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ScienceDirect
Journal of Power Sources 165 (2007) 701–707
JOURNAL OF POWER SOURCES
www.elsevier.com/locate/jpowsour

Morphology study of sulfonated poly(ether ether ketone ketone)s (SPEEKK) membranes: The relationship between morphology and transport properties of SPEEKK membranes

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Received 29 October 2006; received in revised form 8 December 2006; accepted 11 December 2006
Available online 16 December 2006

Abstract

The morphological changes of sulfonated poly(ether ether ketone ketone) (SPEEKK) membranes with different sulfonated degrees (Ds) were investigated by small angle X-ray scattering (SAXS), atom force microscopy (AFM) and transmission electron microscope (TEM). The small angle scattering maximum shifts to little vectors with sulfonated degree increasing. Porod analysis for SPEEKK and Guinier analysis for silver exchanged SPEEKK (SPEEKK-Ag) were carried out to study the microstructures of SPEEKK membranes. All the results showed that: more clearly phase-separated structures will be formed with the increasing of Ds of SPEEKK membranes. The membranes with high Ds will provide much larger and more continuous transport channels for protons. The properties changes that derived from the structures' difference were discussed in detail. The relationship between the properties and microstructures of SPEEKK membranes was established. The study will provide more instructive information on the molecular design of excellent proton exchange membranes.

Keywords: Proton exchange membrane; Morphology; SAXS; SPEEKK

1. Introduction

The proton conductive membrane is central to solid polymer electrolyte membrane fuel cell (PEMFC). The membrane should include the following properties: good proton conductivity, good mechanical and thermal stability and low gas and methanol permeability, etc. The membranes traditionally used in PEMFC are perfluorosulfonic acid membranes such as Nafion. Although they show superior performances in fuel cells operating at moderate temperatures (<90 °C) and high relative humidity with pure hydrogen as fuels, the high cost, low conductivity at low humidity or high temperatures and high methanol permeability of Nafion® hinder their further commercial applications. Alternative materials such as sulfonated poly(aryl ether ketone) (SPAEK), sulfonated poly(aryl ether sulfone)s (SPAES), sulfonated poly(imide) (SPI) have been explored for PEM usages [1–3]. These proton membrane materials usually contain two domain regions: hydrophilic and hydrophobic ones. The hydrophobic domains formed by none sulfonated polymer segment provide the hydrated PEMs with mechanical strength whereas the hydrophilic domains contain sulfonated groups ensure the proton conductivity. The existence of the two regions may lead to the microphase-separated structures, which will determine the properties of PEM such as water swelling methanol cross over and proton conductivity etc. To the micro phase-separated structure of Nafion, many models were given according to SAXS SANS studies. Gieke postulated a cluster-network model that describes the existence of sphere domains (diameter ca. 2–5 nm) containing absorbed water. The acid groups are situated at the water polymer interface, shielding the water molecules from fluorocarbon phase. The micellar structure is interconnected by narrow pores [4]. In this model: the conductivity of wet membranes is dependent on the distribution and connectivity of the conductive pathways through the cluster network, and it can be quite well explained

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doi:10.1016/j.jpowsour.2006.12.011

by percolation theory. Other suggested that the period structure suggested by Gierke is not realistic. They proposed more random or diffuse ionic clusters, with the fluorocarbon backbone intruding into the ionic regions and isolated sulfonic acid groups that located predominantly fluorocarbon regions. More recently Gebel et al. proposed a model based on the existence of local order between ionic aggregates [5]. This model is based on SAXS and SANS data and considers that each ionic aggregate is spherical and surrounded by for aggregates in a tetrahedral coordination. This study suggests that: from low to high water content, the structure of Nafion realizes the inversion from percolation to polymer rods. Regarding of which structure model used, there is an agreement on that: the phase separation is a result of the tendency to reduce the surface interaction between the water filled ionic region and the hydrophobic polymer backbones. The hydrophilic domains are believed to be responsible for the transport of water and the protons while the hydrophobic domains provide the morphology stability and prevent the dissolution of the polymer in water [6]. The development of new membrane materials for fuel cell application requires a better understanding of how the membranes work. To date, Nafion membrane shows the best electrochemical properties and it is believed that the phase-separated morphology of those materials plays a dominant role in the hydration and conductivity of membranes. We have explored series of SPAEKs proton conductive materials in our previous work [7–10]. Although they show good prospective usages in PEM, the morphology of SPAEK membranes was seldom studied. The objective of this paper is to investigate the morphological changes of SPEEKK membranes with different sulfonated degrees (Ds). Further the transport property changes resulted from the morphology will be researched. This work will favor to explore excellent membranes for PEMFC. For this paper SPEEKK membranes with different sulfonated degrees were prepared, this polymer system facilitates the control of hydrophilic and hydrophobic domains, which allows one to obtain the different properties of SPEEKKs, which is related to different morphology of membranes.

Table 1
The data of the sufonated polymers

Polymer	[a]m (mmol)	[a]k (mmol)	$m\,k^{-1}$	[b]Yield (%)	[c]$\eta_{sp}\,c^{-1}$	[d]Ds
SPEEKK-1	16	24	4:6	93	0.89	0.78
SPEEKK-2	20	20	5:5	90	1.10	0.97
SPEEKK-3	24	16	6:4	93	1.41	1.23

[a] The amount of monomer m and monomer k.
[b] The yield of resulted polymers.
[c] The specific viscosities of resulted polymers.
[d] Sulfonated degree of resulted polymers.

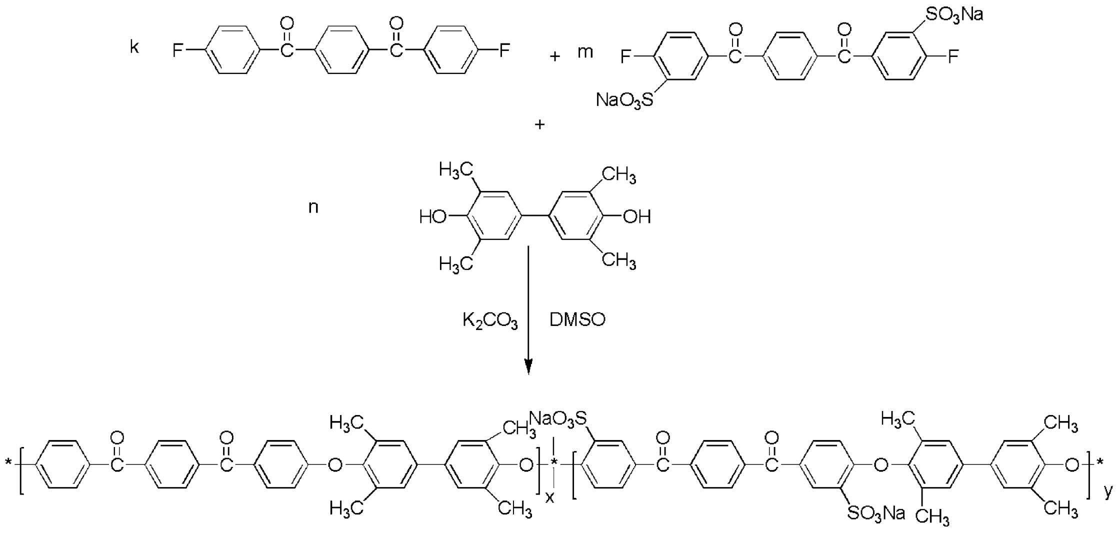
2. Experimental

2.1. Polymer preparation

The polymers used in this paper were prepared by direct aromatic nucleophilic substitution step polymerization (Scheme 1). Three types of monomers participated in this reaction: monomer m monomer k and monomer n [7–8]. The amount of monomer n was fixed at 40 mmol, which is equal to the total mixture of monomer m and monomer k. The sulfoanted degree was controlled by adjusting the ratio of monomer m to monomer k. The detailed synthesis procedure was reported in our previous work [8]. The analytical data of polymers used in this paper was shown in Table 1.

2.2. Membrane preparation

The sulfonated polymers were first dissolved in DMF to form with 5–10 wt% solutions. The resulting mixtures were cast onto glass plates, in which were placed into an oven at 50 °C and dried for 3 days. Dry membranes were peeled off from the substrate with deionized water and immersed into 1.5 M H_2SO_4 solutions overnight to make the membranes into H^+ forms. Finally, the membranes were rinsed with deionized water to remove any excess H_2SO_4 and dried under vacuum for 24 h.



Scheme 1. The preparation of SPEEKKs.

2.3. *Transmission electronic microscopy (TEM)*

TEM was determined by JEM-2000EX. Before test the polymers were first converted into Ag forms (SPEEKK-Ag) by dissolving the polymers in $AgNO_3$ solutions for 24 h. The SPEEKK-Ag in DMF solutions was then cast onto copper grids for TEM use. All the tests were carried out in the unhydrated condition.

2.4. *Atomic force microscopy (AFM)*

Tapping mode AFM images were obtained at ambient conditions using a SPA-300HVwith a SPI3500Ncontroller (Seiko Instruments Industry Co., Ltd.). Both height and phase images were recorded simultaneously using the retrace signal. Etched Si tips with a resonance frequency of approximately 250–300 kHz and a spring constant of about 2 Nm^{-1} were used, the scan rate was in the range from 1.0 to 2.0 Hz. Each scan line contains 256 pixels, and a whole image is imposed of 256 scan lines. The membranes were obtained by spin-coating a polymer solution in 0.05 g ml^{-1} DMF onto freshly cleaned silicon wafer at 3000 rpm for 50 s at room temperature.

2.5. *Small angle X-ray scattering (SAXS)*

SAXS was performed on SPEEKK and SPEEKK-Ag membranes. All the measurements were carried out at room temperature at dehydrated condition with Kratky small angle X-ray scattering, with Cu Kα (Philips) radiation.

The water desorption measurement was tested by Pyris 1TGA(Perkin-Elmer). During measurement, the temperature was kept at 80 °C, the pressure of the test cell was kept constant. Pyris 1TGA was used to determine the weight changes of samples with time. The diffusion coefficient of water was calculated by the Okamoto's report [11].

The salt diffusion coefficients of membranes were determined by using a cell basically consists of two half cells separated by the membrane, which was fixed between two rubber rings. The 1 M KCl and NaCl were placed on one side of cell and water was placed on the other side. DDS-11C was used to record the conductivity changes versus time in solution B. Salt diffusion coefficients of membranes were obtained by the slope of conductivity versus time liner [19]. The properties of membranes such as water uptake, ion exchange capacity (IEC) and proton conductivity were carried out by the usual method. The detailed procedure was presented in our previous publications [7–8].

3. Results and discussion

3.1. *The morphology of SPEEKK membranes*

Two regions exist in SPEEKK membranes, the hydrophobic domains containing non-sulfonated polymer segments and the hydrophilic domains containing the sulfonate groups. The distribution of hydrophilic and hydrophobic domains may determine the membrane proton conductivity. In another word, the morphology of SPEEKK membranes plays a critical role on the membrane electrochemical properties. SAXS, SANS AFM and TEM were usually used to study the ionic clusters in ionic polymers [12–15]. Several small angle X-ray scattering structures have characterized the details of morphology including the ionic clusters. The clustering of the ionic groups in the low dielectric constant polymer matrix is usually indicated by the existence of a scattering maximum. The scattering maximum is usually called "ionomer peak" in SAXS. According the fundamental theory of SAXS, the scattered intensity $I(q)$, oscillates with increasing wave vector (Eq. (1)):

$$q = \frac{4\pi \sin\theta}{\lambda} \tag{1}$$

where λ is the wavelength and 2θ is the scattering angle. The Bragg spacing d is related to q as (Eq. (2)):

$$d = \frac{2\pi}{q} \tag{2}$$

The origin of the "ionomer peak" has been widely studied. Usually two models have been proposed to interpret the SAXS observations: the "intraparticle model" and "interparticle model" [20–21]. The "intraparticle model" attributes the ionomer peak to the interference within the ionic clusters, implying that the scattering maximum is related to the internal structure of the cluster. On the other hand the ionomer peak was attributed to the interference between different ionic clusters. The Bragg spacing refers the "center to center distance" between two clusters, which may indicate the size of the ionic clusters. SAXS data for SPEEKK-1, SPEEKK-2 and SPEEKK-3 was shown in Fig. 1. The maximum at large angle is the Bragg peak, which is derived from the ionic cluster. The scattering maximum is clearly related to the ionic groups of SPEEKK. With the content of sulfonated groups increasing, the scattering maximum shifts to lower scattering vectors (Fig. 1a). SPEEKK-1, SPEEKK-2 and SPEEKK-3, respectively show the scattering maximum at 0.1615, 0.1542 and 0.1368 A^{-1}, respectively. The "center to center distance" calculated from "interparticle model" was 3.88, 4.07 and 4.59 nm, respectively for SPEEKK-1 to SPEEKK-3. This result indicates that SPEEKK membranes show the larger size of ionic clusters or more clearly phase-separated structures with Ds increasing. [12–13]. The asymptotic behavior at large angles of the scattering curve reflects the nature of the interface between the hydrophilic and hydrophobic domains [14–16]. According to Porod analysis, to the obvious phase-separated system, the intensity of scattering at large angles follows formula (3):

$$\lim_{s\to\propto} s^4 I(s) = k_\mathrm{p} \tag{3}$$

where k_p is Porod constant, $I(s)$ is the scattering intensity. The slope of $\ln[s^4I(s)]$ versus s^2 line at large angle can give the information about the thickness between the hydrophilic and hydrophobic interfaces[17]. The Porod plots of membranes in Fig. 1b show "positive departure" (Fig. 2).

The slope of SPEEKK-1 to SPEEKK-3 is 1.43, 1.53 and 1.57 $Å^2$, respectively. The increased interface thickness between the hydrophilic and hydrophobic phases indicates more clearly

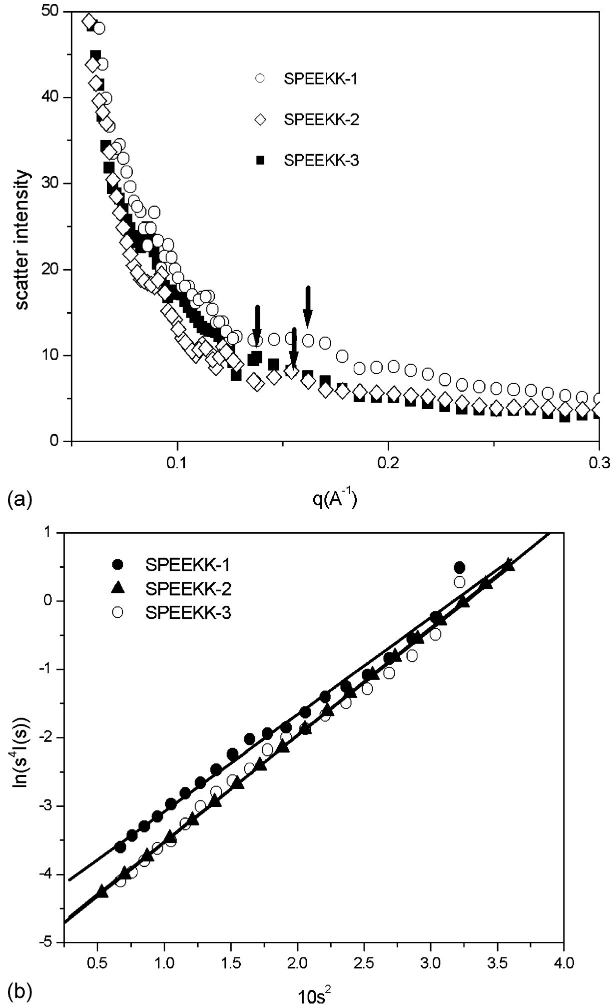


Fig. 1. The SAXS data of SPEEKKs.

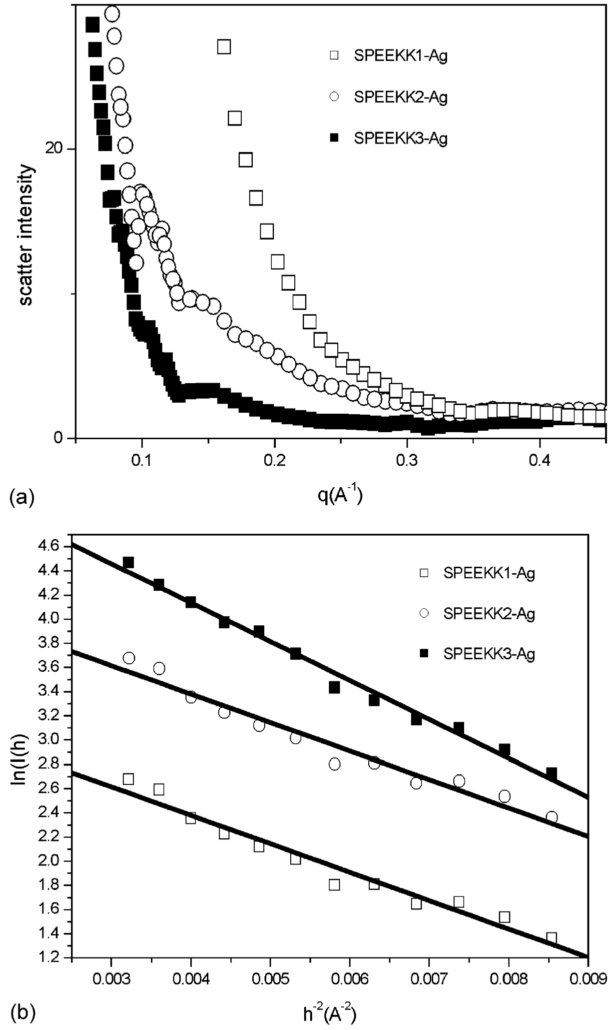


Fig. 2. The SAXS analysis of SPEEKK-Ag,.

phase-separated structures of the SPEEKK membranes with increasing Ds. It has been known that silver ions can chelate with the sulfonate groups, resulting in formation of silver clusters within the S-PEEK matrix. The result of our previous work has indeed shown the formation of silver particles within the SPEEKK matrix [8]. TEM in Fig. 3 can clearly give the distribution of silver particles in SPEEKK membranes. The formation of silver particles can be explained by the hydrophilic (sulfonate) and hydrophobic (main polymer chain) nature of the S-PEEK. The sulfonate groups aggregate and form clusters of hydrophilic nature to create pathways for ions transport. When hydrophilic domains are hydrated, proton charge carriers dissociate from

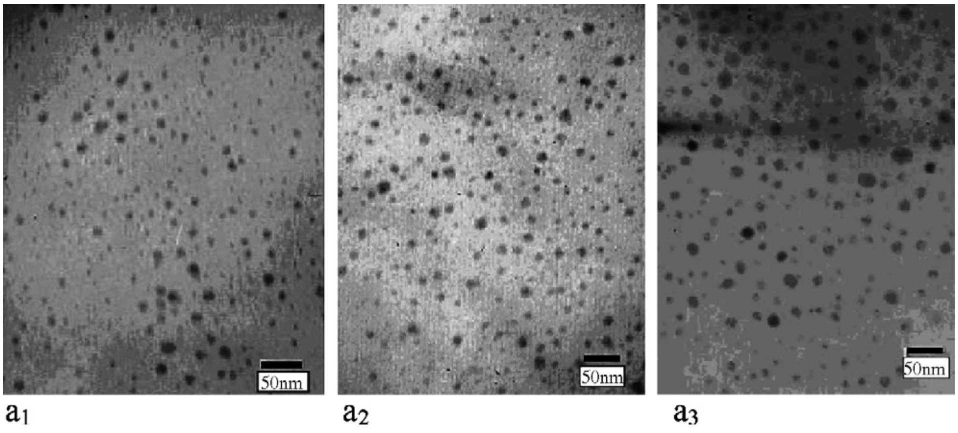


Fig. 3. The TEM of SPEEKK-Ag: (a$_1$), SPEEKK-1; (a$_2$), SPEEKK-2; (a$_3$), SPEEKK-3.

Table 2
The analytical data of SPEEKK membranes

Polymer	SPEEKK-1	SPEEKK-2	SPEEKK-3	Nafion
Water uptake (%)	16	24	27	22
IEC (meq)	1.01	1.36	1.57	0.92
Proton conductivity (s cm^{-1})	1.3×10^{-2}	3.0×10^{-2}	4.8×10^{-2}	8×10^{-2}
[a]R_g (nm)	2.8	3.3	3.4	–
Water diffusion coefficient (m^2 s^{-1})	3.01×10^{-10}	2.24×10^{-9}	7.13×10^{-9}	–
KCl diffusion coefficient (m^2 s^{-1})	3.94×10^{-11}	8.13×10^{-11}	19.1×10^{-11}	–
NaCl diffusion coefficient (m^2 s^{-1})	8.54×10^{-11}	19.1×10^{-11}	31.4×10^{-11}	–

[a] Average radius of gyration for SPEEKK-Ag.

the $SO_3{}^-$ functional groups and proton conductance assisted by water dynamics occurs. The size of silver particles will illustrate the size of clusters or the characteristic of proton conductive channels. From the TEM, the size of silver particles increases with Ds increasing, which shows the increasing size of clusters or the proton transport channels.

SAXS may also give the information about the size of particles. To analyze the experimental curves corresponding to a set of particles that developed with SPEEKK-Ag, we have applied the Guinier equation [18]:

$$\left[I(h) = I(0)\ \exp\left(\frac{-h^2 R_g^2}{3}\right) \right] \tag{4}$$

The average radius of gyration, R_g, of the silver clusters is determined from the slope of the liner part of Guinier plot [$\ln(I(h))$ versus h^2]. And the value of $I(0)$ is obtained by liner extrapolation to $h = 0$. The scattering maximun of SPEEKK-Ag shown in Fig. 2a indicates the same tendency with SPEEKK curves. The size of clusters increases with the content of sulfonate groups increasing. The Guinier plots of SPEEKK-Ag were shown in Fig. 2b. SPEEKK-1 to SPEEKK-3 show increasing slope of 269, 362, and 391 Å^2, respectively. The calculated R_g from Guinier plots in Table 2 shows increasing tendency with increasing Ds. The R_g of silver particles in SPEEKK matrix, which calculated from SAXS data, is 2.8, 3.3 and 3.4 nm with Ds of 0.8, 1.0 and 1.2. The result of SAXS well conform to the TEM results. The hydrophilic domains in SPEEKK matrix may determine the proton conductive property. TEM and SAXS analysis show that the hydrophilic groups, which form proton conductive channels, will have great influence on the micro-structures of SPEKK membranes. With the increasing Ds, the membranes will provide more and larger proton transport channels. To note: the TEM and SAXS analysis were carried out at anhydrate con-

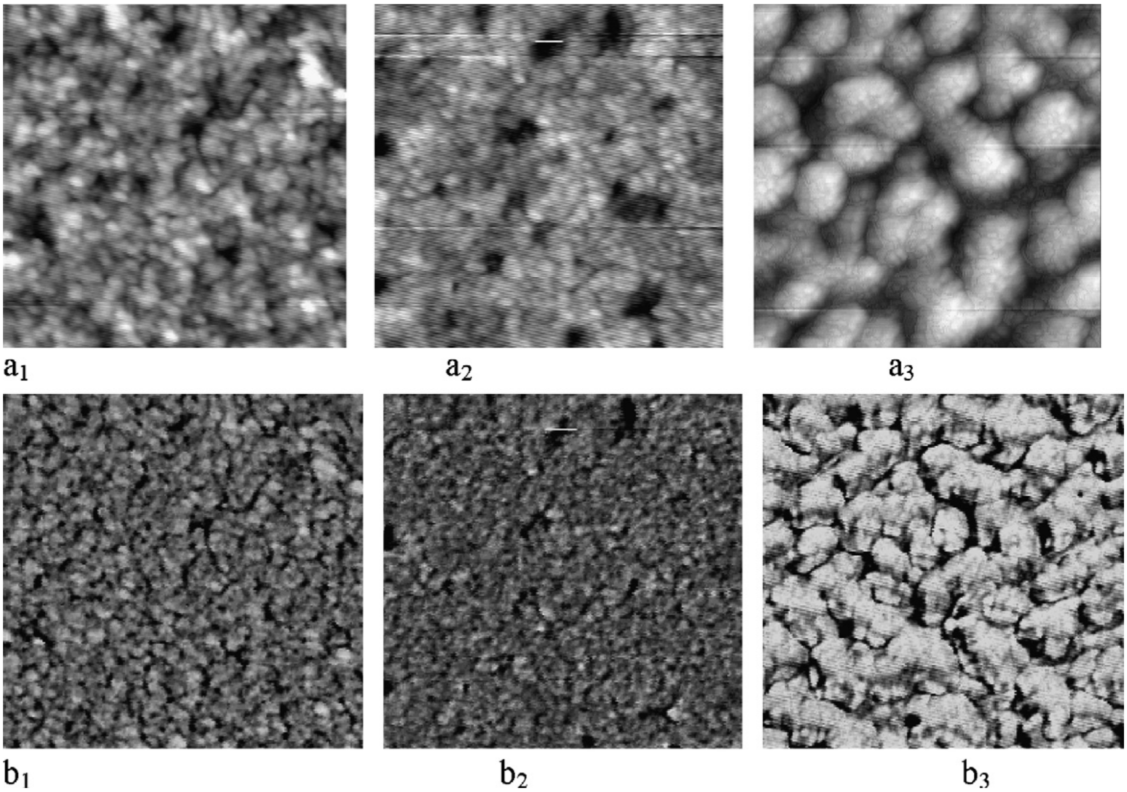


Fig. 4. The AFM of SPEEKKs: (a_1, b_1), SPEEKK-1; (a_2, b_2), SPEEKK-2; (a_3, b_3), SPEEKK-3; (a_1, a_2, a_3), topgraph of SPEEKK; (b_1, b_2, b_3), the phase images of SPEEKK.

dition so in a practical application, the sulfonate clusters would probably be more evenly distributed. The distribution of sulfonated groups may lead to the separation of hydrophilic and hydrophobic domain. The phase structures of SPEEKK were characterized by AFM. The topography and phase images of SPEEKK membranes were shown in Fig. 4, the scale of the images was 1 μm × 1 μm.

The topographs in Fig. 4a show the surface morphology of the membranes. All the membranes show very disordered surface from the results. To the phase images of SPEEKK membranes dark regions are assigned to softer regions, which represent the hydrophilic sulfonated groups. And the light regions are assigned to hydrophobic polymer backbone [1]. The size and the continuous of these two regions have great influence on the transport properties of membranes. Larger and more continuous of hydrophilic regions were found with Ds of SPEEKK increasing from 0.8 to 1.2. The phase-separated structures may be benefit to form proton transport channels, which further lead to the improvement of proton conductivity.

4. The properties of SPEEKK membranes

The properties of proton exchange membranes are closely related to their microstructures. The extreme hydrophobicity of the polymer backbone and extreme hydrophilicity of the sulfonic acid groups lead to a spontaneous hydrophilic/hydrophobic nano-separation. The separation structure will have great influence on the properties of membranes such as proton, water and methanol transport properties. The water uptake, ion exchange capacity and proton conductivity in Table 2 show increased tendency with Ds increasing. The water uptake and proton conductivity of SPEEKKs are much lower than Nafion despite of the high IEC of SPEEKKs. Such results suggest the influence of the position of sulfonate groups in polymer on the microstructures of polymers. To Nafion the sulfonated groups are on the chain side of polymers, which may easily aggregate into clusters. Otherwise in these SPEEKK polymers, the sulfonate groups are dispersed throughout the polymer matrix, and are not easily aggregated. Nafion shows more clearly phase-separated structures than SPEEKK. All these will lead to the high water uptake and proton conductivity of Nafion membranes. To SPEEKKs, the increasing content of sulfonate groups will lead to good phase separation structures, which are benefit to form transport channels. When the membranes were hydrated, the microstructures of membranes become loosen; the size of transport channels will become larger. With the increasing of Ds the size of transport channels increases, which is benefit to water, proton and methanol transport in membranes. Water retention of proton exchange membranes plays a very important role in determining the proton conductivity, especially the water retention of membranes at high temperatures. Low water retention of Nafion at high temperatures is one of drawbacks, which hinder their further commercial applications. Water retention of membranes is closely related to the microstructure of membranes. In this section, water retention was characterized by water desorptions, the temperature was kept at 80 °C. The desorption isotherms of SPEEKK were shown in Fig. 5. The relationship between the water desorption and time may follow Ficker diffusion. Plots of M_t/M_∞ versus $t^{1/2}$ initially are linear for Ficker diffusion. Diffusion coefficients for desorption are determined from the initial slope according to Eq. (5).

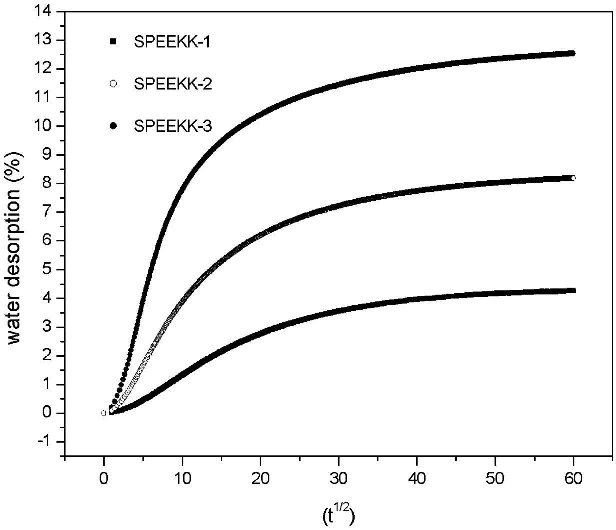


Fig. 5. Water desorption curves of SPEEKK membranes.

$$\frac{M_t}{M_\infty} = 4\left(\frac{Dt}{\pi l^2}\right)^{1/2} \tag{5}$$

where l is membrane thickness, D is water diffusion coefficient and M_t/M_∞ is the water desorption.

Plots of M_t/M_∞ versus $t^{1/2}$ for SPEEKKs were shown in Fig. 5. The thickness of membranes is about 110 μm, water content of SPEEKK membranes increases with the increasing content of sulfonate groups, which is consistent with the water uptake of membranes. The water diffusion coefficients of SPEEKK-1 to SPEEKK-3, which calculated from Ficker diffusion were 3.01×10^{-10}, 2.24×10^{-9}, 7.13×10^{-9} $m^2\,s^{-1}$, respectively. This may be due to the different microstructures of SPEEKK membranes. From the study of membranes' morphology, more and more clearly separated structures were indicated with increasing Ds. The size of hydrophilic domains becomes larger and the structures of them become loosen with increasing content of sulfonated groups. The loosen structures of SPEEKKs with high sulfonated degrees will make the water in the membranes more easily evaporate and the diffusion coefficients of water in membrane increase. The transport properties of membranes may reflect the microstructures properly. The size and continuous of transport channels have great influence on the transport properties of membrane, especially salt permeability. Salt such as NaCl, KCl diffusion coefficient through membranes were investigated. Both the diffusion coefficients of NaCl and KCl (Table 2) increase with increasing Ds of membranes. This might be due to the percolation of ion-conductive channels in the membrane matrix. With the content of sulfonated groups increasing, the membrane structures become loosen and the transport channels of cations become larger and more continuous. All these results will lead to the increasing diffusion coefficients of salts.

5. Conclusion

The microstructures of SPEEKKs membranes were studied in detail with AFM, TEM and SAXS. The water desorption and cation transport properties of membranes with different morphology were characterized. This study established the relationship between the properties and morphology of SPEEKK membranes. The work may have good instructive usages in designing and selecting excellent proton exchange membranes.

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