force field, have been performed for a commonly used PEM like Nafion to understand the effect of ordering of side chain groups on proton transport [26] as well as the details of the hydrated nanostructure of Nafion at different hydration levels and different temperatures and their effect on the proton transport [27–29]. The water and proton transport were found to agree with experimental trends for Nafion classical MD simulations [26,29,30]. Water phase clustering and percolation phenomenon has also been studied for Nafion using classical MD [31,32]. In addition to Nafion, other PFSA membranes like Aciplex [33], Hyflon [34], PFSI (Perfluorosulfonyl Imide) [35] have also been analysed using classical MD, and their corresponding diffusive transport parameters for water molecules and hydronium ions were also found to be consistent with experimental data. There are also many recent studies to analyse the hydrated structure, morphology and percolation transition of aromatic [36–44] and PFSA [45,46] PEMs using classical MD simulations. Classical MD simulations of aromatic backbone PEMs like SPEEK and PEEK have demonstrated transport properties in agreement with experiments [38,40]. A classical MD study showed the amount of phase separation to be a key factor affecting the transport behaviour inside hydrated sulfonated block co-polyimide PEMs [47]. Predictions of water uptake of sulfonated poly ether imide PEM were consistent with experiments in a classical MD simulation study [48]. Classical MD

<sup>1</sup> Nafion 117 is a 183  $\mu\text{m}$  thick Nafion membrane.

<sup>2</sup> Nafion™ 212 is a 50.8  $\mu\text{m}$  thick Nafion membrane.

<sup>3</sup> NAFION NR™ 211 is a 25.4  $\mu\text{m}$  thick Nafion membrane.

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