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Prediction of proton conductivity of graphene oxide-containing polymeric membranes



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ABSTRACT

In the present work we examined the capability of a simple Nernst–Planck based model to predict the proton conductivity of polymeric membranes which contained pristine or functionalized graphene oxide sheets (GO or F-GO, respectively). A wide comparison with experimental data on both fluorinated and non-fluorinated membranes has been made. It was found that the expression employed for calculating the tortuosity factor of the model played an important role in whether the experimental data was accurately predicted. A modification of the tortuosity factor expression was proposed to enable the model to provide the best agreement between the experimental and theoretical values of proton conductivity. The results showed that in the case of fluorinated membranes at low amounts of GO or at high test temperatures the modified model was able to represent the experimental data more accurately than the original model. However, the selection of the best expression for the tortuosity factor calculations in non-fluorinated membrane systems depended on the ion exchange capacity values of the host membranes.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are one of the most promising clean energy technologies due to advantages such as efficiency, reliability, manufacturability and cost-effectiveness [1,2]. The performance of a fuel cell is affected by various parameters including the cell operating conditions, the electrodes geometric factors, and physical and kinetic properties of the membrane [3–5]. Among the cell operating parameters, the operating temperature plays a critical role in the cell overall performance [6]. The potential operation of PEMFC at high temperatures (above 100 °C) is beneficial for high tolerance to CO poisoning [7], water and heat management system and enhanced

electrochemical kinetics [8,9]. However, currently used perfluorosulfonic acid membranes (e.g. Nafion) are unstable at high temperatures, and their proton conductivity decreases by the evaporation of water from the membrane [10]. Various approaches have been employed to develop proton exchange membranes, capable of being stable above 100 °C. For example, utilizing alternative membrane materials such as phosphoric acid-doped polybenzimidazole (PBI) has been proposed for use in high temperature PEMFCs due to their excellent thermal stability, low gas permeability and good proton conductivity at elevated temperatures (100–200 °C) [11]. Moreover, the use of polymeric nanocomposite electrolytes as fuel cell membranes has attracted much attention in recent years. Actually, incorporation of inorganic as well as hygroscopic [12] nanoparticles such as

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SiO₂, TiO₂, ZrO₂, zeolites, and zirconium phosphate into polymer matrices can substantially enhance water retention properties of the polymer and, as the result, the performance of the fuel cell at high temperatures [13–17]. Recently, a great deal of attention has been paid to graphene oxide (GO) containing membranes for use in PEMFCs [18–21]. GO has special characteristics like high surface area (2630 m²/g) [22], good chemical and mechanical stability and low cost. The carboxylic acid groups on the edges of graphene oxide sheets can easily convert to –COO[–] and H⁺ at room temperature, providing protons to enhance ionic/protonic conductivity of the polymer matrix [21]. However, the number of carboxylic acid groups on the graphene oxide surface is low and it does not exhibit significant enhancement in ionic conductivity [23,24]. Fortunately, the existence of functional epoxide, hydroxyl and carboxyl groups on the surface of GO enables it to be functionalized through covalent and non-covalent bonds to obtain versatile new materials. Therefore, many research groups have used these functional groups for direct synthesis of functionalized GOs (F-GO), specially sulfonated GOs, to improve the proton conductivity of GO containing membranes [18–20].

Despite past efforts on the synthesis and applications of polymeric nanocomposite electrolytes, few studies have been devoted to model and predict the proton transport phenomenon and conductivity within them. Three approaches are usually used to construct the proton transport models: phenomenological models based on the non-equilibrium thermodynamics [25,26], models based on the Nernst–Planck equation [27] and those based on the Stefan–Maxwell equation [28].

In the Nernst–Planck based models, different diffusion coefficients of protons are involved; while in the Stefan–Maxwell based models, the frictional coefficients for interaction of components are incorporated.

In this study, we report the results of calculations of proton conductivity for various GO and F-GO containing polymeric membranes using a Nernst–Planck based model, developed by Choi et al. (the Choi model) [29]. Moreover, some modifications of the Choi model parameters are proposed to account for the exact role of GOs in the proton conductivity mechanism of the membranes. A wide comparison with existing experimental data in the literature was made. The accuracy of the modified model in prediction of proton conductivity of GO/polymer systems was determined by the statistical parameters and compared with other ones calculated by the Choi model.

2. Theory

2.1. The Choi model

A general equation for the prediction of proton conductivity of PEMs was derived by Choi et al. [29] which has been found to be valid for various neat and spherical nanoparticle-containing polymeric electrolytes [30]. The equation, leading to calculation of the overall proton conductivity, σ_{H^+} , is based on the different proton transport mechanisms within a polymeric electrolyte:

$$\sigma_{H^+} = \varepsilon_i \tau \left[\frac{F^2}{RT} \left(D_{H^+}^{\sum} C_{H^+}^{\sum} + D_{H^+}^G C_{H^+} + D_{H^+}^E C_{H^+} \right) \right] \quad (1)$$

where F is the Faraday constant (96485 C mol^{–1}), R is the molar gas constant (8.314 J mol^{–1} K^{–1}), T is temperature (K) and $D_{H^+}^{\sum}$, $D_{H^+}^G$ and $D_{H^+}^E$ are diffusion coefficients of protons for the surface, Grotthuss and en masse diffusion mechanisms, respectively. Also, $C_{H^+}^{\sum}$ is concentration of protons participating in surface diffusion while C_{H^+} is concentration of protons participating in Grotthuss and en masse diffusion. ε_i and τ represent porosity of membrane and the tortuosity factor, respectively.

2.1.1. Protons diffusion coefficients

In the nanocomposite membranes, surface diffusion coefficient depends not only on the type of surface acid groups of the host membrane and nanoparticle, but on their concentration as well [30]:

$$D_{H^+}^{\sum} = \frac{1}{4} \left[\frac{\left(\frac{k_B T}{h}\right)(1+q)}{\left(\frac{1}{\sum_M} \right) \exp\left(\frac{\Delta G_{\sum_M}^{e,0}}{k_B T}\right) + \left(\frac{q}{\sum_P} \right) \exp\left(\frac{\Delta G_{\sum_P}^{e,0}}{k_B T}\right)} \right] \quad (2)$$

where q , k_B and h are moles of acid sites of nanoparticle/moles of acid groups of membrane, Boltzmann constant and Planck constant, respectively. l_{\sum_M} and l_{\sum_P} are jump length of the surface proton for acid groups of membrane and nanoparticles, respectively. $\Delta G_{\sum_M}^{e,0}$ and $\Delta G_{\sum_P}^{e,0}$ are effective Gibbs free energy of activation of surface diffusion around the acid groups of the membrane and the nanoparticles, respectively and can be calculated by [29]:

$$\Delta G_{\sum_i}^{e,0} = \frac{(q_e)^2}{4\pi\epsilon_0\epsilon_r} \left[\frac{l_{\sum_i}}{\left(R_f + R_i + l_{\sum_i}\right)(R_f + R_i)} \right] \quad (3)$$

$i = M, P$

where q_e , ϵ_0 , ϵ_r , R_f and R_i are the electrostatic charge, the permittivity of free space, the relative permittivity of the medium, jump length of surface proton in the membrane or nanoparticle, the effective radius of acid groups of the membrane or nanoparticles and the radius of the hydronium ion, respectively.

The Grotthuss diffusion coefficient of nanocomposite membranes is the same as for the host membrane ($D_{H^+}^G$) [29]:

$$D_{H^+}^G = \frac{l_G^2 \mu_w (z_{H^+} q_e)}{192\pi^2 \eta (\epsilon_r \epsilon_0) R^3 \delta^2} \left[\ln \left\{ \frac{\tan(\theta_I/2)}{\tan(\theta_F/2)} \right\} \right] \quad (4)$$

where l_G , μ_w , z_{H^+} , θ_I , θ_F , η , R and δ are jump length of proton in the Grotthuss mechanism, the dipole moment of water, the charge number of a proton, the initial and the final angle of rotating water molecule, water viscosity, the hydrodynamic radius of the water molecules and distance between protons in the hydronium ion and proton accepting water molecules, respectively. The Grotthuss diffusion coefficient depends only on temperature and it is calculated as $D_{H^+}^G \approx 7 \times 10^{-5}$ cm²/s at room temperature [29].

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