



# Effect of the incorporation of sulfonated chitosan/sulfonated graphene oxide on the proton conductivity of chitosan membranes



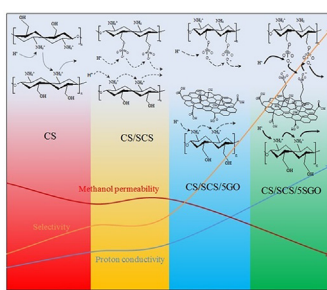
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## HIGHLIGHTS

- Sulfonated chitosan (SCS) and SGO are added to CS to prepare nanocomposite membranes.
- Nanocomposite membranes show better thermal/mechanical properties than pure CS.
- SCS and SGO enhance proton conductivity of CS in a synergistic manner.
- Adding 5 wt% SGO to CS/SCS causes about 6-fold gain in conductivity and selectivity.
- Experimental proton conductivity data are predicted by a Nernst–Planck based model.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Chitosan biopolymer (CS) has been attracting considerable interest as polymer electrolyte in fuel cells. However, proton conductivity of chitosan is low and it is necessary to enhance its conductivity. In this work, 10 wt% sulfonated chitosan (SCS) and different amounts of sulfonated graphene oxide (SGO) nanosheets are incorporated into a chitosan membrane to investigate their effects on the electrochemical properties of the membrane. The proton conductivity and methanol permeability tests conducted on the CS/SCS/SGO membranes show that the conductivity is increased by 454%, the permeability is reduced by 23% and hence the selectivity is increased by 650%, relative to the neat chitosan, at SGO content of 5 wt%. Furthermore, combined addition of SCS and SGO to chitosan causes much more proton conductivity enhancement than the individual additives due to the synergistic effect of SCS and SGO. The observed synergistic effect reveals the importance of the chemical functionality of chitosan and nanofillers in the formation of ionic cluster domains with enhanced size within the membranes for proton transport. Finally, a Nernst–Planck based model is applied to the experimental proton conductivity data in order to shed more light on the role of GOs in the proton conductivity mechanism of chitosan.

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## 1. Introduction

In the past decade, direct methanol fuel cells (DMFCs) have gained considerable attention as power sources for portable power applications owing to many advantages such as high energy density, no requirement of fuel reforming process, simplicity and

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convenience [1–3].

Proton exchange membrane (PEM) is one of the major components which directly govern the DMFC performance. Perfluorosulfonic acid (PFSA) membranes (e.g. Nafion) are currently the most widely used fuel cell membranes for DMFCs, due to their high proton conductivity and good chemical stability [4]. However, these membranes suffer from high methanol permeability, which diminishes the fuel cell efficiency and performance [5]. Moreover, the high cost of Nafion has impeded the commercialization of DMFC technology so far. In recent years, chitosan (CS), an abundant and inexpensive polysaccharide with low toxicity, has been suggested as a promising membrane material for DMFC applications, mainly due to its inherent low methanol permeability [6]. Nevertheless, chitosan membranes show low proton conductivity, and therefore, there is an urgent need to enhance their conductivity. There are two main approaches to improve proton conductivity. The first is the functionalization of chitosan with different groups, especially sulfonic acid,  $-\text{SO}_3\text{H}$ , groups. For example, Xiang et al. [7] prepared a sulfonated chitosan (SCS) polymer by grafting the chitosan monomers with sulfonic groups in order to be used as PEM [7]. Due to the excessive swelling of the SCS, it was blended with pure chitosan in different weight ratios and cross-linking was occurred by the bonds reaction between the sulfonic groups in SCS and the amide groups in the pure chitosan monomers. It was found that the developed CS/SCS membranes had enhanced proton conduction and methanol resistance compared to pure CS membrane. Nevertheless, the proton conductivity enhancement and methanol permeability reduction were not sufficient enough to result in a high selectivity (the ratio of proton conductivity and methanol permeability) compared to Nafion. Addition of inorganic fillers has been another approach to improve the proton conductivity of chitosan membranes [8–10]. Embedding inorganic fillers within the membrane also plays important roles in enhancing mechanical and thermal properties and suppressing methanol crossover. A variety of fillers, including montmorillonite, silica, titania, metal oxides, metal phosphates and zeolites have been incorporated in chitosan membranes for fuel cell applications [11–15].

Recently, Bai et al. [15] fabricated chitosan nanohybrid membranes containing halloysite nanotubes bearing sulfonate polyelectrolyte brushes (SHNTs) for potential DMFC PEMs. It was shown that the high aspect nanotube and long polyelectrolyte brush allow SHNTs to construct continuous and wide pathways along which sulfonic acid–amide acid–base pairs are formed and work as low-barrier proton-hopping sites, imparting an enhanced proton transfer via Grotthuss mechanism.

Compared with HNTs, functionalized graphene oxide (F-GO) nanosheets allow protons to permeate through them with selectively rejecting other substances, such as methanol, due to the ability to form unique two-dimensional nanochannels between the sheets [16]. Thus, fabricating and investigating F-GO containing chitosan membranes would facilitate the development of promising PEMs with high selectivity for DMFC applications.

In this work, we prepared nanocomposites consisting of a chitosan/sulfonated chitosan blend (CS/SCS) as the matrix and sulfonated graphene oxide (SGO) nanosheets as the filler to study the effects of both SCS and SGO on the proton conductivity and selectivity of the chitosan. The results demonstrated the synergistic effect of SCS and SGO on the proton conductivity enhancement of CS. In addition, the facily functionalized GO nanosheets were found to be highly efficient in improving the selectivity of chitosan.

On the other hand, compared with a huge amount of experimental studies regarding the effects of micro/nano particles on the proton conductivity of polymeric membranes, studies devoted to predict the proton conductivity are scarce in the literature [17,18]. Consequently, another objective of this work was to apply a

recently developed Nernst–Planck based model [17] to our experimental proton conductivity data in order to describe the role of GOs in the proton conductivity mechanism of chitosan as well as to extend the applicability of the model to a broader category of PEMs.

## 2. Theory

A Nernst–Planck based model has been proposed by Choi et al. [19] to predict the proton conductivity ( $\sigma_{H^+}^0$ ) of neat and spherical nanoparticle-containing polymeric electrolytes:

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

where  $F$  is the Faraday constant ( $96485\text{C mol}^{-1}$ ),  $R$  is the molar gas constant ( $8.314\text{ J mol}^{-1}\text{K}^{-1}$ ),  $T$  is temperature (K) and  $D_{H^+}^{\Sigma}$ ,  $D_{H^+}^G$  and  $D_{H^+}^E$  are diffusion coefficients of protons for the surface, Grotthuss and en masse diffusion mechanisms, respectively. Also,  $C_{H^+}^{\Sigma}$  represents concentration of protons participating in surface diffusion while  $C_{H^+}$  is concentration of protons participating in Grotthuss and en masse diffusions. The detailed equations for calculating diffusion coefficients and concentrations of protons can be found in Ref. [17]. Furthermore,  $\varepsilon_i$  and  $\tau$  are porosity of the membrane and the tortuosity factor, respectively.

The porosity of nanocomposite membranes can be given as follows [20]:

$$\varepsilon_i = \frac{\lambda_w(1/EW_M + w/MW_p)}{\lambda_w(1/EW_M + w/MW_p) + r_{M/W}/EW_M + w.r_{p/w}/MW_p} \quad (2)$$

where  $w$ ,  $\lambda_w$ ,  $r_{M/W}$  and  $r_{p/w}$  represent the weight percent of nanoparticles, 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. Moreover,  $EW_M$  is equivalent weight of the host membrane and  $MW_p$  is the molecular weight of nanoparticles, estimated by equivalent weight of the nanoparticles,  $EW_p$ .

Recently, our group [17] developed the Choi model to consider the exact role of graphene oxide based nanosheets in the proton conductivity mechanism of polymeric membranes. It was found that the expression employed for calculating the tortuosity factor, as the ratio of the actual distance to the shortest distance that a proton travels through a membrane, of the Choi model played an important role in whether the experimental data was accurately predicted. The following equation was then suggested for calculating the overall tortuosity factor ( $\tau'$ ) of GO containing PEM's [17]:

$$\tau' = \frac{\tau \left( 1 + \frac{a\phi}{6} \right)}{(1 - \phi) \left( 1 + \frac{a\phi}{6} \right) + \tau\phi} \quad (3)$$

where,  $\tau$ ,  $a$  and  $\phi$  are the host membrane tortuosity, aspect ratio of nanoparticles and volume fraction of nanoparticles, respectively. The membrane tortuosity factor ( $\tau$ ) in eq. (3) can be obtained from Prager [21] or Yasuda models [22] ( $\tau_p$  or  $\tau_{Y,K}$ , respectively):

$$\tau_p = \frac{2(1 - \varepsilon_i) + 2\varepsilon_i \ln \varepsilon_i - 0.5\varepsilon_i (\ln \varepsilon_i)^2}{\varepsilon_i(1 - \varepsilon_i) + \varepsilon_i^2 \ln \varepsilon_i} \quad (4)$$

$$\tau_{Y,K} = \exp(K((1/\varepsilon_i) - 1)) \quad (5)$$

In eq. (5), the  $K$  parameter is a size coefficient whose value has been reported to be 0.7 or 3 depending on the chemical structure of

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