

An effective strategy to enhance phosphoric acid retention and proton conductivity stability: Construction of proton transfer channels with starch rather than H₃PO₄



Xiuping Li ^{a,*}, Jiyuan Zhang ^a, Xiao Zhang ^c, Xiudong Liu ^a, Shuhua Chen ^a, Yue Qiao ^b, Qian Li ^{d,**}, Cheng Liu ^{b,***}

^a Dalian Key Laboratory of Green Manufacturing Technology for Fine Chemicals Production, College of Environmental and Chemical Engineering, Dalian University, Dalian, 116622, China

^b State Key Laboratory of Fine Chemicals, Frontier Science Center for Smart Materials, School of Chemical Engineering, Dalian University of Technology, Dalian, 116024, China

^c College of Science, State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Changping, Beijing, 102249, China

^d School of Life and Health, Dalian University, Dalian, 116622, China

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ABSTRACT

To enhance the phosphoric acid (PA) retention as well as maintain high proton conductivity of phosphoric acid doped proton exchange membranes at high temperature, we successfully design a series of phosphoric acid doped biobased composite membranes by incorporation of starch and graphene oxide (GO) into poly arylene ether ketones (PAEK). Proton transfer channels should be mainly built through dense hydrogen bonds formed from massive oxygen-containing groups of starch mainchain, which is confirmed by Molecular dynamics (MD) simulation, FT-IR and XRD analysis. The dense hydrogen-bond structure could construct fast proton transfer channels with extreme low doping level (0.00484 molH₃PO₄). The excellent PA retention properties with almost unchanged proton conductivity at high temperature (200 °C) for 600 min indicates that PA molecules are firmly fixed into membranes. Thus, in this study, we suggest a novel strategy for stabilizing proton conductivity at high temperature and improving PA retention properties of PA doped membranes, which is building dense hydrogen-bond structure with low PA doping level.

Based on the results in this study and the Grotthuss proton transfer mechanism, dense hydrogen-bonds from oxygen-containing groups in polymer backbones should be more stable than hydrogen-bonds from massive H₃PO₄ molecules with high acid doping levels to promote proton conduction.

1. Introduction

High temperature proton exchange membrane fuel cells (HT-PEMFCs) [1–4] have received immense attentions due to their advantage of enhancing catalysts tolerance to CO poisoning, increasing oxygen reduction reaction kinetics, simplifying water and heat management compared with traditional low temperature proton exchange membrane fuel cells [4]. As the key components of HT-PEMFCs, high temperature proton exchange membranes (HT-PEMs) should meet the following requirements: excellent thermal resistance, high proton conductivity, stable mechanical property, good chemical stability, long durability and

low cost. Thus, the structural design and preparation of membrane materials with above properties become the hotspots during the development of HT-PEMFCs. Aromatic-based membranes with strong rigid backbones should be good candidates for HT-PEM materials due to their excellent thermal stability and mechanical properties [5–8].

Poly (arylene ethers) based membranes possess rigid and aromatic structure characterizations, which lead to high thermal stability and excellent mechanical properties [9–12]. As a family of poly (arylene ethers), poly (ether ketone)s (PAEK) [13,14] which has outstanding comprehensive properties especially excellent solubility and low cost, which should be good candidate of HT-PEM materials.

* Corresponding author.

** Corresponding author.

*** Corresponding author.

E-mail addresses: lixp0204@sina.cn (X. Li), liqian@dlu.edu.cn (Q. Li), liuch1115@dlut.edu.cn (C. Liu).

The pristine PAEK membrane without acid doping present almost no intrinsic conductivity, because proton transfer channels would hardly form depending on just polymer mainchain of PAEK. Doping polymer membranes with phosphoric acid (PA) is an effective method to constructing proton transfer channels, which makes membranes possess proton conductivity. The proton strategy in PA doped membranes is that protons are transferred through hydrogen bonds formed with PA molecules, especially at high doping levels. Membranes with high doping levels could perform high proton conductivity because high doping levels indicate more PA molecules which could form denser hydrogen bonds network, facilitating proton transfer.

However, phosphoric acid (PA) doped membranes face dilemma among PA doping levels, PA leaching, mechanical stability and proton conductivity. High PA doping levels will lead to high proton conductivity but decrease the mechanical strength of membrane due to the strong plasticization of PA at high temperatures [15]. Besides, the PA leaching resulting from high doping levels is another major obstacle for application of PA doped membranes for HT-PEMs [16,17]. Therefore, the further understanding of proton transfer mechanism in PA doped membranes are valuable to investigate novel HT-PEMs with high proton conductivity, stable mechanical strength and good PA retention.

As previously reported, proton transfer mechanisms have been recognized as the vehicle mechanism and the Grotthuss mechanism [16, 18,19]. In the vehicle mechanism, protons are transferred by the carriers, such as H_3O^+ [19,20]. While in the Grotthuss mechanism, protons are transferred through hydrogen bonds [21,22].

In PA doped membranes, proton transfer mainly follows the Grotthuss mechanism: at low PA doping levels, the Grotthuss mechanism is the main transformation between H_3O^+ and H_2O , while at high doping levels, the hopping number of protons increased between H_4PO_4^+ and H_3PO_4 molecules, considerably increasing its proton conductivity [23, 24]. Protons are transferred through hydrogen bond network formed among PA molecules connected in polymer backbones, but mainly among massive free PA molecules when at high doping levels [24–26]. This could explain why high doping levels lead to high proton conductivity and severe PA leaching. The pattern that high doping level leads to high proton conductivity is because more PA molecules in high doping level membranes could form more dense hydrogen bond network. Then proton exchange channels are constructed through polymer-fixed PA molecules and free PA molecules in the membranes, facilitating proton conduction. But meanwhile, massive free PA molecules should degrade and most of them leach out of the membranes especially at the temperature above 180 °C [8,27]. The severe PA leaching causes dramatic decreased proton conductivity at high temperatures, which limit the durability of the membranes.

Preparation of membranes with low PA doping levels is an effective strategy to solve the PA leaching problem [27,28], because low PA doping levels leads to decreased free PA molecules in the membranes. But meanwhile, low PA doping level should reduce the proton conductivity due to the reduced proton exchange channels by hydrogen bond network formed from free PA molecules. Considering this, other proton exchange channels should be designed and established without free PA molecules. Structural design of PA doped membranes at high proton conductivity with low doping levels should introduce other functional groups instead of PA molecules to form dense hydrogen bond networks.

Oxygen-containing groups, such as hydroxyl, would be good candidates to form hydrogen bond networks. Previous research should confirm this deduction. Ma investigated the proton transport mechanism of PA doped PBI membrane, and proposed that protons transfer the fastest through -OH and $\text{H}_3\text{PO}_4(\text{H}_2\text{PO}_4^-)$ [24]. More studies indicate introduction hydroxyls into polymer backbone should enhance the proton conductivity of PA doped membranes [15,29].

Starch is a kind of low-cost natural macromolecules with massive hydroxyl groups, which would facilitate forming hydrogen bond network [30,31]. The backbones of starch contain abundant oxygen atoms, which means introduction small quantities of starch into

aromatic-based membranes should import considerable amounts of oxygen-containing groups, facilitating constructing hydrogen bonds in membranes. Hydrogen bonds structure in membranes should facilitate proton conduction due to the Grotthuss mechanism.

Above all, in this study, a novel series of PA doped starch-graphene oxide-PAEK HT-PEM with low PA doping levels are designed. We suggest novel proton transfer channels through PAEK fixed PA molecules, massive oxygen-containing groups of starch mainchains and graphene oxide (GO). This structure may promote proton conduction, PA retention and mechanical strength with no need of high PA doping levels, which could solve the dilemma between proton conductivity and PA leaching.

2. Experimental details

2.1. Preparation of biobased starch graphene oxide PAEK (st-GO-PAEK) proton exchange membrane

The preparation of St-GO-PAEK proton exchange membranes mainly includes two steps: solution casting St-GO-PAEK membranes and phosphoric acid doping.

Firstly, a series of St-GO-PAEK membranes with variation of starch/PAEK mass ratio were prepared by solution casting method. The starch master batch and the poly (aryl ether ketone) (PAEK) containing 2-adamantane structure (2-ADMPEK) polymer with different mass proportion (starch/PAEK: 0/100, 5/95, 10/90, 15/85) were put into single layer graphene oxide (GO) dispersion (2 mg/ml, N-Methylpyrrolidone, NMP). After starch master batch and PAEK dissolving uniformly with stirring, the starch graphene oxide PAEK solution mixture was obtained (m/v:10 %, 0.1 g/ml). The starch graphene oxide PAEK solution (10 % w/v, GO-NMP) was spread uniformly onto clean glass slides, and then heated at 60 °C on an aclinic warm table for at least 10 h. After the N-Methylpyrrolidone (NMP) solvent evaporated, the St-GO-PAEK membranes were peeled off from the glass slides, further dried under vacuum at 100 °C for 24 h to remove residual solvent.

Then the St-GO-PAEK membranes were doped in 85 wt% phosphoric acid for 72 h at 25 °C to prepare acid doped St-GO-PAEK proton exchange membranes. After doping, the membranes were taken out from phosphoric acid, wiped with tissue and dried under vacuum at 80 °C for 12 h. The membranes with different starch/PAEK mass ratio were named as St-GO-PAEK-aabb, of which aabb represents the mass ratio of starch/PAEK is aa/bb. For example, St-GO-PAEK-1585 means the mass ratio of starch/PAEK is 15/85, and St-GO-PAEK-00100 means the mass ratio of starch/PAEK is 0/100.

2.2. Materials and characterization

Full biobased starch master batch was purchased from Changzhou Nuoxin Polymer Technology Co.,Ltd. The poly (aryl ether ketone) containing 2-adamantane structure (2-ADMPEK) [32] was purchased from Shenyang University of Chemical Technology. Single layer graphene oxide (GO, diameter>500 nm, NMP solvent) dispersion was obtained from Jiangsu XFNANO Materials Tech. Co.,Ltd. All the other chemicals were obtained from commercial sources and used as received.

The Fourier Transform Infrared Spectroscopy (FT-IR) spectra were performed on a Thermo Nicolet Nexus 470 Fourier transform infrared spectrometer. The wide-angle X ray diffraction (XRD) was conducted on a SmartLab 9 KW x-ray diffractometer.

The characterization methods of PA doping levels, proton conductivity, oxidative stability and mechanical strength are similar with the previously study [15,33,34].

The proton conductivity of PAEK membranes was measured using two-probe electrochemical impedance spectroscopy technique in a muffle furnace. The test details are as follows. The PAEK membrane sample was sandwiched between the two electrodes of the test cell, and the test cell was put into a muffle furnace at the test temperature. After

the test cell with the membrane being stayed and stabilized in the muffle furnace for 10 min at the test temperature, the resistance of the sample was measured by CHI660E with amplitude of 5 mV in the frequency range of 1–10⁵ Hz. The proton conductivity (σ) was calculated by the following equation:

$$\sigma = \frac{L}{S \times R} \quad (1)$$

where R is the measured resistance of the membrane, L is the thickness of the membrane, and S is the cross-sectional area of the membrane. The relative humidity is 0–10 % during the proton conductivity test.

The PA doping level was calculated as the difference in weight of the membrane with and without PA, thereby determining the moles of PA per mole of St-GO-PAEK repeat unit from the following equation:

$$\text{Doping level} = \frac{(W_2 - W_1)/M_{H_3PO_4}}{W_1/[M_{PAEK}(1 - X) + M_{St}X]} \quad (2)$$

Where $M_{H_3PO_4}$, M_{PAEK} , and M_{St} present the molecular weight of PA, PAEK and Starch repeat unit, respectively. W_1 and W_2 are the weight of undoped membrane and acid doped membrane, respectively. X is the starch (St) mole ratio.

The PA retention ability of PBI membranes was investigated by measuring the proton conductivity decreasing at temperature of 200 °C. More proton conductivity decreasing indicates more PA are leaching out of the membranes [34].

2.3. Molecular dynamics (MD) simulation methods

The initial configurations were generated according to the structure of PA doped St-GO-PAEK membranes by randomly arranging the 44 PAEK chains, 2 starch chains, 18 phosphoric acid molecules and 2 oxidized graphene molecules in an initial cubic cell with a side length of 65 nm using the Packmol software.

All molecular dynamics (MD) simulations were carried out using Materials Studio 2020, and the modeling structure was modified in Forceit modules. All molecules were adopted Compass II force field and modified in 5 × 10⁵ step in Ultra-fine precision. Molecular dynamics (MD) simulations conditions are as follows: In the NPT system of 289.15 K and 1 GPa, Nose temperature-controlled instrument and Berendsen pressostat were used for calculating in 100 ps? Hydrogen bond statistics were performed on the last frame of the box by script.

3. Results and discussion

3.1. Structure simulation

Fig. 1 shows abundant uniformly distributed oxygen-containing groups in the membrane structure. The membrane overview structure exhibit abundant uniformly distributed oxygen atom (the red atoms in the background) in the simulation box, which should be due to the abundant even-distributed oxygen-containing groups in polymer chains as well as oxidized graphene and phosphoric acid in membrane

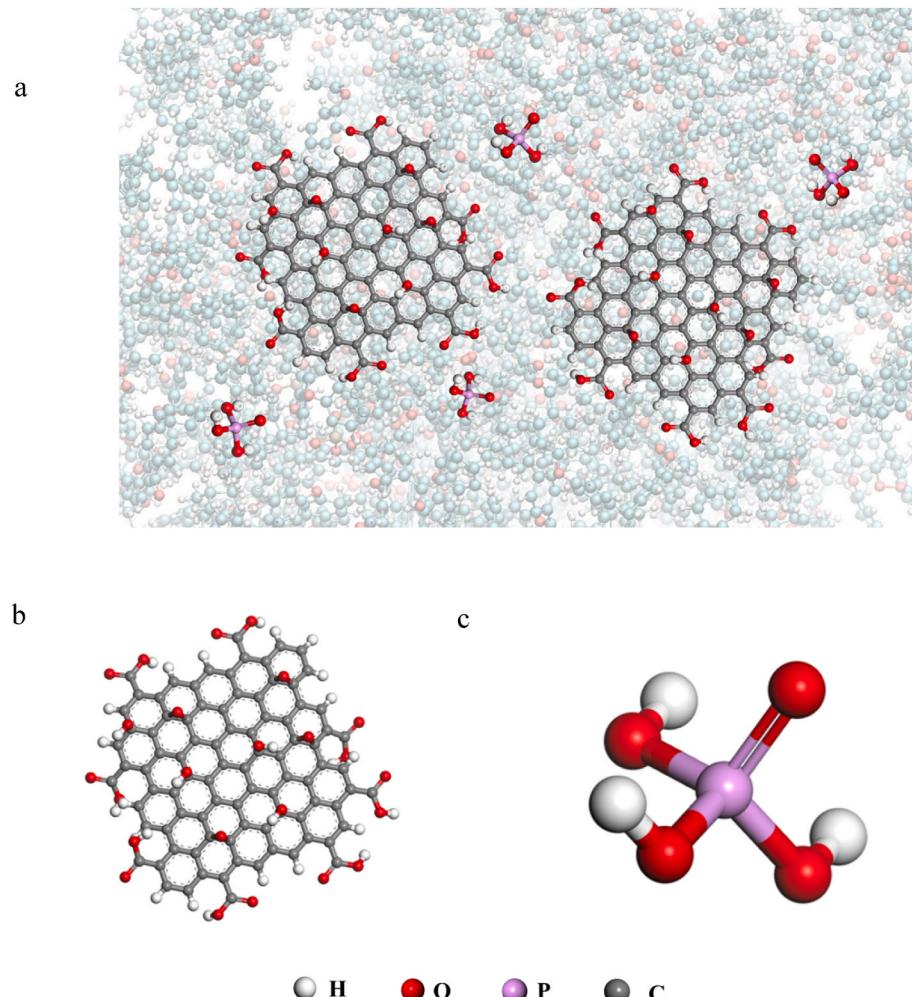


Fig. 1. Molecular dynamics (MD) simulation of phosphoric acid doped St-GO-PAEK-1090 membrane (a: simulated chemical structure of PA doped St-GO-PAEK membrane in this study; b: simulated chemical structure of graphene oxide; c: simulated chemical structure of phosphoric acid).

structure. These oxygen-containing groups should form dense hydrogen bond networks in the whole membrane structure, as shown in Fig. 2. Dense hydrogen bond networks could facilitate proton conduction according to the Grotthuss mechanism [21,35]. Otherwise, dense hydrogen bond networks could enhance intermolecular forces, which may lead to good tensile strength. Further, hydrogen bond networks should protect oxygen-containing groups from attacking by oxygen free radicals in the Fenton's reagent, which may be beneficial for the oxidative stability.

The simulated structure in Fig. 2 shows a promising membrane structure with excellent proton conductivity and PA retention due to the dense hydrogen bond structure and firmly fixed PA molecules in the structure. The hydrogen bonds are mainly formed on the starch chain, demonstrating that incorporation of starch should facilitate formation of hydrogen bonds, which could facilitate proton conduction according to the Grotthuss mechanism. Moreover, almost all the PA molecules are firmly fixed into hydrogen bonds network, which would indicate improved PA retention properties compared with membranes with massive free PA molecules.

Fig. 2a presents the structure of PAEK repeating unit, of which the bulk non-coplanar adamantine structure could create more space among polymer chains to the benefit of accommodating oxidized graphene (GO) and phosphoric acid (PA). Moreover, oxygen atoms in PAEK structure should lead to more connection among PAEK, starch, PA and GO. Fig. 2b shows the structure of starch repeating unit, which contains abundant oxygen atoms. These abundant oxygen atoms of starch should facilitate hydrogen bond formation as shown in Fig. 2c. Hydrogen bond statistics in Fig. 2c were performed on the last frame of the MD simulation box by script. It can be observed that a large amount of hydrogen bonds are formed among those oxygen atoms in starch chains, PAEK chains, oxidized graphenes (GO) and phosphoric acids (PA). Dense hydrogen bond networks are built in the St-GO-PAEK membrane structure. The dense hydrogen bond networks should facilitate proton conduction, PA retention, tensile strength and oxidative stability of the membrane.

3.2. FT-IR analysis of phosphoric acid (PA) doped st-GO-PAEK membranes

As shown in Fig. 3, the FT-IR spectra confirm the structure of PA doped St-GO-PAEK membranes and indicate abundant hydrogen bonds are formed due to introduction of starch. Compared with pure PEAK(St-GO-PAEK-00100) sample, St-GO-PAEK membranes with starch present more obvious characteristics peaks of hydrogen bonds at 2853 cm^{-1} , 1157 cm^{-1} , 1008 cm^{-1} and 920 cm^{-1} [36] in FT-IR spectra, indicating that the introduction of starch effectively promote formation of hydrogen bonds in membranes. Further, the peak intensity of hydrogen bonds increases with the increasing content of starch, indicating that the starch facilitates hydrogen bonds formation. In the structure of PA doped St-GO-PAEK membranes, hydrogen bonds could be built among

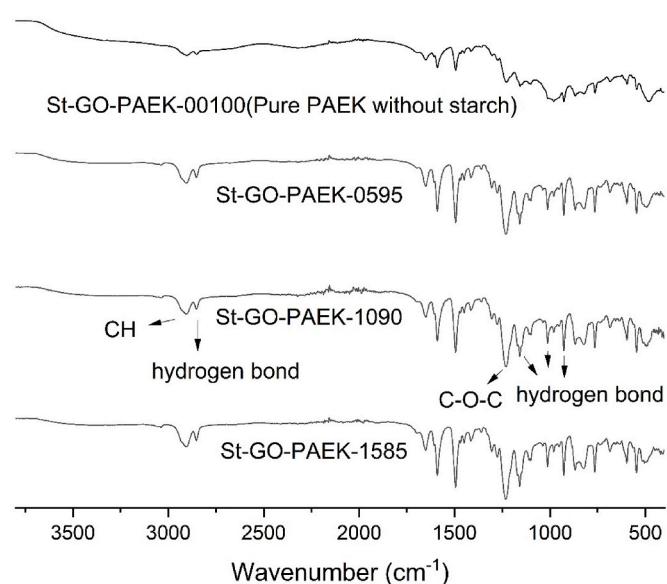


Fig. 3. FT-IR spectra of PA doped St-GO-PAEK membranes.

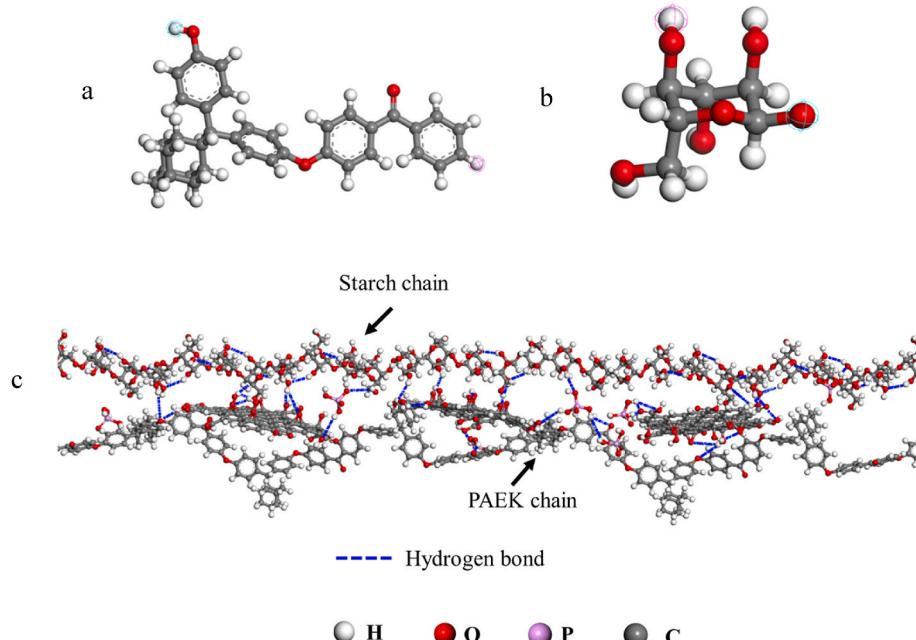


Fig. 2. a: simulated chemical structure of PAEK repeating unit; b: simulated chemical structure of starch repeating unit; c: simulated chemical structure of hydrogen bonds in PA doped St-GO-PAEK membrane.

oxygen-containing groups, such as hydroxy (-OH), carbonyl (C=O), ether linkage (C-O-C) and phosphate groups (H_3PO_4 , $H_2PO_4^-$, HPO_4^{2-}) [36], which is consistent with MD simulation in 3.1.

The peaks at 2910 cm^{-1} and 1229 cm^{-1} could be ascribed to vibration of C-H and C-O-C, respectively. These two peaks appear in the FTIR spectrum of all samples. The peaks at 2910 cm^{-1} and 1229 cm^{-1} in the spectrum St-GO-PAEK-00100 could be ascribed to C-H and C-O-C of GO and PAEK. Meanwhile, St-GO-PAEK-0595, St-GO-PAEK-1090 and St-GO-PAEK-1585 present obviously strengthened peaks at 2910 cm^{-1} and 1229 cm^{-1} , and those peak intensity increases with the increase of starch content of the membranes, which could be due to the introduction of C-H and C-O-C of starch [30,31].

3.3. XRD studies

Fig. 4 shows that the XRD patterns of all samples exhibit amorphous characteristics with broad hump at $2\theta = 12\text{-}23^\circ$. This amorphous character would enhance the ionic conductivity [37] and increase the ion mobility of polymer structure as previously proved [38]. The broad peaks of St-GO-PAEK-0595, St-GO-PAEK-1090, and St-GO-PAEK-1585 present a little sharper than the peak of pure PAEK membrane (St-GO-PAEK-00100), indicating more hydrogen bond interaction due to introduction of starch. These results are consistent with the FT-IR analysis in part 3.2 and MD simulation in part 3.1. Some literatures have reported that pure starch membrane should present some crystalline peaks due to B-type crystallites formed by interchain hydrogen bonding between starch backbones [30]. In this study, the crystallites of starch structure could be destroyed by non-coplanar-structured PAEK, graphene oxide (GO) and doped H_3PO_4 , which could be shown in MD simulation in **Fig. 2c**, so that all samples present amorphous character with no crystalline peaks.

3.4. Phosphoric acid (PA) doping levels and proton conductivity

As shown in **Fig. 5** and **Table 1**, St-GO-PAEK-1090 (doping level: 0.0484 molH_3PO_4) and St-GO-PAEK-1585 (doping level: 0.0799 molH_3PO_4) show obviously higher proton conductivity than that of St-GO-PAEK-0595 (doping level: 0.0481 molH_3PO_4) and PAEK-00100 (pure PAEK, doping level: 1.9280 molH_3PO_4) samples. Even St-GO-PAEK-0595 with such low doping level of 0.0481 molH_3PO_4 shows a little higher proton conductivity than PAEK-00100 (pure PAEK) with much doping level of 1.9280 molH_3PO_4 .

Those starched St-GO-PAEK membranes with lower doping levels

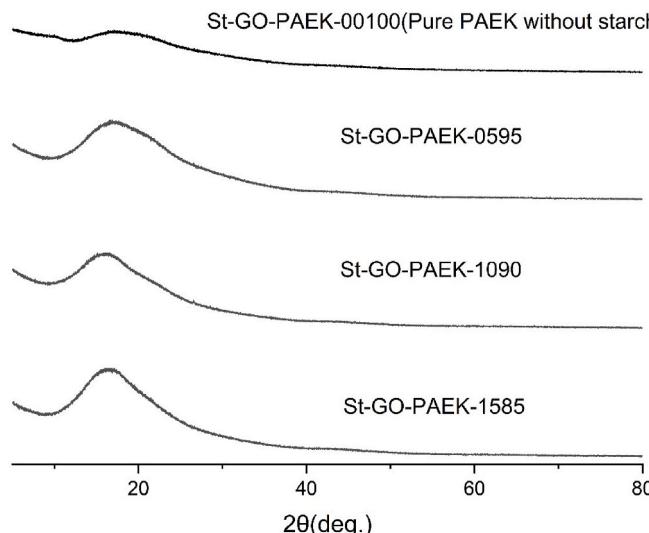


Fig. 4. XRD spectra of PA doped St-GO-PAEK membranes.

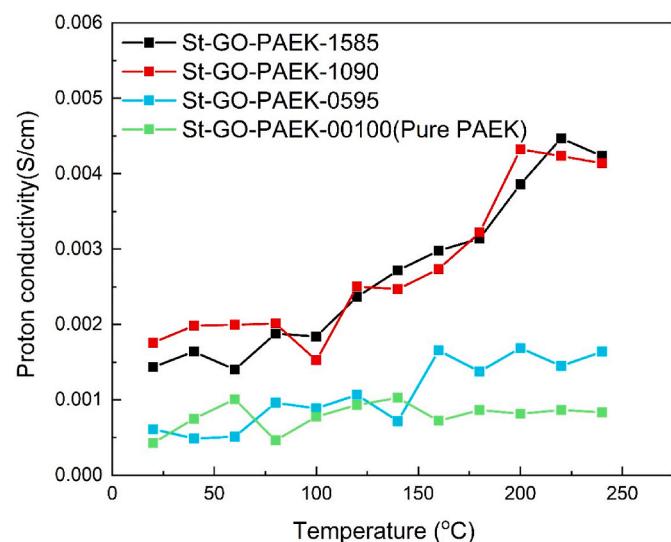


Fig. 5. Proton conductivity of PA doped St-GO-PAEK membranes.

Table 1

PA doping levels, Tensile strength and Weight residual after oxidation of St-GO-PAEK membranes.

Sample	Doping levels (molH_3PO_4)	Tensile strength (MPa)	Weight residual after oxidation (%)
St-GO-PAEK-00100(Pure PAEK)	1.928	12.82 ± 1.13	99.78
St-GO-PAEK-0595	0.0481	12.71 ± 1.40	95.55
St-GO-PAEK-1090	0.0484	7.66 ± 0.86	94.62
St-GO-PAEK-1585	0.0799	3.53 ± 0.74	92.41

show higher proton conductivities than that of non-starched St-GO-PAEK-00100 membrane with much higher doping levels. The results indicate that the introduction of starch would increase proton conductivity as well as decrease the doping levels sharply. The PA doping levels of St-GO-PAEK are much lower than that of other reported PA doped membranes [9,15,33,34], but exhibit much higher proton conductivity with such low doping levels [34]. PA doped St-GO-PAEK-0595, PA doped St-GO-PAEK-1090 and PA doped St-GO-PAEK-1585 with starch present much lower doping levels than that of pure PAEK membrane (St-GO-PAEK-00100) without starch, indicating that the introduction of starch could impede PA doping into the membranes. This may be due to the oxygen groups in PAEK prefer binding with starch to form hydrogen bond rather than binding with PA molecules, which reduced PA doping levels by incorporation of starch. Further, after incorporation of starch into PAEK, PA doping levels increase with starch content, which could be due to the increasing oxygen groups with increasing starch content facilitates PA adsorption. Such low doping level value indicates all PA molecules should be bonded to polymer mainchain as reported: when PA doping level value is below 2 molH_3PO_4 , the PA molecules should almost be bonded PA [24]. The bonded PA in membranes should enhance PA retention of the membranes, which is consistent with the results of PA retention in 3.5.

From above, we suppose that the proton conduction of St-GO-PAEK membranes should not only be related to PA doping levels and other proton conduction channels should be built in St-GO-PAEK membrane structure to enhance proton conductivity. From MD simulation of membrane structure, we suggest that proton conduction fast channels should be formed through dense hydrogen bonds networks from oxygen-containing groups of starch. Usually in PA doped membranes, proton transfer should rely on acid-acid paths of H_3PO_4 [33]. In this work, the H_3PO_4 domain should be too small to construct effective proton

conduction paths due to such low doping levels. Thus, the influence of PA doping levels on conductivity is weak.

The proton conduction mechanism in PA doped St-GO-PAEK membranes could be as follows.

The abundant oxygen-containing groups in PA doped St-GO-PAEK membranes construct proton conduction fast channels through hydrogen bonds formed mainly by starch, leading to enhancement of proton conductivity of PA doped St-GO-PAEK membranes with such low doping levels.

The abundant oxygen-containing groups of starch backbones in the membrane structure could construct such dense hydrogen bonds networks. The dense hydrogen-bond network could maintain H_3PO_4 effectively and abundant oxygen-containing groups in polymer chains would not be loss at high temperatures. Thus, the proton conduction enhancement by hydrogen-bonding interactions should be much more stable than other PA doped membranes. This explains why St-GO-PAEK membranes with low doping levels present such excellent proton conditions during high temperature test.

3.5. retention

Almost all the PA doped St-GO-PAEK membranes show excellent PA retention due to the undiminished proton conductivities when testing at high temperature of 200 °C for such long time as 600 min. For other reported PA doped membranes [34], proton conductivity would decrease obviously during the high temperature test due to the loss of free H_3PO_4 , which could reduce the hydrogen-bonding interaction in membrane structure. In this study, the results from Fig. 6 indicate that proton conductivity of St-GO-PAEK membranes are much more stable, which should not be easily destructed during high temperature process. Their remarkable PA retention property should mainly be due to the extremely low PA doping levels, which indicates almost no free PA in the membranes [24] to leach at high temperature. Usually, decreasing proton conductivity (PA leaching) during high temperature operation mainly result from PA lose or PA decomposition [34], which destroy the proton conduction paths from hydrogen bond networks among PA molecules. But in this study, PA doping levels are too low to influence high proton conductivity. St-GO-PAEK membranes with starch, especially St-GO-PAEK-1090 and St-GO-PAEK-1585, mainly build their proton conduction paths among hydrogen bond networks of oxygen-containing groups of starch, which show less dependence on PA molecules.

Otherwise, St-GO-PAEK-1585 presents a slightly conductivity

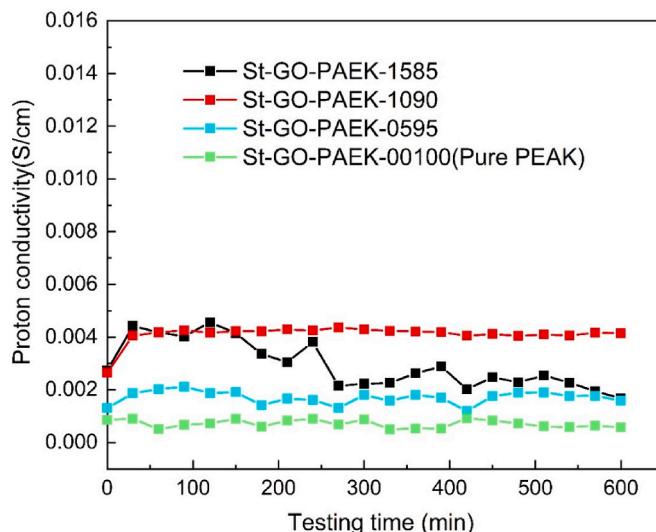


Fig. 6. Proton conductivity changes at 200 °C of PA doped St-GO-PAEK membranes.

decrease compared with other samples. The slightly conductivity decrease should be due to starch decomposition of St-GO-PAEK-1585 at high temperature, which indicate starch facilitate proton conduction from another aspect. St-GO-PAEK-1090 and St-GO-PAEK-0595 shows no conductivity decrease indicate the starch should be integrate with graphene and PAEK firmly which protect starch from decomposition.

These results are consistent with the doping levels of St-GO-PAEK membranes: the H_3PO_4 molecules should not be the main reason that influence the proton conductivity since doping levels of St-GO-PAEK membranes are much lower than other reported PA doped membranes [15,33,39]. The small amount of H_3PO_4 molecules in St-GO-PAEK membranes could be also incorporated into hydrogen-bonding networks tightly, which lead to excellent PA retention.

3.6. Mechanical properties

From Fig. 7 and Table 1, we found the starch content should be the main influence factor of tensile strength rather than doping levels. St-GO-PAEK membranes show a decreasing tendency of tensile strength with increasing of starch content. This should be due to the flexible character of starch backbone. PAEK should present much higher tensile strength than that of starch due to the much more rigid polymer backbone of PAEK. It is reasonable that starch introduction into PAEK should reduce the tensile strength, which may obscure the influence of tensile strength from doping levels.

Otherwise, the dense hydrogen-bonded structure of St-GO-PAEK membranes with low doping levels may improve the mechanical strength by reducing the influence of doping levels. The tensile strength of St-GO-PAEK membranes present no correlation with doping levels, which is quite different from other acid doped membranes [15,39]. Usually, tensile strength of acid doped membranes should decrease with the increasing of doping levels because doping acid should reduce the interaction force among polymer mainchains thus decrease the tensile strength.

This may be because the doping levels of St-GO-PAEK membranes should be too lower to decrease the tensile strength. Doping levels of St-GO-PAEK membranes locate in much lower levels than other acid doping membranes [10,34]. Lower doping levels should reduce the influence of doping levels on tensile strength.

3.7. Oxidative stability

As shown in Fig. 7 and Table 1, all the St-GO-PAEK samples exhibit excellent oxidative stability during the Fenton test. All the membranes stay unbroken after soaking in Fenton's reagent for 120 h and keep almost unchanged weight (weight residual after oxidation in the range of 92.41–99.78 %). St-GO-PAEK samples present much better oxidative stability than other reported membranes [34], of which the weight residual is 40 % during the same test condition. The excellent oxidative stability could be due to the main content of PAEK backbones, which present rigid characters due to the aromatic structure of PAEK's main-chain. The chemical structure of starch containing abundant hydroxy should show little disadvantage of oxidative stability because oxygen groups could more easily react with oxygen free radicals in the Fenton's reagent, leading to destruction of the samples in the oxidation environment of Fenton's reagent. But the St-GO-PAEK samples with starch still show excellent oxidative stability, which should be due to the dense hydrogen bond networks as discussed and simulated in Fig. 2.

4. Conclusion

We discover that dense hydrogen bonds networks formed from abundant oxygen-containing groups of starch in PA doping St-GO-PAEK membranes could facilitate proton conduction stability, PA retention and oxidative stability. Molecular dynamics (MD) simulation has been carried out to investigate the membrane structure, which indicates

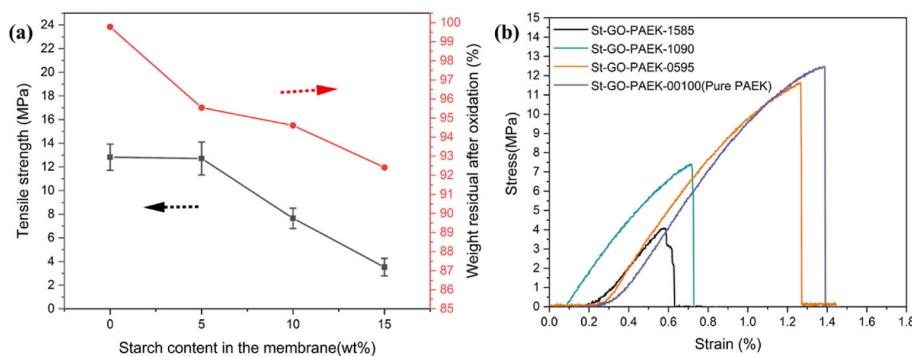


Fig. 7. (a) Tensile strength and Weight residual after oxidation of St-GO-PAEK membranes; (b) Tensile curves of St-GO-PAEK membranes.

dense hydrogen bonds formed through oxidized graphene (GO), phosphoric acid (PA), starch and PAEK chains. This structure has been further confirmed by FT-IR and XRD analysis.

The membranes exhibit excellent PA retention properties with almost unchanged proton conductivity at high temperature (200 °C), and present inconceivably good proton conductivity with such low PA doping levels. These excellent properties should indicate a novel proton conduction mechanism in PA doped membranes. The proton conduction mechanism in St-GO-PAEK membranes is that protons could prefer transferring through dense hydrogen bonds networks rather than PA molecules in St-GO-PAEK membranes. PA doping levels may not be the most influence factor of proton conduction. Novel strategy of designing proton transfer channels with dense hydrogen-bonds structure with low doping levels should be effective to solve the PA leaching problem.

CRediT authorship contribution statement

Xiuping Li: Writing – original draft, Supervision, Methodology, Funding acquisition, Conceptualization. **Jiyuan Zhang:** Visualization, Validation, Investigation, Formal analysis. **Xiao Zhang:** Software, Methodology, Investigation. **Xiudong Liu:** Project administration, Methodology. **Shuhua Chen:** Project administration, Data curation. **Yue Qiao:** Formal analysis. **Qian Li:** Writing – review & editing, Funding acquisition. **Cheng Liu:** Writing – review & editing, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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