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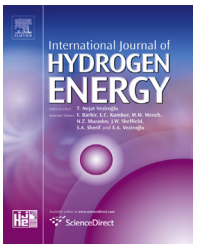

Molecular dynamics simulation study of carboxylated and sulfonated poly(arylene ether sulfone) membranes for fuel cell applications

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ABSTRACT

The performance of poly(arylene ether sulfone) as a proton exchange membrane, for application in a fuel cell, such as carboxylic acid side chain effects on the structural and dynamical properties have been studied by molecular dynamics simulation at 353 K. Different percentage of carboxylated monomer were simulated and the radial distribution function, water cluster size and mean square displacement were evaluated. The results showed that monomer carboxylation up to 10%, decreased the conductivity according to vehicular mechanism and then at 15% of monomer carboxylation the conductivity increased. Also, the greatest water clusters were formed at 15% carboxylated monomer and the increase in acidic sites made the polymer more hydrophilic. In addition, the diffusion and solubility of the gases, O_2 and H_2, into the membrane were studied and the results indicated that H_2 has a higher diffusion coefficient than O_2 and the diffusion phenomenon has a determining effect on the performance of proton exchange membrane.

Introduction

Recently, because of energy crisis, limitation of fossil fuels and environmental problems, fuel cells which convert chemical energy to electrical energy [1] are recognized as a promising alternative source of energy with high efficiency, high energy density, low environmental pollution and low greenhouse gas emission for providing energy and machine power [2–6]. Polymer electrolyte membrane fuel cells (PEMFCs) due to higher efficiency, lower cost and simplicity of operation, have attracted much attention [2,7]. Proton exchange membrane (PEM) is an important part of PEMFC that conducts the protons generated in the anode to the cathode and prevents occurrence of two processes, namely (i) the passage of electron and (ii) the crossover of the fuel (O_2 and H_2) [7–9]. Perfluorinated membrane such as Nafion, due to high proton conductivity and good stability, is a commonly used polymer as fuel cell membrane, but it has some disadvantages such as; high production cost, low proton conductivity as a result of dehydration at high temperatures (T > 80 °C) and poor resistance to methanol crossover in the direct methanol fuel cells [10–14]. Sulfonated aromatic polymers such as sulfonated poly(ether

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ether ketone) (SPEEK), sulfonated poly(phenylene sulfide), sulfonated poly(arylene ether sulfone) (SPAES), sulfonated poly imide (SPI) due to their high proton conductivity, thermal and mechanical stability and low production cost, are considered as favorable alternatives to the Nafion [9,11,15–17]. An advantage of sulfonated aromatic polymers is their thermal stability which increases with aromatic groups [18].

However, researchers are making effort to develop the proton exchange membrane for operation at high temperatures [19–23] with low co-catalyst poisoning, better water management and system efficiency and higher diffusivity to increase the rate of reaction in the fuel cells [19]. The main problem with proton exchange membranes is their dehydration at high temperatures [24]. The poly(arylene ether sulfone) (PAES) is a thermoplastic polymer that due to excellent thermal, mechanical and oxidative stability, high glass transition temperature, low methanol permeability, low cost and easy preparation is considered as a suitable material for utilization as a proton exchange membrane [17,20,25–27]. This type of membrane has higher thermal properties compared with Nafion and other hydrocarbon polymers such as SPEEK [23]. Due to these properties, PAES is known as a promising alternative for usage as a high temperature proton exchange membrane in the fuel cells. Kim et al. [15] used sulfonated poly(ether sulfone) membrane for three different kinds of polymer electrolyte fuel cells, proton exchange membrane fuel cell (PEMFC), direct formic acid fuel cell (DFAFC) and direct methanol fuel cell (DMFC). It was found that the performance of these fuel cells was improved at higher temperature and as a result it was proposed that the sulfonated poly(ether sulfone) is the best candidates for application as a fuel cell membrane. Park et al. [28] synthesized crosslinked sulfonated poly(arylene ether sulfone) and found that the crosslinked membrane has less water uptake, low level of methanol permeability, and good thermal and mechanical properties. Chun et al. [20] reported that addition of carboxylic acid groups as the side chain in the sulfonated poly(arylene ether sulfone) increases the resulting copolymer hydrophilicity and can act as active acid sites for reaction with cross linking agents such as silica to form polymer crosslinked membrane. An important role of PEM relies on its performance as a barrier to penetration and reaction between the gases (H_2 and O_2) which are separated by the membranes [29,30]. High gas permeation into the membrane decreases the performance and durability of fuel cell [31], that is, the membrane should have low gas permeability. James Jr. et al. [32] investigated the transport behavior of O_2 in disulfonated poly(arylene ether sulfone) (BPSH) and Nafion 112 membrane and found that the sorption of O_2 followed Henry's law under dry condition and sorption of O_2 was increased by water content and this increase in the BPSH membrane is more significant than in the Nafion membrane.

Molecular dynamics (MD) simulation is a useful method for modeling of systems in molecular scale by application of atomistic approach and can provide better understanding of the relationship between material structure and dynamics of system as a function of time [33,34]. Utilizing these advantages has led the researchers to use MD simulation for predicting the properties of polymer exchange membranes for applications in the fuel cells. Cordova-Mateo et al. [35] used atomistic MD simulations for investigating the effects of electric field on the diffusion, velocity and conductivity of hydronium ions inside the sulfonated poly(styrene-co-divinyl benzene) membranes and they found that the mobility and diffusion coefficient of hydronium ions increased by the applied electric field strength in the parallel direction more than of the perpendicular direction of the applied electric field. Ahadian et al. [30] investigated the effect of side chain and backbone flexibility of short-side-chain perfluorosulfonic acid (SSC PFSA) membrane, in addition to variation of temperature and hydration level on the proton transfer at low humidity of the membrane by using *ab initio* MD simulations and found that the side chain or backbone flexibility of the SSC PFSA are more effective on proton transfer. However, at low hydration level no proton transfer occurs from membrane to the water molecules. Mahajan and Ganesan [36,37] investigated the structure of solvated sulfonated poly(ether ether ketone) (SPEEK) membrane by atomistic simulation and compared the resulting structure with that of solvated Nafion. Their simulations were performed in two parts; (i) by investigating nanophase segregation and hydrophilic domains they found that the nanophase segregation in SPEEK was less profound than in Nafion (ii) by investigating structure and transport properties of water, hydronium ion (H_3O^+) and methanol they found that the localization of H_3O^+ was more profound than in the Nafion. Ohkubo et al. [38,39] by using MD simulation studied the hydration of Nafion and sulfonated poly ether sulfone (SPES) membranes as well as the effect of the hydration on aqueous phase structure and dynamics of water and H_3O^+ in these membranes. They also reported higher proton conductivity diffusion coefficients of water and H_3O^+ for the Nafion membrane. Choe et al. [25] by *ab initio* calculations on sulfonated poly ether sulfone (SPES) reported that, the proton was not completely separated from the sulfonic groups of SPES at low hydration level compared with that of Nafion.

Considering the works done on fuel cells, it seems that most suitable membranes for application in the fuel cells are crosslinked organic–inorganic hybrid membrane where the cross links between polymer chains and nano particles (silica) are formed by reaction between nano particles and the side chains such as carboxylic groups of the polymer chain.

In the present study, the effect of carboxylation on properties of sulfonated poly(arylene ether sulfone) for utilization as the essential polymer component, which is used in preparation of a polymer exchange membrane for application in the fuel cells is investigated and the behavior of this carboxylated polymer on the performance of the fuel cell membrane is considered and discuss in the light of the obtained results.

For this purpose different level of carboxylic acid in polymer was used and its effect on the structural properties, nanophase segregation, hydrophilic domain and dynamics of hydronium ion and water were evaluated. Also, the diffusion of hydrogen and oxygen and their effect on proton conductivity of the membranes with and without carboxylic acid were studied. Density, radial distribution function (RDF), cluster size, mean square displacement (MSD), coordination number and energy of cells were used for analysis of the simulation results.

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