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# Investigation on Structure and Behaviours of Proton Exchange Membrane Materials by TEM

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## 1. Introduction

H<sub>2</sub>/O<sub>2</sub> fuel cells and direct methanol fuel cells (DMFC) are one of the most promising efficient and environmental friendly energy generation systems because of their low emissions and high working efficiency, which are extensively applied in stationary power, automobiles and portable electrical source [1-2]. The proton exchange membrane (PEM), the key component of fuel cell, acts as a separator to prevent the mixing of the fuel and the oxidant and serves as an electrolyte to transfer protons from the anode to the cathode [3]. The PEM must be satisfied with following peculiarities such as high proton conductivity, low electronic conductivity, long-term chemical stability, good mechanical strength under fuel cell operation conditions and low cost. In the early 1960s, sulfonated polystyrene copolymers membranes were used as the PEM in proton exchange membrane fuel cells (PEMFCs) [4]. However, short lifetime and relatively high price limited their further applications. In the later 1960s, Nafion<sup>®</sup> perfluorosulfonated membranes produced by DuPont company have been extensively used because of their high conductivity and chemical stability [5-7]. However, there are some drawbacks, such as high methanol permeability, relatively low proton conductivity at high temperature and high price, which baffle their further developing. Recently many researchers have been devoted to developing new hydrocarbon PEM materials that are of good mechanical performance and thermo-oxidative stability, low price and high proton conductivity. Nowadays, the developed novel polymer electrolyte membranes include sulfonated poly(arylene ether sulfone)s [8-10], sulfonated poly(arylene ether ketone)s [11-15], sulfonated polyimides [16-19], sulfonated polybenzimidazoles [20-22], block sulfonated copolymers and their composite membranes [23-28], etc. Sulfonated polymers may be prepared either by postsulfonation of the polymers or by polycondensation of sulfonated monomer with other non-sulfonated monomers [29]. The postsulfonation polymers were prepared by electrophilic aromatic sulfonation using concentrated sulfuric acid, fuming sulfuric acid, chlorosulfonic acid or

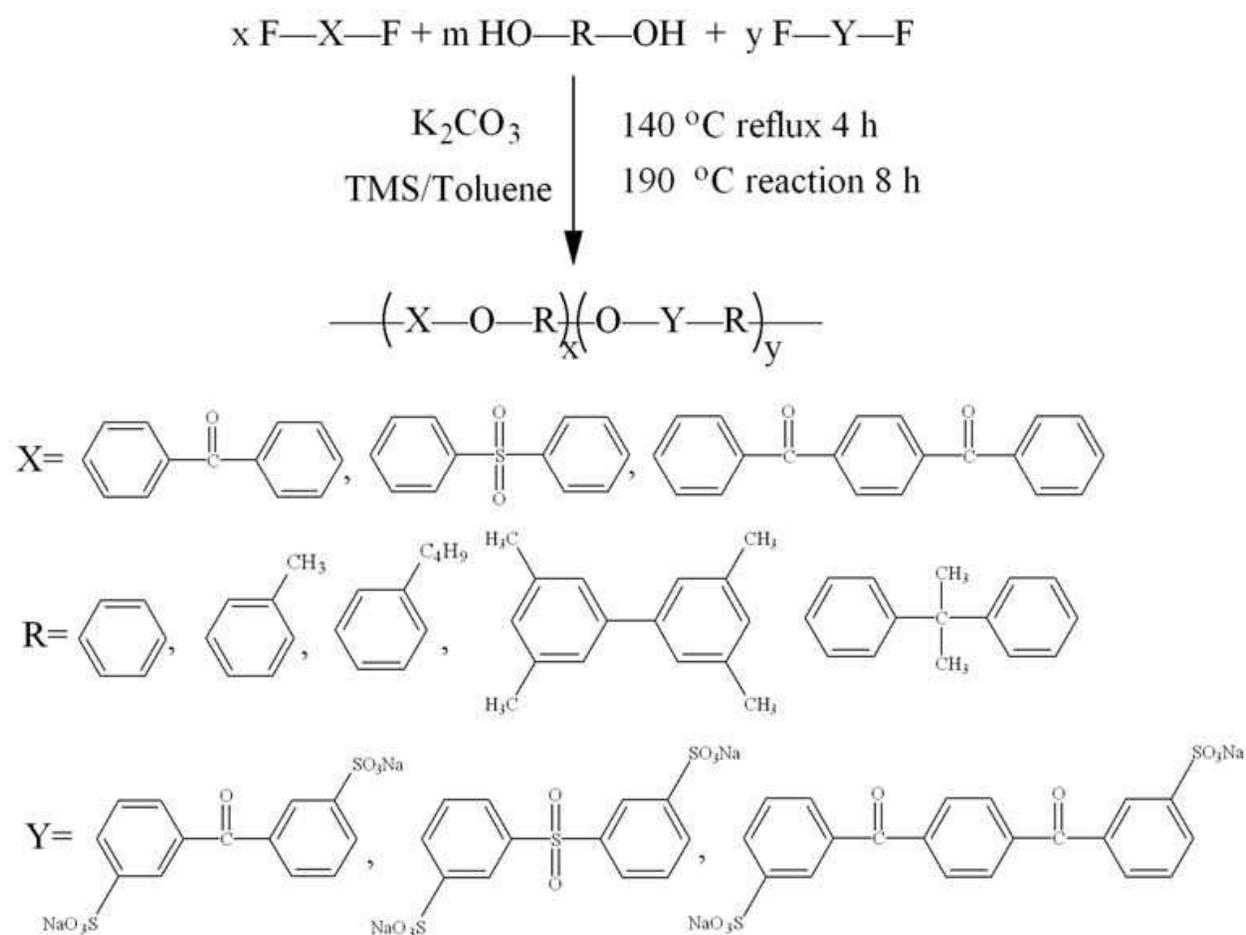
sulfur trioxide as sulfonating agents. The postsulfonation reaction usually has some drawbacks such as not ease to precisely control on the degree of sulfonation (DS) and the location of sulfonic groups, the possibility of side reaction, and the degradation of polymer. The direct polycondensation sulfonated copolymers with different sulfonation degrees were synthesized by varying the ratios of the sulfonated monomers to the non-sulfonated monomers [30-35]. The latter method has been proved to be more advantageous than postsulfonation. Some of the advantages are: (1) the position and the content of sulfonated groups can be easily controlled and (2) cross-linking and other side reactions can be avoided. In order to investigate more available the relationship between structures and properties, sulfonated aromatic copolymers were obtained by aromatic nucleophilic substitution polycondensation reaction in most literatures. As PEM materials, these sulfonated aromatic copolymers showed relatively good properties including high proton conductivity, good water transport properties, thermo-oxidative stability, good mechanical performance and methanol permeability. To further develop these sulfonated polymers, which can be potentially suitable for applications in proton exchange membrane fuel cell or direct methanol fuel cell systems, some researchers have modified sulfonated polymers. The sulfonated polymers/heteropolyacid and sulfonated polymers/TiO<sub>2</sub> composite membranes exhibited high proton conductivity at high temperature, which are satisfied with the requirement of fuel cell operation at high temperature[36-38]. The sulfonated polymers/polyaniline and sulfonated polymers/polypyrrole composite membranes decreased methanol permeability with a little lower proton conductivity change, thus showing very good prospective in DMFC application [39, 40]. The cross-linked sulfonated aromatic polymer membranes displayed higher mechanical strength, thermo-oxidative stability and lower methanol diffusion coefficient than those of non-crosslinked membranes, which were particularly attractive as the PEM for DMFC. The important parameters of proton exchange membranes included ion-exchange capacity, water uptake, water diffuse coefficient, thermo-oxidative stability, proton conductivity, methanol permeability and mechanical performance, which directly decide proton exchange membrane behaviors. These parameters are determined by their chemical structures and morphology. In this paper, series of sulfonated aromatic polymers with different chemical structures were synthesized. The measured and studied methods about PEM were detailed discussed as well as the relationship between structure and properties were investigated by transmission electron microscope (TEM).

## 2. Experiment

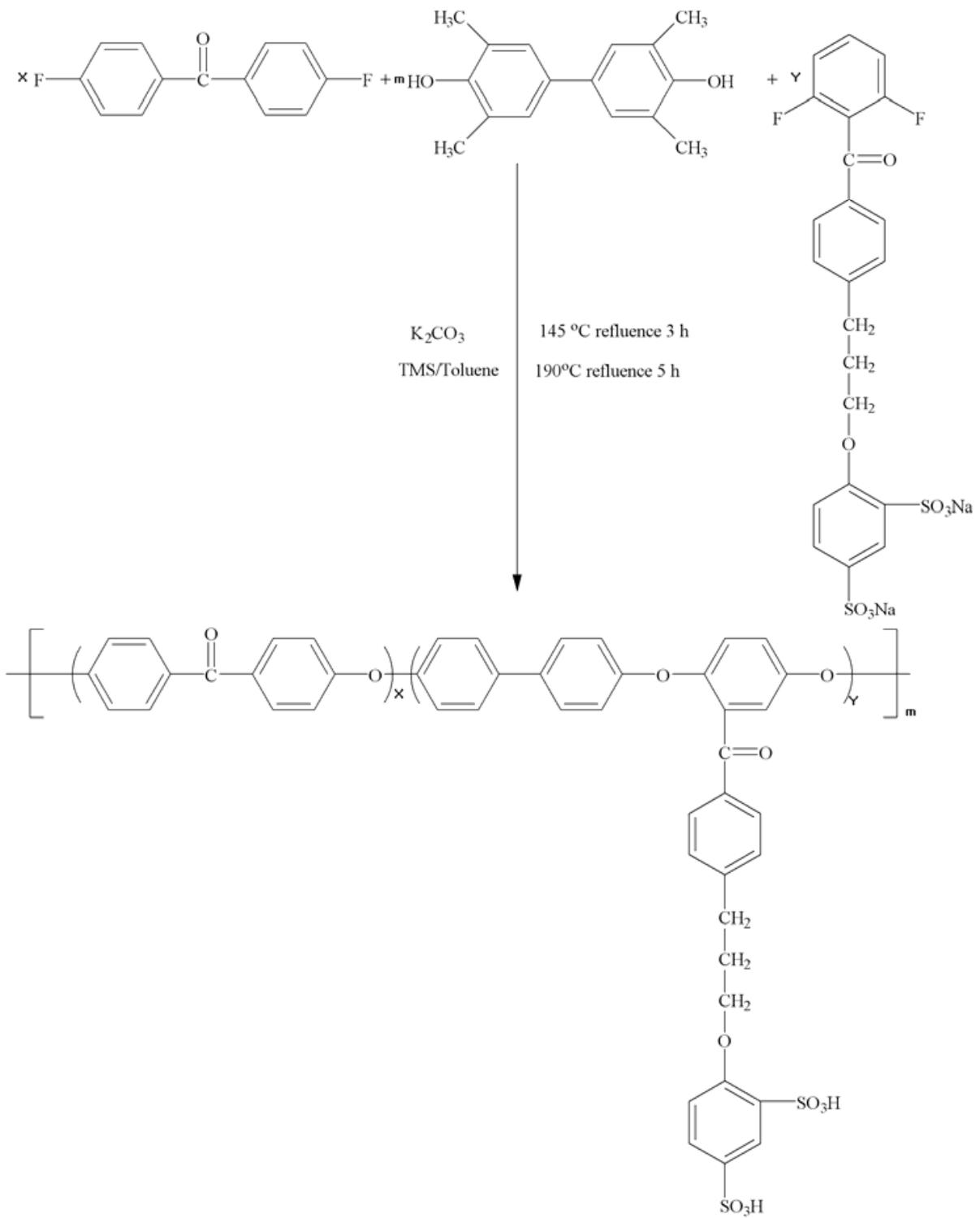
### 2.1 The synthesis of sulfonated copolymers

It has been proved that direct copolymerization have some advantage, for example, it can enhance the stability and the acidity of sulfonic groups due to introducing two sulfonic groups in each repeating unit. A series of sulfonated poly(aryl ether sulfone)s, sulfonated poly(aryl ether ketone)s and sulfonated poly(aryl ether ketone sulfone) copolymers with different DS were synthesized by aromatic nucleophilic substitution polycondensation. The detailed procedure is described as following: sulfonated monomer, non-sulfonated monomer, double hydroxybenzene monomer and potassium carbonate were added into a 500 mL three neck round bottom flask with an atmosphere of nitrogen inlet, a mechanical

stirrer, and a Dean-Stark trap with a reflux condenser. Tetramethylene sulfone (TMS) was used as a solvent and toluene was used as an azeotropic agent. The reaction mixture was refluxed at 145 °C for 4 h until water was fully removed from the reaction system by azeotropic distillation, and then the excess toluene was distilled out. The reaction temperature was then slowly raised to 200 °C and kept at this temperature for another 10 h. After the reaction mixture became highly viscous, TMS was added to dilute the solution, and then the solution was cooled to room temperature. The cooled copolymers with low DS solutions were directly poured into deionized water. While the copolymers with high DS solutions were poured into acetone. The precipitated copolymers were washed by boiling deionized water several times and dried at 80 °C for 48 h. This process is shown in **Scheme 1** and **Scheme 2**. The sulfonated aromatic polymers with different main chain structure were named as SPAEKS-M and the sulfonated aromatic polymers with side chain structure were defined as SPAEKS-S.



Scheme 1. A series of sulfonated aromatic polymers with different main chain structures.



Scheme 2. The sulfonated aromatic polymer with a side chain structure.

### 3. Results and discussion

#### 3.1 The FT-IR characterization of SPAEKS copolymers

The chemical structure of the SPAEKS copolymers was verified by fourier transform infrared (FTIR) spectroscopy using a Perkin Elmer recording in  $4\text{ cm}^{-1}$  of spectral resolution in the range  $400\text{-}4000\text{cm}^{-1}$ . The FTIR spectra of SPAEKS copolymers are presented in **Fig.1**, where the peaks at  $1078\text{ cm}^{-1}$ ,  $1020\text{ cm}^{-1}$  and  $1028\text{ cm}^{-1}$  corresponded to the stretching of the sodium sulfonate groups and at  $1660\text{cm}^{-1}$  was assigned to double bond of phene stretching. The S=O stretching band of sodium sulfonate groups was observed at  $1243\text{ cm}^{-1}$ . These results confirmed that the sodium sulfonate groups were successfully incorporated into the copolymers as expected.

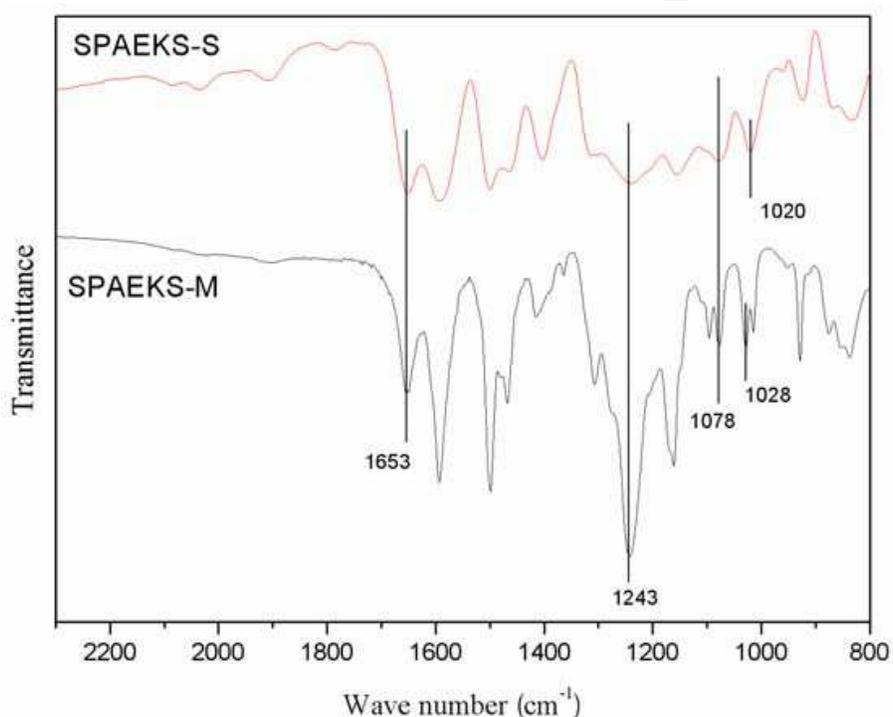


Fig. 1. The FTIR spectra of SPAEKS copolymers.

#### 3.2 Ion exchange capacity

Ion exchange capacity (IEC) is usually defined as the mole of fixed  $\text{SO}_3$  sites per gram copolymer, which indicates the ability of proton exchange membrane transferring proton. The higher IEC values are, the better membranes transfer proton. The IEC values of membranes were determined by the titration and calculation. The detailed procedures are descibled as following: Membranes in acidic form were immersed into a 50 ml 1 M NaCl solution for 24 h in order to achieve complete ion exchange of  $\text{H}^+$  with  $\text{Na}^+$ . The released  $\text{H}^+$  was titrated with 0.1 M NaOH solution, in which phenolphthalein was used as an indicator. The IEC values were calculated from the titration data via the following equation.

$$\text{IEC} \left( \text{mequiv. / g} \right) = \frac{\text{consumed NaOH} \times \text{molarity NaOH}}{\text{weight dried membrane}}$$

The IEC values measured by titration increased with DS increasing and accorded with the calculated IEC values. It indicated that IEC values could be readily controlled by varying the feed ratio of sulfonated monomers to non-sulfonated monomers. This has the advantage over the postsulfonated reaction of introducing sulfonic groups into the copolymers without a sulfonation degradation reaction on the polymer chain by direct copolymerization.

### 3.3 Water transport properties

It is well known that water plays a critical role for proton exchange membrane applications. On the one hand, adequate water uptake is desired to maintain good proton conductivity; on the other hand, water sorption should be minimized to ensure the membrane mechanical performance and the dimensional stability. Nafion with low water retention at high temperatures resulting in conductivity falls is one of the drawbacks, which limited its further commercial application. Water uptake and swelling ratio of membrane were calculated using the following formula.

$$\text{Water uptake} = \frac{W_w - W_d}{W_d} \times 100\%$$

The swelling ratio was defined as:

$$\text{Swelling ratio} = \frac{L_w - L_d}{L_d} \times 100\%$$

Where  $W_d$  and  $L_d$  are the weight and length of dried membrane, respectively. The dried membranes were immersed into deionized water until constant weight and length were obtained, which was recorded as  $W_w$  and  $L_w$ .

Water retention of proton exchange membrane has significant effects on its proton conductivity, especially at high temperature. In our work, water retention of membrane was expressed by water diffusion coefficient, which TGA recorded the weight change with time. The relationships between the water desorption and time might follow the Ficker diffusion law. The water diffusion coefficient of membranes was calculated according to the following formula.

$$\frac{M_t}{M_\infty} = 4 \left( \frac{D_t}{\pi l^2} \right)^{1/2}$$

Where  $D$  is the water diffuse coefficient;  $l$  is the membrane thickness;  $M_t/M_\infty$  is the water desorption, which can be obtained by the slope of water desorption curves because the plots of  $M_t/M_\infty$  versus  $t_{1/2}$  are linear for Ficker diffusion [39].

The state of water in the sulfonated copolymers has a critical influence on the electrochemical and physical properties of the membranes, which may be very important for PEM fuel cells. The water within sulfonated aromatic polymers membranes exists into two states: the loosely bound water and the tightly bound water. The loosely bound water

content can be calculated by DSC instrument [3]. Thermo-gravimetric analysis as an excellent method was used to study the tightly bound water. It is well known that the relative weight loss before sulfonic groups decompose due to water evaporation corresponded to water retention capacity of the membrane. The temperature of water desorption best fasten recording as  $T_{\max}$  in TGA differential curves served as an indication of the water retention capacity of a given membrane. The higher the  $T_{\max}$  was, the better the membrane hold water. In this paper, we select two samples with main chain structure and side chain structure at the same IEC values as comparing. The results showed that the water uptake, swell ratio and water diffusion coefficient of SPAEKS-S were higher than those of SPAEKS-M at the same DS.

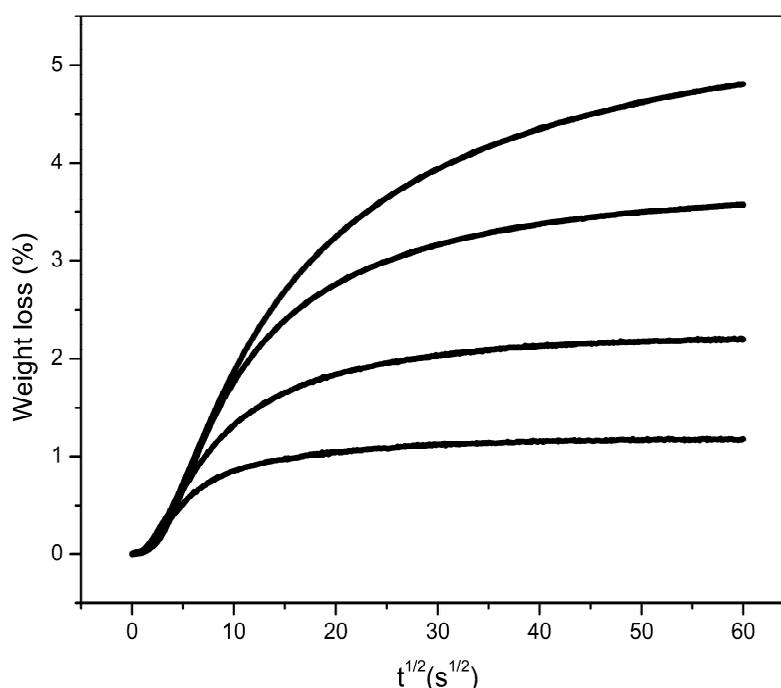


Fig. 2. The water desorption curves of SPAEKS membrane at 80 °C.

Samples	IEC (mmol/g)	Water uptake (%)	Swelling ratio (%)	Water diffusion coefficient (cm <sup>2</sup> /s)
SPAEKS-M	1.88	35	9	$1.21 \times 10^{-9}$
SPAEKS-S	1.90	41	11	$8.96 \times 10^{-8}$

Table 1. The data of SPAEKS-M and SPAEKS-S membrane.

### 3.4 Thermal properties, thermo-oxidative stability, mechanical strength of membrane

Proton exchange membrane must hold good thermal properties due to fuel cell operation at a relatively high temperature. In our previous works, thermal properties were performed on thermo-gravimetric analysis (TGA) and different scanning calorimetry (DSC) analyzer. It can be seen from TGA curves that the membrane in acid form has two degradation steps. The first weight loss about range from 160 °C to 200 °C was assigned to the elimination of sulfonic groups. The second weight loss around 400 °C was attributed to the decomposition of polymer backbone. The onset weight loss temperature ( $T_{\text{onset}}$ ) of membrane in acid form

gradually decreased with increment of DS. Thermo-oxidative stability may be very decisive with respect to proton exchange membrane life span. Sulfonated aromatic polymers are amorphous and only one glass transition temperatures ( $T_g$ ) due to rigid polymer backbone, which is proved by differential scanning calorimetry (DSC). All sulfonated polymers exhibited relatively high  $T_g$  that increased with DS increasing. It was well explained that the introduction of sulfonate groups increased intermolecular interaction and molecular bulkiness. Both effects hinder the internal rotation, which leads to increase  $T_g$  of sulfonated copolymers.

Thermo-oxidative stability was studied by immersing the membrane into Fenton's reagent (3%  $H_2O_2$  containing 2 ppm  $FeSO_4$ ), which is a routine testing method for oxidative stability. The consumed time that the membrane started to break into pieces was used to evaluate oxidative stability of membrane. Good mechanical strength is necessary for a proton exchange membrane material. Aromatic polymers including poly(aryl ether sulfone)s, poly(aryl ether ketone)s and polyamides as a series of typical thermal plastics, are well known for their excellent thermal and mechanical properties as well as their resistance to oxidation and their stability under acidic conditions. Sulfonated aromatic polymers also exhibited good mechanical strength, which the tensile strength and tensile modulus of membrane reached up to 40 MPa and 1 GPa, respectively. It indicates that they are tough enough to be performed as a functional membrane material. The mechanical strength of membrane can be obtained by electro-tensile machine at a tensile speed of 2 mm/min under ambient conditions, the size of samples is 15 mm×4 mm. Three samples of each membrane were analyzed and average value was obtained.

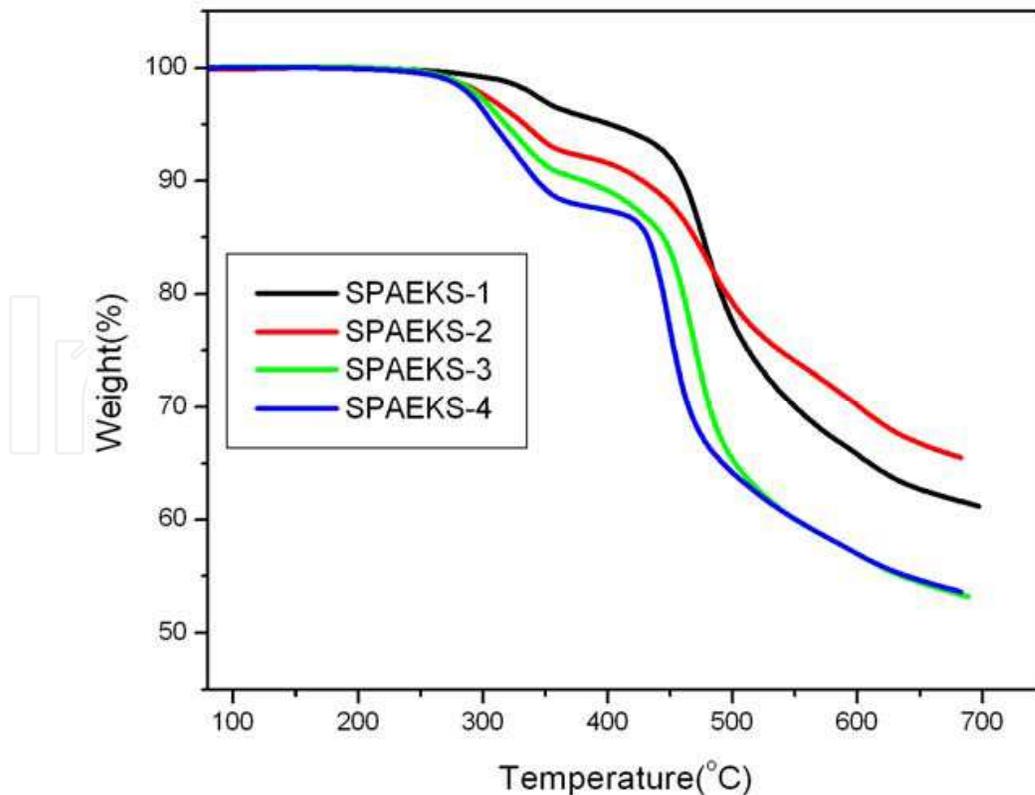


Fig. 3. The TGA curves of SPAEKS copolymers.

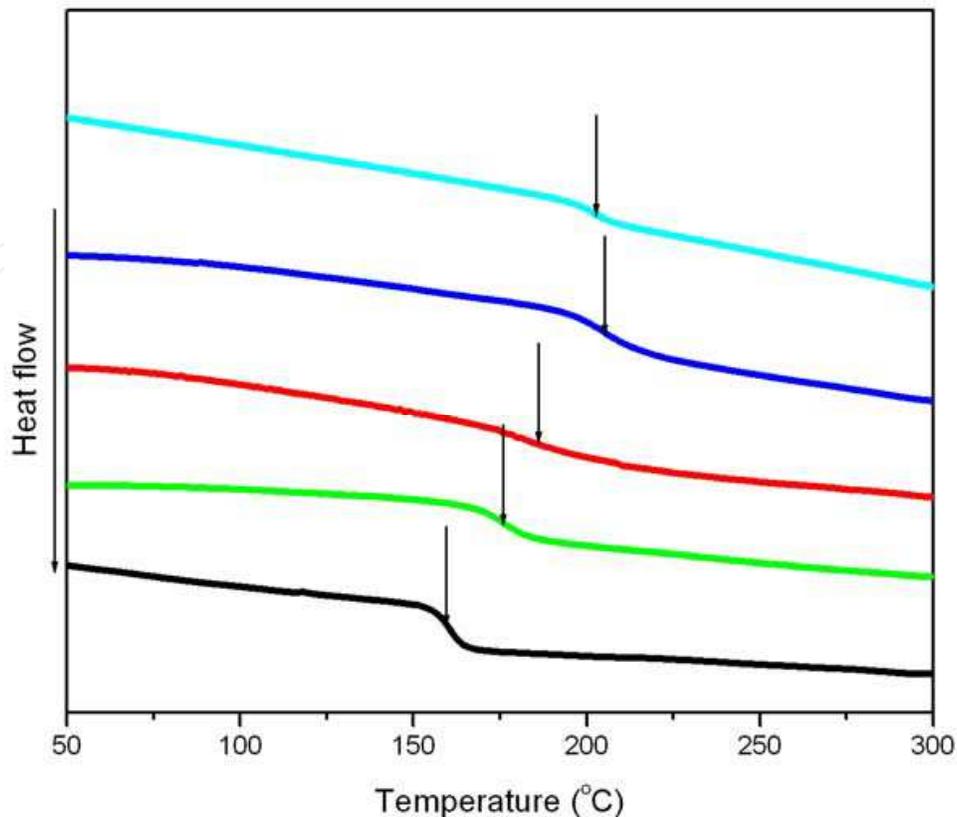


Fig. 4. The DSC curves of SPAEKS copolymers.

Sample	T <sub>g</sub> (°C)	T <sub>d</sub> (°C)	Oxidative time (h)	Tensile strength (MPa)	Tensile modulus (GPa)	Maximum elongation (%)
SPAEEKS-M	160	252	225	47	1.15	8.2
SPAEEKS-S	153	227	198	45	1.02	10.1

Table 2. The data of SPAEEKS-M and SPAEEKS-S membrane.

### 3.5 Morphology of the proton exchange membrane

The physical and electrochemical properties of proton exchange membrane are related to their microstructure and morphologies, especially the spatial distribution of ionic sites. The sulfonic groups in SPAEKS copolymers aggregated into hydrophilic ionic clusters are related to water uptake and proton transport. The transporting of proton in PEM occurs through three mechanisms, Grotthus, vehicular and surface transport. The Grotthus mechanism is that protons transfer via structural diffusion (proton charge carriers dissociate from water molecular to next water molecular). However, proton transport through the movement of larger cations (such as  $H_5O_2^+$ ,  $H_9O_4^+$ ) was defined as vehicular mechanism. It is likely that proton transport predominate through Grotthus and vehicular mechanisms in SPAEKS membrane with relatively high water contents. Surface

mechanism refers that proton transmission occurs between sulfonic groups located on the walls of hydrophilic channels. Surface mechanism becomes increasingly important at low humidity. The distribution of hydrophilic and hydrophobic domains may determine the proton conductivity of SPAEKS membrane. The water serving as proton carrier plays an important role in determining the proton conductivity of PEM. Some researchers have used Atomic Force Microscopy (AFM), Small-angle X-ray scattering (SAXS) and TEM to study the distribution of hydrophilic and hydrophobic domains in PEM. In order to find the distribution of sulfonic groups in copolymers matrix, in this paper, TEM experiments were performed on a JEM-2000EX microscope with an acceleration voltage of 200 kV. The detailed operation procedures are described as following: The SPAEKS copolymers in acidic form were obtained by immersing the SPAEKS copolymers in sodium form into a 2M HCl solution for 24 h. Sulfonated copolymers in acid form were immersed in  $\text{AgNO}_3$  solution for 24 h in order to make  $\text{Na}^+$  forms convert into  $\text{Ag}^+$  form because  $\text{Ag}^+$  particles can provide a good contrast. Copolymers in  $\text{Ag}^+$  form were filtrated and vacuum dried at  $80^\circ\text{C}$  overnight, and then were dissolved in DMF forming 5% DMF solutions and dropped on carbon coated copper grids for TEM investigation. The sulfonic groups in sulfonated polymers aggregate into hydrophilic ionic transport channels in copolymers matrix contributing to transport proton and the nonsulfonated copolymers backbone form hydrophobic domains providing their mechanical strength. The TEM pictures of  $\text{Ag}^+$  chelated SPAEKS membranes were shown in Figure 1. The dark domains ( $\text{Ag}^+$  particles) in pictures represent hydrophilic sulfonic groups, while the light domains refer to hydrophobic copolymer backbone. It can also be seen that the sulfonic groups randomly disperse in sulfonated copolymer matrix. With an increment in DS from SPAEKS-10 (DS=0.2) to SPAEKS-60 (DS=1.2) membrane, the density and the size of sulfonic groups become larger. The diameter of sulfonic groups increases from 5 nm to 10 nm. Thus, it is concluded that the ionic groups could aggregate to relatively large transport pathways at high contents of sulfonic acid groups. This may be likely to enhance proton or ion transport properties of SPAEKS membranes. The conclusion about the density of  $\text{Ag}^+$  particles can not be definitely made due to the different thickness of the TEM samples. The size of  $\text{Ag}^+$  particles will denote the size of proton conductive channels in SPAEKS membranes. It is also important to note that the membranes observed under TEM do not hydrate, so in a practical application, the ionic clusters would probably be more evenly distributed. When this hydrophilic domain is hydrated, protonic charge carriers dissociate from the  $\text{SO}_3^-$  functional groups (Grotthus mechanism) and proton transfer by  $\text{H}_3\text{O}^+$  (vehicular mechanism). The micrograph of sulfonated copolymers with side chain sulfonic acid groups was shown in Figure 1(k). It can be seen that the sulfonic acid groups spreading as a cloud-like belt were also observed for side chain sulfonated copolymers. These wide and well-connected ionic domains can provide large proton transport channels, which are responsible for fast proton transport and high proton conductivity. From here we see that sulfonic groups disperse throughout the polymer matrix and phase separation does not happen for random SPAEKS copolymers. While for block and graft sulfonated copolymers, sulfonic groups aggregated into hydrophilic ionic clusters and form phase separation. The morphology of PEM explained why the water uptake and proton conductivity of membrane increased with increasing DS. The relationship between micro-structure and properties is established by TEM.

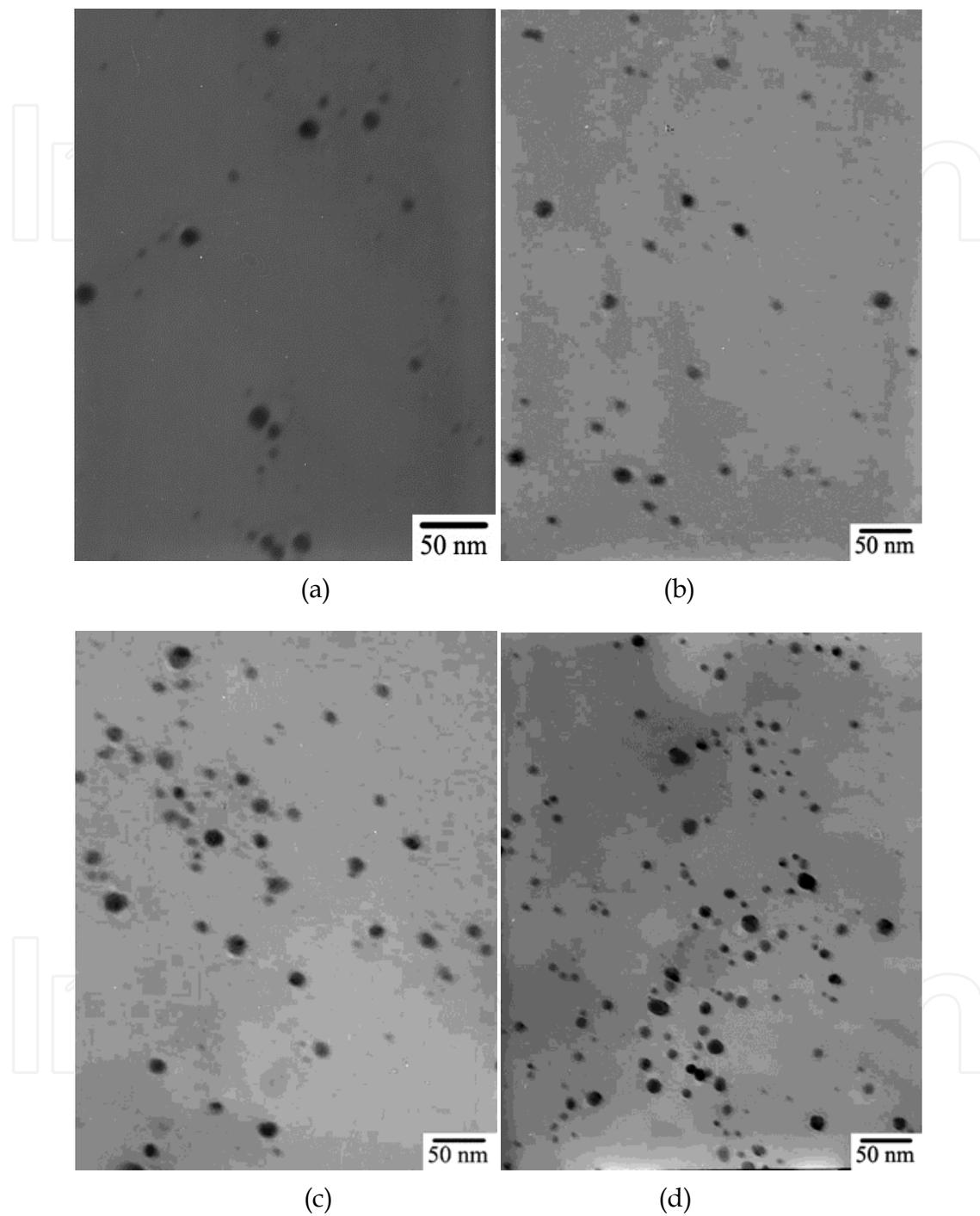


Fig. 5. The micrographs of SPAEKS membranes: (a) SPAEKS-M1-10; (b) SPAEKS-M1-20; (c) SPAEKS-M1-30; (d) SPAEKS-M1-40; (e) SPAEKS-M1-50; (f) SPAEKS-M1-60; (g) SPAEKS-M2-20; (h) SPAEKS-M2-30; (i) SPAEKS-M2-40; (j) SPAEKS-M2-50; (k) SPAEKS-S-50.

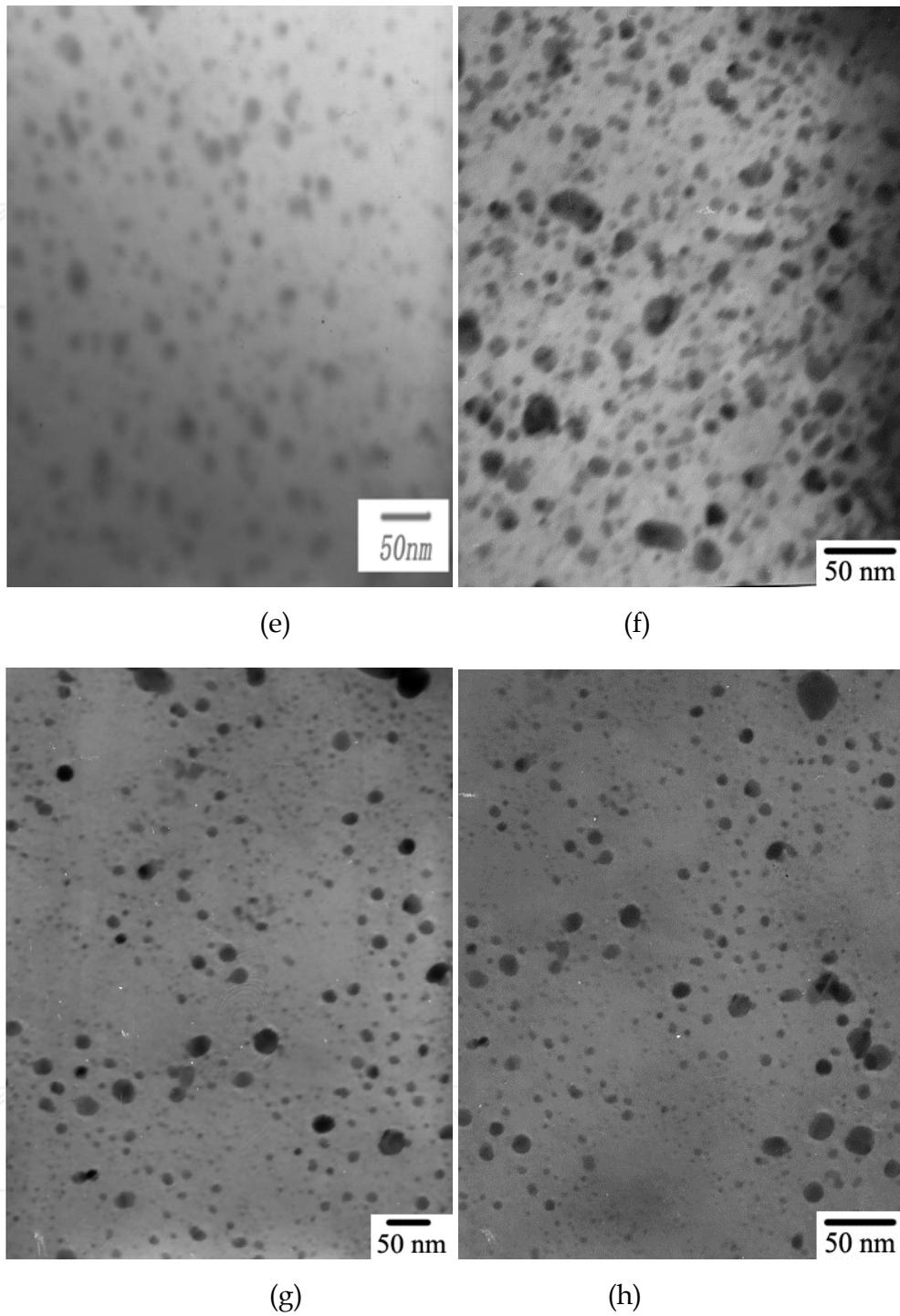


Fig. 5. The micrographs of SPAEKS membranes: (a) SPAEKS-M1-10; (b) SPAEKS-M1-20; (c) SPAEKS-M1-30; (d) SPAEKS-M1-40; (e) SPAEKS-M1-50; (f) SPAEKS-M1-60; (g) SPAEKS-M2-20; (h) SPAEKS-M2-30; (i) SPAEKS-M2-40; (j) SPAEKS-M2-50; (k) SPAEKS-S-50. (Continuation)

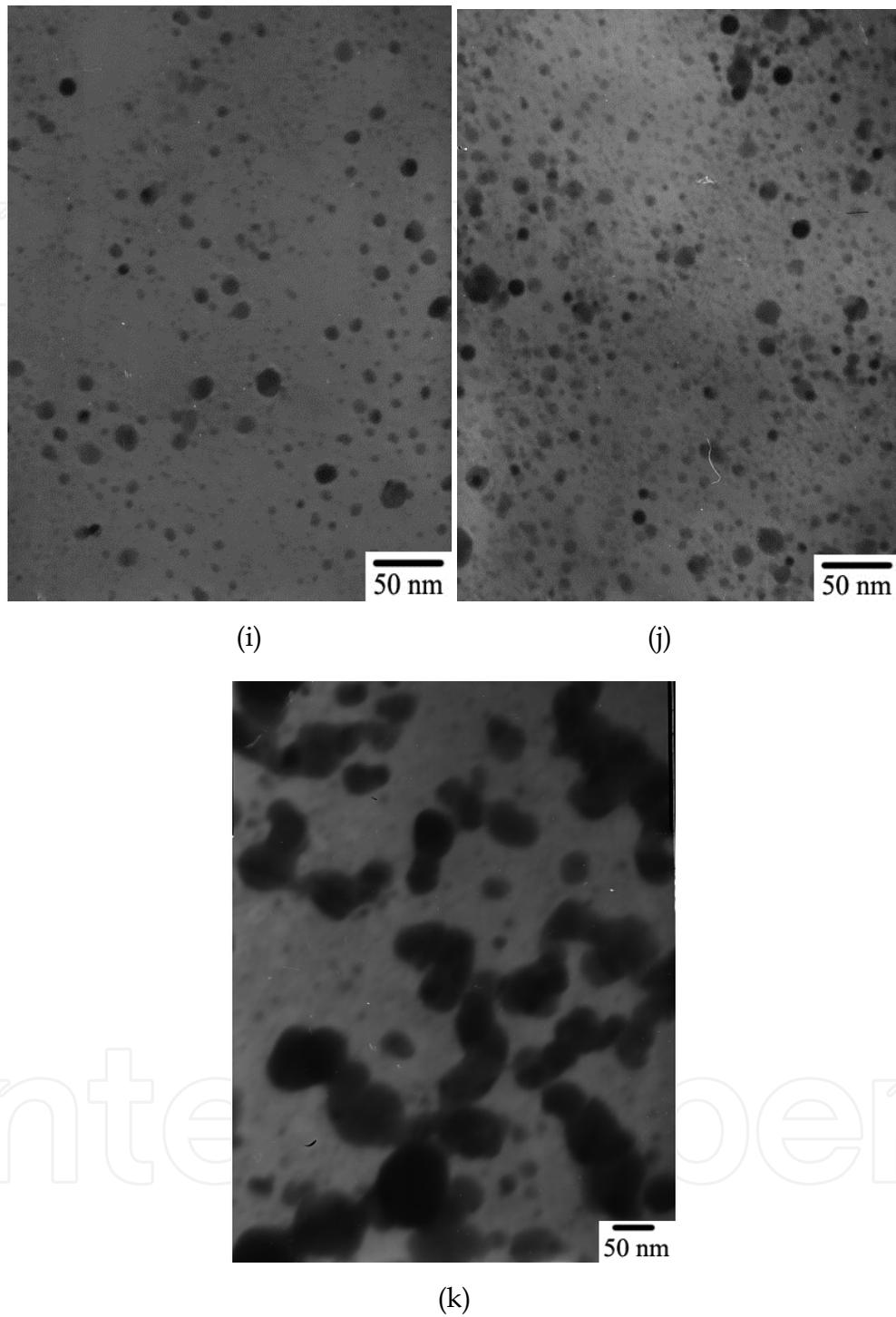


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### 3.6 Proton conductivity

Proton conductivity is a particularly important parameter for proton exchange membranes. Without sufficient proton conductivity, a membrane will never be applicable to H<sub>2</sub>/O<sub>2</sub> fuel cells or direct methanol fuel cells. Proton conductivity may have different results with different measured approaches and instruments. In our work, Nafion 117 was selected as a reference to compare the proton conductivity of membrane. The proton conductivity ( $\sigma$ ) of membrane was determined by AC impedance spectroscopy over a frequency range of 10 Hz–1 MHz. The membrane in acid form was immersed in deionized water for at least 24 h prior to the test. Conductivity measurements of fully hydrated membranes were carried out with the cell immersed in liquid water (water resistance is 18.2 MO; 100% RH). The resistance value related to the proton conductivity of membranes was determined from the low intersect of the high frequency semicircle on a complex impedance plane with the real axis. High temperature conductivity measurements were performed in water vapour. This experimental set up allowed the membranes to equilibrate with saturated water vapour at the desired temperature. The temperature was controlled by a wrap-around resistance heater and feed back temperature controller. The proton conductivity of membranes was calculated from the resistance based on the following formula:

$$\sigma = l/RS$$

Where  $l$  is the distance between the two electrodes,  $R$  is the membrane resistance, and  $S$  is the cross-sectional area of membrane. For a series of sulfoanated copolymers membrane, it can be found from measurement results that the proton conductivity increased with DS and temperature. This might be attributed to the increasing of size and density of ion domains

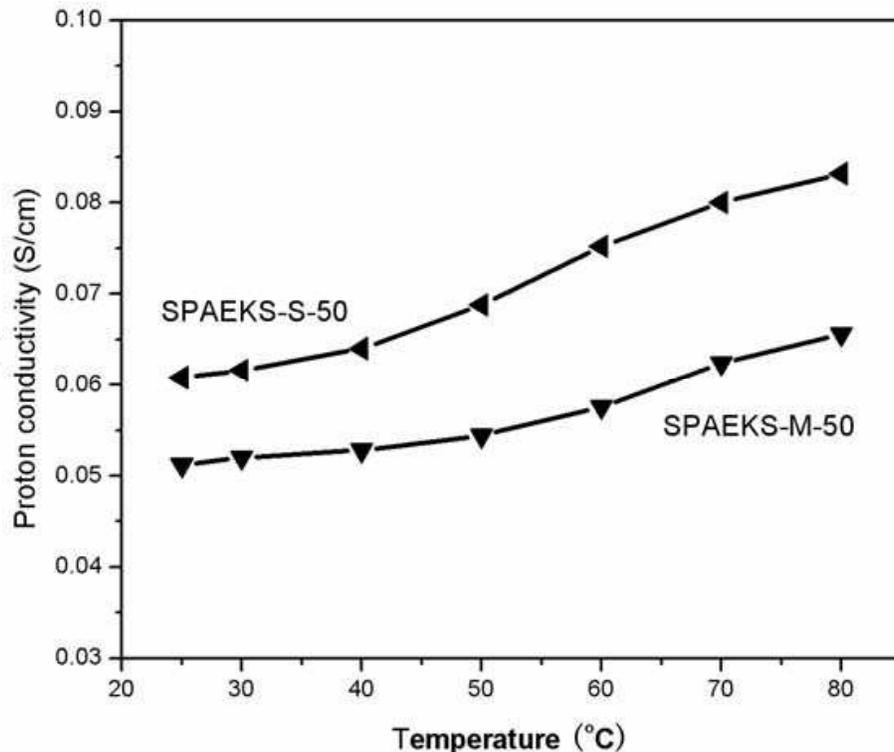


Fig. 6. The proton conductivities of SPAEKS-M-50 and SPAEKS-S-50 membranes from 25 °C to 80 °C.

when DS increases, which can be concluded from the structure and morphology of membrane (TEM, SAXS and AFM). Also, the speed of H<sup>+</sup> transmitting in membrane was fastened with increasing temperature, which greatly improved the proton conductivity. The proton conductivity of membrane was closely related to their microstructure. In order to improve proton conductivity, McGrath and co-workers have synthesized a series of block sulfonated copolymers, which shows higher proton conductivity than that of random sulfonated copolymers at the same of degree of sulfoantion and IEC values [52-54]. This is attributed to the different distribution of ion domains in membranes. In this paper, the proton conductivity of SPAEKS-M membrane was lower than that of SPAEKS-S at the same Ds. This is because that the existence of the two distinct hydrophobic and hydrophilic regions may lead to the micro-phase separation structure. Also, the concentrated sulfonic groups may provide much larger proton transport channels, which are beneficial to enhance the proton conductivity of the membranes. However, for the random sulfonated copolymers, the sulfonic groups were dispersed throughout the copolymers matrix and not easily phase separated, which may lead to the relativity lower proton conductivity than the side chain ones.

### 3.7 Methanol permeability

Methanol permeability of membranes is one of the most significant roles for DMFC, which directly affects the work efficiency of a DMFC. The high methanol diffusion coefficient of Nafion membrane in the DMFC application is one of the most drawbacks, which limits its further development in DMFC applications. The methanol permeability of membrane was expressed by methanol diffusion coefficient, which was measured using a cell that consists of two half cells divided by the membrane. Pure methanol was placed on one side of the diffusion cell (A cell) and water was placed on the other side (B cell). In order to ensure solution uniformity, magnetic stirrer was used in each compartment. The concentration of the methanol in the cell B was determined by a gas chromatograph. The methanol diffusion coefficient was calculated by following formula.

$$C_{B(t)} = \frac{A}{V_B} \frac{DK}{L} C_A (t - t_0)$$

Where DK is the methanol diffusion coefficient (cm<sup>2</sup>/s), C<sub>B(t)</sub> is the concentration of methanol in B cell (mol L<sup>-1</sup>), C<sub>A</sub> is the concentration of methanol in A cell (mol L<sup>-1</sup>), A is the membrane area (cm<sup>2</sup>) and L is thickness of membrane (cm).

The methanol diffusion coefficients of sulfoanted aromatic polymers were lower than that of Nafion membrane and increased with degree of sulfonation increasing. This may be because that the sulfonic groups in Nafion distribute on the side chains of polymers, which may easily form a phase-separation structure. Furthermore, these sulfonic groups can provide much larger methanol transport channel than aromatic polymers.

	Proton conductivity (S/cm)		Methanol permeability (cm <sup>2</sup> /s)
	25°C	80°C	
SPAEEKS-M-50	0.052	0.062	4.65×10 <sup>-7</sup>
SPAEEKS-S-50	0.061	0.083	7.36×10 <sup>-7</sup>

Table 3. The data of SPAEKS-M and SPAEKS-S membrane.

It can be seen from Table 3 that the methanol permeability of SPAEKS-S-50 was higher than that of SPAEKS-M-50 ( $4.65 \times 10^{-7} \text{cm}^2/\text{s}$ ). This may be because the sulfonated groups of SPAEKS-M copolymers are dispersed throughout the copolymer matrix and not easily lead to phase separation. While sulfonate groups of SPAEKS-S copolymers are located on the side chains of polymers, which may easily form phase separation, thus providing much larger transport channel than SPAEKS-M copolymers. The separation of copolymer chains generated unoccupied volume in the form of pores lined with sulfonic acid groups and formed transport pathways, which should absorb more methanol.

#### 4. Conclusions

This paper has attempted to introduce the basic research method for evaluating the performance of proton exchange membrane and reveal the relationship between structure and properties by TEM. In our previous works, a series of random sulfoated poly(arylene ether sulfone)s, sulfonated poly(arylene ether ketone)s and sulfonated poly(aryle ether ketone sulfone)s were synthesized by the direct copolymerization. These sulfonated copolymers membrane exhibited relatively high proton conductivity, good thermal-oxidative stability and mechanical performance. The newly synthesized side chain sulfonated poly(ether ether ketone) copolymer membranes showed higher proton conductivity than that of random sulfonated poly(ether ether ketone) membranes at the same of IEC values, which was attribute to a greater degree of phase separation. All these results relating to their micro-structure and morphology have been characterized by TEM. It is assured that new proton exchange membranes materials with low cost, high proton conductivity, low water uptake and methanol diffusion coefficient, good mechanical performance and thermal-oxidative stability, long life-span and good fuel cell performance will appear at short time.

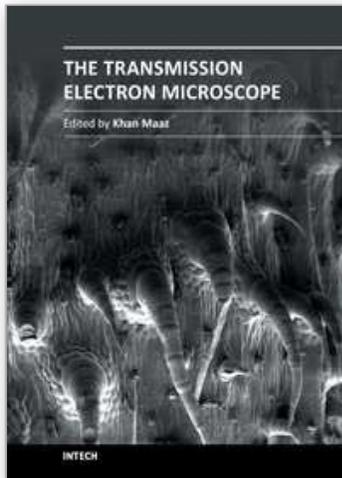
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