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ARTICLE TYPE

Composite proton exchange membranes from poly(aryl ether sulfone)s with pendant sulfonated aliphatic side chains nanofiber electrospun mats

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A series of cardo poly(aryl ether sulfone) copolymers bearing pendant sulfonated aliphatic side chains were synthesized and electrospun to nanofibers. The sulfonated poly(aryl ether sulfone) (SPES) nanofibrous mats were filled by appropriate amount of Nafion solution. The composite membranes showed significantly reduced swelling behavior and excellent mechanical properties as well as appropriate proton conductivity. Especially, the composite membrane exhibits much lower methanol permeability in the range of 10^{-7} cm^2 s^{-1} and higher selectivity about 10^5S s cm^{-3} compared to Nafion117. The results showed that the fabricated nanofiber-based composite membranes can be used as a promising proton exchange membrane for direct methanol fuel cell (DMFC) applications.

1. Introduction

The direct methanol fuel cell (DMFC) are the focus of most attention because of their versatile and multiple applications in the automobile and portable fields.[1−2] As a key element of DMFC, proton exchange membranes (PEMs) have been highly developed owing to the contribution of perfluorinated acid polymers (e.g., Nafion) with high proton conductivity, good mechanical properties, and excellent stability.[3] However, these membranes have some drawbacks such as high cost, low conductivity at elevated temperatures, and high methanol crossover, hinder the widespread commercialization of DMFC.[4]

To overcome the defects above, inorganic nanoparticles, for example silica,[5] titania,[6] etc., have been incorporated into Nafion to form hybrid membranes. Unfortunately, most filler particles lacked protogenic groups, which restricted the fast proton transport. Meanwhile, the filler materials, such as the sulfonic acid functionalized single-walled carbon nanotubes, could offer additional protogenic groups for acid-water clusters.[7] However, the low content of dispersed filler particles made it difficult to form effective proton-transport pathways in membranes. Recently, Nafion has been entrapped within a poly(vinyl pyrrolidone) (PVP) network as a semi-IPN membrane.[8] In this association, acid−base interactions between the PVP amino groups and the sulfonic acid groups of Nafion form an ionically cross-linked ionomer network, which decreases methanol permeation and promotes proton transfer. The overall performance of these Nafion-based modified membranes did not meet the requirement of practical fuel cell applications yet. Therefore, new strategies would be significant and need further exploration.

Electrospinning is a straightforward method for producing fine polymeric fibers with a small diameter.[9] The electrospun nanofibrous mats have drawn considerable interest owing to provide high porosity and three-dimensional network structure[10]. These distinct features make electrospun mats very useful for numerous applications and ideal porous substrates for filters[11] or conductivity materials,[12] etc. The Nafion-filled electrospun nanofibrous poly(vinylidene fluoride) membranes have been reported by Choi el al.[13] The composite membranes showed the improvements in the mechanical properties, but decreased with the addition of the non-ionic nanofiber mats in the proton conductivity. Pintauro reported that Nafion film reinforced by poly(phenyl sulfone) nanofibers. The nanofiber composite membranes exhibit very low in-plane water swelling and better mechanical properties.[14] Shabani and coworkers,[15-16] prepared composite PEMs which are sulfonated poly(ether sulfone) nanofiber webs filled with Nafion. On the effects of the polyelectrolyte nanofibers, the obtained composite PEMs have higher electrochemical performance than commercial Nafion membranes. However, they used the main-chain-type sulfonated poly(ether sulfone) as electrospinning material, that lead to high water uptake of the composite film(i.e. the SPES-N-N, SPES-N-N112, was 13.5% and 16.3%, respectively). According to the results, Methanol permeability of the bilayer or triple-layer membrane is still in the same order of magnitude with Nafion117.

For optimizing the DMFC performance, it is necessary to look for satisfied polyelectrolyte nanofibers which should have many extraordinary properties, such as small diameter, high resistance to swelling properties, low methanol permeability, superior proton conductivity and good mechanical properties.

The water uptake and swelling ratio of the side-chain-type sulfonated poly(aryl ether sulfone)(SPES) were lower than that of the main-chain-type sulfonated polymers with similar IEC.[17] Moreover, sulfonic acid groups on the flexible aliphatic side chain of the SPES could decrease the limitation of main-chain rigidity on the mobility of sulfonic acid groups, thus enhancing proton conductivity.[18] Therefore, in this work, we first prepared the side chain SPES samples with different degree of sulfonation, and then electrospun to nanofibers. The fabricated composite membrane based on Nafion-filled was evaluated to identify the effects of nanofibers compared to a pristine membrane using proton conductivity, dimensional stability, morphologies and so forth.

2. Experimental

2.1.Materials

Phenolphthalein was purchased from Beijing Chemical Reagent Company and purified by recrystallization from mixed solvent of ethanol and water. 4,4-Difluorodiphenylsulfone (DFDPS) was obtained from Jiangyan Jiasheng Chemical Co., Ltd., China. 1,3-Propanesultone were obtained from Alfar and used as received. Nafion 5wt% solution and Nafion117 membrane were obtained from DuPont Co. All other chemicals were reagent grade and used as received.

2.2. Synthesis of cardo poly(aryl ether sulfone)s with pendant sulfonic acid groups(SPES-X)

Preparation and characterization of cardo poly(arylene ether sulfone)s containing amide groups(PES-NH) was reported in a previous paper.[19] Then the cardo-poly(arylene ether sulfone)s with pendant sulfonated aliphatic side chains were synthesized as Scheme1. The obtained polymers are denoted by SPES-X, where X represents the degree of sulfonation.

A typical procedure for SPES-60: PES-NH (10.632g, 0.02mol) and NaH (0.96g, 0.04mol) were added to 100mL of NMP at room temperature and stirred for 30min. Then 1,3-propanesultone (1.4657g, 0.012mol) was added and the reaction was allowed to proceed at room temperature for 12h. The viscous solution was precipitated into ethanol. The isolated white polymer was washed with deionized water several times before being dried under vacuum at 120℃overnight. Yield: 97%. Other sulfonated polymers were prepared by the same method described above, except with different amounts of 1,3-propanesultone.

SPES-X: ^{1}H NMR(DMSO-d$_6$): 9.80ppm 1H; 7.93-7.96ppm 4H; 7.57-7.84 4H; 7.32-7.41ppm 4H; 7.17-7.24ppm 8H; 3.43ppm 2H; 2.26ppm 2H; 1.23ppm 2H.

2.3.Preparation of electrospun SPES-X nanofiber mats

SPES-X solutions with 25, 30, and 35wt% in DMAc were prepared. The resulting clear and homogeneous solutions were electrospun with electrical voltages 15kV. A syringe pump was used to feed the polymer solution into the needle tip at a fixed feed rate of 0.1 mL/h. The electrospun fibers were collected on an aluminum target with a distance of 15cm from the spinneret. The mats were dried under vacuum to remove residual DMAc, and had specific weights of about 25g/m^2. The porosity of the electrospun mats was about 60%.[20]

2.4.Fabrication of the composite membranes containing nanofibers

The appropriate amount of 5wt% Nafion solution were poured on the SPES-X nanofiber porous mats, and the solution was dried at room temperature for 3 days. The resulting membranes were then dried under vacuum at 100℃ for 12h. Finally, the composite membranes in their salt form were then converted to a corresponding acid form by soaking in 1M H_2SO_4 solution for 48h followed by immersion in deionized water for 48h. Tough, ductile ionomer membranes were obtained with a controlled thickness of 40-60μm.

2.5.Characterizations

^{1}H NMR spectra were measured at 300MHz on an AV 300 spectrometer. The morphologies of the electrospun nanofibers and composite membranes were examined by scanning electron microscope (Hitachi XE-100 SEM, Japan).

The proton conductivity (σ, S/cm) of each membrane coupon (size: 1cm×4cm) was obtained using $\sigma = d/L_S \times W_S \times R$ (d is the distance between reference electrodes, and L_s and W_s are the thickness and width of the membrane, respectively). Here, ohmic resistance (R) was measured by four-point probe alternating current impedance spectroscopy using an electrode system connected with an impedance/gain-phase analyzer (Solatron 1260) and an electrochemical interface (Solatron 1287, Farnborough Hampshire, ONR, UK). All samples were equilibrated in water for at least 24h before the conductivity measurements. At a given temperature, the samples were equilibrated for at least 30min before any measurements.

The membrane sample (30-40 mg per sheet) was dried at 120 ℃ under vacuum for 12 h until constant weight as dry material was obtained. It was immersed into deionized water at 20℃ for 8 h and then quickly taken out, wiped with tissue paper, and quickly weighted on a microbalance. The water uptake was calculated using the following equation: water uptake (wt%) = $(W_s - W_d)/W_d$, where W_d and W_s are the weight of the dry and wet membranes, respectively. The water swelling ratio of the membranes was investigated by immersing the round-shaped samples into water at 20℃ for 8h and the swelling ratio was calculated from the following equation: swelling ratio(%)=$[l_{wet}-l_{dry}]/l_{dry}$, where l_{dry} and l_{wet} are the length of the dry and wet samples, respectively.

The methanol permeability was determined by using an H's test cell with a solution containing (2mol L^{-1}) methanol in water in one side and pure water in the other side. Magnetic stirrers were used in each compartment to ensure uniformity. Methanol concentration within the water cell was monitored by SHIMADZU GC-1020A series gas chromatography. The methanol permeability was calculated by the following Eq. (1):

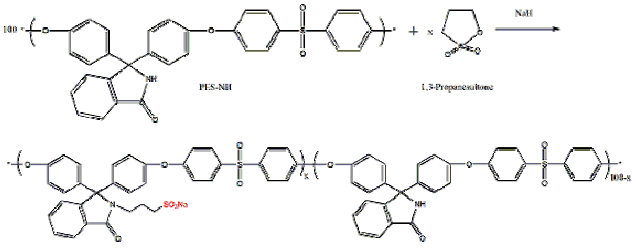
$$C_B(t) = \frac{A}{V_A}\frac{DK}{L}C_A(t - t_0) \qquad (1)$$

where $C_A$and C_B are the methanol concentration of feed side and permeated through the membrane, respectively. A, L and V_A are the effective area, the thickness of membrane and the volume of permeated compartment, respectively. DK defined as the methanol permeability, and t_0 is the time lag.

Tensile measurements were performed with a mechanical tester Instron-1211 instrument (Instron Co., USA) at a speed of 2mm/min at ambient humidity (～30% relative humidity).

3. Results and discussion

3.1. Synthesis and characterization of the polymers



Scheme 1 The typical synthetic route for cardo poly(arylene ether sulfone)s containing sulfonated side chains.

Synthetic procedure of cardo poly(arylene ether sulfone)s containing sulfonated aliphatic side chains is shown schematically in Scheme1. The as-synthesized polymers(PES-NH)

contained an amide group in each repeating unit, which provided reaction sites to introduce various functional groups, such as sulfonated aliphatic side chains. The sulfoalkylation reaction of PES-NH and 1,3-propanesultone was carried out at room temperature for 12h with NaH as the base.

Useful information can be extracted simply from studying the ^{1}H NMR spectrum of the SPES-X copolymers. Fig.1 shows ^{1}H NMR spectra of SPES-60, SPES-70 and SPES-80. The peak at 9.80ppm (proton in amide) still part of the present, and new peaks appear at 3.43ppm, 2.26ppm and 1.23ppm which correspond to the protons in the sulfoalkyl group, which confirms that part of the amide groups reacted with 1,3-propanesultone to produce N-alkylated product. The integration ratio of H(c) to that of H(1-8) was close to 2X:20, suggesting a quantitative conversion of proton in amide(NH) to sulfopropyl groups. The content of the sulfonic acid groups in the copolymers was readily controlled through the feed ratios.

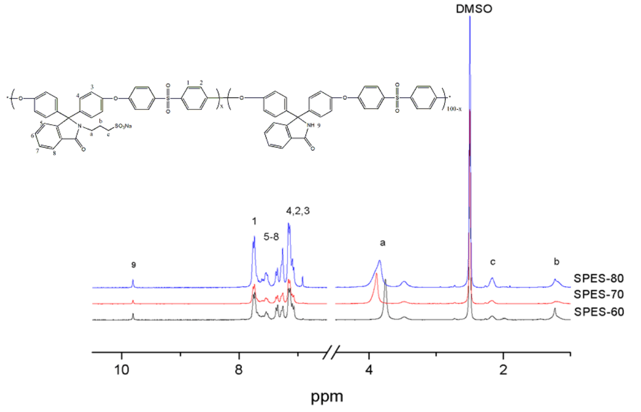


Fig.1 ^{1}H NMR spectra of SPES-X copolymers in DMSO-d_6.

Table 1 shows the properties of the synthesized SPES-X membranes. IEC is a constant representing the amount of the exchangeable protons in ionomer membranes. The IEC values were determined by a titration method, which were close to the theoretical values calculated according to the content of -NH groups, indicating a quantitative reaction between -NH groups and 1,3-propanesultone. The IEC values in the range of 0.90-1.51mequiv./g were readily controlled by adjusting the feed ratios.

As shown in Table 1, the water uptake increased from 7.3% for SPES-60 to 20.0% for SPES-100. Also, the swelling ratio increased from 4.4% for SPES-60 to 7.5% for SPES-100. With the increasing IEC, the proton conductivity was also enhanced from 0.0126 to 0.0560S/cm for SPES-60 and SPES-100, respectively. The increased proton conductivity with IEC implies that the water uptake values were reasonable in enhancing the proton transfer through the fully hydrated membrane.

Table 1 properties of the cast SPES-X membranes.

Samples	IEC(meq./g)		Water uptake(%)		Swelling ratio(%)		σ(S/cm)
	IEC[a]	IEC[b]	20℃	80℃	20℃	80℃	20℃
SPES-100	1.53	1.51	20.0	30.0	7.5	9.8	0.0560
SPES-80	1.27	1.18	14.4	22.3	6.2	8.0	0.0456
SPES-70	1.13	1.08	12.6	20.1	4.8	5.6	0.0392
SPES-60	0.99	0.90	7.3	12.2	4.4	5.0	0.0126

[a] Calculated IEC values based on complete reaction of –NH groups with 1,3-propanesultone.

[b] Determined from titration.

[c] The composite membrane reinforced to Nafion by SPES-X nanofibers, denoted as CSPES-60, CSPES-70, and CSPES-80, respectively. CSPES-70-3 and CSPES-70-5 represented 3wt% and 5wt% Nafion solution, respectively.

The homopolymer SPES-100 can achieve suitable conductivities only at high ion-exchange capacities(IECs), resulting in high water uptake and large membrane dimensional changes which are unsuitable for practical PEM applications. Therefore, it is more suitable to select copolymer electrospun mats as reinforcer in Nafion matrix.

3.2. Electrospun fiber and membrane morphology

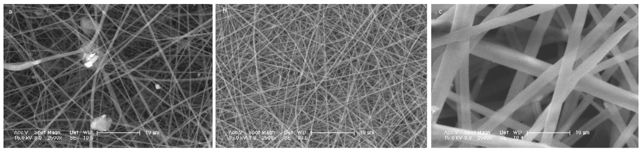


Fig.2 SEM images of the SPES-70 electrospun nanofibers with different concentrations: a(25%), b(30%), c(35%)

Three types of copolymer, which are SPES-60, SPES-70 and SPES-80 respectively, were electrospun to nanofiber. The SEM micrographs of electrospun fibers from SPES-70 in DMAc solution with different concentrations, ranging from 25% to about 35%, are shown in Fig.2. At concentration below 25wt%, the electrospinning process generated a mixture of fibers and droplets. In contrast, the electrospinning fiber population exhibits wider size distribution of the 300-500nm at a concentration above 35wt%. Continuous fibers without beads are obtained at the polymer concentration of 30wt% (Fig.2b) and the diameter distribution of the fibers is shown highly uniform with 120-150nm range. This observation is consistent with the literature on the effect of concentration.[21] The fiber mat is highly porous and cannot be used as a fuel cell membrane, so further processing of the mat is required to create a dense and defect-free film. Moreover, SPES-60 and SPES-80 were also electrospun to nanofibrous mats in the optimized conditions (e.g. 15kV, 30wt%, 0.1mL/h and 15cm et al.).

Fig.3a show the cross-section SEM photographs of the SPES-70 electrospun nanofiber mats, which revealed high porosity and interconnected open pore structure. The SPES-70 nanofibers are clearly visible and uniform throughout the membrane which was pore-filled completely in Fig.3b and Fig.3c. Absence of fiber pull out or crack indicates good interfacial surface compatibility between SPES-70 nanofibers and Nafion matrix(Fig.3c). Fig.3d and Fig.3e show the morphology of the composite membrane containing 5%Nafion, where there is a uniform distribution of SPES-70 nanofibers embedded in Nafion. However, image analysis of nanofibers (Fig.3e) revealed that SPES-70 nanofibers had slightly dissolved due to a strong interaction between nanofiber and Nafion. The nanofiber structures could be clearly seen in the micrographs of CSPES-60-3 composite samples (Fig.3f). Nevertheless, cracks appear in the composites show poor compatibility between the Nafion matrix and SPES-60 nanofiber. Furthermore, preparation of CSPES-60-5 composite was not successful in this work. Fig.3g confirmed designed composite structures but a lot of voids. Based on the above results, the following discussions are only about SPES-70 and the related materials.

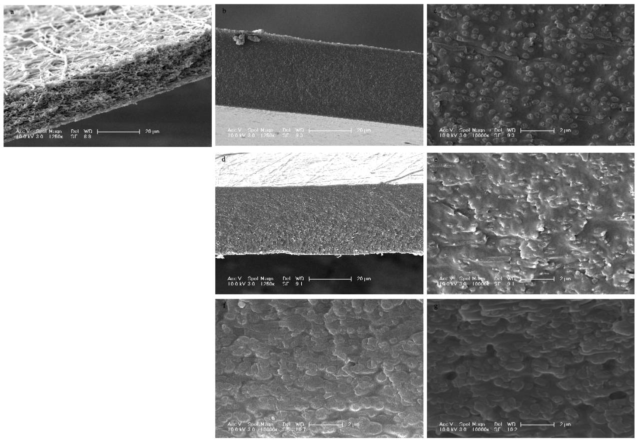


Fig.3 the cross-section SEM images of the prepared samples for (a)SPES-70 nanofiber mat, (b) and (c)the CSPES-70-3 composite membrane(b for low magnification and c for high magnification), (d) and (e)the CSPES-70-5 composite membrane,(f)the CSPES-60-3 composite membrane,(g)the CSPES-80-3 composite membrane.

As shown in Fig.4, the swelling ratio of composite membranes were greatly reduced compare to Nafion117, from 15.2 to 5.1 for CSPES-70-5 and 15.2 to 4.5 for CSPES-70-3. Meanwhile, the water uptake of composite membranes also showed similar trend. The three-dimensional network structures formed by nanofibers within the composite membranes eventually restrict the swelling ratio.[22] These results imply that the Nafion matrix were efficiently reinforced by nanofibers, and the electrospun nanoporous mat was suitable for use as a supporting materials in a pore-filling membrane.

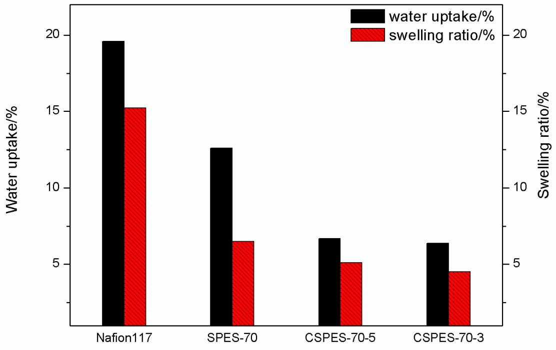


Fig.4 the water uptake and swelling radio of the membranes at 20℃

The proton conductivity of the membranes plays particularly important role in fuel cell performance, higher levels of ion conductivity lead to higher power density. Proton conductivities of the fabricated membranes were subsequently examined at 20℃ under 100% RH conditions. Fig.5 shows the dependence of membrane proton conductivity on temperature over the range 20-80℃. The conductivity of all membranes steadily increases with temperature because the free volume, in favor of ion transport and the mobility of cations, is increased as the temperature rises. The composite membranes contain nanofibers displayed the higher proton conductivity at all measured temperature compared to that of neat SPES-70. The proton conductivity of CSPES-70-5 is lower than that of CSPES-70-3, which was associated with slightly dissolved nanofibers from SEM (Fig.3e).The observed increase in conductivity is mainly attributed to Nafion with several sulfonic groups. On the other hand, it is also the contribution of nanofibers. The proton channel structure due to the network of the sulfonic acid groups formed within the nanofiber may lead to the rapid transport of the proton.[23]

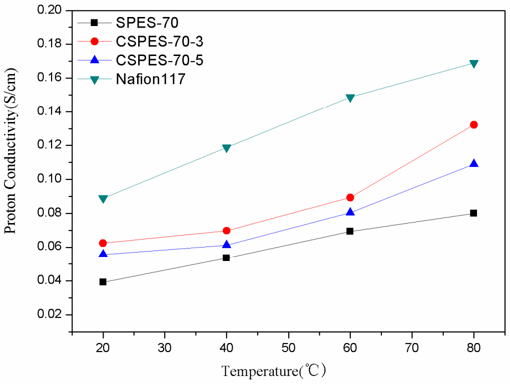


Fig.5 Impact of temperature on proton conductivity

One of the most significant limitations to the use of Nafion membranes in DMFC is methanol crossover, which is detrimental to the performance of the fuel cell.[24] Table 2 lists the methanol transport behavior of the CSPES-70-3 membranes in comparison with Nafion117 and SPES-70 cast film.

Table 2 methanol permeability and selectivity of membranes

Samples	σ(S cm^{-1}) 20℃	P_M(×10^{-7}cm^2 s^{-1}) 20℃	Selectivity (×10^5 S s cm^{-3})
SPES-70	0.0392	4.98	0.79
CSPES-70-3	0.0624	1.02	6.12
Nafion117	0.0900	24.0	0.38

The methanol permeability of the CSPES-70-3 from 1.02×10^{-7}cm^2 s^{-1} are much less than the Nafion117 measured under the same experimental conditions (2.4×10^{-6}cm^2 s^{-1}). The SPES-70 membrane exhibited methanol permeability of 4.98×10^{-7}cm^2 s^{-1}, which was also higher than CSPES-70-3. The methanol permeability reduction occurs from the longer and tortuous diffusive pathway in the presence of nanofibers.[16]

The possibility of using a membrane in DMFC is often evaluated using the selectivity parameter, which is the ratio of proton conductivity to methanol permeability. The selectivity values of the CSPES-70-3 is about 6.12×10^{5}S s cm^{-3} compared to 7.9×10^4 and 3.8×10^{4}S s cm^{-3} for SPES-70 and Nafion117, respectively. An improvement in the composite membrane selectivity has been achieved due to the incorporation of nanofiber three-dimensional network into the Nafion.

Table 3 mechanical properties of membranes

samples	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
SPES-70	72.9	1490.4	38.6
CSPES-70-3	25.5	362.2	38.7
CSPES-70-5	33.5	634.2	36.9
Nafion117	18.3	164.0	190.0

The actual stress strain curves for the two composite membranes and for Nafion117 are shown in Fig.6. Mechanical properties are summarized in Table 3. As can be seen, the neat SPES-70 membrane has excellent mechanical properties, which were Young's modulus of 1.5GPa, a tensile strength of 72.9MPa and an elongation at break of 38.6%. For the nanofiber composite membranes, it is observed that the Young's modulus and tensile strength of CSPES-70-3 and CSPES-70-5 are much higher than Nafion117. This is attributed to SPES-70 in the fiber form as a reinforcing nonwoven network. The interfacial adhesion between nanofibers and 5%Nafion matrix is stronger compared to 3%Nafion matrix (as evidence by SEM examinations).

Conclusions

We have developed Nafion composite membrane reinforced by electrospun side-chain cardo-SPES nanofibers. The morphological evaluations revealed that the nanofibrous mat was successfully filled by Nafion. The swelling ratio of composite membranes were reduced due to the incorporation three-dimensional network of SPES nanofibers into the Nafion matrices.

With the effects of the polyelectrolyte nanofibers, the obtained composite membranes have exhibited enhanced proton conductivity compared to the neat SPES-70 films. Methanol permeability results showed that the incorporation of SPES nanofibers into the Nafion matrix can act as a methanol barrier. Moreover, the nanofiber composite membranes exhibited better mechanical properties. Such membrane may prove to be promising as a polymer electrolyte membrane and may be potentially useful for application in fuel cells.

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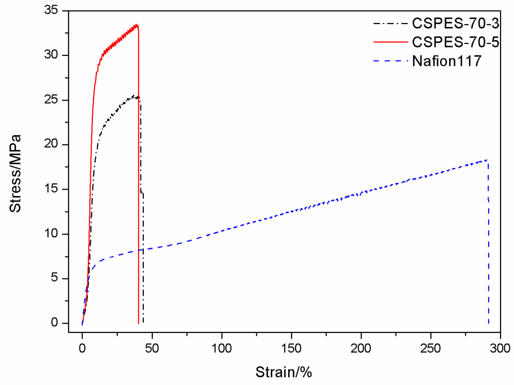

Fig.6 Stress-strain curves for Nafion117 and composite membranes

Notes and references

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Graphical Abstract

The electrospun nanofiber mats revealed high porosity and interconnected open pore structure. The nanofibers are clearly visible and uniform throughout the composite membrane which was pore-filled completely.