



Oxygen diffusion in cation-form Nafion membrane of microbial fuel cells



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ABSTRACT

The diffusion process of O₂ in the cation-form Nafion membrane is investigated by molecular dynamics simulations. Moreover, the effects of cation species and concentration on O₂ diffusion are elucidated systematically. The results show that for the H⁺-form Nafion membrane, the average size of hydrophilic clusters in the membrane increases and these clusters will interconnect gradually as the membrane water content increases. Thus, the diffusion coefficient of O₂ increases with the increase of water content. In addition, O₂ molecules tend to diffuse along the hydrophilic/hydrophobic phase interface and within the hydrophobic phase of the membrane. Na⁺ or Ca²⁺ promotes while K⁺ hinders O₂ diffusion compared with H⁺ when there is only one kind of cation in the Nafion membrane. As to the membrane contains both H⁺ and one kind of metal cations mentioned above, although the ratios of these two kinds of cations change linearly, the diffusion coefficient of O₂ changes nonlinearly. It is mainly because that the factors affecting O₂ diffusion in the Nafion membrane have different priorities under different cation species and concentration conditions. In general, the factors such as the large free volume fraction of the membrane, the large average size of hydrophilic clusters with better connectivity and the wide distribution of O₂ molecules close to the hydrophobic phase are conducive to O₂ diffusion in the cation-form Nafion membrane.

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1. Introduction

Power generation from renewable energy is one of the central issues of researches recently because of the severe shortage of fossil fuel [1]. Microbial fuel cell (MFC) can convert the chemical energy of organic compounds into electric energy directly via microorganism. It has dual effects of productivity and environmental restoration [2–4]. In an MFC, organic materials in the anodic chamber are degraded to produce electrons, which travel from the anode to the cathode via an external circuit. Meanwhile, protons migrate from the anode to the cathode through a separator [5]. The separator is utilized to physically separate the anodic and cathodic chambers (or cathode for a single-chamber MFC). One of the most commonly used MFC separators is Nafion (product of DuPont Inc., USA) [6]. Due to perfluorination, this membrane exhibits excellent chemical, thermal, and electrochemical stability. Although ferricyanide has been used for cathodic electrolyte in some reports,

oxygen-based cathodes provide a more sustainable method of power generation [7]. However, the leakage of oxygen in the cathode phase through the separator into the anodic chamber can either lower energy recovery due to the substrate loss from aerobic respiration by facultative bacteria, or inhibit the growth of obligate anaerobes [8]. Furthermore, Kim et al. [7] has reported that Nafion is the most permeable membrane to oxygen among the commercially available membranes tested in their study. Therefore, oxygen diffusion through Nafion membrane is a serious problem for MFC usage which cannot be ignored.

A few experimental attempts have been made to study the diffusion properties of oxygen inside Nafion membranes in different kinds of MFCs [7–9]. In reference [7–9], the diffusion coefficient of oxygen in Nafion117 membrane is determined by monitoring the dissolved oxygen (DO) concentration over time and calculated by the same mass balances equation. This first order linear differential equation establishes the relationship between the O₂ diffusion coefficient and the O₂ concentration in the two sides of the membrane, and the O₂ diffusion coefficient is assumed to be independent of time. MFC solution components in these three

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references are different, then the obtained O_2 diffusion coefficients are $4.4 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ (single-chamber MFC) [9], $2.4 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ (two-chamber MFC) [7], and $5.35 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ (two-chamber MFC which catholyte is phosphoric acid buffer) [8] respectively. Especially, when the catholyte changes to distilled water in reference [8], the O_2 diffusion coefficient is reduced to $5.27 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. It is suggested that the ion species and concentration of MFC solution indeed have an effect on O_2 diffusion in the Nafion membrane. Therefore, the O_2 diffusion coefficient during MFC operation process is not constant because the solution ion concentration changes constantly. Nafion has a hydrophobic CF_2 backbone and perfluorinated side chains with terminating sulfonic acid groups ($-SO_3H$) [10]. After swelling, the membrane separates in at least two phases on the nanometer scale, a hydrophobic phase containing the backbone and a hydrophilic phase containing the sulfonic acid groups and water [11]. In addition, cations in the MFC medium (e.g., Na^+ , K^+ , Ca^{2+} , and others), typically present at 10^5 higher concentrations than protons, are primarily responsible for the transport of positive charge across Nafion membranes [7]. Therefore, the sulfonic acid groups are more likely to equilibrate with the above cations present in the anolyte and catholyte. This equilibration rapidly turns the Nafion membrane from its proton form to a form in which mainly other cation species (Na^+ , K^+ , NH_4^+ , Mg^{2+} , and Ca^{2+}) occupy the negatively charged sulfonate groups [12]. Thus, studies on the mechanism of O_2 diffusion in the cation-form Nafion membrane are of practical interests, and may provide a novel method to decrease the cathodic oxygen leakage from the aspect of MFC medium.

There have been various experimental investigations of the oxygen permeation (including diffusion and sorption) through H^+ -form Nafion membranes [13–18]. Recently, the aim of these studies is not only determining the coefficients of gas permeability, but also establishing the physical model to elucidate this process [19–21]. For example, a resistor network model accounting for the alternating pathways of gas (including oxygen) permeation through the aqueous and solid phase of fully hydrated Nafion has been presented [20,21]. However, there are few experimental studies on the diffusion of O_2 in the cation-form Nafion membrane. Sakai et al. [22] have pointed out that the oxygen permeability of Nafion greatly depends not only on water content but also on cation form and ion-exchange capacity. Metal cations (K^+) exchanged to the hydrogen of the Nafion membrane will hinder oxygen diffusion through the inter-chain of the polymer. This conclusion is consistent with reference [23]. It has been found that K^+ -form Nafion membrane has smaller oxygen diffusivity than the H^+ -form one in reference [23]. Furthermore, this reference also believes that oxygen mainly diffuses through the portion of the water contained in clusters inside Nafion membrane. Besides K^+ , Hirata et al. [24] have determined the mobility of hydration water and the dissolved oxygen permeability through other cation forms of Nafion membranes. In this study, two alkali metals (Na^+ and K^+) and two amino sugars (D -glucosamine (GLU) and an equivalent molar mixture of D -glucopyranosyl- $\alpha(1 \rightarrow 6)$ -2-amino-2-deoxy- D -mannitol and its sorbitol (GPA) are used as counter ions, and the dissolved oxygen permeability through the Nafion membrane containing GPA is the lowest value. In addition, Fan et al. [25] have compared the physical and gas transport properties of Li^+ , Na^+ , K^+ , and Ca^{2+} neutralized Nafion to its acid form. All metal complexed Nafion samples have a rise in permeation and solubility versus the acid form. However, a relationship between gas diffusion and cation type is not present. On the basis of the wide-angle X-ray diffraction (WAXD) experiment, they think correlations between inter-chain spacing and gas transport are impossible. The above studies generally believe that the presence of foreign cations in the Nafion membrane indeed have different effects on O_2 diffusion, and O_2 mainly diffuse

through the portion of the water contained in the ionic phase. However, the macroscopic experiments cannot obtain the microstructure of Nafion membrane after ion exchange. Moreover, the relationship between O_2 diffusion and cation concentration inside the membrane is still unclear. Thus, it is difficult to explain the mechanism of O_2 diffusion from a deeper level.

Due to the inability of experiments on elucidating the micro mechanism, molecular dynamics (MD) simulations have already been extensively applied to study the structure and the properties of Nafion membranes. However, these studies are mainly focused not on O_2 transport but on water and/or proton transports [26–30]. Actually, there are few types of researches discuss O_2 transport in the hydrated Nafion membrane because of difficulties in simulating the complex polymeric system [31–33], and the simulation results of O_2 diffusion coefficient are only consistent in the order of magnitude. MD simulations of O_2 diffusion in the bulk Nafion are executed by systematically changing the hydration level λ in reference [31]. The results indicate that the O_2 diffusion coefficient increases with the rise of λ . O_2 molecules are considered to move through the hydrophilic/hydrophobic interfacial regions of the Nafion matrix, unlike water molecules and protons which move through the water channels comprised of the hydrophilic clusters. Ban et al. [32,33] demonstrate that H_2 diffusion in Nafion membranes is nearly an order of magnitude faster than O_2 diffusion due to its small molecular size. In addition, the binding interaction between O_2 and Nafion is relatively stronger than that of H_2 . The change of porous nanostructures of Nafion has a significant effect on gas diffusion. Consistent with reference [31], gas molecules tend to move along the interface between Nafion framework and water. All of the above studies are on gas molecules diffusion in the H^+ -form Nafion membrane. However, there have been scarce investigations on the gas diffusion inside cation-form Nafion membranes. In fact, detailed MD studies on the cation-form Nafion membrane itself are deficient. Nick et al. [34,35] have used molecular dynamics simulations to investigate the structure and the transport properties of the hydrated Na^+ -Nafion membranes. They find that the main factors controlling the structure of the membrane are the hydration energies and the electrostatic interactions. While the diffusion coefficient of both water and Na^+ increases with increasing hydration. Reference [34] and [35] provide the concept and basis for the construction of the cation-form Nafion membrane model, but these two references do not involve gas diffusion. To the best of our knowledge, the theoretical MD simulation studies of O_2 diffusion in the cation-form Nafion membrane have not been reported in previous scientific efforts. In addition, the experimental and simulated studies mentioned above have significant differences in the location of O_2 diffusion in the Nafion membranes. Therefore, researches on the diffusion mechanism of O_2 in the cation-form Nafion membrane and the interactions between O_2 molecules, water molecules, and cations are of scientific interests.

The objective of our work is to investigate the effect of cations on the diffusion of oxygen inside the Nafion membranes. Hereto, the diffusion process of O_2 in the Nafion membrane has been simulated by MD method. The variation laws of O_2 diffusion coefficient changing with cation species and concentration have been analyzed systematically. The factors affecting O_2 diffusion and their priority under different conditions have also been investigated. Furthermore, the membrane microstructure differences and their causes have been compared when there is only one kind of cations in the membrane. Combined with our previous work [36], the results may provide a novel method to reduce oxygen leakage and increase the performance of batteries at the same time from the aspect of MFC medium. Besides MFC, the results can also apply to polymer electrolyte fuel cells (PEFCs), membrane-based gas

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