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Preparation and characterization of side-chain poly(aryl ether ketone) anion exchange membranes by superacid-catalyzed reaction

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ABSTRACT

The poly(aryl ether ketone) with spatial cardo structure is prepared from 4,4'-bis(phenoxy)benzophenone and 1-(4-bromobutyl)indoline-2,3-dione through a facile polyhydroxyalkylation reaction catalyzed by superacid. The number average molecular weight of the resultant polymer is achieved as high as 105.6 kg mmol⁻¹. Three anion exchange membranes were prepared by reacting the polymer with trimethylamine, N-methyl-piperidine, and N, N,N',N','Pentaethylguanidine, respectively. Among the prepared membranes, N-methyl-piperidine based anion exchange membrane exhibited the highest OH⁻ conductivity of 99.8 mS cm⁻¹ at corresponding IEC of 1.54 meq g⁻¹. In addition, the prepared membranes also exhibit excellent mechanical properties, in which the tensile strength and elongation at break can reach up to 50 MPa and 35%, respectively. Moreover, the anion exchange membranes exhibited good alkaline stability. When they were treated with 1 M KOH at 60 °C for 600 h, their conductivity decreased by less than 5%.

1. Introduction

Anion exchange membrane fuel cell (AEMFC) is an environmentally benign electrochemical device, which offers several advantages such as non-noble metal based electro-catalysts, insignificant fuel cross-over, controlled catalyst corrosion, and fast kinetics of oxygen reduction at the cathode [1–3]. In AEMFCs, anion exchange membranes (AEMs) are used, which simultaneously act as a separator between opposite electrodes and as a solid-state polymer electrolyte to transport anions from cathode to anode [4]. Since the AEMs are recognized as a key component, the development of high-performance and stable AEMs is a hot area of fuel cell technology. An ideal AEM possesses high alkaline stability, good dimensional/thermal stability, high mechanical properties, and excellent conductivity. All of these characteristics mainly originate from polymer backbone architecture and stability of cationic groups attached to the polymer electrolyte [5].

AEMs derived from aromatic polymers such as poly(ether ketone)s

(PEKs) [6-8], poly(phenylene oxide) (PPO) [9-11], and poly(ether sulfone)s (PESs) [12–16] have been extensively studied due to their high mechanical strength, excellent chemical and thermal stability. Commercial PPO and polysulfone are easily functionalized to convert into AEMs, in contrast, similar functionalization to an engineering polymer, commercial poly(ether ether ketone) (PEEK) is relatively difficult due to solubility in common solvents. Although its poor the post-functionalization process is possible, it requires a carcinogenic chloromethylation reagent, i.e., chloromethyl methyl ether [17-19]. Another major disadvantage of post-functionalization is poor control on level and sites of functionalization [20-24]. Bromination of benzyl groups is another alternate method, which is relatively cleaner but involves a reaction to undesired sites of aromatic rings [21]. Our research group already explored and validated a new method of direct polymerization of bisphenol monomers containing benzylic tertiary amine groups [25,26]. Nevertheless, all these routes lead to the product in which cationic functional groups and the main chains is spaced through

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a single $-CH_2$ - group. This spacer introduces poor stability to cationic groups, and also enhances the possibility of polymer backbone degradation due to presence of electron-withdrawing groups in the vicinity [27,28]. Increasing the length of the interval between the main chain and the ionic group is a feasible method to improve the stability of the main chain (the number of C in the interval > 3) [29–33]. However, most of the quaternary ammonium salts are directly connected to the benzyl group, and the benzyl quaternary ammonium salt has poor alkaline stability. Therefore, a simple approach to develop high-performance AEMs based on poly(aryl ether ketone)s (PAEKs) remains an attractive and challenging.

In the present study, a simple and effective method is investigated to synthesize side-chain-type PAEKs with various cationic groups for AEMs development. The proposed method depends on the polyhydroxyalkylation reaction between 4,4'-bis(phenoxy)benzophenone (BPBP) and 1-(4-bromobutyl)indoline-2,3-dione (BID) using trifluoromethane sulfonic acid (TFSA) as a catalyst, which successfully introduced bromoalkyl side chain groups into PAEKs. Typical tertiary amines including trimethylamine, N-methyl-piperidine and N,N,N',N',N''-pentaethylguanidine were selected for subsequent Menthukin reaction to obtain OPAEK, PPAEK and GPAEK ionomers (Scheme 2). Meanwhile, cardo structure can increase the space between chains and would be in favor of the aggregation of ionic clusters. This generated hydrophilic-hydrophobic microphase separation morphology, which confirmed by atomic force microscopy (AFM). The AEMs containing three different cationic functional groups showed some differences in the properties of water management, ionic conductivity as well as mechanical property, which have been studied in detail to evaluate the potential of these membranes for fuel cell application.

2. Experimental

2.1. Materials

Trifluoromethanesulfonic acid (TFSA), phenol, 4,4'-difluorobenzophenone, isatin, 1,4-dibromobutane, N-methyl-piperidine, and trimethylamine were of reagent grade and purchased from Aladdin Reagents. Ethanol, dichloromethane, petroleum ether, diethyl ether, ethyl acetate, toluene, chloroform, N,N-Dimethylformamide (DMF), N, N-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO) and potassium carbonate (K_2CO_3) used in this study were also of reagent grade and provided by Sinopharm Group Chemical Reagent. All chemicals were used as received.

2.2. Synthesis of 4,4'-bis(phenoxy)benzophenone (BPBP)

The synthetic route of BPBP is shown in Scheme 1a. The reagents including K_2CO_3 (228.00 g, 1.65 mol), 4,4'-difluorobenzophenone (200.00 g, 0.91 mol), and phenol (155.00 g, 1.65 mol) were added to a three-necked round bottom flask equipped with a condenser, stirrer, a

water separator, and a nitrogen supply tubing. Dehydration process was performed in 500 ml DMSO and 200 ml toluene at 150 °C. Then, toluene was removed by heating, and the mixture was continuously stirred at 165 °C for 2 h. Finally, the product was extracted with chloroform/water system, washed repeatedly with methanol, and dried. The yield obtained of 4,4'-bis (phenoxy) benzophenone was 85%. The ¹H NMR spectra of BPBP is shown in Fig. S3.

2.3. Synthesis of 1-(4-bromobutyl)indoline-2,3-dione (BID)

The synthetic route of BID is shown in Scheme 1b. Isatin (30.00 g, 0.20 mol) and anhydrous DMF (200 ml) were added in a 500 ml threenecked flask. Once isatin was dissolved, the K_2CO_3 (56.39 g, 0.41 mol) was added to the solution along with stirring and continued for 30 min at room temperature. Then 1, 4-dibromobutane (121 ml) was slowly dripped through a constant pressure dropping funnel and the reaction was performed at room temperature. The degree of reaction completion was monitored by TLC. After filtration to remove K_2CO_3 , excess 1, 4dibromobutane was distilled off under reduced pressure. The red needle-like crystal product was further purified by recrystallization using ethanol as solvent. The product yield was 80%. The ¹H NMR spectra of BID is shown in Fig. S2.

2.4. Synthesis of poly(aryl ether ketone) (BPAEK)

In a 75 mL pressure bottle, 10 mol BPBP (3.66 g, 10 mmol) and 10 mol BID (2.82 g, 10 mmol) were dissolved in 15 mL CH_2Cl_2 . The mixture was slowly added to 15 mL CF_3SO_3H in ice water bath. Then the system was magnetically stirred at room temperature for 1 h in a sealed environment. Finally, the viscous solution was slowly poured into ethanol for precipitation. A white solid was obtained which was then washed with ethanol repeatedly and dried under vacuum. The product yield was 97%.

2.5. Synthesis of QPAEK/PPAEK/GPAEK ionomers

BPAEK was dissolved in DMAc and then trimethylamine aqueous solution (30%) (3 eq), N-methylpiperidine (3 eq) or N,N,N',N',N''-pentaethylguanidine (1 eq) were added respectively for functionalization reaction. Each reaction mixture was stirred and heated at 80 °C for 24 h followed by cooling to room temperature. The reaction product was then precipitated in ethyl acetate to obtain ionomers, which then washed repeatedly with ethyl acetate and dried under vacuum for 12 h to obtain ionomers QPAEK/PPAEK/GPAEK.

2.6. Preparation of AEMs

QPAEK and PPAEK were dissolved in DMF to prepare casting solutions. The GPAEK is found insoluble in common solvents, thus the solution prepared in the previous step for quaternization reaction was



Scheme 1. The synthetic route of BPBP (a) and BID (b).



Scheme 2. The synthetic route of the polymer BPAEK and subsequent QPAEK/PPAEK/GPAEK AEMs.

directly used as the casting solution. After filtration and degassing, acquired solution was casted onto a smooth flat glass plate and heated at 70 °C for 24 h to constant weight. The membranes were separated from the glass plate through immersion of it into DI water. Thoroughly washed membranes are subsequently immersed in 1 M KOH aqueous solution at 60 °C for 24 h to exchange Br⁻ with OH⁻. Each membrane converted in OH⁻ form followed by thorough washing with DI water and then stored in DI water till its use for testing.

2.7. Characterization and measurements

The ¹H NMR spectra were recorded with a Bruker AV500 spectrometer. FT-IR transmissions spectroscopy was undertaken using a Bio-Rad Digilab Division FTS-80 spectrometer infrared spectrophotometer (ATR-IR; Bruker Vertex 70). The spectra were obtained by examining the power in the 4000-500 cm⁻¹ range. The thermostability of the AEMs is assessed with a simultaneous TGA/DSC system (METTLER TOLEDO) at a N₂ atmosphere. All samples were maintained at 100 °C for 30 min to eliminate residual moisture during the thermostability test. Mechanical properties are evaluated by INSTRON-1121 with a stretching rate of 1 mm min⁻¹ at room temperature. Molecular weights were measured by GPC with POLYMER LABORATORIES-GPC120, where polystyrene was used as standard and DMF was used as an eluent. After the 1 wt% polymer solution was dripped on the mica flakes and dried, the microstructure of the AEMs were observed by a silicon-based n-type cantilever in the tapping mode on a Bruker AFM instrument.

2.8. Ionic conductivities

The ionic conductivities of the membranes were measured by a fourelectrode AC impedance analyzer in the range of 10 Hz–100 kHz using a BioLogic VSP. The cell was placed in a beaker filled with N₂-saturated ultrapure water. The conductivity values are validated by performing each measurement in replicates. The hydroxide conductivity is calculated according to the following formula,

$$\sigma = \frac{L}{AR} \tag{1}$$

where L is the distance between the two electrodes, R is the membrane resistance obtained from impedance analysis and A is the cross-sectional area of the membrane.

2.9. IEC values

IEC values were determined by simple titration. The membranes were initially exchanged to Cl⁻ form and dried at 60 °C to a constant weight that is recorded as W_{dry} . Then, the samples were soaked in 0.5 M Na₂SO₄ aqueous solution (100 ml) for 24 h to release Cl⁻ completely. The solution consisting Cl⁻ ions is titrated against 0.01 M AgNO₃ aqueous solution with K₂CrO₄ as indicator. The IEC values were calculated with following formula,

$$\text{IEC} \quad (\text{mmol/g}) = \frac{V_{\text{AgNO}_3} \times C_{\text{AgNO}_3}}{W_{\text{dry}}} \tag{2}$$

Where V_{AgNO3} is the volume of AgNO₃ consumed and C_{AgNO3} is concentration of AgNO₃ solution used for titration.

2.10. Water uptake and swelling ratio

The flat films were dried in a vacuum oven at 60 °C for 12 h till the constant weight was achieved. These completely dried membranes were cut into size of 4 cm \times 1 cm and weighed. After that, these samples were soaked in deionized water for 12 h to saturate the membranes with DI water at different temperatures. Before measurement, the extra water on these swollen membranes were gently wiped off using filter paper followed by quick measurement of weight and length of these membranes that is recorded as W_w and L_w , respectively. The WU and SR of AEMs was calculated using formula (3) and (4),

$$WU = \frac{W_w - W_d}{W_d} \times 100\%$$
(3)

$$SR = \frac{L_W - L_d}{L_d} \times 100\%$$
(4)

2.11. Alkaline stability

The long-term alkaline stability of the membranes is investigated by treating the membranes with 1 M KOH solution for different time intervals at 60 °C. Alkaline stability is estimated by analyzing the membranes through ¹H NMR spectra for any change in chemical composition upon exposure to alkaline solution. Moreover, the change in conductivities of the AEMs upon exposure to alkaline environment is taken another parameter to observe alkaline stability.

2.12. Membrane electrode assembly (MEA) and single cell performance

The PPAEK membrane (75 \pm 3 μ m thick) was used to fabricate the catalyst coated membrane (CCM). The anode and cathode were prepared by spray coating the catalyst ink evenly onto both sides of the membrane. The catalyst ink was prepared by mixing Pt/C (40 wt% Pt on high-surface area C) catalysts in an ionomer solution consist of 5 wt% solution of QPAEK in THF/water (50 wt%/50 wt%) as solvent. The catalyst loading at anode and cathode with reference to Pt metal was maintain as 0.4 mg cm⁻². Finally, the MEA was prepared by sandwiching the CCM between two pieces of carbon paper. The single fuel cell tests were carried out using fully humidified H₂ and O₂ with the flow rate of 200 mL min⁻¹ at 60 °C.

3. Results and discussion

3.1. Synthesis of the polymer and the ionomers

The concept of super-electrophilic activation was proposed for the first time by Olah in the 1970's [34], who explained the high reactivity of electrophilic reactions and their application in the synthesis of diarylated compounds. Zolotukhin [35–40] and co-workers developed a superacid catalyzed polyhydroxyalkylation as novel polymerization route, which can be classified as an unusual $A_2 + B_2$ step-growth polymerization, resulting ultrahigh molecular weight polymers. The dramatic acceleration in polymerization rate was observed with a small excess of the carbonyl compound, known as the "nonstoichiometric effect." [38].

The molecular weight and polydispersity coefficient of the polymer developed in this study "BPAEK" are 105.6 kg mmol⁻¹ and 1.53, respectively, which is measured through a gel permeation chromatograph using DMF as eluent (Fig. S4). The high molecular weight of synthesized polymer indicates that the two monomers used have good reactivity under provided conditions. The other advantages of this process are simple operation, low cost, a mild reaction condition, and environmentally friendly.

The structure of BPAEK was determined by ¹H NMR (Fig. 1a). Trimethylamine, 1-methylpiperidine, N,N,N',N',N''-pentaethylguanidine (Scheme S1) were used for polymer quaternization. These reagents were selected because trimethylamine is one of the most commonly used quaternization agents, while it is established through literature that AEMs with cycloaliphatic QAs or ethyl substituted guanidinium exhibits good alkaline stabilities [41,42,47]. QPAEK, PPAEK, and GPAEK ionomers were synthesized by simple Menshutkin reaction. The chemical structures for QPAEK and PPAEK were analyzed by ¹H NMR (Fig. 1b and c). The two peaks appeared at 2.98 ppm and 3.34 ppm are corresponding to the protons of -CH2- and -CH3 connected to the N atom of QAs, confirmed the successful quaternization reaction. The formation of guanidinium salt was determined by FT-IR (Fig. 2). The new band at 1538 cm^{-1} is attributed to the -C=N of the guanidinium salt. The prepared GPAEK membrane was subjected to elemental analysis after immersing in KOH aqueous solution, and it was found that there was no bromine element. This result shows that the quaternization reaction is complete, and all Br⁻ have been exchanged for OH⁻.

3.2. Mechanical property and thermal stability

The ability to convert into thin and robust membranes is critical for any polymer to be considered for its commercial application as AEMs. In the membrane electrode assembly (MEA), a fragile membrane may cause fuel leakage, which results in significantly efficiency loss and is also dangerous. Therefore, good mechanical properties are necessary. All three membranes showed excellent mechanical properties, with the tensile strength of 50 MPa. The elongation at break of QPAEK and GPAEK were 13% and 8.5%, respectively. However, the elongation at break for PPAEK is relatively higher as 35% at room condition (Fig. 3a).



Fig. 1. ¹ H NMR spectra of the polymer BPAEK (a), QPAEK (b) and PPAEK (c).

The difference may be due to the higher water uptake of PPAEK in air, and a small amount of water acts as a plasticizer to make its elongation at break greater. The mechanical properties of these membranes are sufficient for the application of AEMFCs.

Thermal gravimetric analysis (TGA) was performed to evaluate the thermal stability of the developed membranes. Fig. 3b shows the TGA curves of different polymers in the range of 50–800 °C. Initially, the decomposition pattern of three AEMs is found similar as the first weigh loss is occurred at 200 °C that is attributed to the decomposition of the QA groups. The second weight loss occurred at 300–400 °C and is assigned to the thermal degradation of the alkyl groups, which happened in all AEMs and BPAEK polymer. The last weight loss stage above 500 °C is attributed to the disintegration of the polymer backbone. It is thus verified by TGA results that the developed PAEK based AEMs have an excellent thermal stability.



Fig. 2. FT-IR spectra of BPAEK and GPAEK.

3.3. Microstructure of the AEMs

The microstructures of the QPAEK and PPAEK membranes make a contribution to the high ion conductivity but moderate WU. AFM phase images show the microstructure of the QPAEK, PPAEK and GPAEK membranes (Fig. 4a, b and c). It can be seen that QPAEK and PPAEK have clear microphase separation structures and the size of the aggregated ion clusters is about 5 nm. The introduction of cardo structure and long alkyl side chain in the membranes increases the divergence of hydrophobic and hydrophilic segments, which derives the formation of ion aggregation and a microphase separation structure. AFM surface topographic images of AEMs made of QPAEK and PPAEK (Fig. 4d and e) explain that the microphase separation morphology appeared in AFM phase diagrams is due to spatial chemical structure rather than the roughness of the membranes surface. Comparing images Fig. 4c and f, it can be found that the difference in brightness in Fig. 4c is basically caused by the difference in surface height reflected in Fig. 4f. Therefore, there is no microphase separation structure in the GPAEK membrane surface, which may be because extremely low hydrophilicity of GPAEK membrane is not conducive to the aggregation of hydrophilic groups.

3.4. Water uptake (WU) and swelling ratio (SR)

According to the Grotthuss mechanism, water is essential for ion transmission in AEMs [43]. Too low WU may reduce the ion transport efficiency and hence cause low conductivity. On the contrary, redundant WU in membranes may weaken the intermolecular interaction, leading to an excessive swelling and then severe loss of strength of the membrane [43]. Therefore, solving the trade-off between the WU and ionic conductivity of the membrane is an important aspect of obtaining an advanced AEM. As shown in Fig. 5a and b, the expected increase in WU and SR of QPAEK and PPAEK is observed with increasing temperature from 30 to 80 °C, while almost no change in WU and SR with increasing temperature is noticed for the GPAEK membranes. It is justified due to the fact that guanidium salt functionalized polymers generally experience very low WU and SR even at high temperatures that may be attributed to its lower hydrophilicity than other anions [41,44]. As a result, GPAEK membrane displayed a lower WU (less than 10%) and a lower SR (less than 5%). In comparison, WU (79% at 80 °C) and SR (25% at 80 °C) of PPAEK are much higher than OPAEK, probably because N-methyl-piperidine has a larger free volume. The titration IEC values of the three membranes are shown in Table 1. All three membranes have SR of less than 30%, which is recommended for application of any membrane in fuel cells.

3.5. Anion conductivity and morphology of AEMs

The hydroxyl conductivities of all AEMs were measured in temperature range 30-80 °C (Fig. 5c). The conductivities followed the normal trend such as it increases with increasing temperature, which simply attributed to fast kinetics at higher temperature. The QPAEK and PPAEK membranes showed excellent OH⁻ conductivities that is as high as 94.8 mS cm⁻¹ and 99.8 mS cm⁻¹, respectively, which may be related to the involvement of spatial cardo structure of PAEKs-based AEMs. The presence of three-dimensional structure of cardo offers formation of nano voids and thus greater free volume within polymer chains, which facilitates the transport of ions between chains, resulting enhanced conductivity [45]. Thus the spatial structure of membranes afforded the control over the trade-off between the conductivity and SR. However, GPAEK membrane exhibited OH⁻ conductivity value as low as 11.8 mS cm⁻¹ at 80 °C that is less than one eighth of OPAEK membrane, and is attributed to much lower WU of the GPAEK membrane. Therefore, the absence of water as an ion carrier in the GPAEK based membranes reduces their efficiency of ion transport. Compared to the reported poly (aryl ether ketone)s and poly(aryl ether sulfone)s based AEMs, QPAEK



Fig. 3. (a) Stress-strain curve of the dry membranes and (b) TGA curves of prepared polymers.



Fig. 4. Microphase separation structure of the QPAEK, PPAEK and GPAEK AEMs in Br⁻ form. AFM phase images of the (a) QPAEK, (b) PPAEK and (c) GPAEK AEMs. (d) The corresponding AFM surface topographic images of (a). (e) The corresponding AFM surface topographic images of (b). (f) The corresponding AFM surface topographic images of (c).



Fig. 5. (a) Swelling ratio, (b) water uptake, (c) ionic conductivity of the prepared AEMs in the OH⁻ form as a function of temperature, and (d) Arrhenius plot: ionic conductivity vs. 1000/T.

Table 1

Property comparison of the AEM obtained in this work with the other AEMs.

Sample	IEC_{theo}^{a} (meq g ⁻¹)	$\text{IEC}_{\text{titr}}^{b} \text{ (meq g}^{-1}\text{)}$	WU ^c (%)	SR ^c (%)	σ (OH ⁻) ^c (mS cm ⁻¹)	σ (OH ⁻) ^d (mS cm ⁻¹)	Ref.
QPAEK	1.59	1.55	31.0	15.3	44.5	94.8	This work
PPAEK	1.54	1.52	58.6	18.5	45.8	99.8	This work
GPAEK	1.30	1.23	8.7	3.1	6.1	11.8	This work
FAA-3-50	2.00	_	108.2	117.8 ^g	16.5	-	[50]
QAPES-BTP-20%	2.15	1.96	53.5 ^e	20.4 ^e	21.7 ^e	50.2	[32]
8C-SfPAES-ImOH	1.76	-	~118 ^e	~35 ^e	~36 ^e	-	[33]
PAES-Q-12	1.84	1.65	10.6 ^e	3.6 ^e	23 ^e	54	[19]
QBz-PEEK-91.6%	1.95	_	96 ^f	20^{f}	-	59 ^f	[30]
QPE _R K-TMA	2.0	1.6	26.6 ± 1.3	$\textbf{6.7} \pm \textbf{0.2}$	$\textbf{22.3} \pm \textbf{1.6}$	-	[31]
PES-PPH-Pi(OH)-100	1.48	1.45	16.7	5.2	27	56	[49]

^a Theoretical IEC.

^b IEC by titration.

^c Measured at 30 °C.

^d Measured at 80 °C.

^e Measured at 20 °C.

 $^{\rm f}$ Measured at 60 °C.

^g Volumetric swelling ratio measured at 25 °C.

and PPAEK are the advanced AEMs exhibiting excellent conductivity but a relatively low IEC and WU (Table 1).

Moreover, the Arrhenius plot in Fig. 5d represents that the hydroxide ion conductivities of all AEMs are extremely temperature-dependent. The activation energies (Ea) for hydroxide conductivity through QPAEK, PPAEK and GPAEK membranes are obtained from the slope of the Arrhenius curves and found 12.8, 13.8 and 11.8 kJ/mol, respectively. The Ea value of PPAEK is slightly higher, indicating that the transportation of hydroxide ion is slightly more sensitive to temperature in PPAEK membranes.

3.6. Alkaline stability

In addition to thermal stability, the PAEK based AEMs also displayed good alkaline stability. In general, alkaline environment causes degradation of ionomeric functional groups so as polymer backbone through different mechanisms [27,46,48]. In the present study, all three membranes remained robust and flexible after immersing in N₂-saturated 1 M KOH at 60 °C. After 600h, the observed decrease in OH⁻ conductivity is less than 5% (Fig. 6), proving that the introduction of a long side chain can ameliorate the alkaline stability of the PAEKs-based membranes. The structural stability of QPAEK and PPAEK was analyzed through ¹H



Fig. 6. The retention of membranes' conductivity measured at 30 $\,^\circ\text{C}$ after immersing in $N_2\text{-saturated}$ 1 M KOH at 60 $\,^\circ\text{C}.$

NMR spectra (Fig. 7b and c) after certain interval of alkaline stability test such as after 360 h and 600 h. The alkaline stability of GPAEK cannot be characterized by ¹H NMR due to its poor solubility. For QPAEK, two new peaks at 5.90 ppm and 4.92 ppm revealed that CH₂—CH- was formed at the head group that was attributed to degradation by Hofmann elimination (Fig. 7b). The same peaks were also observed in Fig. 7c, revealing that PPAEK also underwent Hofmann elimination. The new peak at 2.07 ppm of Fig. 7b and the new peaks at 2.10–2.45 ppm of Fig. 7c indicate that nucleophilic substitution degradation occurred. The possible degradation routes of the QPAEK and PPAEK membranes are shown in Fig. 7a. Moreover, no change in the peak of the aromatic region represents that the polymer backbone is still intact when treated in 1 M KOH solution at 60 °C.

3.7. Single cell performance

Considering the conductivity, mechanical properties, stability, etc., OPAEK and PPAEK membranes were selected for AEMFC testing in H₂/ O2 fuel cell system. Since the ionomer has similar composition and structure with the membrane thus offered good compatibility. As shown in Fig. 8, the open circuit voltage of 1.03 and 1.05 V which represents that the membrane electrode assembly (MEA) prepared through the developed membranes are of good quality and free from gas leakage. QPAEK membrane exhibits a peak power density of 69 mW cm⁻² at a current of 120 mA cm⁻². For PPAEK membrane, a high peak power density of 92 mW cm⁻² was achieved at a current density of 154 mA cm⁻². The comparison of the single cell performance of the AEMs obtained in this work with the other reported AEMs is shown in Table 2. The PPAEK membrane is at a medium level. In addition to the performance of the AEMs, several factors can influence the single cell performance such as compatibility of ionomers and membranes, Pt loading, gas flow rate and MEA fabrication procedures, etc.

4. Conclusions

Spatial architecture poly(aryl ether ketone)s (PAEKs) are successfully prepared by the superacid-catalyzed polycondensations of the bromobutyl substituted isatin with the aryl ether ketone monomer. The polymerization process reported herein is a simple and an efficient method to prepare novel designed AEMs. The performance of AEMs can be tuned by varying the fixed cation functional groups. The AEMs comprising of cyclic quaternary ammonium salts have shown improved WU, SR, conductivity, and elongation at break compared to AEMs having simple quaternary ammonium salts, while AEMs with guanidinium salts experienced lowest values of WU, SR, so as conductivity.



Fig. 7. (a) The possible degradation routes of the QPAEK and PPAEK membranes in 1 M KOH solution at 60 °C. ¹H NMR spectra of (b) the QPAEK membrane and (c) PPAEK membrane after the alkaline stability test for 360 h and 600 h.



Fig. 8. H₂/O₂ AEMFC performance for the QPAEK and PPAEK AEMs at 60 °C.

However, the properties such as thermal and alkaline stability were not much effected by changing the cation group, thus assumed to be dependent on the polymer backbone. Among different AEMs, PPAEK exhibited the highest WU of 79% and the highest conductivity of 99.8 mS cm⁻¹ at 80 °C. The peak power density of PPAEK membranes achieved is 92 mW cm⁻² at a current density value of 154 mA cm⁻², rendered these membranes as potential AEM candidate for fuel cell application.

 Table 2

 The single cell performance of the AEMs obtained in this work with the other AEMs.

AEM	T (°C)	Pt loading (mg cm ⁻²)	Ionomer	H ₂ /O ₂ (mL/ mL)	Pmax (mW cm ⁻²)	Ref.
PPAEK	60	0.4	QPAEK	200/ 200	92	This work
QPAEK	60	0.4	QPAEK	200/ 200	69	This work
PPO-6QA	60	0.5	PS-6C- QA-40	1000/ 1000	53.5	[9]
SDQ	60	0.5	PTFE	100/ 100	98	[11]
Tokuyama	60	0.5	QTBPCE	100/ 100	41.8	[51]
QAPIB	60	0.4	QAPPT	500/ 500	940	[45]
QAPES- BTP-25%	60	0.5	AS-4	200/ 200	137	[32]
QBz-PEEK- 76.0%	70	0.5	QPPO	1000/ 1000	391	[30]

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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