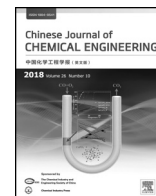




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Article

Poly (ether ether ketone ketone) based imidazolium as anion exchange membranes for alkaline fuel cells☆

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ABSTRACT

An imidazolium functionalized poly (ether ether ketone ketone) (PEEKK-DImOH) anion exchange membrane (AEM) readily soluble in certain low-boiling-point solvents (isopropanol) is prepared. The solubility results are consistent with the results of molecular dynamics simulations. By varying the chloromethylation reaction temperature or concentrated sulfuric acid concentration of PEEKK, the degrees of chloromethylation of PEEKK are changed from 54% to 92%, the corresponding PEEKK-DImOH AEMs with the ion exchange capacities (IECs) of 1.14–1.65 mmol·g⁻¹. The PEEKK-DImOH 92% AEM shows high hydroxide conductivity (31 mS·cm⁻¹), suitable water uptake (94%) and acceptable swelling ratio (39%) at 60 °C. In addition, the PEEKK-DImOH AEMs possess good thermal and alkaline stability. The maximum power density (46.16 mW·cm⁻²) of fuel cell prepared with PEEKK-DImOH 92% AEM as exchange membrane and ionomer is much higher than that with commercial AHA membranes. All the above results indicate that the PEEKK used in this study is a promising AEM matrix material for alkaline fuel cells.

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1. Introduction

Since the operation environment of alkaline anion exchange membrane fuel cell (AAEMFC) is basic, it has some advantages compared to the proton exchange membrane fuel cell [1–4]: electrode reaction kinetics is high and thus dropping the over potential, so the AAEMFC can use non-noble metals act as catalysts [5, 6] (e.g. nickel [7], silver [8], or cobalt [9]), in addition, the stability of the catalyst is improved. The above reasons make the AAEMFC receive more and more attention [10–13].

The performance of AAEMFC depends to a large extent on the anion exchange membrane (AEM). This is because AEM plays a role of conducting hydroxide ions and separating fuel/oxidant in the fuel cell [14]. AEM needs to have high hydroxide conductivity, excellent hydrolysis resistance to meet the increasingly demanding application

requirements of AAEMFC; moreover, to ensure long-term stable operation of the AAEMFC, AEM also needs to have good alkaline stability, thermal stability and excellent mechanical behavior [6]. In addition, with the purpose of establishing an effective triple-phase-boundary for high electrode performance, the AEM material also requires to have good solubility in the specific low-boiling-point solvent so that it can be dispersed as the ionomer in the catalyst layer. Simultaneously, the material to prepare AEM must not be soluble in water, methanol or ethanol to ensure the membrane's barrier effect on the fuel. Therefore, developing new AEMs with high performance becomes one of the most challenging works [6, 15, 16].

The chloromethylation-functionalization route has been indicated to be a simple and efficient way to synthesize AEM materials [17]. The chloromethyl groups are introduced onto the benzene ring of the polymer by a chloromethylation reaction. The chloromethylated polymer is reacted with tertiary amine, hydrazine, 1-alkylimidazole or tertiary phosphine to give a functionalized polymer [1, 18–21]. Hydroxide conducting functional groups has great effects on the AEM properties of solubility, conductivity, and stability [17, 22]. Due to the low volatility, excellent thermal stability and good electrochemical performance of imidazoles [23], we have conducted many studies on imidazole-functionalized anion exchange membranes in our previous work [24–26]. For example, imidazole-functionalized poly

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(ether ether ketone) anion exchange membranes have high hydroxide conductivities, good dimensional stabilities and excellent mechanical properties. The polymer matrix also has important effects on the properties of conductivity, dimensional stability, and thermal stability. Some aromatic polymers were chosen as substrates to prepare imidazole-functionalized AEMs by chloromethylation route, including polyfluorene [16, 27], poly-ether-ether-ketone [1, 26], polysulfone [15, 28–31], and fluorinated poly (arylether oxadiazole)s [27].

In this study, PEEKK is developed as anion exchange membrane (AEM), aiming to explore novel AEM materials with comprehensively excellent properties. Chemical composition of PEEKK [32–34] is shown in Fig. 1.

Because of the good thermal stability, excellent resistance to hydrolysis and other outstanding properties of polyether ketones they are often selected as the main chain material of anion exchange membranes. In our previous work, a series of PEEK based AEMs with high hydroxide conductivity, proper degree of swelling ratio, and good chemical stability were prepared [1, 25, 35], but these membranes are not easily soluble in low-boiling-point solvents or can only be dissolved in acetone or tetrahydrofuran aqueous solution with high chemical toxicity [26]. Furthermore, according to Hansen solubility parameter (HSP) theory [36], the closer the solubility parameter of the material is, the better the compatibility is, namely the so-called “like dissolves like”. Our previous work has found that PEEK used as a membrane skeleton material is insoluble in the common low-boiling solvent n-propanol, isopropanol [26]. The result of molecular dynamics simulation found that the solubility parameter of PEEK-DImCl was $21.1 \text{ MPa}^{1/2}$, much smaller than n-propanol $24.5 \text{ MPa}^{1/2}$, isopropanol $23.5 \text{ MPa}^{1/2}$. The physical meaning of the solubility parameter δ was the open square of the cohesive energy, which is mainly composed of three parts: $\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2$, where δ_D is the open square of the dispersion cohesive energy, δ_P is the square of the polar cohesive energy, δ_H is the open square of hydrogen bond [36, 37]. Compared with PEEK, the increased carbonyl group in the PEEKK structure is an electron-withdrawing group. When the carbonyl group is attached to the benzene ring, it forms a π - π conjugate with the ring, which increases the δ_P value. Based on the above analysis, it is inferred that when using PEEKK to synthesis the AEM, the increase of the δ_P value can increase the solubility parameter to make the result closer to that of n-propanol and isopropanol, so as to obtain a membrane material with higher solubility, thereby constructing an effective triple-phase boundary with high electrode performance. The PEEKK has better thermal stability due to the fact that the ratio of ketone and ether linkages in the polymer chain is increased as compared to the polyetheretherketone (PEEK) [33, 38–41]. Hence, PEEKK is a promising AEM matrix.

Insofar as we know, there is currently no report on the preparation of AEM using PEEKK as a matrix. In this work, sulfuric acid was used as solvent, and catalyst chloromethylated PEEKK (CMPEKK) was synthesized by the chloromethylation of PEEKK for the first time. The imidazolium functionalized PEEKK (PEKK-DImCl) was then obtained from the reaction of 1, 2-dimethylimidazole with CMPEKK, and an imidazolium-functionalized PEEKK anion exchange (PEKK-DImOH) membrane was further synthesized by solution casting. To examine the performance of PEEKK-DImOH AEM, the IEC, hydroxide conductivity, water uptake, swelling ratio, thermal and alkaline stability, solubility, as well as the performance of AAEMFC prepared from PEEKK-DImOH AEM were tested and characterized. Molecular dynamics simulations were also used to verify solubility results.

2. Experimental

2.1. Materials

PEKK power was obtained from Changchun Jida Plastics Engineering Research Co. Ltd. According to Ref. [1, 42] chloromethyl octyl ether (CMOE) was prepared. Sulfuric acid, ethanol, 1-methyl-2-pyrrolidone (NMP), 1, 2-dimethylimidazole and dimethyl sulfoxide- d_6 (DMSO- d_6) were commercially obtained. To prevent CO_2 from affecting the experimental results, deionized water was boiled for 15 min before being used.

2.2. Preparation of CMPEKK

The chloromethylated PEEKK (CMPEKK) was prepared by reacting PEEKK with CMOE at different temperatures with different volumes of concentrated sulfuric acid as the solvent. After addition of CMOE (5 ml), the reaction was maintained in a cold trap set at different temperatures (-10°C , -5°C , 0°C , 5°C) for 2 h. The white fibrous product, CMPEKK, was obtained by pouring the reacted mixture into ice water after the reaction, then rinsed with boiled deionized water and dry at room temperature. By dissolving in NMP, remove impurities completely, and then use ethanol for precipitation and cleaning. Finally, 6 h of air drying at 60°C would provide further purification of CMPEKK. Fig. 1 shows the chemical structure and the synthesis route of CMPEKK.

2.3. ^1H NMR test

The chloromethylation of PEEKK was affirmed by ^1H NMR spectroscopy, which was also adopted to measure the degree of chloromethylation (DC). Varian Unity Inova 400 spectrometer at a resonance frequency of 399.73 MHz was used to record the ^1H NMR spectra of CMPEKK. Using tetramethylsilane as the internal standard, CMPEKK was dissolved into DMSO- d_6 to prepare the solution with a mass fraction of about 2%.

2.4. Preparation of PEEKK-DImOH AEMs

An appropriate amount of 1, 2-dimethylimidazole was added to the PEEKK/NMP solution and stirred at room temperature for 4 h to synthesize the imidazolium chloride-functionalized PEEKK (PEKK-DImCl) by quaternization. The reacted solution was dropped into anhydrous ethanol to obtain white fibers, which were washed multiple times with ethanol and deionized water to get pure PEEKK-DImCl. In this study, AEM was prepared by solution casting method. The appropriate amount of PEEKK-DImCl was dissolved in NMP to prepare casting solution. An amount of PEEKK-DImCl/NMP solution was poured onto the grooved glass plate. After the casting solution was dried in the oven at 60°C for 3 d, a PEEKK-DImCl membrane was obtained. Exchange of Cl^- with OH^- was performed by immersing the PEEKK-DImCl membrane in the $1 \text{ mol} \cdot \text{L}^{-1}$ KOH solution for 48 h. After completion of the exchange, the membrane was treated with deionized water for 2 d to finally attain pure PEEKK-DImOH AEM. Fig. 2 shows the synthetic routes for PEEKK-DImCl and PEEKK-DImOH.

By adjusting the ratio of concentrated sulfuric acid and PEEK in the chloromethylation reaction, a chloromethylation level of 98% CMPEKK was obtained, which was quaternized with a suitable amount

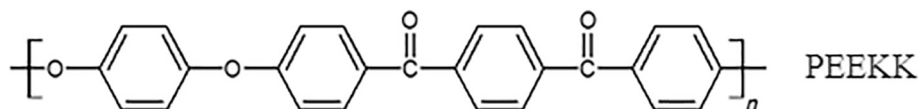


Fig. 1. Chemical structure of PEEKK.

and then the mass and size of the dry membrane were measured after vacuum drying at 60 °C for 12 h. Water uptake and swelling ratio were calculated as follows:

$$\text{Water uptake} = \frac{W_w - W_d}{W_d} \times 100\% \quad (3)$$

$$\text{Swelling ratio} = \frac{l_w - l_d}{l_d} \times 100\% \quad (4)$$

where W_d and W_w represent the mass of dry and wet membrane samples, respectively, l_d [$l_d = (l_{d1} \cdot l_{d2})^{1/2}$] and l_w [$l_w = (l_{w1} \cdot l_{w2})^{1/2}$] are the average lengths of dry and wet membrane sample, respectively, in which, l_{d1} , l_{d2} and l_{w1} , l_{w2} represent the lengths of dry and wet membrane sample, respectively.

2.8. Thermogravimetric analysis (TGA)

Thermodynamic property of the PEEKK-DImOH AEM was processed on TGA analyzer (Mettler Toledo TGA/SDTA851e). The test temperature range is 100–800 °C at 10 °C·min^{−1} with the protection of nitrogen. Samples were vacuum dried completely prior to testing to eliminate the effect of moisture on the experimental results.

2.9. Alkaline stability

In this study, the alkaline stability of PEEKK-DImOH AEMs was investigated by comparing the changes of hydroxide conductivity and IEC after immersing PEEKK-DImOH 92% AEM in 1 mol·L^{−1} KOH solution at 60 °C for a period of time. To ensure the accuracy of the results, the AEMs were washed to neutrality before each test.

2.10. Alkaline fuel cell performance test

The catalyst ink was prepared by mixing the Pt/C (70 wt%, Johnson Matthey Co.), isopropanol and ionomer solution (1 wt%, PEEKK-DImOH 92%) together. The mixture after 2 h of ultrasonic

dispersion was evenly sprayed on both surface PEEKK-DImOH 92% membrane (thickness: (35 ± 5) μm). The prepared CCM was sandwiched between two carbon cloths (ETEK) to form a membrane electrode assembly (MEA) without hot pressing. The Pt loading on the MEA with an effective area of 5 cm² was 0.5 mg·cm^{−2}. The humidity, back pressure, and temperature of the fuel cell performance test were 100%, 0.1 MPa, 60 °C respectively, and the hydrogen and oxygen carrier gas flow rate were 500 cm³·min^{−1}. The test was conducted using the Associates Co. Scribner Associates 850e.

2.11. Molecular dynamics simulation

Molecular dynamics (MD) simulations of the PEEKK-DImCl and PEEK-DImCl were carried out to investigate the solubility. 10 repeat units and 5 chains were used to construct the polymer. By annealing the atomic structure, the amorphous cell is completely balanced. The simulated density of PEEK-DImCl is 0.89 g·cm^{−3} and PEEKK-DImCl is 0.95 g·cm^{−3}, consistent with the experimental phenomena, in anhydrous ethanol (0.79 g·cm^{−3}) in the bottom, in deionized water (1 g·cm^{−3}) suspension. The solubility parameter of each system was determined.

2.12. Mechanical properties

The mechanical strength of the wet membranes were measured by a SANS mechanical analyzer at room temperature and the tensile speed was 5 mm·min^{−1}. The width of the sample was ~50 mm and the length was ~300 mm. The tensile strength and elongation at break were recorded during the test.

3. Results and Discussion

3.1. Characterization of PEEKK-DImCl

Fig. 3 shows the ¹H NMR spectra of PEEKK, CMPEKK, and PEEKK-DImCl. The success of chloromethylation of PEEKK was determined

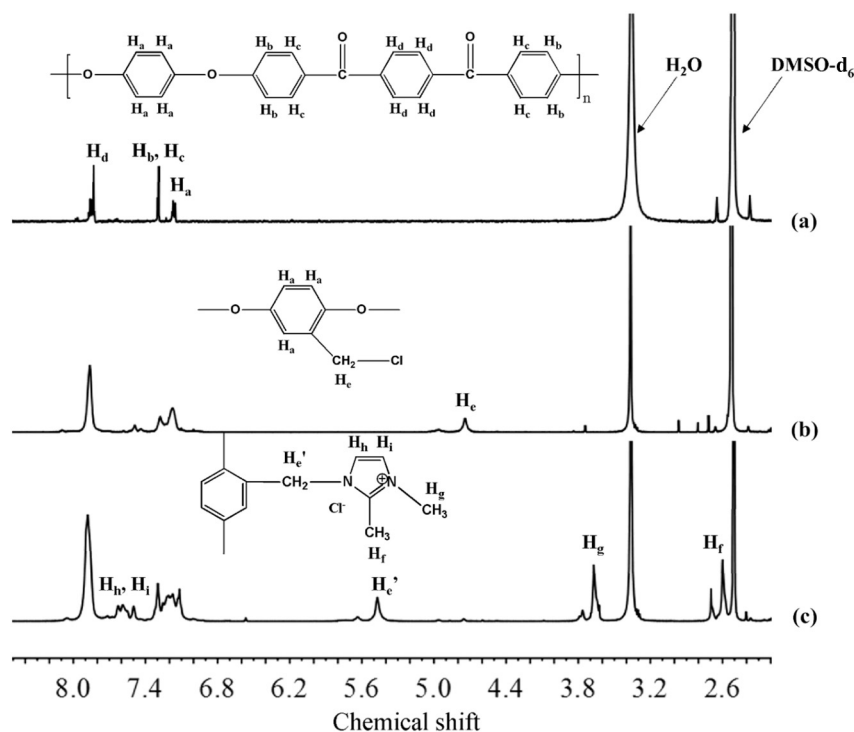


Fig. 3. ¹H NMR spectra of (a) PEEKK, (b) CMPEKK, (c) PEEKK-DImCl.

by the new signal at $4.78 \mu\text{L} \cdot \text{L}^{-1}$ in ^1H NMR spectrum of CMPEEKK (H_e of $-\text{CH}_2-$).

Electrophilic substituted chloromethylation reactions occurred on H_a , which with the highest electron density in PEEKK. And H_d with the lowest electron density is not conducive to chloromethylation. The formula: $\text{DC} = 4A(\text{H}_e)/A(\text{H}_d)$, was used to calculate the CMPEEKK's DC, $A(\text{H}_e)$ and $A(\text{H}_d)$ stand for the integral area of the H_e and H_d peak, respectively.

Significant new characteristic peaks appeared due to quaternization of CMPEEKK and 1,2-dimethylimidazole: multiple-peak at $7.58 \mu\text{L} \cdot \text{L}^{-1}$ (H_h, H_i) and single peak at $3.64 (\text{H}_g)$ and $2.59 \mu\text{L} \cdot \text{L}^{-1}$ (H_f) result from the protons at C4 and C5 position in the imidazole ring and the methyl protons attached to the imidazole ring, respectively. In addition, the methylene signal (H_e) in CMPEEKK is completely shifted to $5.43 (\text{H}_e')$. The successful synthesis of PEEKK-DImCl was confirmed by the results.

The degree of chloromethylation (DC) of the chloromethylated polymer determines the IEC of AEM so it is an important parameter. Fig. 4 shows that the DC of CMPEEKK increases with low concentration of sulfuric acid due to good reaction condition (appropriate temperature and selected solvent) of PEEKK and CMOE to H_2SO_4 which was used as solvent and catalyst, because the PEEKK concentration is higher with lower H_2SO_4 , so that DC is higher, indicating an excellent DC controllability and preparing PEEKK-ImOH AEMs with low cost due to utilized low concentration of sulfuric acid to get high hydroxide conductivity with high DC. Also, the DC of CMPEEKKs increases with the increase of reaction temperature as shown in Fig. 4. This was because the chloromethylation reaction is an endothermic reaction, and high temperatures favor the reaction. The results in Fig. 4 show that when the reaction temperature is 5°C , the DC of CMPEEKK has reached 108%, the obtained CMPEEKK is white powder, and the yield is reduced and the product after reacting with 1,2-dimethylimidazole is not easy to form the membrane. In addition, although the CMPEEKK with high degree of chloromethylation can obtain the AEM with a higher IEC, the swelling ratio of the AEM may also be too high so that the mechanical strength of the AEM is decreased, which is not favorable for assembling the MEA. In summary of the above discussion, we have controlled the reaction at low temperatures to obtain CMPEEKK with a suitable DC in this study. From these, it can be seen that by changing the amount of PEEKK and the chloromethylation reaction temperature, DC can be easily controlled.

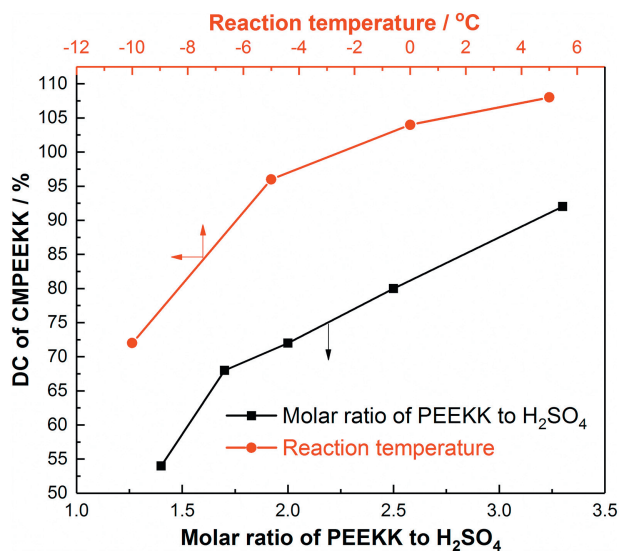


Fig. 4. The effect of sulfuric acid concentration and reaction temperature on the DC of CMPEEKKs.

Through the above discussion, it can be seen that CMPEEKK with high chloromethylation can be obtained by low sulfuric acid concentration and suitable reaction temperature. Therefore, the preparation route of CMPEEKK for preparing anion exchange membranes is simple, the operating conditions are mild and easy to control, which is convenient for large-scale production and thus provides material support for the assembly of AAEMFCs.

3.2. IEC and hydroxide conductivity

Table 1 lists the IEC (IEC_m : measured IEC, IEC_t : theoretical IEC) of PEEKK-DImOH AEMs. As DCs increase from 54% to 92%, IEC_m s of PEEKK-DImOH AEMs rise from 1.14 to $1.65 \text{ mmol} \cdot \text{g}^{-1}$. At the same time, since all of the IEC_m s are very close to the IEC_t s, the thorough conversion of chloromethylated groups to imidazolium groups can be reconfirmed from another aspect. Fig. 5 shows the hydroxide conductivities of PEEKK-DImOH AEMs with different IECs. It can be seen that, the PEEKK-DImOH AEM's hydroxide conductivity increases from $3 \text{ mS} \cdot \text{cm}^{-1}$ to $19 \text{ mS} \cdot \text{cm}^{-1}$ as the IEC grows from $1.14 \text{ mmol} \cdot \text{g}^{-1}$ to $1.65 \text{ mmol} \cdot \text{g}^{-1}$.

Table 1
IEC of PEEKK-DImOH AEMs prepared by different DCs CMPEEKKs

AEMs	DC/%	$\text{IEC}_t/\text{mmol} \cdot \text{g}^{-1}$	$\text{IEC}_m/\text{mmol} \cdot \text{g}^{-1}$
PEKK-DImOH 54%	54	1.17	1.14
PEKK-DImOH 68%	68	1.42	1.15
PEKK-DImOH 72%	72	1.49	1.46
PEKK-DImOH 80%	80	1.62	1.62
PEKK-DImOH 92%	92	1.81	1.65

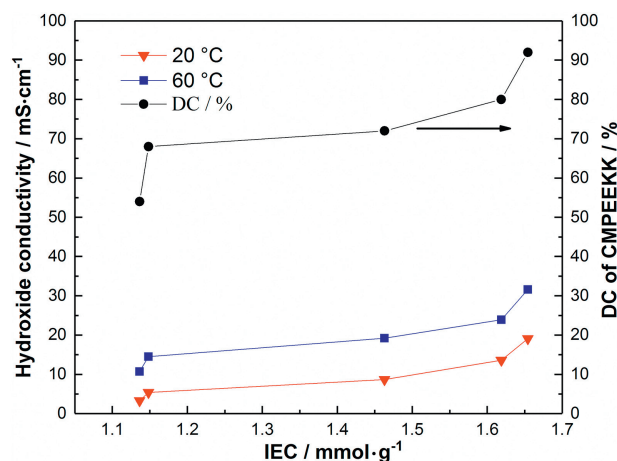


Fig. 5. Hydroxide conductivity (20°C and 60°C) of PEEKK-DImOH AEMs against IECs.

From the results of Fig. 6 we can see that hydroxide conductivity increases as temperature rises. The highest hydroxide conductivity ($31 \text{ mS} \cdot \text{cm}^{-1}$) was obtained from PEEKK-DImOH 92% AEM at 60°C . $10.9 \text{ kJ} \cdot \text{mol}^{-1}$ and $23.5 \text{ kJ} \cdot \text{mol}^{-1}$ for PEEKK-DImOH 92% and PEEKK-DImOH 54% membranes were the apparent activation energies (ΔE_a s) calculated by Arrhenius relationship formula. These results indicate that the hydroxide conductivity of AEMs is closely related to temperature, the lower the apparent activation energy, the smaller the ion transfer resistance, and the ion channels were more interconnected, so the PEEKK-DImOH 92% AEM had the highest conductivity.

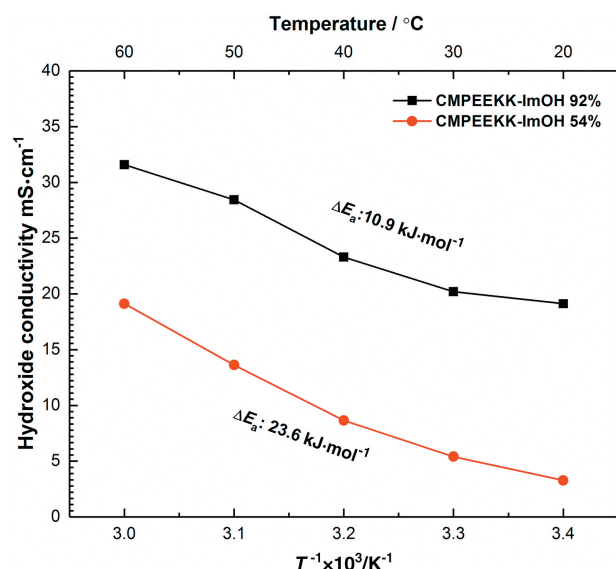


Fig. 6. Hydroxide conductivity of PEEKK-DImOH AEMs at different temperatures.

3.3. Water uptake and swelling ratio

Fig. 7 shows the water uptakes of PEEKK-DImOH AEMs. At 20 °C the water uptakes of PEEKK-DImOH AEMs arise from 48% to 135% with DC increasing from 54% to 80%. For PEEKK-DImOH 92% AEMs, the water uptake increases from 244% (20 °C) to 278% (60 °C). Higher IEC induces the hydrophilic domain easier to be connected, thus increasing the hydrophilic domains of PEEKK-DImOH AEMs, eventually leading to more water uptake, especially at elevated temperatures [1, 23].

The swelling ratio of PEEKK-DImOH AEMs at different temperatures is illustrated in Fig. 8. Swelling ratio also increases as temperature and IEC increase. The swelling ratio of PEEKK-DImOH AEMs at 20 °C increases from 20% to 39% with DC increasing from 54% to 80%. For DC of 92%, the swelling ratio of PEEKK-DImOH AEM rises from 53% to 79% with temperature increasing from 20 °C to 60 °C. In the meantime, the water uptake of the PEEKK-DImOH AEM with a DC of 54%–72% is 48%–94% and the swelling ratio is 20%–39%, measured at 60 °C, this result is acceptable.

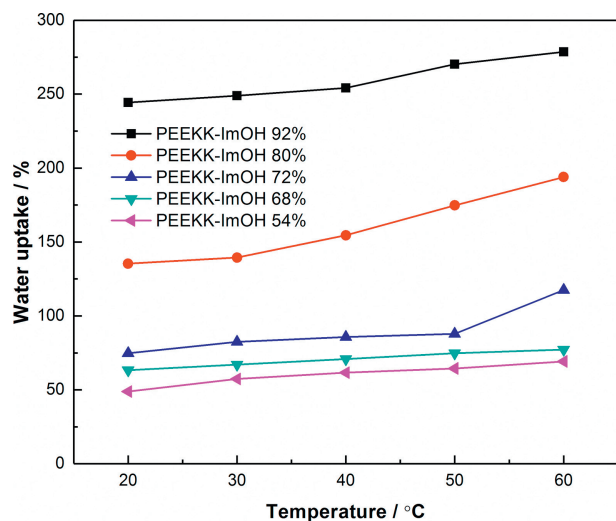


Fig. 7. Water uptake of PEEKK-DImOH AEMs at different temperatures.

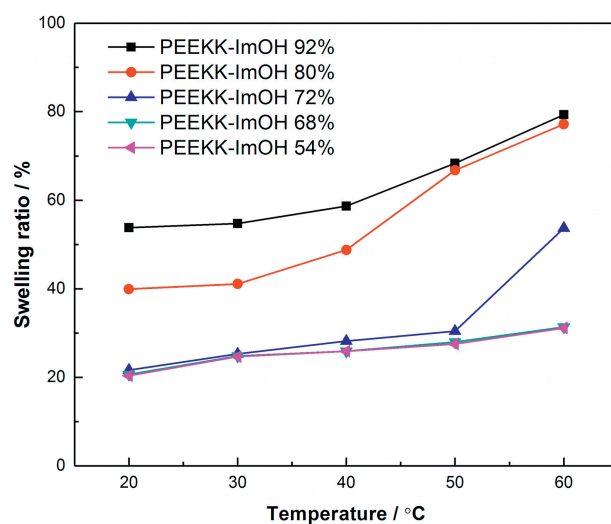


Fig. 8. Swelling ratio of PEEKK-DImOH AEMs at the function of temperature.

3.4. Thermal stability

The thermodynamic property of the PEEKK-DImOH 92% AEM was investigated by the changing of TGA and DTG (Fig. 9). In addition to the mass loss due to evaporation of water below 191 °C, the PEEKK-DImOH 92% AEM has three major mass loss steps. OH[−] attacks the spacer between the imidazole and PEEKK by SN₂ nucleophilic substitution, leading to the removal of imidazolium. This result caused the first step of mass loss (the onset decomposition temperature, T_{OD1} : 191 °C, the fastest decomposition temperature, T_{FD1} : 204 °C) [23, 31]. Decompose of hydroxymethyl or methyl groups results in the second step of mass loss (T_{FD2} : 251 °C). The degradation of polymer caused the third step of weight loss (T_{FD3} : 546 °C) [31].

As listed in Table 2, the onset decomposition temperature, T_{OD} : 191 °C is much higher than 148 °C of (QAPEEKOH) [1] and 180 °C of QAPEEKOH [42]. The results show that the thermal stability of the PEEKK-DImOH AEM is high enough for application in AAEMFCs.

3.5. Alkaline stability

Since the AEM works in the alkaline environment, the alkaline stability has an effect on ensuring stable operation of the fuel cell.

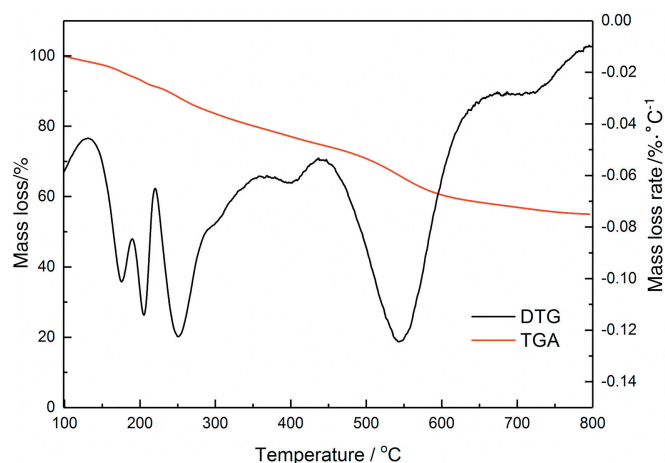


Fig. 9. TGA and DTG curves of PEEKK-DImOH 92% AEM.

Table 2

Thermal characteristic temperatures (T_{OD} and T_{FD}) of PEEKK-DImOH 92% AEM, QAPEEKOH, QAPEEKOH and QAPEK-OH

Sample	$T_{OD}/^{\circ}\text{C}$	$T_{FD1}/^{\circ}\text{C}$	$T_{FD2}/^{\circ}\text{C}$	$T_{FD3}/^{\circ}\text{C}$	Ref.
PEKK-DImOH92%	191	204	251	546	This work
QAPEEKOH	148	172	320	454	[1]
QAPEK-OH	180	200	320	–	[43]

From the results showed in Fig. 10, after 8 d the IECs and hydroxide conductivities of PEEKK-DImOH 92% AEMs at 60 °C remain 75%, suggesting that PEEKK-DImOH AEM has a good alkaline stability.

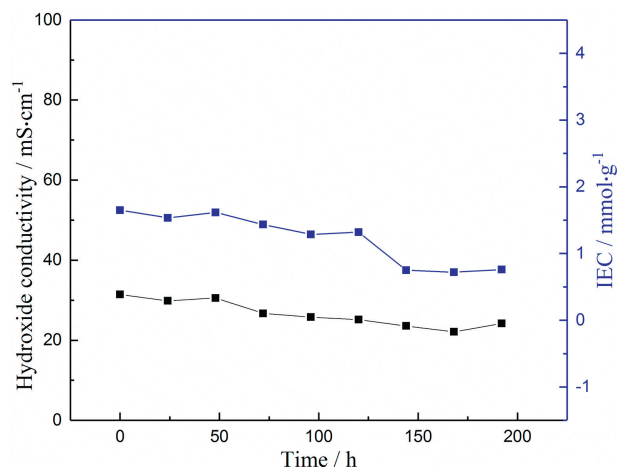


Fig. 10. The hydroxide conductivity and IEC of PEEKK-DImOH 92% AEM after immersed in 1 mol·L⁻¹ KOH at different times.

3.6. Solubility and molecular dynamics simulation

Table 3 shows the solubility of PEEK-DImCl 98% (prepared by the quaternization reaction between CMPEEK and 1, 2-dimethylimidazole)

Table 3

Solubility of PEEK-DImCl and PEEKK-DImCl in low-boiling-point solvents

Sample	Water	Methanol	Ethanol	N-propanol	Isopropanol	Acetone
PEEK-DImCl 98%	–	–	–	–	–	–
PEKK-DImCl 92%	–	–	–	+	+	–

Note: +: Soluble; –: Insoluble.

and PEEKK-DImCl 92% in six typical low-boiling-point solvents. It can be seen from the table that PEEKK-DImCl is insoluble in methanol and ethanol which shows good alcohol resistance. Together, as expected, PEEKK-DImCl is slightly soluble in the low-boiling-point solvent *n*-propanol, which is soluble in isopropanol, while PEEK-DImCl cannot dissolve all the solvent tested.

To investigate the mechanism of solubility enhancement, molecular dynamics simulations were used to calculate the solubility parameters of PEEK-DImCl and PEEKK-DImCl. The solubility parameter refers to the open square of the cohesive energy. According to the Hansen solubility parameter theory [36], the polymer is easily soluble and similar to its own solubility parameter that is “like dissolves like” principle. As shown in Fig. 11, in order to equilibrate the amorphous cells, the molecular dynamics simulation was used to optimize the computational object in the compass force field. The solubility parameters of PEEK-DImCl and PEEKK-DImCl were then calculated by universal force field. The obtained results and the solubility parameters of the six common low-boiling-point solvents are shown in Table 4. Compared with the solubility parameter of PEEK-DImCl (22.4 MPa^{1/2}), the solubility parameter of PEEKK-DImCl increases to 23.75 MPa^{1/2} due to the increase of δ_p value, much closer to that of *n*-propanol (24.5 MPa^{1/2}) and isopropanol (23.5 MPa^{1/2}), indicating better solubility of PEEK-DImCl in low-boiling-point solvent, which is consistent with the previous analysis. Hence, when assembling the fuel cell, PEEKK-DImCl can be dissolved as ionomer in isopropyl alcohol to form a catalytic layer to construct an effective three-phase interface. On the other hand, according to the calculation result, the solubility parameter of PEEK-DImCl is different from the solubility parameter of several solvents, so its solubility is poor, which is not conducive to constructing an effective three-phase interface as ionomer. The above results prove that PEEKK-DImCl is easier than PEEK-DImCl when it is used to construct an effective three-phase interface for the assembly of fuel cells, which is beneficial for improving the performance of the fuel cell.

Table 4

Solubility parameters of solvent, PEEK-DImCl, PEEKK-DImCl

Chemicals	Solubility parameters /MPa ^{1/2}			
	δ_d	δ_p	δ_h	δ_t
Water	15.5	16.0	42.3	47.8
Methanol	15.1	12.3	22.3	29.6
Ethanol	15.8	8.8	19.4	26.5
N-propanol	16.0	6.8	17.4	24.5
Isopropanol	15.8	6.1	16.4	23.5
Acetone	15.5	10.4	7.0	20.0
PEEK-DImCl	–	–	–	22.40
PEKK-DImCl	–	–	–	23.75

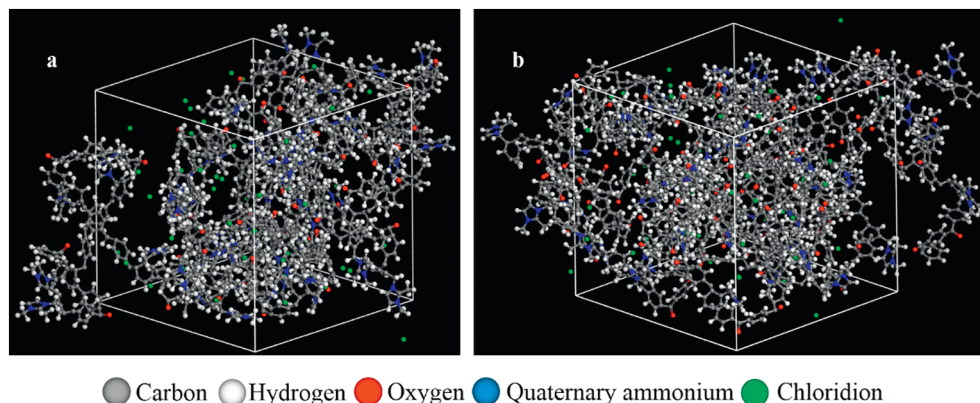


Fig. 11. Photos of PEEK-DImCl (a) and PEEKK-DImCl (b) from the molecular dynamic simulations.

3.7. Alkaline fuel cell performance

Pt/C (70%) was dispersed in 1 wt% PEEKK-DImCl 92% solution, the mass ratio of Pt/C to PEEKK-DImCl 92% is 1:4. It was assembled as membrane electrode assembly (MEA) for AAEMFC after both surfaces of the PEEKK-DImOH 92% AEM with a thickness of (40 ± 5) μm are sprayed with the aforementioned catalyst solution. Fig. 12 shows the performance of MEA based on PEEKK-DImOH 92% AEM and the commercial AHA membrane [44]. The initial fuel cell performance was quite low compared with recently reported AEMs [45–48], the reason may be attributed to the absence optimization of MEA assembly process and low hydroxide conductivity of PEEKK-DImOH AEM, respectively. However, the open circuit voltage (OCV) of the PEEKK-DImOH 92% AEM was 0.95 V, demonstrating the membrane meets the requirements of the fuel cell that separates hydrogen and oxygen [49]. The single cell prepared by PEEKK-DImOH 92% AEM possessing the maximum power density was $46.16 \text{ mW} \cdot \text{cm}^{-2}$, much higher than that of AHA membrane ($2.45 \text{ mW} \cdot \text{cm}^{-2}$), illustrating that PEEKK, as anion exchange membrane main chain, can satisfy the demand of AAEMFC application. The performance of AAEMFC can be improved by optimized MEA assembly process or using PEEKK anion exchange membrane with other quaternary ammonium group to improve hydroxide conductivity.

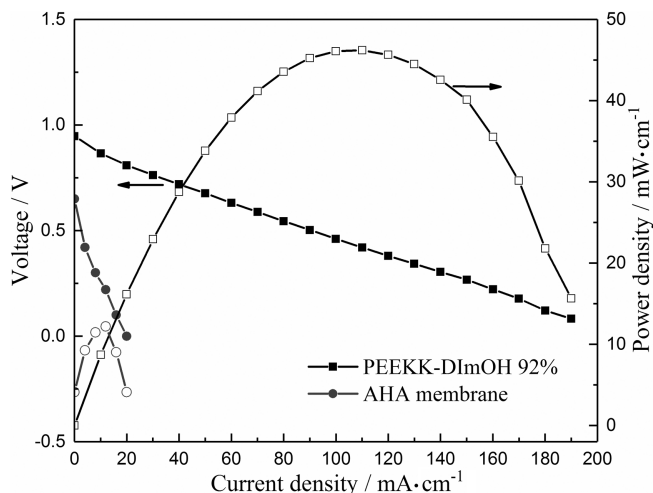


Fig. 12. Single cell performance of PEEKK-DImOH 92% AEM at 60 °C and AHA membranes at 60 °C [49].

3.8. Mechanical properties

As the AEM is squeezed by external force during assembly of the MEA and undergoes tension and pressure during the operation of the fuel cell, which may cause cracks or damage to the membrane, this would cause short circuit of the fuel cell due to fuel permeation and affect the service life of the fuel cell. Therefore, the AEM is required to have good mechanical properties. Table 5 shows the results of mechanical properties of PEEKK-DImOH AEMs with different DCs. Since the introduction of

functional groups will cause the mechanical strength of the AEMs to be impaired, the mechanical strength of the AEM decreases as the DC increases, but the lowest mechanical strength is 22 MPa, which is higher than that of the Nafion 212 [50], and the membrane remains intact during assembly of the fuel cell. The fuel cell is able to operate normally without fuel permeation, indicating that the PEEKK-DImOH AEMs in this study has good mechanical properties.

4. Conclusions

Chloromethylated poly (ether ether ketone ketone) (CMPEKK) was synthesized, the changing of the reaction temperature or the molar ratio of PEEKK to sulfuric acid could easily control the degree of chloromethylation (DC: 54%–92%). Then imidazolium chloride-functionalized PEEKK (PEKK-DImCl) with IECs $1.14 \text{ mmol} \cdot \text{g}^{-1}$ to $1.65 \text{ mmol} \cdot \text{g}^{-1}$ were synthesized by the quaternization reaction of CMPEKKs and 1, 2-dimethylimidazole. PEEKK-DImOH 92% AEM exhibits high hydroxide conductivities $19 \text{ mS} \cdot \text{cm}^{-1}$ (20 °C). PEEKK-DImOH AEMs with DC of 54%–72% have moderate water uptake of 48%–94% and appropriate swelling ratio of 20%–39% (60 °C). In addition, PEEKK-DImOH AEM shows a good alkaline stability. Molecular dynamics simulation reveals that better solubility of PEEKK-DImCl in low-boiling-point solvent results from increase of solubility parameter. The maximum power density ($46.16 \text{ mW} \cdot \text{cm}^{-2}$) of the fuel cell prepared from PEEKK-DImOH 92% membrane was much higher than that from the commercial AHA membrane. All these suggest that PEEKK-DImOH AEM is promising for applications in AAEMFCs.

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Table 5

Mechanical properties of PEEKK-DImOH AEMs (wet state, room temperature)

AEMs	DC/%	IEC _m /mmol · g ⁻¹	Tensile strength/Mpa	Elongation-to-break/%
PEKK-DImOH 54%	54	1.14	42	85
PEKK-DImOH 68%	68	1.15	39	72
PEKK-DImOH 72%	72	1.46	30	61
PEKK-DImOH 80%	80	1.62	25	43
PEKK-DImOH 92%	92	1.65	22	37

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