High durable PEK-based anion exchange membrane for elevated temperature alkaline fuel cells

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Highly durable quaternary ammonium polyetherketone hydroxide (QAPEK-OH) membranes were developed for alkaline fuel cells operating at elevated temperatures via chloromethylation, quaternization and alkalinization method. The chemical reaction for chloromethylated polymer (CMPEK) was confirmed by nuclear magnetic resonance (1H NMR) and the QAPEK-OH membranes were characterized by Fourier transform infrared spectroscopy (FT-IR). The thermal properties of the membranes were determined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The ion-exchange capacity (IEC), water uptake, mechanical properties and anion conductivity of the QAPEK-OH membranes were measured to evaluate their applicability in alkaline fuel cells at elevated temperature. The anionic conductivity of the QAPEK-OH membrane varied from 8 × 10−4 to 1.1 × 10−2 S cm−1 over the temperature range 20–100 °C. The QAPEK-OH membrane showed excellent alkaline stability in 1 M KOH solution at 100 °C. The excellent temperature durability of QAPEK-OHs makes them promising membrane materials for alkaline fuel cells.

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1. Introduction

Anion exchange membrane fuel cells (AEMFCs) are attracting considerable interest relative to proton exchange membrane fuel cells (PEMFCs) in recent years, primarily due to the distinct advantages when operating in an alkaline environment such as cathode reaction kinetics and resistance polarization [1,2]. The inherently faster and much easier kinetics of the oxygen reduction reaction (ORR) in alkaline environment than in acid medium leads to the use of non-noble and non-precious metal electrocatalysts such as silver (Ag) and nickel (Ni), making the AEMFC a potentially low cost technology compared to PEMFCs, which employ platinum (Pt) catalysts [3,4]. Moreover, due to the less corrosive nature of an alkaline medium, higher durability is expected for AEMFCs. However, AEMFCs need to overcome strenuous technical and economic challenges which are specifically associated with fabrication of a cost effective anion exchange membrane (AEM) possessing (i) high anionic conductivity and (ii) exemplary physico-chemical and temperature stability [1,2,5]. Due to the poor thermal, chemical and physical stability of current AEMs, the typical operating temperature of AEMFCs is limited to 50 or 60 °C [6]. However, AEMFC performance can be increased by operation at elevated temperatures which can be explained as follows. Increasing the operating temperature enhances both the charge (i.e., hydroxide) conduction within the membrane and the mass transfer, reducing the ohmic and mass transfer overpotentials, respectively. Moreover, the electrochemical kinetics of both the fuel oxidation reaction at the anode and the ORR at the cathode increase, resulting in minimized thermodynamic voltage losses and higher overall cell voltages. Thus, in order to successfully employ AEMFCs for applications such as vehicle propulsion, high temperature stable AEMs must be produced [2,7–11]. Accordingly, one of the primary challenges with AEMs is the membrane physico-chemical stability, especially at elevated temperatures.

Unlike polymer electrolyte membranes where highly chemically stable perfluorinated membranes such as perfluorosulfonic acid (DuPont™ Nafion®), control the market, commercially available AEMs are usually based on quaternary ammonium (QA) cross-linked polystyrene which albeit having been applied for water processing, cannot be used for AFCs due to low chemical and thermal stability, as well as weak mechanical property. Distinctively, the polystyrene backbone is too rigid to produce flexible thin films, and the QA functional group attached on polystyrene tends to degrade at 40–60 °C [5]. Furthermore, the blended amminated cross-linked polystyrene with other polymers limits the anion conductivity and may also reduce the chemical stability of the membrane [7]. So far, many types of polymers, such as polybenzimidazole (PBI) [12], polyphenylene oxide (PPO) [13], carbolyetherketone (PEK) [14], polyethersulfone (PES) [15], and radiation-grafted FEET [16] and FEFP [17] have been used to produce AEMs for application in alkaline fuel cells. Yet, the main problems stayed with many known AEMs, such as the low chemical
stability in concentrated alkaline environments, due to the decay of the anion exchange groups (e.g., QA functional groups) in concentrated alkali solution; or the weak thermal stability which limits them to be used for elevated temperature alkaline fuel cells [18].

In this paper, in order to accomplish the aforementioned objectives, a modified quaternary ammonium polyetherketone (QAPEK) based block copolymer electrolyte has been developed through the chloromethylation and quaternization method, demonstrating the requirements for AEMs with improved thermal, chemical and mechanical stability for AEMFCs at elevated temperatures. Among different polymeric structures for AEMs, block copolymers possess higher water uptake and ion conductivity which can be assigned to their sequential hydrophilic/hydrophobic structure with ionic groups in the hydrophilic blocks, resulting in a helpful hydration effect [13,14]. Since one of the requirements and a key challenge for AEMs is the satisfactory chemical stability, fully aromatic polymers are expected to have notably high chemical resistance, leading to the desirable durability for AEMFCs. Specifically, polyetherketones (PEKs) and their derivatives are the focus of many investigations, and the synthesis of these materials has been widely reported. This family of aromatic copolymers is attractive for use in AEMs because of their well-known chemical and hydrolytic stability under harsh conditions [19–21]. The reason for that behavior is a microphase separation between the chemically different and incompatible blocks which are attached to each other by covalent bonds, and which does not occur in random copolymers or in blends (macrophase separation) of the same composition [22]. Moreover, AEMs containing QA functional groups as the cation exhibit higher thermal and chemical stability than other quaternary cations such as quaternary phosphonium (QP) or tertiary sulfonium (TS) groups [23–26]. This is mainly due to the higher basicity of QA (pKa = 31.9) than TS (pKa = 17.8) and QP (pKa = 17.4) compounds, respectively [27,28]. For the obtained QAPEK copolymer, the water uptake, ion exchange capacity (IEC), ion conductivity, mechanical properties, thermal stability and chemical durability were investigated.

2. Experimental methods

2.1. Materials

4,4′-isopropylidenediphenol (Bisphenol A/BPA), 4,4′-dihydroxybenzophenone (DHBP) and 4,4′-difluorobenzophenone (DFBP) were purchased from TCI America and used as received. Chloromethyl methyl ether (CMME), anhydrous zinc chloride (ZnCl₂), triethylamine (TEA), N-methylpyrrolidone (NMP) and 1,1,2,2-tetrachloroethane (TCE) were purchased from Sigma-Aldrich and used as received. All other reagents such as toluene and potassium hydroxide (KOH) were obtained from other commercial sources and used as received.

2.2. Synthesis of PEK block copolymer via polycondensation

The PEK block copolymer was synthesized through aromatic nucleophilic substitution polycondensation reaction of activated aromatic halide (DFBP) with BPA and DHBP in the presence of a weak base, potassium carbonate, and a dipolar aprotic solvent, NMP (Fig. 1). In a 50 mL 3-neck round-bottom flask Bisphenol A (7.5 mmol, 1.7122 g) and K₂CO₃ (8.25 mmol, 1.6585 g) were mixed in 6 mL of NMP and 6 mL toluene, equipped with a Dean-Stark receiver under nitrogen flow. The reaction temperature was maintained at 150 °C for 4 h until the produced water was extracted and collected in the Dean-Stark trap via toluene. After cooling the solution to the room temperature, DFBP (10 mmol, 2.182 g) was added to the flask and then, the temperature was increased to 165 °C for 2 h to obtain the hydrophilic oligomer. In order to generate the hydrophobic oligomer block, DHBP (2.5 mmol, 0.5356 g) and K₂CO₃ (2.75 mmol, 0.3795 g) were added to the solution with 12 mL of toluene and 6 mL of NMP, connected to the Dean-Stark trap under nitrogen flow. The temperature was kept at 150 °C for 4 h until the water was removed by toluene from the system. The reaction was continued under nitrogen flow at 175–180 °C for another 2 h until gaining a viscous copolymer. The mixture was diluted with 12 mL of NMP at 100 °C and added dropwise into a large excess of methanol with vigorously mechanical stirring. The precipitated PEK block copolymer was washed and purified with double deionized (DDI) water and methanol three times. After being dried at 80 °C under vacuum, the white PEK copolymer fibers were dissolved in 12 mL of NMP and then, re-precipitated in methanol, washed with DDI water and methanol three times, and finally dried vacuum at 80 °C in the oven.

2.3. Chloromethylation of PEK and membrane casting

According to Fig. 2, the Friedel-Crafts chloromethylation reaction of the PEK occurs at the activated aryl ring between the isopropylidene and ether bond by adding chloromethyl methylether (CMME) and a Lewis acid catalyst (e.g., ZnCl₂). The product will be a halomethylated polymer. A 50 mL round-bottom flask was charged with PEK block copolymer (0.8 g) and 20 mL of 1,1,2,2-tetrachloroethane (TCE) as the solvent. After stirring the mixture under nitrogen at room temperature (until PEK was completely dissolved), a solution of CMME (29.28 mmol, 2.22 mL) and anhydrous ZnCl₂ (0.0998 g, 0.732 mmol) was added dropwise to the mixture and stirred at 35 °C for 48 h. The mixture was poured slowly into a large excess of methanol, and washed with methanol three times. Then, the dried chloromethylated PEK (CMPEK) copolymer was dissolved in NMP and filtered via a frieted disk funnel. The filtrate was cast on a flat glass plate and heated at 80 °C for 1 day, resulted in a thin 35–40 μm thick, transparent and tough membrane.

2.4. Quaternization and alkalinization of CMPEK membrane

The solid-state alkaline electrolytes are typically prepared by amination of halomethylated polymers with tertiary amines such as triethylamine (TEA). Fig. 3 clearly indicates the conversion from a chloromethyl group into a quaternary ammonium (QA) group by immersing the CMPEK membrane in a 35 wt% TEA aqueous solution at room temperature for 48 h. The last step corresponds to the final product, i.e., QAPEK-OH. To replace the Cl⁻ anion in the QAPEK with OH⁻, the membrane was placed in 1 M sodium hydroxide (KOH) aqueous solution at room temperature for 48 h, and then, washed with DDI water three times. The obtained QAPEK-OH membrane was stored in a closed vessel filled with DDI water before being used for any performance test.

2.5. Measurements and characterization tests

Nuclear magnetic resonance (¹H NMR) spectra were measured at 500 MHz on a Bruker Analytik GmbH spectrometer. FT-IR spectra were recorded on 35–40 μm thick membrane samples using an Avatar 320 FT-IR spectrometer. Thermogravimetric analysis (TGA) was performed under nitrogen with a TGA Q500 V20.10 instrument in the temperature range from 50 to 900 °C at the heating rate of 10 °C min⁻¹. Differential scanning calorimetry (DSC) analysis was performed under nitrogen through the heating–cooling–heating cycle from 0 to 400 °C with a DSC Q2000 V24.4 Build 116 instrument. Tensile measurements were carried out with an UMT-CETR mechanical testing instrument at a speed of 0.05 mm min⁻¹.
2.5.1. Water uptake (WU) and ion exchange capacity (IEC)

The membrane was vacuum-dried at 80 °C for 10 h until constant weight for the dried membrane was obtained. They were then immersed in DDI water at given temperature for 4 h. After this time, the membranes were taken out, wiped with tissue paper, and quickly weighed on a microbalance. The water uptake of membranes was calculated according to Eq. (1):

\[
WU (\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100
\]

where \( WU (\%) \), \( W_{\text{wet}} \) and \( W_{\text{dry}} \) are the water uptake by weight percentage, the weight of wet membrane and the weight of dry membrane, respectively.

The IEC of membrane samples was determined by using the back titration method. At first, the samples were dried until the weight was constant, after which each sample was immersed in DDI water overnight. Then, they were soaked in 0.01 M hydrochloric acid (HCl) for 48 h to exchange Cl\(^-\) ions with hydroxides. Back titration was then accomplished with 0.01 M NaOH (aq.) standardized solution with phenolphthalein as an indicator. The IEC values were calculated using Eq. (2)

\[
IEC = \frac{M_1 V_{1\text{HCl}} - M_2 V_{2\text{NaOH}}}{W_{\text{dry}}}
\]

where IEC is the ion exchange capacity (mequiv. g\(^{-1}\)), \( M_1 \) (molar) and \( V_1 \) (mL) are the concentration and volume of HCl solution, respectively, before the titration; \( M_2 \) (molar) and \( V_2 \) (mL) are the concentration and volume of NaOH solution, respectively, used in the titration; \( W_{\text{dry}} \) (g) is the mass of dry sample.
2.5.2. Anion conductivity

The anion conductivities of all QAPEK-OH membrane samples were obtained by a four-electrode AC impedance spectroscopy [29] with a CHI760D potentiostat control model. The impedance was measured in the frequency range between 1 MHz and 0.1 Hz with perturbation voltage amplitude of 5 mV. The membranes and the electrodes were set in a Teflon cell, and the distance between the reference electrodes was 1 cm. The cell was placed in a thermo-controlled chamber in DI water for measurement. Conductivity measurements under fully hydrated conditions were carried out with the cell immersed in DI water. All samples were equilibrated in water for at least 24 h prior to the conductivity measurement. At a given temperature, the samples were equilibrated for at least 30 min before any measurements. Repeated measurements (four times) were then taken at that given temperature with 10 min interval until no more change in conductivity was observed. The anion conductivities ($\sigma$) of all samples were then determined along the longitudinal direction, using Eq. (3) [30–32].

$$\sigma = \frac{L}{AR}$$ (3)

where $\sigma$, $L$, $R$, and $A$ denote the ionic conductivity, sample length (or distance between the reference electrodes in the membrane), the resistance of the membrane, and the cross-sectional area of the membrane, respectively.

2.5.3. Alkaline stability

To measure the alkaline stability, the QAPEK-OH samples were kept in a stirred aqueous solution of 1 M KOH at 60 and 100 °C. Then, after different specific time, each sample was rinsed and stored in DI water before re-testing the anion conductivity. Furthermore, the FT-IR and tensile strength tests were re-tested for samples after the stability test.

3. Results and discussion

As shown in Figs. 2 and 3, the AEM was prepared through three stages of chloromethylation, quaternization, and alkalization chemical reactions. Among them, chloromethylation and quaternization are two chief reactions which demonstrate the anion conductivity [6]. The chloromethylation of polymer is a valuable procedure that was identified about four decades ago. Because of the high reactivity of the tethered chloromethyl group, chloromethylated polymer is the starting point for the synthesis of “polymer-bound reagents” for the ion-exchange polymer electrolytes [33].

The $^1$H NMR spectra of the PEK and CMPEK block copolymers were well assigned to the supposed chemical structure (Fig. 4). In the $^1$H NMR spectrum of CMPEK (denoted as h in Fig. 4), a peak assignable to the methylene protons of the chloromethyl groups on the polymer main chain was observed at 4.6 ppm, which was
absent in the $^1$H NMR spectrum of the bare PEK. The signals with chemical shifts between 6.8 and 7.9 ppm were assigned to the aromatic protons of PEK and CMPEK copolymers.

In order to demonstrate whether the quaternary ammonium (QA) groups are attached on the polymer chain, the elemental composition of QAPEK-OH membrane was investigated through the FT-IR spectroscopy (Fig. 5). The absorption bands at 3290 and 2359 cm$^{-1}$ were characteristic of QA groups [34,35]. The absorption bands at 2873 and 2968 cm$^{-1}$ arise from the stretching vibrations of symmetric and asymmetric methylene (–CH$_2$–) groups, respectively [34–40].

The thermal stability of PEK, CMPEK and hydrated QAPEK-OH membrane were investigated by TGA curves, shown in Fig. 6. The pure PEK copolymer started the degradation process around 461 °C. For CMPEK the weight loss (14%) observed at 320 °C was attributed to the chloromethylene groups. In QAPEK-OH membrane, as a result of the strong hydrophilicity of the quaternary ammonium groups and attracting water from the atmosphere, a slight weight loss (5.4%) was observed between 150 and 180 °C, corresponding to the
evaporation of absorbed water. This behavior has been commonly found in other polymeric ion-exchange membranes. The weight loss (9%) observed for QAPEK-OH started at 200 °C was related to the degradation of QA groups and the one at 320 °C can be assigned to chloromethylene groups (18%), satisfying alkaline fuel cell applications at high temperatures.

The DSC analysis was performed to identify their glass transition temperatures \(T_g\) of PEK, CMPEK and QAPEK-OH polymers (Fig. 7). For unmodified PEK copolymer, \(T_g\) was about 142 °C. It can be seen that the \(T_g\) for CMPEK and QAPEK-OH has been shifted to higher temperature of 155 and 167 °C, respectively. The increase of \(T_g\) for the CMPEK and QAPEK-OH, implies that they are thermomechanically more stable than unmodified PEK membrane. The membrane thus becomes more elastic in nature and can withstand higher temperatures. Thus, the results obtained from TGA and DSC shows the improved potential of the PEK based AEMs for high temperature operations of alkaline fuel cells applications.

The water uptake of aminated polymers is known to have a profound effect on the anion conductivity and mechanical properties of AEMs. Water molecules dissociate the alkaline functionality and facilitate hydroxide transport. However, excessively high levels of water uptake can result in membrane fragility and dimensional change, which lead to the loss of mechanical properties [41]. Basically, the amount of water uptake of QAPEK-OH membrane is strongly dependent upon the amount of quaternary ammonium hydroxide groups [42]. The deep effect of water uptake on the anion conductivity as well as the mechanical property of AEMs is remarkable. Basically, when the membrane absorbs higher amount of water, the number of available anion exchange sites increases, resulting in an increment in the anion conductivity. Although the higher water uptake leads to the higher anion conductivity, excessive uptake can also cause swelling and decrease the mechanical strength of the membrane [43–46]. The measured water uptake and IEC were 16.67% (Eq. (1)) and 0.41 mequiv. g\(^{-1}\) (Eq. (2)), respectively. To reach a high anion-conductive membrane, 16.67% water uptake was not enough for the developed QAPEK-OH membrane. The low water uptake value of the block QAPEK-OH membrane can be related to (i) low ion exchange capacity and (ii) the developed hydrophilic/hydrophobic phase-separated morphology [43,45].

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**Fig. 7.** DSC curves for PEK, CMPEK and QAPEK-OH copolymers in N\(_2\).

**Fig. 8.** Anion conductivities of fully hydrated QAPEK-OH and commercial FAA membranes at different temperatures.

**Fig. 9.** FT-IR spectrum of QAPEK-OH membranes treated in 1 M KOH solution at 100 °C after 24 and 72 h.

**Fig. 10.** Stress–strain curves of the QAPEK-OH membranes under hydrated condition in ambient atmosphere (25 °C) before and after alkaline stability test at 100 °C.
The anion conductivity of the QAPEK-OH membrane was compared to the commercial fumapem® FAA from FuMA-Tech GmbH (35–40 μm thickness, 0.59 Ω cm² at 20 °C), after the hydration in DDI water for 24 h at the room temperature. FAA is a hydrocarbon membrane-polymer of aminated polyarylene (polysulfone) chloride, hydroxide and carbonate salts anion exchange membrane, used for alkaline fuel cells without the need of liquid electrolyte. In Fig. 8, the anion conductivity values of the membranes were shown and compared versus the temperature. In general, an anion conductivity above $10^{-2}$ S cm⁻¹ is required for AEM materials used in fuel cells. As expected, an increase in temperature resulted in an increase in hydroxide conductivity based on the simplified diffusion mechanism and thermal motion of hydroxides within the membrane [37]. This is attributed to the increase of free volume in the membrane at elevated temperatures which expands the required channels for ion conduction [14]. For the FAA membrane, the enhancement of the anion conductivity with the increase of the temperature was in a gradual fashion, whereas for the QAPEK-OH membrane the temperature had much higher effect on the improvement of the anion conductivity. The possible
4. Conclusions

In summary, polyetherketone (PEK) polymer backbone was successfully modified with quaternary ammonium groups through direct chloromethylation followed by reaction with triethylamine reagent. The obtained quaternized ionomers exhibited an excellent solubility and formed flexible and tough membranes by casting from an NMP solution. These AEMs based on quaternary ammonium hydroxide groups, denoted QAPEK-OHs, presented excellent thermal stability, satisfactory mechanical property, and good alkaline stability. The preliminary properties have demonstrated their potential as electrolytes for high temperature anion exchange membrane fuel cells. The obtained results will aid in designing superior stable membranes for high temperature alkaline fuel cell application; yet, to enhance and increase the anion conductivity at high temperature AEMFCs, further modifications on the membrane morphology and ionomer structure must be performed.

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References


