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Synthesis and characterization of novel sulfonated naphthalenic polyimides as proton conductive membrane for DMFC applications

Yuming Shang [a], Xiaofeng Xie [a,*], Hao Jin [a,b], Jianwei Guo [a], Yaowu Wang [a], Shaoguang Feng [a], Shubo Wang [a], Jingming Xu [a]

[a] *Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084, China*
[b] *The Key Laboratory of Beijing City on Preparation and Processing of Novel Polymer Materials, Beijing University of Chemical Technology, Beijing 100029, China*

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Abstract

To prepare proton conductive membrane for direct methanol fuel cells (DMFC), a novel sulfonated aromatic diamine monomer, 1,4-bis(4-amino-2-sulfonic acid-phenoxy)-benzene (DSBAPB) was synthesized and characterized by ^{1}H NMR and FT-IR. Then a series of sulfonated polyimides (SPIs) were prepared from DSBAPB with 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA) and a non-sulfonated diamine, 4,4′-oxydianiline (ODA) via one-step high-temperature polymerization method. The sulfonation degree of the SPIs can be controlled by changing the mole ratio of sulfonated monomer to non-sulfonated monomer. The obtained SPI membranes exhibit desirable proton conductivity ranged from 7.9×10^{-3} to 7.2×10^{-2} S cm^{-1} and low methanol permeability of less than 2.85×10^{-7} cm^2 s^{-1}. Furthermore, the hydrolysis stability of the obtained SPIs is better than the BDSA based SPIs caused by the flexible structure.

Keywords: Sulfonated polyimides; Proton conductive membrane; Methanol permeability; Fuel cell; DMFC

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1. Introduction

Direct methanol fuel cells (DMFC) have been considered as promising power source in transportation and portable applications for their high efficiency, high power density, low noise, reduced pollution, and the simplicity of system [1,2]. Proton conductive membranes are the key components of DMFC systems. Up to now, the major used membranes in DMFCs are perfluorosulfonic acid membranes such as Dupont's Nafion. However their undesirable property, high methanol crossover, greatly reduces the cell performance, which limits the actually commercial applications of DMFCs. Therefore, much work has been focused on developing new proton conductive membranes with low methanol crossover and high proton conductivity to replace Nafion [3,4].

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[*] Corresponding author. Tel.: +86 10 62784827.
E-mail addresses: ymshang@mail.tsinghua.edu.cn (Y. Shang), xiexf@mail.tsinghua.edu.cn (X. Xie).

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There are two main stratagems to get proton conductive membranes with low methanol crossover. One is the modification of perfluorosulfonic acid membranes such as blending Nafion with other polymers, compositing Nafion with inorganic nanoparticles or sputtering metallic blocking layers on Nafion surface [5–8]. The second is preparation of non-fluorinated membranes such as sulfonated poly (ether ether ketone), sulfonated polysulfon or polyphosphazene and so on [9–12]. The introduction of sulfonic acid groups into polymer backbone is usually by sulfonation of the base polymers. However, the disadvantage of this method is the sulfonation degree is difficult to control. Another approach to get sulfonated polymers is by the polymerization directly from sulfonated monomers. This approach makes it easily to control the sulfonation degree only by changing the mole ratio of the sulfonated monomers to non-sulfonated ones.

Among the numerous polymers, aromatic polyimides are widely used in many fields due to their excellent thermal stability, high mechanical strength, and superior chemical resistance [13]. Recently, much attention has been paid to sulfonated polyimides (SPI) for their potential use as polymer electrolyte membranes for polymer electrolyte fuel cells (PEFCs) including DMFCs [14–16]. Furthermore, the introduction of –SO_3H group can be achieved by the second sulfonation method. Up to now, the widely reported SPIs were mainly synthesized from commercial sulfonated diamine monomer, 2,2′-benzidinedisulfonic acid (BDSA). However, the hydrolysis stability of these SPIs is relatively poor. Changing the molecular structure can improve the hydrolysis stability of polymers. Mercier et al. reported six-member ring SPIs derived from naphthalenic dianhydride were more stable than five-member ring SPIs from phthalic dianhydride [17,18]. Okamoto et al. studied the relationship between the hydrolysis stability and the structure of sulfonated diamine monomer [19,20], they found that the SPIs synthesized from flexible sulfonated diamine exhibited better stability. However, till now, there are very few sulfonated diamine monomers could be commercially available. Hence, it is very important to synthesis more diamines to prepare SPIs with desirable properties.

In this study, a novel sulfonated aromatic diamine monomer with flexible structure, 1,4-bis(4-amino-2-sulfonic acid-phenoxy)-benzene (DSBAPB) was synthesized and then polymerized with 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA) and a non-sulfonated diamine via high-temperature polymerization method to get a series of sulfonated polyimide (SPI) membranes with different sulfonation degree. The properties of the obtained SPIs were also investigated in this paper.

2. Experimental

2.1. Materials and measurements

5-Amino-2-chlorobenzenesulfonic acid, hydroquinone and benzoic acid (purchased from Beijing Chemical Reagent Co.) were used as received; naphthalene-1,4,5,8-tetracaboxylic dianhydride (NTDA) and 4,4′-oxydianiline (ODA) were purchased from Acros Organics and purified by sublimation before use; dimethyl formamide (DMF), triethylamine (Et_3N), *m*-cresol, dimethylsulfoxide (DMSO) (purchased from Beijing Yili Fine Chem. Co.) were distilled and stored over molecular sieves before used.

^1H NMR spectra were performed on a Varian Unity 200 spectrometer operation at 300 MHz in DMSO-d_6. FT-IR spectra were obtained with a Shimadzu-FTIR-8400 Fourier transform infrared spectrophotometer; Inherent viscosities of the samples were measured using an Ubbelohde viscometer at a concentration of 0.5 g dl^{-1} in DMSO solution at 30 °C. Thermo-gravimetric analysis (TGA) was recorded on a Perkin–Elmer 7 series thermal analysis system at a heating rate of 20 °C/min under N_2 atmosphere. Water uptake was measured by weighing the changes in a sample (5.0×5.0 cm) before and after immersion in water at 30 °C for 24 h.

Proton conductivity was measured using Princeton Potentiostat/Galvanostat model 263A by four-point probe electrochemical impedance spectroscopy technique over the frequency ranging from 100 Hz to 3 MHz according to the method described in Ref. [19].

The methanol permeability of membrane was measured at 30 °C using a liquid permeation cell composed of two compartments containing solution A and B. Where solution A is 20 wt% methanol/water and solution B is deionized water. The tested membrane was immersed in water for hydration before measurements and then vertically placed between the two compartments by a screw clamp. Both the compartments were kept stirred slightly during the permeation experiments. The concentration of methanol in solution B was measured by a gas chromatograph (Shimadzu, GC-14B). The methanol permeability *P* was calculated by the following equation [14]:

$$P = \frac{k \cdot V_B \cdot L}{A \cdot C_A}$$

where k is the slope of the straight-line plot of methanol concentration in solution B versus permeation time, V_B, L, A are the volume of solution B, thickness and effective area of the tested membrane respectively.

2.2. Synthesis of monomer (DSBAPB)

To a completely dried four-necked round-bottom flask equipped with nitrogen inlet, mechanical stirrer, Dean-stark trap and condenser were added 1.10 g (0.01 mol) of hydroquinone, 3.0 g of K_2CO_3, 4.16 g (0.02 mol) of 5-amino-2-chlorobenzenesulfonic acid and 20 ml of DMF. After the mixture was stirred for 1 h, 10 ml toluene was added and the mixture was heated to reflux for 4 h. The toluene was then removed off under reduced pressure. The reaction temperature was raised to 130 °C for 24 h. After cooling to room temperature, the mixture was poured into access of water. The solution was filtered and acidified with HCl solution. The precipitate was collected, washed with water for several times. Then the crude product was neutralized with Et_3N and recrystallized in ethanal/H_2O (1/1) solution to get 4.98 g of DSBAPB–Et_3N salt (72 wt%). FT-IR (KBr, cm^{-1}): 3388, 3339, 3241, 2998, 2689, 1643, 1494, 1231, 1325, 1180, 1080, 1030, 856, 777, 706; ^1H NMR (DMSO-d_6, δ): 7.06 (s, 2H), 6.73 (s, 4H), 6.50 (d, 2H), 6.47 (d, 2H), 4.97 (s, 4H). Elemental analysis: calculated for $C_{30}H_{46}N_4O_8S_2$: C, 55.02, H, 7.08, N, 8.56; Found: C, 54.62%, H, 7.11%, N, 8.61%.

2.3. Synthesis of polymers and membrane formation

To a dried 100 mL three-neck flask were added 0.6682 g (1 mmol) of DSBAPB–Et_3N salt, 0.2004 g (1 mmol) of ODA and 10 mL of *m*-cresol, the mixture was stirred for 0.5 h under N_2 flow until the diamines dissolved, then 0.5361 g (2 mmol) of NTDA and 0.4 g of benzoic acid were added. The mixture was heated to 60 °C for 4 h and 180 °C for 20 h, the obtained viscous solution was cooled to 80 °C and poured into acetone to get fiber-like sulfonated polyimide (SPI-2). Other SPIs with different sulfonated degree were prepared through the above method.

The SPI membranes were prepared by casting the polymer solutions in DMSO on glass substrate which were then heated in a schedule of 80 °C, 10 h; 120 °C, 2 h; 150 °C, 2 h. The obtained SPI membranes were immerged in methanol to remove the residual solvent. Then the membranes were acidified with 10% H_2SO_4 solution for 24 h, washed with distilled water and finally dried at 50 °C under vacuum overnight.

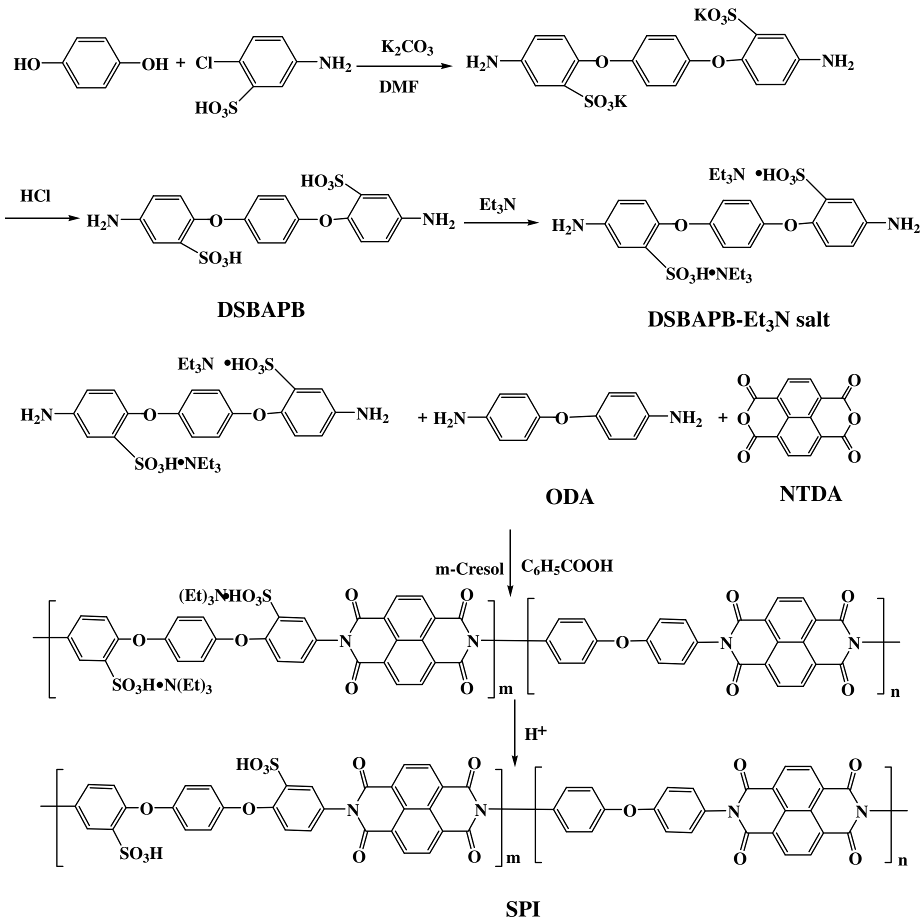
3. Results and discussion

3.1. Monomer synthesis

As shown in Scheme 1, the sulfonated diamine monomer DSBAPB was synthesized from hydroquinone and 5-amino-2-chlorobenzenesulfonic acid in DMF via one step coupling reaction at the present of strong base. Because DSBAPB cannot dissolve in common organic solvents, the purification was carried out in its Et_3N salt form. The chemical structure of the obtained diamine was confirmed by ^1H NMR, ^{13}C NMR, FT-IR and elemental analysis. In the ^1H NMR spectrum of DSBAPB (Fig. 1), the absorption peak at 4.97 ppm is assigned to the protons of amino group. The signals in range of 6.47–7.06 ppm are clearly assigned to the aromatic protons. In the ^{13}C NMR spectrum, the chemical shift signals of aromatic carbon appear in the range of 113.8–153.8 ppm, which agree with the predicted structure of DSBAPB. The FT-IR spectrum (Fig. 2) shows characteristic absorption bands of amino and sulfonic group at around 3388 and 1080 cm^{-1} respectively. Further more, the elemental analysis values are in good agreement with the calculated ones.

3.2. Polymer synthesis

Sulfonated polyimides were synthesized in *m*-cresol via one-step high temperature polycondensation catalyzed by benzoic acid. By changing the mole ratio of the sulfonated diamine monomer (DSBAPB) to the non-sulfonated one (ODA), the sulfonated degree of SPIs can be easily controlled, and there were totally 4 SPIs with different sulfonated degree prepared in this study (Table 1). The inherent viscosities of the resultant polymers (Et_3N salt form) are in the range of 1.25–0.82 dl/g measured at 30 °C in DMSO, which indicates the high molecular weight of the polymers. Because the structure of sulfonated diamine (DSBAPB) is more flexible than ODA, furthermore, its reactive activity is lower than ODA, which may lead to the lower polymerization degree of polymers at high sulfonation degree level. These two factors cause the viscosity decreases with the



Scheme 1. Synthesis of DSBAPB and SPIs.

increase of sulfonation degree. The obtained SPIs were in Et_3N salt form and should be transformed to proton form treated with HCl solution in order to get proton conductivity.

After proton exchange, the resulting SPIs were characterized by FT-IR. As can be seen from the FT-IR spectrum of SPI-2 (Fig. 2), the wide absorption band around 3000–3600 cm^{-1} is assigned to absorbed water in the sample due to the highly hydrophilic sulfonic acid group. The characteristic absorption of imide ring is observed at 1713 cm^{-1} and 1671 cm^{-1} (C=O asymmetric and symmetric stretching). And the sulfonic group absorption (S=O) bond appears at 1246 $cm^{-1}$and 1080 cm^{-1}.

3.3. Thermal stability of SPIs

The thermal stability of the obtained SPIs was investigated by means of TGA and the analysis results are given in Fig. 3. There are three stage of weight loss in the TGA curves. The first weight loss before 200 °C is attributed to the absorbed water elimination. The second weight loss corresponding to the decomposition of sulfonic acid group occurs from 280 °C to 400 °C. The third weight loss due to the degradation of polymer backbone starts at the temperature of higher than 400 °C. The above-described thermal stability is quite enough for DMFCs, which are usually operated at the temperature of lower than 200 °C.

3.4. Proton conductivity and methanol permeability of SPIs

As proton conductive membranes for DMFCs, the crucial properties are proton conductivity and methanol permeability. In this study, the above properties of SPIs were investigated as a function

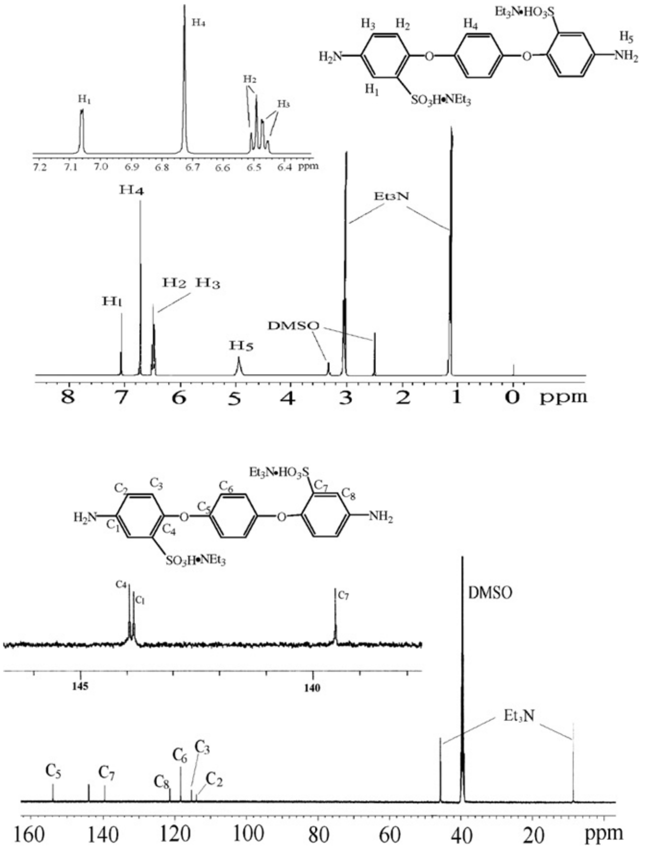


Fig. 1. ^{1}H NMR and ^{13}C NMR spectra of DSBAPB (Et_3N salt form) in DMSO-d_6.

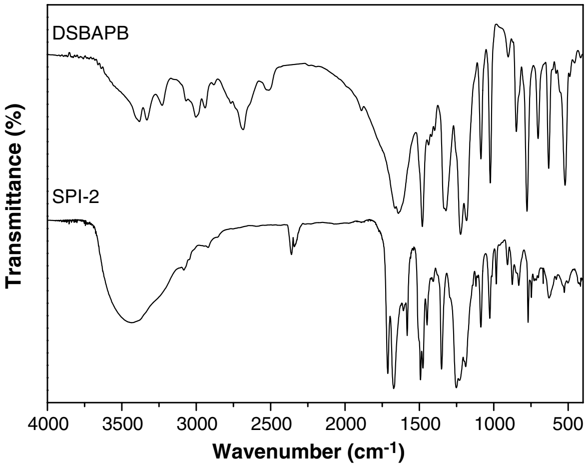


Fig. 2. FT-IR spectra of DSBAPB (Et_3N salt form) and SPI-2.

of the sulfonation degree. Prior to measurements, all the membrane samples were soaked in water over night for hydration. For comparison, these properties of Nafion115 were also determined at the same conditions.

The proton conductivity of SPI membranes at 30 °C and 100%RH is listed in Table 2. At low sulfonation degree of 33%, the membrane has a poor proton conductivity of only 7.9×10^{-3} S cm^{-1}, which is lower than 10% of Nafion. With the increase of sulfonation degree, proton conductivity rises caused by the increase of protonated sites ($-SO_3H$) and the water mediated pathways. At the highest sulfonation degree level (100%), the proton conductivity can reach to 7.2×10^{-2} S cm^{-1}, which is near the value of Nafion.

The methanol permeability of the obtained SPI membranes rise from 2.37×10^{-8}cm^{2} s^{-1} to 2.85×10^{-7}cm^{2} s^{-1} with the increment of sulfonation degree, which is considerably lower than that of Nafion115. This can be explained by the difference of the microstructure of these two polymers. It is well known that in Nafion membranes, the extremely high hydrophobicity of perfluorinated backbone and the extremely high hydrophilicity of sulfonic acid group make it quite easy to form hydrophobic/hydrophilic micro-phase separation.

Table 1
Monomer ratio and inherent viscosity of SPIs

Sample	Monomer ratio (mol) DSBAPB: ODA:NTDA	Sulfonated degree (%)	IEC[a] (mmol/g)	η[b] (dl g^{-1})
SPI-1	1:2:3	33	1.27	1.25
SPI-2	1:1:2	50	1.78	1.12
SPI-3	2:1:3	66	2.21	1.03
SPI-4	1:0:1	100	2.91	0.82

[a] Ion exchange capacity.

[b] Inherent viscosity of SPIs in Et_3N salt form.

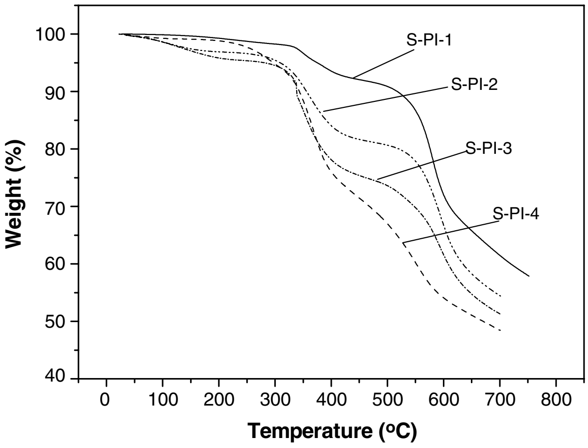


Fig. 3. TGA curves of SPIs (acid form).

Table 2
Proton conductivity, methanol permeability, water uptake and hydrolysis stability of SPIs

Sample	Proton conductivity (S cm^{-1})	Methanol permeability (cm^2 s^{-1})	Water uptake (%)	Hydrolysis stability (h)
SPI-1	7.9×10^{-3}	2.37×10^{-8}	18	180
SPI-2	3.1×10^{-2}	9.12×10^{-8}	38	42
SPI-3	4.9×10^{-2}	1.31×10^{-7}	49	17
SPI-4	7.2×10^{-2}	2.85×10^{-7}	63	2
Nafion	8.4×10^{-2}	1.42×10^{-6}	25	–

The sulfonic acid groups aggregate to form hydrophilic domains. The well-connected hydrophilic domains provide a substance transport channel through which not only proton and water but also some smaller polar molecules such as methanol can penetrate the membrane. The penetration of methanol is called methanol crossover. While in sulfonated polyimides, the backbone is rigid and less hydrophobic, the sulfonic acid group is less acidic and therefore less hydrophilic. So the hydrophobic/hydrophilic domain is less separated, in other word, the substance transport channel is narrower in SPIs, which results in the lower methanol permeability compared with Nafion.

3.5. Water uptake and hydrolysis stability of SPIs

As shown in Table 2, with the increase of sulfonation degree, the water uptake of obtained SPI membranes rises from 16% to 63% caused by the increase of strongly hydrophilic sulfonic acid group in polymer chain.

The hydrolysis stability was measured by immerging the samples in distilled water at 80 °C and judged by the loss of mechanical strength (broken when lightly bent). As can be seen from Table 2, SPI-4 can only maintain its mechanical strength less than 2 h because of the high sulfonation degree. With the decrease of sulfonation degree, the hydrolysis stability is greatly improved by the introduction of non-sulfonated diamine. Compared with BDSA based SPI with the similar sulfonation degree, NTDA–BDSA/ODA (BDSA/ODA = 1/1, mole ratio) lose mechanical strength within 5.5 h at 80 °C [20], whereas DSBAPB based SPI-2, NTDA–DSBAPB/ODA (1/1) in this paper, can maintain mechanical strength for 42 h. Okamoto reported that the SPIs with flexible chain structure could undergo relaxation more easily than rigid ones, which may cause better hydrolysis stability of the former [19,20]. In this study, the sulfonated diamine DSBAPB has two flexible ether bond linkages, so the corresponding polymers are more flexible than the SPIs derived from BDSA. As a result, DSBAPB based SPIs exhibit much better hydrolysis stability than the BDSA based ones. It should be noted that the hydrolysis stability of the obtained SPIs is still relatively poor for the practical applications, but it can be further improved by selecting more favorable non-sulfonated diamine monomers because the hydrolysis stability is not only effected by sulfonated diamines.

4. Conclusions

A series of sulfonated polyimides (SPIs) were synthesized from a novel sulfonated aromatic diamine monomer, 1,4-bis(4-amino-2-sulfonic acid-phenoxy) benzene (DSBAPB) with 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA) and a non-sulfonated diamine (ODA). The proton conductivity of the SPI membranes ranges from 7.9×10^{-3} to $7.2 \times$

10^{-2} S cm^{-1}. The methanol permeability is less than $2.85 \times 10^{-7} cm^2 s^{-1}$, which is considerably lower compared with Nafion. The obtained SPIs exhibit much better hydrolysis stability than the BDSA based ones attributed to their flexible chain structure.

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