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Prediction of proton conductivity of graphene oxide-containing polymeric membranes



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ARTICLE INFO

Article history:

Received 20 October 2013

Accepted 12 November 2013

Available online 15 December 2013

Keywords:

Fuel cell

Proton conductivity

Prediction

Tortuosity factor

Graphene oxide

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].

Also, in en masse diffusion mechanism, hydronium ions diffuse through components of the membrane system and for nanocomposite membranes $D_{H^+}^E$ can be calculated as follows [30]:

$$D_{H^+}^E = \left\{ \frac{(\lambda_w + 1)(1 + q)}{\lambda_w(1 + q) + \sqrt{2}\left(\frac{r_M}{W}\right)^{\frac{2}{3}} + \sqrt{2}\left(\frac{r_p}{W}\right)^{\frac{2}{3}}q} \right\} D_{H^+}^w \quad (5)$$

where λ_w , $r_{M/W}$ and $r_{p/W}$ are the moles of water sorbed per acid site, the ratio of partial molar volume of membrane to that of water and the ratio of partial molar volume of nanoparticles to that of water, respectively. $D_{H^+}^w$ is the diffusion coefficient of hydronium ion through water that may be obtained by Stokes–Einstein equation, assuming the hydronium ion as a diffusing entity in a continuum of water [31]:

$$D_{H^+}^w = \frac{K_B T}{6\pi\eta R_i} \quad (6)$$

In Eq. (6), R_i is the hydrodynamic radius of a hydronium ion which can be replaced by $R_{H_2O}^* = 0.108$ nm, where $R_{H_2O}^*$ is the effective water radius [32]. Therefore, $D_{H^+}^w$ is calculated as 2.2×10^{-5} cm²/s at room temperature.

2.1.2. The bulk and surface proton concentrations

Protons generated from dissociation of acid groups are divided into two groups: protons closed to the channels surfaces that participate in the surface diffusion mechanism and those which are in the pore bulk region of the channels and participate in the Grotthuss and en masse diffusion mechanisms. The total concentration of protons, $C_{H^+,0}$, in the membrane is calculated as [29]

$$C_{H^+,0} = 1/\lambda_w \bar{V}_w \quad (7)$$

where \bar{V}_w is the partial molar volume of water. Also, In nanocomposite membranes, the surface proton concentration, $C_{H^+}^\Sigma$, can be obtained from [30]:

$$C_{H^+}^\Sigma = \left\{ \frac{1}{1+q} \left[\frac{K_{1,M} a_w (1-a_w) (1+K_{2,M} a_w)}{(1-a_w)(1+K_{1,M} a_w) + K_{1,M} K_{2,M} a_w^2 (1-a_w^{-1})} \right] + \frac{q}{1+q} \left[\frac{K_{1,p} a_w (1-a_w) (1+K_{2,p} a_w)}{(1-a_w)(1+K_{1,p} a_w) + K_{1,p} K_{2,p} a_w^2 (1-a_w^{-1})} \right] \right\} \times 1/\lambda_w \bar{V}_w \quad (8)$$

where ν is the number of equilibrium reactions occurred between the acid groups and water molecules. Also, the equilibrium constant K_1 and K_2 are taken as 1000 and 200, respectively [32]. Furthermore, a_w is the activity of water in the electrolyte membrane. The bulk proton concentration can also be obtained by subtracting the surface proton concentration from the total concentration of protons.

2.1.3. Porosity

Porosity is a measure of volume fraction of water in a membrane, and for nanocomposite membranes it can be given as follows [30]:

$$\varepsilon_i = \frac{\lambda_w (1/EW_M + w/MW_p)}{\lambda_w (1/EW_M + w/MW_p) + r_{M/W}/EW_M + w \cdot r_{p/W}/MW_p} \quad (9)$$

where EW_M is equivalent weight of the host membrane and MW_p is the molecular weight of nanoparticles, estimated by equivalent weight of the nanoparticles, EW_p . Also the solvent loading, λ_w , can be obtained by the following expression [32]:

$$\ln \left(\frac{\lambda_w - \lambda_w^c}{\lambda_w + r_{M/W}} \right) + \left(1 - \frac{1}{r_{M/W}} \right) \left(\frac{\lambda_w^c + r_{M/W}}{\lambda_w + r_{M/W}} \right) + \chi \left(\frac{\lambda_w^c + r_{M/W}}{\lambda_w + r_{M/W}} \right) - \ln a_w = -\frac{\bar{V}_i}{RT} \left\{ \left[\frac{2}{3} G \left[\left(\frac{r_M}{W} \right)^{1/3} - \left(\frac{r_M}{W} \right)^{7/3} \right] - S \sigma \cos \theta \left(1 + \frac{r_M}{\lambda_w} \right) \right] \right\} \quad (10)$$

where λ_w^c , G , S , σ and θ are the number of chemically bound water molecules per acid sites of the polymer and nanoparticles, the shear modulus of the membrane, specific pore surface area, surface tension of water and contact angle of saturated water vapor in the membrane, respectively.

2.1.4. Tortuosity factor

Tortuosity factor (τ), as the ratio of the actual distance to the shortest distance that a proton travels through a membrane, can be calculated using different models such as Mackie–Meares [33] Prager [34] and Yasuda [35] models. The Mackie–Meares model is based on the lattice model of polymer solutions and has been used in the case of highly swelable membranes [36]. On the other hand, the Prager, Eq. (11), and Yasuda, Eq. (12), models, have been frequently used to calculate the tortuosity factor of proton exchange membranes [37–39]:

$$\tau_p = \frac{2(1 - \varepsilon_i) + 2\varepsilon_i \ln \varepsilon_i - 0.5\varepsilon_i (\ln \varepsilon_i)^2}{\varepsilon_i (1 - \varepsilon_i) + \varepsilon_i^2 \ln \varepsilon_i} \quad (11)$$

$$\tau_{Y,K} = \exp(K((1/\varepsilon_i) - 1)) \quad (12)$$

The parameter K in Eq. (12), is a size coefficient whose value has been reported to be 0.7 or 3 depending on the chemical structure of the membrane and the relative size of the penetrant molecules [40]. Inserting $K = 0.7$ or 3 into Eq. (12) gives $\tau_{Y,0.7}$ or $\tau_{Y,3}$ expressions, respectively.

2.2. The Choi model for prediction of σ for GO containing polymer electrolytes

In order to predict σ_{H^+} for GO containing polymer electrolytes using the Choi model, one needs to calculate the molar ratio of acid sites of GO nanoparticles per gram of the polymer matrix, q , as:

$$q = \frac{2 \cdot w}{t \cdot \rho_{f_GO}} EW_M \cdot C_{H^+,f_GO}^* \quad (13)$$

where w , t , ρ_{f_GO} and C_{H^+,f_GO}^* were amount (g), thickness, density and effective surface site density of acid groups of GO (pristine or functionalized), respectively. C_{H^+,f_GO}^* is given by:

$$C_{H^+,f_GO}^* = \frac{IEC_{f_GO}}{A} \quad (14)$$

where IEC_{f_GO} is the ion exchange capacity of GO and A is the surface area of GO. A is obtained from $A = 2/(\rho_{f_GO} \cdot t)$, assuming a uniform thickness for all GO layers.

Table 1 – Parameters required for calculating the proton conductivity of the membrane systems by Eq. (1).

Parameters	Values	Units	Comments
SGO/Nafion1100			
SGO properties			
t	2.04	nm	Thickness of F-GO [45]
ρ_{f-GO}	2.2	g/cm ³	Density of F-GO [45]
$l_{\Sigma,f-GO}$	0.255	nm	Jump length of surface proton for acid groups of F-GO
IEC_{f-GO}	1.39	mmol/g	IEC of F-GO [19]
$C_{H^+f-GO}^*$	3.747×10^{-6}	mol/m ²	Effective surface site density of acid groups of F-GO
MW_{f-GO}	719.42	g/mol	Molecular weight of F-GO
$R_{f(f-GO)}$	0.254	nm	Radius of acid site of F-GO
a	376.483		Aspect ratio of F-GO layers
$\epsilon_r(f-GO)$	6		Relative permittivity of F-GO
$r_{f-GO/W}$	19.98		Molar volume ratio of F-GO to water
Nafion1100 properties			
EW_M	1100	g/mol	Equivalent weight of the membrane [19]
IEC_M	0.9	mmol/g	IEC of the membrane
$r_{M/W}$	29.83		Molar volume ratio of the membrane to water
$l_{\Sigma,M}$	0.255	nm	Jump length of surface proton for acid groups of the membrane
SGO/Nafion112			
SGO properties			
t	2.04	nm	Thickness of F-GO [45]
ρ_{f-GO}	2.2	g/cm ³	Density of F-GO [45]
$l_{\Sigma,f-GO}$	0.255	nm	Jump length of surface proton for acid groups of F-GO
IEC_{f-GO}	4.91	mmol/g	IEC of F-GO [19]
$C_{H^+f-GO}^*$	11.018×10^{-6}	mol/m ²	Effective surface site density of acid groups of F-GO
MW_{f-GO}	203.66	g/mol	Molecular weight of F-GO
$R_{f(f-GO)}$	0.254	nm	Radius of acid site of F-GO
a	376.483		Aspect ratio of F-GO layers
$\epsilon_r(f-GO)$	6		Relative permittivity of F-GO
$r_{f-GO/W}$	5.143		Molar volume ratio of F-GO to water
Nafion112 properties			
EW_M	1100	g/mol	Equivalent weight of the membrane [46]
IEC_M	0.91	mmol/g	IEC of the membrane
$r_{M/W}$	38.639		Molar volume ratio of the membrane to water
$l_{\Sigma,M}$	0.255	nm	Jump length of surface proton for acid groups of the membrane
SGO/SPEEK1			
SGO properties			
t	2.04	nm	Thickness of F-GO
ρ_{f-GO}	2.2	g/cm ³	Density of F-GO
$l_{\Sigma,f-GO}$	0.255	nm	Jump length of surface proton for acid groups of F-GO
IEC_{f-GO}	16.495	mmol/g	IEC of F-GO [24]
$C_{H^+f-GO}^*$	37×10^{-6}	mol/m ²	Effective surface site density of acid groups of F-GO [24]
MW_{f-GO}	60.624	g/mol	Molecular weight of F-GO [24]
$R_{f(f-GO)}$	0.254	nm	Radius of acid site of F-GO
a	376.483		Aspect ratio of F-GO layers
$\epsilon_r(f-GO)$	6		Relative permittivity of F-GO
$r_{f-GO/W}$	1.53		Molar volume ratio of F-GO to water
SPEEK1 properties			
EW_M	1333.33	g/mol	Equivalent weight of the membrane [24]
IEC_M	0.75	mmol/g	IEC of the membrane
$r_{M/W}$	56.116		Molar volume ratio of the membrane to water
$l_{\Sigma,M}$	0.255	nm	Jump length of surface proton for acid groups of the membrane
SGO/SPEEK2			
SGO properties			
t	2.04	nm	Thickness of F-GO
ρ_{SGO}	2.2	g/cm ³	Density of F-GO
$l_{\Sigma,f-GO}$	0.255	nm	Jump length of surface proton for acid groups of F-GO
IEC_{f-GO}	1.842	mmol/g	IEC of F-GO [23]
$C_{H^+f-GO}^*$	4.133×10^{-6}	mol/m ²	Effective surface site density of acid groups of F-GO [23]
MW_{f-GO}	542.888	g/mol	Molecular weight of F-GO [23]
$R_{f(f-GO)}$	0.254	nm	Radius of acid site of F-GO
a	376.483		Aspect ratio of F-GO layers
$\epsilon_r(f-GO)$	6		Relative permittivity of F-GO
R_{f-GO}	13.7091		Molar volume ratio of F-GO to water

(continued on next page)

Table 1 – (continued)

Parameters	Values	Units	Comments
SPEEK2 properties			
EW_M	584.79	g/mol	Equivalent weight of the membrane [23]
IEC_M	1.71	mmol/g	IEC of the membrane
$r_{M/W}$	24.99		Molar volume ratio of the membrane to water
$l_{\Sigma,M}$	0.255	nm	Jump length of surface proton for acid groups of the membrane
GO/SPI			
GO properties			
t	0.95	nm	Thickness of F-GO [46]
ρ_{F-GO}	2.2	g/cm ³	Density of F-GO
IEC_{F-GO}	0	mmol/g	IEC of F-GO [47]
$C_{H^+_{F-GO}}^+$	0	mol/m ²	Effective surface site density of acid groups of F-GO
a	808.447		Aspect ratio of F-GO layers
SPI properties			
EW_M	384.024	g/mol	Equivalent weight of the membrane [47]
IEC_M	2.6	mmol/g	IEC of the membrane
$r_{M/W}$	14.919		Molar volume ratio of the membrane to water
$l_{\Sigma,M}$	0.255	nm	Jump length of surface proton for acid groups of the membrane
General constants used in the model			
k_B	1.38×10^{-23}	J/K	Boltzmann constant
h	6.626×10^{-34}	J s	Planck constant
$r_{f(M)}$	0.254	nm	Radius of acid sites of membranes
$r_{(H_2O)}$	0.143	nm	Radius of a water molecule
ϵ_0	8.854×10^{-12}	C ² /J m	Permittivity
$\epsilon_{r(M)}$	6		Relative permittivity of membranes
q_{e-}	1.602×10^{-19}	C	Electronic charge
l_G	0.255	nm	Proton jump length in Grotthuss mechanism
S	0		The orientation parameter of the nanosheets

Moreover, the tortuosity factor, obtained from Eqs. (11 or 12), depends only on the porosity which in turn varies with water vapor activity (or RH) and equivalent weight of the membrane (or EW). On the other hand, it is well known that other parameters such as the nanoparticles content and geometry significantly affect the overall tortuosity of nanocomposites [41,42]. Therefore, we aimed to take into account the exact role of graphene oxide nanosheets on the tortuosity of the GO containing membranes by estimating the overall tortuosity (τ') via the inverse rule of mixture:

$$\frac{1}{\tau} = \frac{(1-\varphi)}{\tau} + \frac{\varphi}{\tau_1} \quad (15)$$

In this equation, φ , τ and τ_1 are volume fraction of nanosheets, tortuosity of the host membrane (calculated by Prager or Yasuda models) and tortuosity caused by the nanosheets, respectively. τ_1 can be calculated as follows [43,44]:

$$\tau_1 = 1 + \frac{a\varphi(2S+1)}{6} \quad (16)$$

where a is the aspect ratio, defined as the ratio of width (w) to thickness (t) of the nanosheets. Also, S , the orientation parameter of the nanosheets, depends on the angle between the sheets normal and the direction of the proton diffusion (θ) [43]:

$$S = (3 \cos^2 \theta - 1)/2 \quad (17)$$

In the case of random sheet orientation S equals zero. The tortuosity decreases with orientation and diffusion is facilitated as opposed to parallel orientation ($S = 1$). In this study, we considered random orientation for nanoparticles in the membranes [40,45].

By substituting Eq. (16) into Eq. (15), an expression for the overall tortuosity factor is obtained:

$$\tau = \frac{\tau \left(1 + \frac{a\varphi(2S+1)}{6} \right)}{(1-\varphi) \left(1 + \frac{a\varphi(2S+1)}{6} \right) + \tau\varphi} \quad (18)$$

The membrane tortuosity factor (τ) in Eq. (18) can be taken from the Prager model, Eq. (11), the Yasuda model ($K = 0.7$, Eq.

Table 2 – The values of λ_w^a for SGO/Nafion1100 membranes, containing 5 or 10 wt% of the SGO, at test temperatures of 80 °C and 120 °C at different RHs.

Membrane	Test temperature 80 °C					Test temperature 120 °C		
	RH %					RH %		
	20	40	60	80	100	20	30	40
SGO5/Nafion1100	1.9	5	7.75	9.5	13.75	1.6	3.4	6.5
SGO10/Nafion1100	2	5.8	9.5	12	15.5	1.8	4.1	5

^a Obtained from Eq. (10).

Table 3 – The values of λ_w for GO/SPEEK1 and SGO/SPEEK1 membranes containing different amounts of GO or SGO, at test temperature of 80 °C [24].

Membrane	GO or SGO wt%					
	SPEEK1	1	3	5	7	10
GO/SPEEK1	41.6	34.153	21.2	18.51	19.91	20.88
SGO/SPEEK1	41.6	33.058	13.71	8.417	6.8	4.6

(12)) or the Yasuda model ($K = 3$, Eq. (12)) to obtain τ'_p , $\tau'_{Y,0.7}$ or $\tau'_{Y,3}$ expressions, respectively, as the overall tortuosity factors.

3. Results

Experimental proton conductivity data of some GO or F-GO (sulfonated GO or SGO) containing membrane systems were used to investigate the accuracy of the Choi model, Eq. (1), to predict the systems behavior. The nanocomposite membrane systems include: SGO/Nafion1100 [19], SGO/Nafion112 [46], GO/sulfonated poly(ether ether ketone), with ion exchange capacity (IEC) = 0.75 mmol/g, (GO/SPEEK1) [24], SGO/SPEEK1 [24], SGO/sulfonated poly(ether ether ketone), with IEC = 1.71 mmol/g, (SGO/SPEEK2) [23] and GO/sulfonated polyimide (GO/SPI) [47]. Table 1 shows the necessary parameters required for calculating the proton conductivity of the membrane systems by Eq. (1). Also Tables 2–5 provide the moles of water sorbed per acid site (λ_w) for the nanocomposite membranes, obtained from the literature or calculated using Eq. (10). To describe the accuracy of the Choi model, we calculated the standard deviation (SD) between the predicted and experimental proton conductivity values of the above membrane systems, Tables 6–11. It should be noted that to assess and compare the role of tortuosity factor on the predictability of Eq. (1), data shown in Tables 6–11 include the corresponding values of SD obtained by using the tortuosity factors taken from the Prager equation (τ_p), Yasuda equations ($\tau_{Y,0.7}$ and $\tau_{Y,3}$) and their modified forms (τ'_p , $\tau'_{Y,0.7}$ and $\tau'_{Y,3}$, respectively) in the Choi model.

Table 6 shows that the use of Prager equation to estimate the tortuosity factor of the Choi model gives the best agreement (the least SD values) between calculated and experimental proton conductivity values of the Nafion membranes containing 5 wt% of SGO (SGO5/Nafion1100) at test temperature of 80 °C and at all relative humidities (RH%) tested. However, by increasing the test temperature to 120 °C, the closest values to the experimental points were obtained by inserting the τ'_p expression into Eq. (1) to calculate the proton conductivities (Table 6).

Table 4 – The values of λ_w for SGO/SPEEK2 membranes containing different amounts of SGO, at test temperature of 65 °C [23].

Membrane	SGO wt%			
	SPEEK2	3	5	8
SGO/SPEEK2	21.659	19.4	29.68	30.765

Table 5 – The values of λ_w ^a for GO/SPI membranes containing different amounts of the GO, at test temperature of 90 °C.

Membrane	GO wt%					
	SPI	0.1	0.3	0.5	0.7	0.9
GO/SPI	6	8	11	20	7	5

^a Obtained from Eq. (10).

As Table 7 demonstrates, in the case of the SGO10/Nafion1100 membranes, the experimental proton conductivity values obtained at 80 °C and at relative humidities up to 40%, could be best predicted when the τ_p expression was utilized to calculate the σ_{H^+} values by Eq. (1), while at the same test temperature but at relative humidities greater than 40%, the best prediction was achieved by using the τ'_p expression for the conductivity calculations. It is also shown in Table 7 that at the test temperature of 120 °C, the τ'_p expression should be inserted in Eq. (1) in order to obtain an accurate prediction of the experimental σ_{H^+} data.

Moreover, Table 8 shows that by incorporating very low amounts of SGO (0.5 wt%) in the SGO0.5/Nafion112 membrane and at different temperatures under saturated humidity condition, this is the τ'_p expression that must be substituted into Eq. (1) to achieve the best agreement between the experimental and theoretical values of σ_{H^+} .

According to the SD values reported in Table 9, the best agreement between the calculated and experimental proton conductivity data of GO/SPEEK1 membranes (containing 1, 3, 5, 7 and 10 wt% of the GO) was achieved by inserting the $\tau_{Y,3}$ expression into Eq. (1) to calculate the σ_{H^+} values. On the other hand, by incorporating more than 1 wt% SGO in the SPEEK1 polymer, the closest results to the experimental data were obtained when the $\tau'_{Y,3}$ expression was used to calculate the σ_{H^+} values by Eq. (1), Table 9.

Also, as Table 10 shows, for the SGO/SPEEK2 membranes (containing 3, 5 and 8 wt% of the SGO), the experimental proton conductivity values were best predicted by inserting the τ'_p expression into Eq. (1) to calculate the proton conductivities.

Finally in Table 11, the experimental proton conductivity values of the GO/SPI membranes, containing up to 0.5 wt% of the GO, could be best predicted when the $\tau'_{Y,0.7}$ expression was utilized to calculate the σ_{H^+} values by Eq. (1), while at higher GO loadings (0.7 and 0.9 wt%), the best prediction was achieved by using the $\tau'_{Y,3}$ expression for the conductivity calculations.

4. Discussion

Based on the above results one can conclude that the Choi model can reasonably predict the proton transport behavior of GO (SGO) containing membranes, depending on the expression used for the tortuosity factor in Eq. (1). In Nafion based membranes the polymer microphases separate into hydrophilic domains of sulfonic acid groups and absorbed water imbedded in a hydrophobic matrix of tetrafluoroethylene (TFE) and perfluoroalkyl ether (PFA) to pass protons through the network of hydrophilic domains [48]. Therefore, the

Table 6 – Standard deviations between calculated results and experimental data for SGO5/Nafion1100 membranes at test temperatures of 80 and 120 °C.

Tortuosity factor	Test temperature 80 °C					Test temperature 120 °C		
	RH%					RH%		
	20	40	60	80	100	20	30	40
τ_p	0.00056	0.00141	0.00071	0.00071	0.01270	0.00190	0.00310	0.00260
τ'_p	0.00141	0.00242	0.00071	0.00141	0.01410	0.00021	0.00042	0.00014
$\tau_{Y,3}$	0.00501	0.02758	0.05650	0.07770	0.08410	0.00849	0.02360	0.04950
$\tau'_{Y,3}$	0.00311	0.02425	0.05218	0.07250	0.07861	0.00594	0.02001	0.04492
$\tau_{Y,0.7}$	0.00495	0.02312	0.02744	0.02600	0.01810	0.00840	0.02290	0.03260
$\tau'_{Y,0.7}$	0.00311	0.02000	0.02440	0.02320	0.01892	0.00594	0.01923	0.02878

Table 7 – Standard deviations between calculated results and experimental data for SGO10/Nafion1100 membranes at test temperatures of 80 and 120 °C.

Tortuosity factor	Test temperature 80 °C					Test temperature 120 °C		
	RH%					RH%		
	20	40	60	80	100	20	30	40
τ_p	0.00005	0.00233	0.00622	0.00250	0.01760	0.00594	0.00871	0.02581
τ'_p	0.00141	0.00346	0.00571	0.00049	0.01351	0.00396	0.00650	0.02353
$\tau_{Y,3}$	0.00566	0.02972	0.06001	0.09150	0.10422	0.01271	0.03352	0.06362
$\tau'_{Y,3}$	0.00382	0.02601	0.05533	0.08601	0.09891	0.01012	0.02952	0.05861
$\tau_{Y,0.7}$	0.00565	0.02061	0.01492	0.01051	0.01982	0.01271	0.03113	0.05643
$\tau'_{Y,0.7}$	0.00375	0.01761	0.01341	0.01130	0.01661	0.01012	0.02731	0.05190

equation derived by Prager [34], assuming a systematic distribution of the regions for proton diffusion, was the best choice for tortuosity factor calculations of the Nafion based nanocomposite membranes. It is also important to note that, depending on the GO (SGO) content in the Nafion polymer and the conditions of proton conductivity tests, τ_p or τ'_p expressions are suggested for the tortuosity factor calculations. For example, it is necessary to use the developed Prager equation (τ'_p) at very low concentrations of GO (SGO), Table 8, due to the well dispersion of the nanosheets inside the Nafion membrane, or at high test temperatures (e.g. 120 °C), due to the drying of the membrane system. In other words, the well-dispersed nanosheets contribute considerably in the proton conductivity of the host membrane and the effect can be well considered by inserting the τ'_p expression in Eq. (1) to calculate the σ_{H^+} values. Also, the role of the graphene oxide nanosheets on the proton conductivity becomes more important as the Nafion membrane loses its water content at high test temperatures, and the τ'_p expression can take this better into account than the τ_p expression.

On the other hand, according to the SD values reported in Tables 9–11 it is reasonable to conclude that the selection of the best expression for tortuosity factor calculations in non-fluorinated membrane systems (SPEEKs and SPI) depends on the IEC values of the host membranes. In the non-fluorinated membranes, possessing low (SPEEK1) and high (SPI) IEC values the results obtained by substituting the Yasuda equation in Eq. (1) are more consistent with experimental data, while in the case of the medium IEC membrane (SPEEK2), the use of the τ'_p expression led to a better agreement between the theory and experiment. In the SPEEK1 based membranes, the continuity of transport channels are less than that in the Nafion system and therefore the equation which was proposed based on the free volume theory, by Yasuda [35], was the best choice for tortuosity factor calculations. It should be noted that since SGO nanosheets could be better dispersed, in comparison with GO ones, in the SPEEK1 membrane, the use of $\tau'_{Y,3}$ expression in Eq. (1) resulted in better agreement between the experimental and theoretical proton conductivity values of the SGO/SPEEK1 membranes. Also, due to the high IEC value of

Table 8 – Standard deviations between calculated results and experimental data for SGO0.5/Nafion112 membranes at different test temperatures under saturated humidity condition.

Tortuosity factor	Test temperature/°C							
	25	40	50	60	70	80	90	100
τ_p	0.0204	0.0164	0.0155	0.0151	0.0181	0.0203	0.0167	0.0145
τ'_p	0.0199	0.0158	0.0149	0.0143	0.0173	0.0190	0.0157	0.0133
$\tau_{Y,3}$	0.0488	0.0535	0.0587	0.0643	0.0735	0.0800	0.0848	0.0883
$\tau'_{Y,3}$	0.0483	0.0528	0.0579	0.0634	0.0724	0.0811	0.0835	0.0869
$\tau_{Y,0.7}$	0.0329	0.0328	0.0346	0.0368	0.0425	0.0469	0.0468	0.0470
$\tau'_{Y,0.7}$	0.0324	0.0321	0.0338	0.0359	0.0416	0.0458	0.0456	0.0458

Table 9 – Standard deviations between calculated results and experimental data for GO/SPEEK1 and SGO/SPEEK1 membranes at test temperature of 80 °C.

Tortuosity factor	GO or SGO wt%					
	SPEEK1	1	3	5	7	10
GO/SPEEK1						
τ_p	0.1006	0.0931	0.0714	0.0651	0.0685	0.0707
τ'_p	0.1006	0.0940	0.0732	0.0669	0.0696	0.0705
$\tau_{Y,3}$	0.0053	0.0023	0.0001	0.0000	0.0001	0.0001
$\tau'_{Y,3}$	0.0053	0.0037	0.0032	0.0039	0.0044	0.0048
$\tau_{Y,0.7}$	0.1162	0.1011	0.0565	0.0443	0.0508	0.0551
$\tau'_{Y,0.7}$	0.1162	0.1019	0.0586	0.0468	0.0527	0.0560
SGO/SPEEK1						
τ_p	0.1006	0.0965	0.0947	0.0884	0.0653	0.0412
τ'_p	0.1006	0.0971	0.0966	0.0924	0.0687	0.0455
$\tau_{Y,3}$	0.0053	0.0036	0.00436	0.0059	0.0055	0.0039
$\tau'_{Y,3}$	0.0053	0.0047	0.0006	0.0001	0.0031	0.0013
$\tau_{Y,0.7}$	0.1162	0.1140	0.0848	0.0560	0.0234	0.0016
$\tau'_{Y,0.7}$	0.1162	0.1144	0.0869	0.0600	0.0247	0.0038

Table 10 – Standard deviations between calculated results and experimental data for GO/SPEEK2 membranes at test temperature of 65 °C.

Tortuosity factor	GO wt%			
	SPEEK2	3	5	8
τ_p	0.0803	0.0370	0.0411	0.0421
τ'_p	0.0803	0.0370	0.0398	0.0378
$\tau_{Y,3}$	0.0503	0.0948	0.0849	0.0831
$\tau'_{Y,3}$	0.0503	0.0915	0.0821	0.0807
$\tau_{Y,0.7}$	0.1073	0.0608	0.0750	0.0765
$\tau'_{Y,0.7}$	0.1073	0.0612	0.0721	0.0704

SPI, the dilution effect [49] would be the dominant mechanism affecting the proton conductivity of the GO/SPI membranes. It seems that the developed Yasuda equations ($\tau'_{Y,0.7}$ and $\tau'_{Y,3}$) could include the above effect in the σ_{H^+} values calculated by the Choi model. However, in the SGO/SPEEK2 system, the weak continuity of transport channels and the occurrence of the dilution effect were balanced by the medium IEC value of the SPEEK2 membrane, and thus the system behaved like the Nafion based nanocomposites.

5. Conclusions

A simple Nernst–Planck based model (the Choi model) was utilized to predict the proton conductivity of polymeric

Table 11 – Standard deviations between calculated results and experimental data for GO/SPI membrane at test temperature of 90 °C.

Tortuosity factor	GO wt%					
	SPI	0.1	0.3	0.5	0.7	0.9
τ_p	0.1383	0.0887	0.0497	0.1789	0.1841	0.1533
τ'_p	0.1383	0.0891	0.0490	0.1784	0.1858	0.1556
$\tau_{Y,3}$	0.0701	0.1542	0.3182	0.4257	0.0435	0.0316
$\tau'_{Y,3}$	0.0701	0.1536	0.3167	0.4244	0.0408	0.0282
$\tau_{Y,0.7}$	0.1044	0.0945	0.0065	0.1097	0.1715	0.0963
$\tau'_{Y,0.7}$	0.1044	0.0945	0.0059	0.1095	0.1732	0.0989

membranes containing GO or F-GO sheets. The values of statistical parameters between experimental data points from literature and calculated proton conductivities showed that the Choi model could reasonably reproduce and predict the proton transport behavior of GO (SGO) containing membranes, depending on the expression used for the tortuosity factor in the model. It was demonstrated that the use of the modified tortuosity factor derived in the present work to account for the exact role of GOs in the proton conductivity mechanism, resulted in the best agreement between theory and experiment for fluorinated membranes at low amounts of GO or at high test temperatures as well as for non-fluorinated membranes with high IEC values.

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