ACS APPLIED MATERIALS & INTERFACES
Research Article
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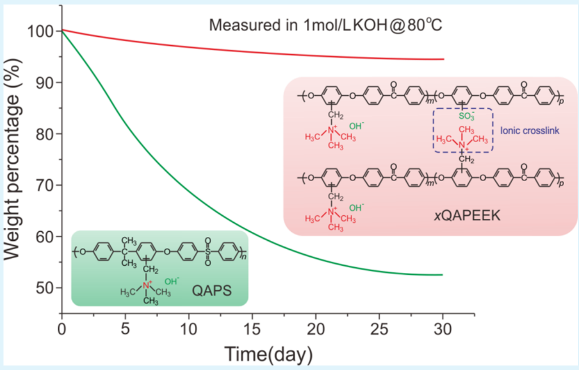
Highly Stable Alkaline Polymer Electrolyte Based on a Poly(ether ether ketone) Backbone

Juanjuan Han, Hanqing Peng, Jing Pan,* Ling Wei, Guangwei Li, Chen Chen, Li Xiao, Juntao Lu, and Lin Zhuang

College of Chemistry and Molecular Sciences, Hubei Key Lab of Electrochemical Power Sources, Wuhan University, Wuhan 430072, China



ABSTRACT: Alkaline polymer electrolyte fuel cells (APEFCs) promise the use of nonprecious metal catalysts and thus have attracted much research attention in the recent decade. Among the challenges of developing practical APEFC technology, the chemical stability of alkaline polymer electrolytes (APEs) seems to be rather difficult. Research found that, upon attachment of a cationic functional group, an originally stable polymer backbone, such as polysulfone (PSF), would degrade in an alkaline environment. In the present work, we try to employ poly(ether ether ketone) (PEEK), a very inert engineering plastic, as the backbone of APEs. The PEEK is functionalized with both a sulfonic acid (SA) group and a quaternary ammonia (QA) group, with the latter as the majority amount. Ionic cross-linking between SA and QA has rendered the thus-obtained membrane (*x*QAPEEK) with high mechanical strength and low swelling degree. More importantly, the *x*QAPEEK membrane exhibits outstanding stability in a 1 mol/L KOH solution at 80 °C for a test period of 30 days: the total weight loss of *x*QAPEEK is only 6 wt %, in comparison to a large degradation of quaternary ammonia PSF (more than 40 wt %) under the same conditions. Our findings not only have demonstrated an effective approach to preparing PEEK-based APE but also cast a new light on the development of highly stable APEs for fuel-cell application.

KEYWORDS: *fuel cell, alkaline polymer electrolyte, poly(ether ether ketone), ionic cross-linking, high chemical stability*

■ INTRODUCTION

The proton-exchange membrane fuel cell (PEMFC) is a clean and efficient power source suitable for applications in vehicles and portable devices.[1,2] The advantages of PEMFC include compact structure, high power density, quick startup, etc.[2,3] However, the inherent strong acidic environment of PEMFC has restricted the choice of catalysts; only noble metals, mostly platinum, can work stably. This has been the main obstacle to the large-scale commercialization of PEMFC.[4−6] To fundamentally get rid of the platinum dependence problem, an alkaline polymer electrolyte fuel cell (APEFC) is considered as a very promising alternative. By substitution of the acidic polyelectrolyte with its alkaline counterpart, many nonprecious materials can possibly be employed as the catalyst for fuel-cell reactions.[5,7−9] The R&D of APEFC has been one of the hot subjects in the fuel cell world in the recent decade.[10−17]

To realize practical APEFC technology, developing high-performance alkaline polymer electrolytes (APEs) is of primary significance. An ideal APE membrane for fuel-cell application should possess high ionic conductivity, low swelling degree (SD %), and high chemical stability.[18] Among these requirements, the chemical stability of APEs has been the toughest challenge. Many efforts have been devoted to improving the stability of the organic cation, quaternary ammonia (QA), in APEs,[19−22] but, recently, degradation of the polymer backbone in an alkaline environment was identified to be a severe issue.[23,24] For instance, although polysulfone (PSF) is a stable engineering plastic and has been employed widely as the backbone of polyelectrolytes,[25−30] the inertness of PSF was found to be broken upon attachment of cations.[23] How to design APE based on practically stable backbones is now an urgent task.

In the present work, we report our recent progress on developing APEs based on a poly(ether ether ketone) (PEEK) backbone. Although PEEK is thought to be much more stable in an alkaline environment than PSF, high-performance APE based on PEEK has hitherto rarely been seen,[31−33] most probably because of the very low solubility of PEEK.[31,33] Our strategy is first to make PEEK soluble in 1-methylimidazole through a sulfonation process and then to functionalize the resulting sulfonated PEEK (SPEEK) with QA using the procedure employed for PSF-based APEs.

Our approach is different from the previously reported attempts on making PEEK-based APEs.[31,33] We deliberately keep both the sulfonic acid (SA) and quaternary ammonia (QA) groups in the polyelectrolyte, with QA being the major functional group, such that SD % of the membrane can be

Received: October 2, 2013
Accepted: November 14, 2013
Published: November 14, 2013

dx.doi.org/10.1021/am4043257 | *ACS Appl. Mater. Interfaces* 2013, 5, 13405−13411

significantly reduced through an ionic cross-linking between SA and QA. The resulting ion-cross-linking quaternary ammonium PEEK membrane (*x*QAPEEK) turns out to be not only superior in ionic conductivity and mechanical strength but also outstanding in chemical stability in strong alkaline solutions.

■ EXPERIMENTAL SECTION

Materials. Poly(ether ether ketone) [PEEK; Victrex PLC (England), 450G], paraformaldehyde (Sinopharm Chemical Reagent Co. Ltd., 95%), trimethylchlorosilane (Shanghai Lingfeng Chemical Reagent Co. Ltd., 98%), stannic chloride (Sinopharm Chemical Reagent Co. Ltd., 99%), methanol (Sinopharm Chemical Reagent Co. Ltd., 99%), sulfuric acid (Sinopharm Chemical Reagent Co. Ltd., 98%), *N*,*N*-dimethylformamide (DMF; Sinopharm Chemical Reagent Co. Ltd., 99%), *N*-methyl-2-pyrrolidone (NMP; Sinopharm Chemical Reagent Co. Ltd., 99%), trimethylamine (Sinopharm Chemical Reagent Co. Ltd., 33% alcohol solution), potassium hydroxide (KOH; Sinopharm Chemical Reagent Co. Ltd., 85%), and hydrochloric acid (HCl; Sinopharm Chemical Reagent Co. Ltd., 37%) were used as received from the companies indicated.

Syntheses. *Sulfonated PEEK (SPEEK).* SPEEK used in this study was synthesized following the procedures reported by Huang et al.[34] Briefly, 10 g of PEEK was dissolved in 190 mL of sulfuric acid at ambient conditions to form a solution, and the reaction proceeded at a temperature of 35 °C. The grafting degree (GD) of the SA group was controlled by the reaction time. The resultant SPEEK was precipitated in deionized ice water and then washed with cold water several times until the filtrate was neutral. Finally, the product was dried in a vacuum oven at 70 °C for 24 h.

Chloromethylation of SPEEK. In a three-necked, round-bottom flask with a mechanical stirrer, 2 g of SPEEK was dissolved in 60 mL of NMP to form a solution. After paraformaldehyde (5.6 g) was added into the solution, trimethylchlorosilane (16.2 mL) and $SnCl_4$ (1.46 mL) were added dropwise. The reaction mixture was stirred at 150 °C for 35 h. The product (CMPEEK) was precipitated in a cold methanol solution of sodium carbonate, washed several times with cold deionized water, and then dried in a vacuum oven for 24 h at 70 °C.

Ion-Cross-Linked Quaternary Ammonium PEEK (xQAPEEK). Dried CMPEEK powders were dissolved in DMF to form a 10 wt % solution, into which trimethylamine was then added, and the resulting solution was stirred for 2 h at 40 °C (GD of QA was determined by the amount of trimethylamine added). The resulting solution was cast onto a clean, flat glass plate, dried in an oven at 65 °C for 20 h, and then further dried in a vacuum oven at 80 °C for 10 h to produce *x*QAPEEK membrane. To replace the Cl^- anion in *x*QAPEEK with OH^-, the *x*QAPEEK membrane was immersed in a 1 mol/L KOH solution for 10 h. This process was repeated four times to ensure complete replacement. Finally, the *x*QAPEEK membrane with the OH^- anion was rinsed repeatedly with deionized water until the pH of the residual water was neutral. Then the membrane was post-treated by immersion in deionized water at 60 °C for 2 h before use.

Measurements. *^1H NMR.* ^1H NMR spectra of SPEEK and CMPEEK were recorded on a Bruker spectrometer at 400 MHz using deuterated dimethyl sulfoxide as the solvent and tetramethylsilane as the internal reference.

Fourier Transform Infrared (FTIR) Spectroscopy. FTIR spectra of membranes were obtained on a Nicolet 6700 FTIR spectrometer with a wavenumber resolution of 4 cm^{-1} and in the range of 400−4000 cm^{-1}.

X-ray Photoelectron Spectroscopy (XPS). XPS measurements were employed for structural characterization of *x*QAPEEK. The measurements were carried out in a Kratos XSAM-800 spectrometer with an Mg Kα radiator. N 1s and S $2p_{3/2}$ signals were collected and analyzed using the software *XPSPeak*.

UV−Vis Spectroscopy. UV−vis measurements were conducted on a Mapada UV-6100PC spectrometer. A clean KOH solution was used as the reference for the detection of degraded APE backbone fragments in a KOH solution.

Ion-Exchange Capacity (IEC). In the cases of SPEEK and CMPEEK, where SA is the anionic functional group, IEC refers to the cation-exchange capacity, while in the case of *x*QAPEEK, where most SA groups have been captured by GA groups, IEC means the anion-exchange capacity. The IEC values of SPEEK, CMPEEK, and *x*QAPEEK were determined by titration. SPEEK (in the H^+ form) or CMPEEK (in the H^+ form) was immersed in a standard KOH solution (0.1 mol/L, 40 mL) for 48 h. The solution was then titrated with a standard HCl solution (0.1 mol/L) to pH = 7. The membrane was washed and immersed in deionized water for 24 h to remove any residual KOH, then dried in a vacuum at 45 °C for 24 h, and weighed to determine the dry mass (in the K^+ form). The IEC of SPEEK or CMPEEK is calculated using eq 1:

$$\mathrm{IEC} = \frac{n_{\mathrm{i(OH^-)}} - n_{\mathrm{f(OH^-)}}}{m_{\mathrm{dry(K^+)}}} \tag{1}$$

where $n_{\mathrm{i(OH^-)}}$ is the initial amount of hydroxide in the KOH solution, $n_{\mathrm{f(OH^-)}}$ is the final amount of hydroxide in the KOH solution determined by titration, and $m_{\mathrm{dry(K^+)}}$ is the mass of the dry membrane in the K^+ form.

An *x*QAPEEK membrane (in the OH^- form) was immersed in a standard HCl solution (0.1 mol/L, 40 mL) for 48 h. The solution was then titrated with a standard solution of KOH (0.1 mol/L) to pH = 7. The membrane was washed and immersed in deionized water for 24 h to remove any residual HCl, and then dried in vacuum at 45 °C for 24 h and weighed to determine the dry mass (in Cl^- form). The IEC of the membrane is calculated using eq 2:

$$IEC = \frac{n_{\mathrm{i(H^+)}} - n_{\mathrm{f(H^+)}}}{m_{\mathrm{dry(Cl^-)}}} \tag{2}$$

where $n_{\mathrm{i(H^+)}}$ is the initial amount of proton in the HCl solution, $n_{\mathrm{f(H^+)}}$ is the final amount of proton in the HCl solution determined by titration, and dry(Cl^-) is the mass of the dry membrane in the Cl^- form.

Ionic Conductivity. To measure the ionic conductivity of *x*QAPEEK, fully hydrated membranes in the OH^- form were assembled into a fuel-cell device with carbon electrodes. Fully humidified N_2 was fed during measurements to exclude the influence of CO_2. The OH^- conductivity of fully hydrated membranes with different IEC values was measured by two-probe electrochemical impedance spectroscopy using an alternating-current impedance analyzer (IviumStat, The Netherlands) with the frequency ranging from 1 Hz to 1 MHz and an oscillating amplitude of 10 mV. The ionic conductivity was calculated using eq 3:

$$\sigma = \frac{l}{R_{\mathrm{mem}}A} \tag{3}$$

where l is the membrane thickness in centimeters, A is the electrode area in centimeters squared, and R_{mem} is the high-frequency resistance in ohms.

SD %. In order to obtain SD % of APE membranes, the dimensions of the dry *x*QAPEEK membranes (in the Cl^- form, denoted as $x_{\mathrm{dry(Cl)}}$) were recorded first. Then the fully hydrated *x*QAPEEK membranes (in the OH^- form, denoted as $x_{\mathrm{hyd(OH)}}$) that were post-treated with water at 60 °C were measured. Accordingly, SD % was calculated via eq 4:

$$\mathrm{SD}\ \% = \frac{x_{\mathrm{hyd(OH)}} - x_{\mathrm{dry(Cl)}}}{x_{\mathrm{dry(Cl)}}} \times 100 \tag{4}$$

GD. GD of the membranes was defined as the percentage of functionalized units to the total units of the polymer backbone. GD of the SA group in SPEEK and CMPEEK and the benzyl chloride group in CMPEEK can be determined by characterizations such as ^1H NMR and IEC titration.

Mechanical Strength. A tensile tester (CMT6503, Shengzhen SANS TestMachine Co. Ltd., China) was employed to analyze the tensile stress−strain behavior of fully hydrated *x*QAPEEK in the OH^- form at room temperature. A constant crosshead speed of 5 mm/min was used for samples of 1 cm width and 3 cm length.

Thermogravimetric Analysis (TGA). TGA was performed on a TGA Q500 (TA Instruments) using samples (5 mg) placed in an Al_2O_3 crucible. The samples were heated from 30 to 600 °C at a rate of 5 °C/min under flowing air (40 mL/min).

Stability Test. A piece of the APE membrane (50 ± 3 μm thickness) was immersed in a 1 mol/L KOH solution and maintained at 80 °C for 30 days. During the stability test, the KOH solution was sampled periodically for UV−vis detection. The absorbance at around 270 nm in the UV−vis spectra (vide infra) was due to the phenyl group on the degraded fragment of APE. After the 30-day test, the APE membrane was rinsed repeatedly with deionized water until the pH of residual water was neutral, and the dried membrane was then weighed. The weight loss of the tested membrane was normalized by the signal strength of the final UV−vis spectrum, and then every UV−vis signal recorded during the test can be converted to a value of weight loss, resulting in the stability curve (weight loss against time). Meanwhile, the IEC and ionic conductivity of APEs were tested before and after the test to evaluate the stability of the QA group.

■ RESULTS AND DISCUSSION

Synthesis of *x*QAPEEK. The synthetic procedure of *x*QAPEEK is schematically illustrated in Figure 1. The first step is sulfonation of the PEEK backbone. The success of attachment of the SA group can be identified from emergence of the peak at 7.5 ppm in the ^{1}H NMR spectrum of SPEEK (Figure 2a), and GD of the SA group can also be calculated based on the strength ratio of such a peak to all hydrogen signals.[35]

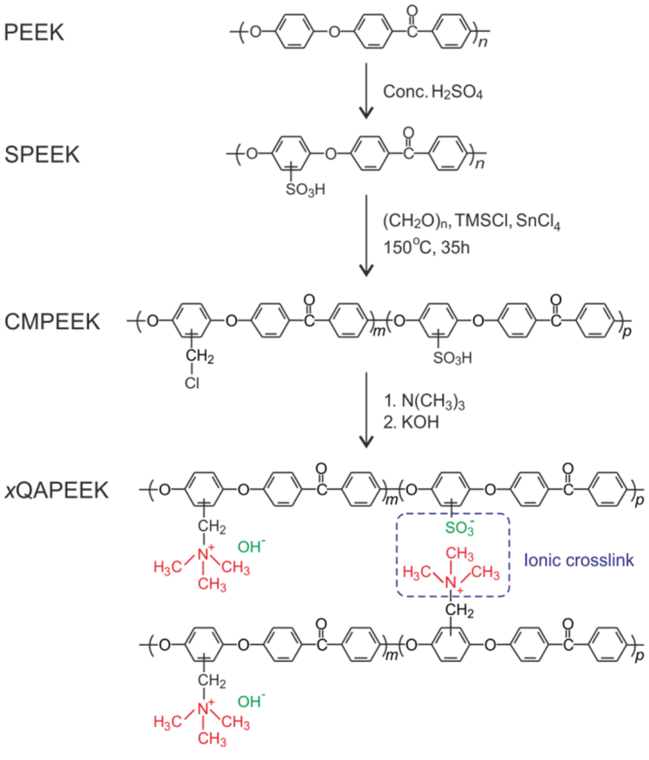


Figure 1. Schematic illustration of the synthesis of *x*QAPEEK.

Unlike pristine PEEK, SPEEK can be dissolved in NMP. During the chloromethylation process, part of the SA groups are substituted by the chloromethyl (CM) group,[31] and more CM groups are directly attached to the aryl ring of PEEK, which have been activated by a Lewis acid catalyst. GD of the CM group can also be determined by the characteristic ^{1}H NMR signal (Figure 2b), and the amount of remaining SA groups after chloromethylation can be determined by titration. Different from previous attempts on PEEK-based APE, where the SA group in SPEEK was completely removed or replaced by the CM group,[31,33] we deliberately increase GD of the SA group and maintain a relatively low temperature for the chloromethylation reaction to keep a sufficient residual amount of SA groups in CMPEEK.

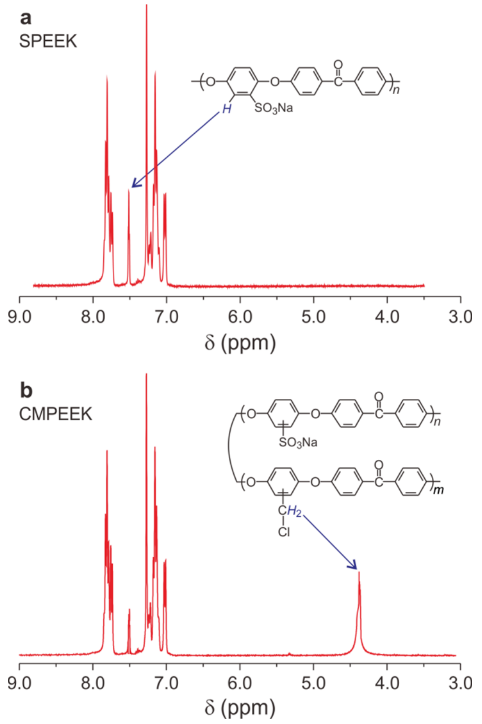


Figure 2. ^{1}H NMR spectra of SPEEK (a) and CMPEEK (b).

The final step of the *x*QAPEEK synthesis is to replace the CM group in CMPEEK with a QA group (Figure 1). FTIR spectra were used to characterize the chemical structure of *x*QAPEEK (Figure 3). In comparison to the FTIR spectrum of SPEEK, the emergence of a C−H bond deformation vibration in the QA group at 1451 cm^{-1} and the asymmetric and symmetric stretch vibrations of the whole QA group at 951 and 750 cm^{-1} have confirmed the success in attaching QA groups. XPS was also employed to analyze the SA and QA groups in the membrane. As shown in Figure 4, the N 1s (binding energy BE = 401.7 eV) and S 2p (BE = 168.6 eV) signals are well

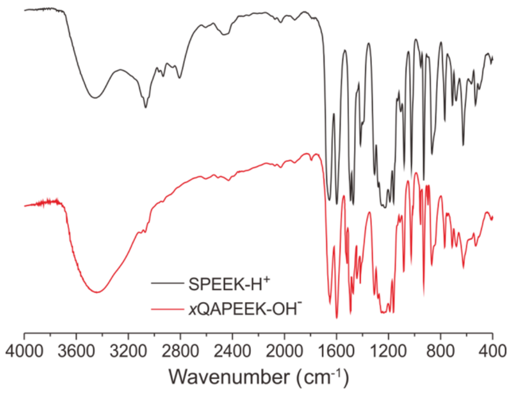


Figure 3. FTIR spectra of the SPEEK membrane with H$^+$ as a free cation and the *x*QAPEEK membrane with OH$^-$ as a free anion.

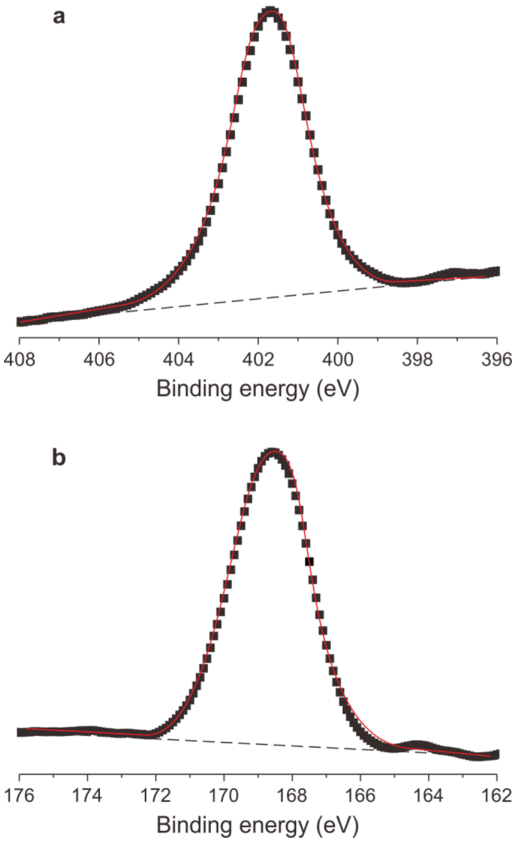


Figure 4. XPS spectra of N 1s (a) and S $2p_{3/2}$ (b) in *x*QAPEEK.

collected, which correspond to the nitrogen and sulfur elements in the QA and SA groups, respectively.[36]

Ionic Cross-Link and Relevant Structural Parameters. In our study, the amount of QA groups is greater than that of SA groups, such that the resulting *x*QAPEEK is still alkaline in nature (after replacement of the anion to OH^-). After casting, the ionic cross-links will form between the SA and QA groups,[37] and the *x*QAPEEK membrane becomes antiswelling and cannot be dissolved in conventional solvents. The transport number of the *x*QAPEEK membrane was found to be 0.88 for t_-, close to the value for typical APE (0.93 for QAPS, for example). This is understandable because most of the SA groups have been captured by the QA groups, and the *x*QAPEEK membrane behaves mainly as an anion-exchange membrane.

There are two important structural parameters that determine the properties of the *x*QAPEEK membrane. The first parameter is the initial GD of the SA group in SPEEK, which determines not only the solubility of SPEEK in NMP[34] but also the cross-linking degree (CD) of the final *x*QAPEEK. Usually, the higher the GD of the SA group in SPEEK, the more the residual SA groups in *x*QAPEEK and the greater the CD of the *x*QAPEEK membrane (Table 1). The second important structural parameter is the GD of the QA group in *x*QAPEEK, which determines the final IEC and ionic conductivity. Because the QA group is excessive in comparison to the SA group, the CD of the *x*QAPEEK membrane is mainly determined by the amount of residual SA groups. Therefore, the CD of an *x*QAPEEK membrane can be defined as the GD of residual SA groups in CMPEEK.[38] For instance, CD = 25.3% means 25.3% of QA groups have been consumed by the SA group to form ionic cross-linking, and the remaining QA groups are free and contribute to ion conduction.

Table 1. Properties of SPEEK, CMPEEK, and *x*QAPEEK Membranes

SPEEK		CMPEEK		*x*QAPEEK
IEC (H^+, mmol/g)[a]	GD (SAH, %)[b]	IEC (H^+, mmol/g)[a]	GD (MeCl, %)[b]	CD (%)[c]
1.18	40.1	0.46	84.7	16.5
1.64	58.1	0.70	75.6	25.3
2.17	66.5	0.90	67.9	32.7

[a] The IEC (H^+, mmol/g) values of SPEEK and CMPEEK were determined by titration. [b] GD values of the $-SO_3H$ and $-CH_2Cl$ groups were calculated from ^1H NMR. [c] CD was calculated based on the amount of $-SO_3H$ groups in SCMPEEK.

Ionic Conductivity and Dimensional Stability of the *x*QAPEEK Membrane. The ionic conductivity and dimensional stability are two important, but usually contradictory, properties of APE membranes. To have high ionic conductivity, the APE membrane should possess sufficient IEC, whereas high IEC always leads to excessive water uptake and membrane swelling. In the case of *x*QAPEEK, this problem can be addressed, to a large extent, by ionic cross-linking. As demonstrated in Figure 5, under the same CD, both the ionic conductivity and SD % increase with the IEC, but with increasing CD, SD % can be remarkably suppressed (Figure 5b), although the ionic conductivity is also reduced to some extent (Figure 5a).[39] Therefore, by optimization of the IEC and CD, the ionic conductivity of the *x*QAPEEK membrane at

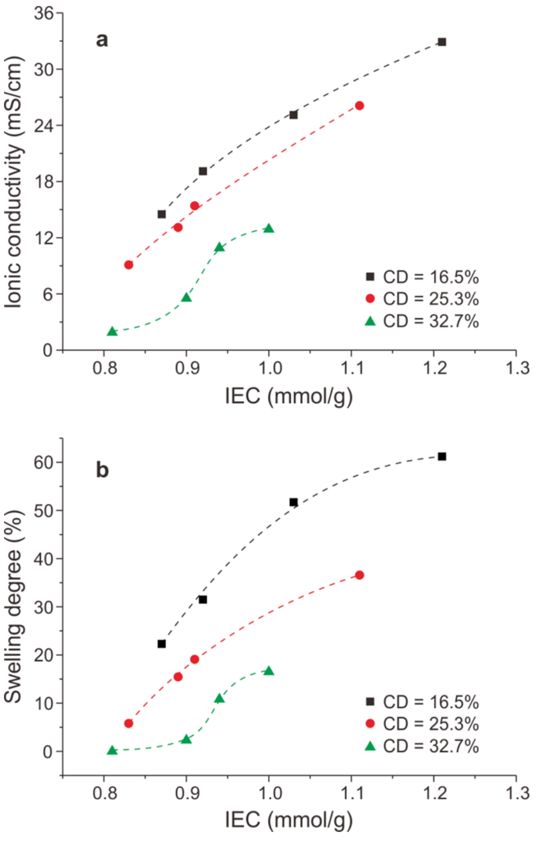


Figure 5. IEC-dependent ionic conductivity (a) and SD % (b) of the *x*QAPEEK membrane with different CD values.

room temperature can be higher than 10 mS/cm, with SD % lower than 20%.

The effect of the ionic cross-linking becomes advantageous at elevated temperatures. As shown in Figure 6, with increasing temperature, the ionic conductivity of the *x*QAPEEK membrane increases as expected (Figure 6a), but SD % remains unchanged (Figure 6b). Such a special feature is very unusual and has not been seen for any APE thus far reported in the literature; it can only be ascribed to the ionic cross-linking in the *x*QAPEEK membrane, which turns out to be very strong and does not break even in hot water. This advantage makes *x*QAPEEK very suitable for fuel-cell applications.

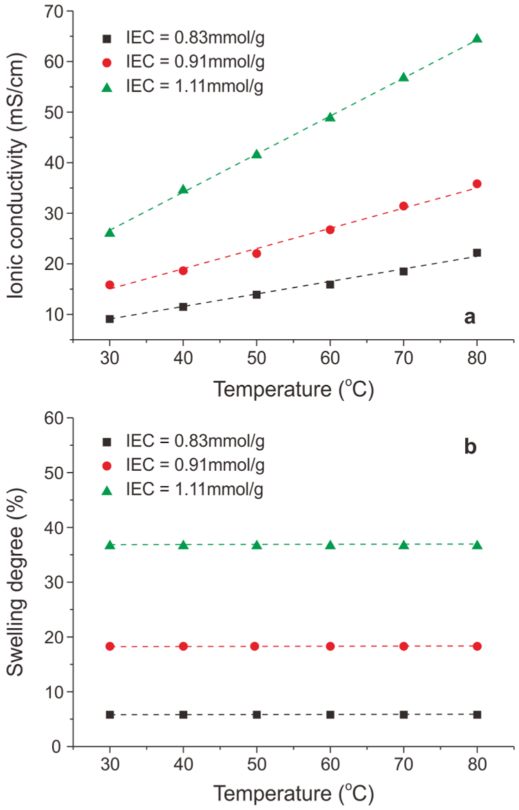


Figure 6. Temperature-dependent ionic conductivity (a) and SD % (b) of *x*QAPEEK (CD = 25.3%) with different IEC values.

Chemical Stability of *x*QAPEEK. As mentioned in the Introduction, the chemical stability of APEs is highly challenging. Even though the pristine polymer backbone is stable in an alkaline environment, it would degrade upon attachment of the cationic functional groups. The motivation of this work is to see if the PEEK backbone, after functionalization, is more stable than the PSF backbone, which has been widely employed in the literature.[23−30] We start the stability test of *x*QAPEEK by looking at the thermal stability using TGA. Figure 7 shows the differential thermogravimetric (DTG) results of SPEEK and *x*QAPEEK. Both SPEEK and *x*QAPEEK contain SA groups, which degrade at 370 °C, while the QA group only exists in *x*QAPEEK, which starts to degrade at 215 °C. Such a degradation temperature of the QA group is much higher than that of benzyltrimethylammonium in quaternary ammonia polysulfone (QAPS).[29]

Testing an APE membrane in an alkaline solution at elevated temperature is currently a standard protocol for chemical stability examination. In the present work, two *x*QAPEEK membranes with a moderate CD (25.3%) were immersed in a 1 mol/L KOH solution at 80 °C for 30 days. The IEC and ionic conductivity of the membranes before and after the test were examined to see how many QA groups have been lost during this test. As shown in Table 2, the IEC of these two membranes only decreased slightly by 1% to 2%. Meanwhile, the ionic conductivity of the membranes remained almost unchanged, suggesting that, subject to nucleophilic substitution, elimination, or rearrangement reactions, the QA group in *x*QAPEEK membranes is outstandingly stable.

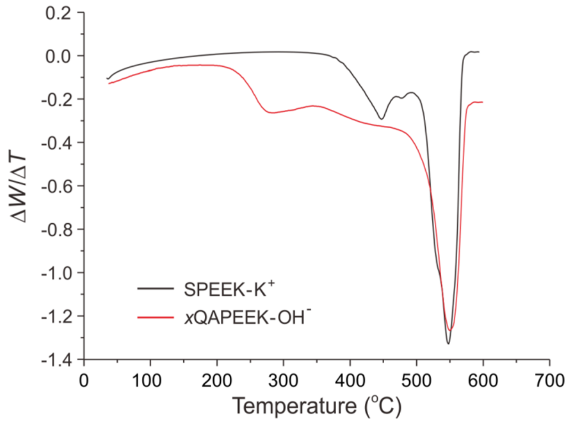


Figure 7. DTG results of SPEEK (IEC = 1.64 mmol/g, with a K^+ cation) and *x*QAPEEK (CD = 25.3%, IEC = 0.91 mmol/g, with a OH^- anion).

To detect any degradation in the polymer backbone during the above test, UV−vis spectroscopy was employed to capture signals of the degraded backbone fragments in a KOH solution (Figure 8a), which was then calibrated and converted to a percentage of weight loss. Figure 8b displays the weight loss of *x*QAPEEK as a function of time, in comparison to the results of pristine PEEK, PSF, and QAPS. Clearly, pristine PEEK pellets are extremely stable in hot alkaline solutions, and pristine PSF only degrades slightly under the same conditions. Upon attachment of the cationic functional groups, QAPS lost its weight gradually and less than 60 wt % remained after the 30-day test period, whereas degradation of the *x*QAPEEK backbone turned out to be much slower; only about 6 wt % weight loss was detected after 30 days of testing. The degradation of *x*QAPEEK in a hot alkaline solution is actually as slow as that of pristine PSF. In addition, the mechanical strength of *x*QAPEEK remained at a high level after the test in a hot alkaline solution for 30 days (Table 2). Unambiguously, APE based on the PEEK backbone is much superior to that based on PSF in terms of chemical stability and thus more suitable for fuel-cell applications.

■ CONCLUSIONS

APEs based on the PEEK backbone have been successfully synthesized, in which QA is the major functional group and SA is the minor one. The interaction between QA and the SA results in an ion-cross-linking network in the resulting *x*QAPEEK membrane, which significantly strengthens the mechanical strength and reduces SD % of the membrane. An outstanding feature is that SD % of the *x*QAPEEK membrane does not change with temperature.

The chemical stability is the main theme of this paper. Benefiting from a highly stable PEEK backbone, the *x*QAPEEK membrane exhibits excellent stability in a 1 mol/L KOH

Table 2. Properties[a] of *x*QAPEEK Membranes (CD = 25.3%) Measured before and after the Stability Test in a 1 mol/L KOH Solution at 80 °C for 30 days

	IEC_{before} (mmol/g)	IEC_{after} (mmol/g)	IC_{before} at 60 °C (mS/cm)	IC_{after} at 60 °C (mS/cm)	MS_{before} (MPa)[b]	MS_{after} (MPa)[b]	EB_{before} (%)[b]	EB_{after} (%)[b]
*x*QAPEEK-1	0.83	0.82	15.9	16.1	30.8	27.15	138.95	115.69
*x*QAPEEK-2	0.91	0.89	26.9	26.4	18.38	16.23	71.49	65.73

[a]The abbreviations IEC, IC, MS, and EB stand for the anion-exchange capacity, ionic conductivity, mechanical strength, and elongation at break, respectively. [b]The mechanical properties were measured at room temperature.

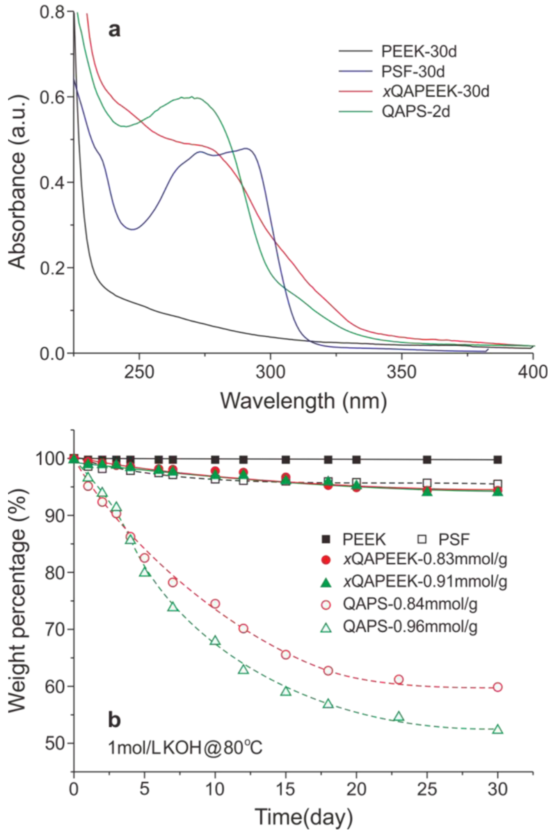


Figure 8. Stability test of *x*QAPEEK in a 1 mol/L KOH solution at 80 °C, in comparison to QAPS. Pristine PEEK and PSF are also tested for reference. The weight change of the polymers (b) was monitored by the UV−vis signal of the KOH solution containing degraded polymer fragments (a).

solution at 80 °C. After 30 days of testing, the weight loss of the *x*QAPEEK membrane is only 6 wt %, in comparison to the great degradation of QAPS (more than 40 wt %) under the same conditions. The present work thus casts a new light on the development of highly stable APEs.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jpan@whu.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was financially supported by the National Basic Research Program (Grants 2012CB215503 and 2012CB932800), the National Science Foundation of China (Grants 20933004, 21125312, 21303124, and 21303123), the National Hi-Tech R&D Program (Grant 2011AA050705), the Doctoral Fund of Ministry of Education of China (Grant 20110141130002), and the Program for Changjiang Scholars and Innovative Research Team in University (Grant IRT1030).

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