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In situ synthesis of star copolymers consisting of a polyhedral oligomeric silsesquioxane core and poly(2,5-benzimidazole) arms for high-temperature proton exchange membrane fuel cells

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**In-situ synthesis of star copolymers consisting of a POSS
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***In-situ* synthesis of star copolymers consisting of a POSS core and poly(2,5-benzimidazole) arms for high temperature PEMFCs**

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Abstract: Star copolymers with good film-forming and mechanical properties were *in-situ* synthesized for fabricating proton exchange membranes. The monomers of 3,4-diaminobenzoic acid were first grafted onto glycidyl-polyhedral oligomeric silsesquioxane (G-POSS) cores and then propagated to the poly(2,5-benzimidazole) (ABPBI) chains. The introduction of the star copolymer improves the movement of the ABPBI polymer chains, resulting in a lower internal viscosity and larger free volume that favor increased membrane flatness and absorptilities of water and phosphoric acid molecules, respectively. It was found that the star copolymers with 1.0 wt% of incorporated POSS (ABPBI-1.0POSS) had the best balance of the acid retentivity and film-forming property as well as mechanical properties that are desirable for proton exchange membranes without PA loss operating at high temperatures. The enhanced cell performance characteristics obtained using the ABPBI-1.0POSS-based membranes indicate that star copolymers are promising materials for use in high temperature proton exchange membrane fuel cells.

Graphical abstract

Keywords: Proton exchange membrane; Poly(2,5-benzimidazole); Polyhedral oligomeric silsesquioxane; Star copolymer; Film-forming

1. Introduction

Due to their wide range of potential applications in electric vehicles, combined heat and power systems, and auxiliary power units, high temperature-proton exchange membrane fuel cells (HT-PEMFCs) (100–200 °C) have attracted intense research attention [1–4]. Raising the working temperature of PEMFCs to above 100 °C is highly favorable compared to their operation at low temperatures (i.e. below 100 °C) due to advantages such as high catalyst tolerance to carbon monoxide, simple heat and water management, and consequently high fuel cell efficiency [5–7]. Phosphoric acid-doped polybenzimidazole (PA-PBI) membrane is still the most widely studied proton exchange membrane (PEM) in the high temperature range of 120–180 °C [7–10]. Among PBI-type polymers (PBIs), ABPBI has been shown to be a promising material due to its unique combination of low cost, single-step synthesis process, and high acid absorptivity [11]. Unfortunately, PBIs-based cells are strictly limited to operation in the 120–180 °C range only in order to avoid free PA leaching in hydrous atmosphere at the temperatures below the lower limit of 120 °C and to avoid degradation above the upper

limit of 180 °C [12, 13]. Furthermore, PA-PBIs-based membranes often show a trade-off relationship between the PA absorbance on the one hand and film-forming and mechanical stability on the other hand [2]. To design PBI-based PEMs with excellent electrochemical performance and stability, the construction of the membrane microstructure and proton transfer channels are critical [14]. Thus, one of the greatest challenges for the commercialization and effective operation of PBI in HT-PEM fuel cells is to achieve high proton conductivity, good film-forming ability and good mechanical stability while avoiding the disadvantages of free PA.

Much effort has been exerted for the development of PBIs-based PEMs for high-temperature applications. The developed approaches [5, 11, 15-17] include: 1) linking PA through either crosslinked polymer matrices or basic; 2) impregnation of hygroscopic inorganic fillers to retain PA, and 3) introduction of immobilized proton carriers to partially or fully replace PA. Among these approaches, the use of inorganic-nanoparticle-embedded composite membranes is the most favorable due to the simple synthesis and low cost of these membranes. These nanocomposite membranes often show the combined advantages of good mechanical strength, high water and/or acid retention capabilities, and good proton conductivity at elevated temperatures and reduced relative humidity (RH) [1, 18]. However, the amount of embedded inorganic fillers has been limited due to their strong tendency to aggregation that leads to the deterioration of the mechanical and film-forming properties [19].

Star-shaped polymers consisting of a multifunctional core from which multiple polymer chains (multiarms) radiate have unique properties compared to their linear

analogues with identical molecular weight and monomer composition [20]. Generally, these star-shaped copolymer have lower internal viscosities than their linear analogues with the same molecular weight, with the internal viscosity dependent on the molecular weight of the arms [21]. Such lower internal viscosity is beneficial for improving the film-forming property. Due to their larger free volume, PEMs with branched polymers show a marked improvement in proton conductivity compared to the corresponding linear polymers. Because their unique three-dimensional networks with enlarged free volume can maintain more water and/or acid, branched polymers have been applied in low-temperature [22-24] and high-temperature PEMs [25, 26].

Polyhedral oligomeric silsesquioxane (POSS) possesses an inorganic core with an Si–O framework that can form links with organic groups or reactive groups at its eight vertices [27]. Due to the ease of controlled modification and rational design of the organofunctional groups on POSS, the water retention property of the material can be enhanced by chemically modifying the branch containing the hydrophilic functional group. Meanwhile, groups with specific functionalities can be grafted to POSS so that on the one hand, protons can be transferred independent of water when these functional groups act as proton receptors and donors [28], while on the other hand, the formation of crosslinked structures enhances the mechanical stability and dimensional stability of the composite membranes [26, 29-32].

In this study, organic-inorganic hybrid composite membranes with star copolymers of ABPBI-POSS were prepared to achieve a balance amongst the PA uptake, film-forming property and mechanical stability. Herein, the star copolymer was

obtained in an efficient *in-situ* synthesis carried out using the “arm-out” method as shown in **Scheme 1**. During the synthesis process, an epoxy ring-opening reaction occurred between Glycidyl-POSS and the 3,4-diaminobenzoic acid (DABA) monomer at a low temperature (approximately 80 °C), and then the grafted DABA continuously propagated into the ABPBI polymer chains at the elevated temperatures (up to 150 °C) to form star copolymers with the typical structure of a POSS as the core and eight ABPBI chains as the arms. The inorganic POSS cores improve the mechanical properties, while the star-shaped copolymers with adjustable arm lengths are expected to reduce the intrinsic viscosity which is desirable for preparing highly flat membranes [33]. Due to the benefits provided by the introduction of POSS, the ABPBI-POSS composite membranes treated by boiling in hot water in order to remove free PA as much as possible show enhanced water uptake, PA retentivity, and proton conductivity. We believe that this study provides a feasible method for the fabrication of a new class of PA-PBIs-based PEMs with a good balance among the PA uptake, film-forming and mechanical properties for use in HT-PEMFCs.

Scheme 1. Schematic illustration of the synthesis procedure.

2. Experimental

Materials: Glycidyl-POSS (G-POSS, 99%) was purchased from Hybrid Plastics (USA). Monomer 3,4-Diaminobenzoic acid (DABA, 98.0%) was purchased from Beijing J&K Technology (China). Methane sulfonic acid (MSA, 99.0%) was purchased from the Aladdin Industrial (China). P_2O_5 (98.0%), PA (85.0%), NaOH (85.0%), $CHCl_3$ (analytical reagent), DMSO (analytical purity), $NaHCO_3$ (analytical reagent), C_2H_5OH (99.7%), HCl (36.0-38.0%) and H_2SO_4 (95.0-98.0%) were obtained from Sinopharm Chemical Reagent (China). All of the chemicals were used as received without further purification.

Synthesis of star copolymer: DABA (1.58 g) and a certain mass fraction (0.5%, 1%, 1.5%, 2%) of POSS were dissolved in MSA and ultrasonicated for 1.5 h. Then, P_2O_5 (10 g) was added to the mixture. The reaction was carried out under nitrogen atmosphere, and the temperature was first increased to 80 °C and held for 0.5 h, and then increased to 150 °C and held for 2.5 h. The product was boiled in a beaker with a 10% NaOH solution at 100 °C for 2 h to remove the remaining MSA, and then boiled in deionized water (D.I. water) until NaOH was completely removed. Finally, the filamentous product was dried in a vacuum oven at 110 °C for 24 h to obtain the ABPBI-POSS hybrid composites. The reactions in the synthesis of ABPBI-POSS are illustrated in **Scheme 1**.

Preparation and characterization of Membranes: Membrane preparation and the characterizations of morphology, thermal stability, intrinsic viscosity, mechanical properties, water uptakes (WUs), PA DLs, oxidative stability and proton conductivities followed the procedures typically used for ABPBI membrane casting [26] as described

in detail in the **ESI**.

Single cell performance: The catalyst 40% Pt/C (Johnson Matthey, UK) was ultrasonically dispersed in an ethanol solution to prepare a catalyst slurry, and then sprayed onto the gas diffusion layer that consisted of Vulcan XC-72 carbon PTFE (20 wt%) coated onto a carbon paper (TGPH060, Toray, Japan) to prepare the gas diffusion electrode (GDE) [34], with the Pt loading controlled to be 0.5 mg/cm². The GDEs and the membrane were assembled by 2 min of hot-pressing at 0.2 MPa and 130 °C to obtain the membrane electrode assembly (MEA). The polarization curve of the single cell was tested using a homemade fuel cell test system, and the inlet pressure on both sides of the cell was 0.8 bar.

3. Results and discussion

Chemical structure analysis: The star copolymers of ABPBI-POSS were prepared by in-situ synthesis in a two-step heating processes that raised the temperature from room temperature to 150 °C. In this study, the successful execution of the epoxy ring-opening reaction between the epoxy groups in G-POSS and the amino groups in monomer DABA to form DABA grafted POSS (POSS-DABA) was easily confirmed by the reaction of the carboxyl protective group as illustrated in the **ESI**. The FTIR and ¹H NMR spectra of the product synthesized using the salt formation of DABA at 80 °C are shown in **Figs. S1** and **S2**, respectively. As shown in **Fig. S1**, characteristic peaks were observed for the Si-O cage structure at 1092 cm⁻¹ and for the telescopic vibration of the benzene ring skeleton at 1631 cm⁻¹ from DABA [26], confirming the presence of the POSS and DABA components in the composite materials. Meanwhile, the

characteristic peak of the epoxy group in G-POSS at 904 cm^{-1} disappeared; this was attributed to the generation of the -NH-O- group, indicating the grafting of the DABA monomer onto G-POSS (POSS-DABA) *via* the epoxy ring-opening reaction. The ^1H NMR curve (**Fig. S2**) further confirms the chemical structure of POSS-DABA. The peaks at 8.31 ppm, 7.20 ppm, and 6.63 ppm are attributed to the three hydrogen in the benzene ring and 5.33 ppm to the amino group [35], while the peak at 2.01 ppm attributed to the secondary ammonia [33, 36] and 0.86 ppm to the hydroxyl. At the same time, the peak at 3.21 ppm corresponding to the proton on the epoxy group [36, 37] does not appear in the spectrum of POSS-DABA. These indicate the occurrence of the epoxy ring-opening reaction between the epoxy groups in G-POSS and the amino groups in monomer DABA.

Fig. 1 FTIR (A), ^1H NMR (B) and XRD (C) spectra of the ABPBI-POSS copolymer.

With the reaction temperature raised to 150 °C, the DABA monomer grafted onto POSS-DABA was expected to continuously propagate into the ABPBI polymer chains and ultimately form star copolymers (ABPBI-POSS) with the typical structure of POSS as the core and eight ABPBI chains as the arms. The chemical structure of the star copolymer was confirmed by FTIR spectroscopy as shown in **Fig. 1A**. The FTIR spectrum of the ABPBI-POSS synthetic product shows the typical characteristics of the ABPBI polymer chain, in particular the benzimidazole group stretching bands at 1631 cm^{-1} and 1570 cm^{-1} [26], and the characteristic stretching modes of the Si–O in the POSS core at 1092 cm^{-1} and the grafted $-\text{CH}_2-$ groups at 2918 cm^{-1} and 2850 cm^{-1} . The epoxy group peak at 904 cm^{-1} disappeared and a broad peak attributed to the $-\text{OH}$ stretching mode appeared at 3425 cm^{-1} , indicating that ABPBI polymer chains were successfully grafted into POSS through the epoxy ring opening reaction to form the ABPBI-POSS copolymer.

In **Fig. 1B**, the signals for the three protons in benzimidazole are observed at 8.11 (c-H), 8.19 (b-H), 8.47 (a-H) [38], and the weak peak at 12.21 ppm corresponds to H of both the $-\text{COOH}$ end group and benzene in the ABPBI chain [39]. It is clearly observed that the peak intensity at 12.21 ppm increases with the increased POSS content, implying that a greater amount of the carboxyl groups was retained for the composites with greater POSS content. As the POSS content increases, the number of the repeating units decreases and the arms or grafted ABPBI chains become shorter. Although the “arm-out” method has the limitation that the arm length of the synthesized

stars cannot be characterized directly, indirect methods such as intrinsic viscosity measurements can be employed to evaluate the characteristics of star copolymers.

The ABPBI polymer has a semi-crystalline structure with the characteristic stacking of ABPBI chains that displays a broad peak at 26.55° in agreement with the previously obtained results [40]. As shown in **Fig. 1C**, both the ABPBI membrane and ABPBI-POSS composite membranes display this characteristic peak indicating the existence of semi-crystalline ABPBI chains. It is also found that the peak intensities of the composite membranes are lower than that of ABPBI membrane and first decreased with the POSS content increasing to 1.5 wt% and then increased with the POSS content increasing to 2.0 wt%. It can be explained that the introduction of the ABPBI-POSS star copolymer must break the ABPBI chain stacking, resulting in the reduction of the peak intensity, while the excessive amount of POSS is responsible for the increasing peak intensity in the ABPBI-2.0POSS sample due to agglomeration.

Film-forming property analysis: The film-forming properties of the membranes were evaluated by intrinsic viscosity measurements and morphology characterization. As observed in **Fig. 2a**, the intrinsic viscosity decreased with increased POSS content. Based on the analysis of ^1H -NMR spectra presented in **Fig. 1B**, this effect is attributed to the ABPBI arms in the star-branched structure of ABPBI-POSS and ABPBI polymer chains becoming shorter, leading to the reduced intermolecular entanglement. Thus, intrinsic viscosity can be used as a measure of the ABPBI arm length changes.

Fig. 2 (a) Intrinsic viscosity; (b-f) SEM images of ABPBI and ABPBI-POSS membranes.

Fig. 3 Evaluation of the surface morphology of the ABPBI membrane (A) and ABPBI-POSS (B) observed with an optical microscope (Keyence VHX-5000).

Fig. 2b-f and **Fig. 3** also show the surface topographies of the ABPBI and ABPBI-POSS membranes. The ABPBI membrane displays an uneven surface with dimples with the lengths of tens of μm (**Fig. 2b**) and the depths of up to 9.17 μm (**Fig. 3A**). It is important to mention that as shown in **Fig. S3**, the ABPBI membrane that did not undergo the acid removal procedure (i.e. before boiling in NaOH and rinsing with water) clearly shows the residual MSA left in the dimples, indicating that these dimples should be attributed to the uneven evaporation of the MSA solvent.

Compared to the ABPBI membrane, the ABPBI-POSS membranes show relatively uniform surfaces that first become more flat as the POSS content increased

from 0.5 wt% to 1.5 wt% (**Fig. 2c-e** and **Fig. 3B**), and then become more rough when the POSS content is further increased to 2.0 wt% (**Fig. 2f**). It is known that the ABPBI polymer has a quasi-crystalline form due to the stacking of the ABPBI chains with a d spacing between the two parallel benzimidazole chains of 3.3 Å [41]. This quasi-crystalline structure makes it difficult for the MSA solvent to escape when the solution casting method is used to form an ABPBI membrane [40]. The destruction of the ABPBI chains stacking by the star copolymer improved the movement of ABPBI chains, resulting in the greatly enhanced film-forming properties. As the POSS content is increased further, the POSS particles begin to agglomerate in the ABPBI-2.0POSS sample, giving rise to a rough topology. The surface morphologies of the ABPBI and ABPBI-POSS membranes were also investigated by AFM. As shown in **Fig. S4**, compared to the relatively flat surface of the ABPBI-POSS membranes, the ABPBI membrane shows a clear pit that is ascribed to the uneven MSA evaporation. Considering the need for a balance between the film-forming and mechanical properties, the ABPBI-1.0POSS sample was considered to have the optimal composition for PEM fabrication.

Thermal stability, mechanical properties, water and phosphoric acid absorbilities, volume swelling rate and oxidative stability: The thermal stabilities of membranes were measured with the results shown in **Fig. S5**. The thermal weight loss before 300 °C is mainly due to the volatilization of the bound water in the polymer and the elimination of low molecular weight polymer [26]. The heavier weight loss before 300 °C of the ABPBI-0.5POSS and ABPBI-1.0POSS samples compared to that of ABPBI indicates

they maintain more bound water [27] due to the effect of the star copolymer, and the composite membranes still maintain a good thermal stability that fully meets the operating temperature requirements of HT-PEMFC.

Fig. 4 (a) Stress-strain curves of the ABPBI and ABPBI-POSS; (b) Water uptake (WU) under 98% RH 50 °C and phosphoric acid (PA) doping level (DL) under 70% PA solution of the ABPBI and ABPBI-POSS membranes; (c) Swelling ratio after phosphoric acid doping (the ABPBI-2.0POSS sample dissolved in the PA solution); (d) Oxidative stability of the ABPBI and ABPBI-POSS membranes in Fenton's reagent at 70 °C.

Fig. 4a and **Table S1** present the mechanical properties of the ABPBI and ABPBI-POSS membranes. With increasing POSS content, the tensile strength of the composite membranes first increased and then decreased. The Young's modulus values of the

ABPBI-0.5POSS and ABPBI-1.0POSS membranes are greatly higher than that of the ABPBI membrane, while the Young's modulus decreased strongly upon the addition of more than 1.0 wt% of POSS. For the content of no more than 1.0 wt%, the well-dispersed POSS in the ABPBI-POSS membranes improves the mechanical properties; with the content exceeding 1.0 wt%, on the one hand, the star copolymer with shorter arms make the movement of the molecular segment more free leading to the decreased mechanical stability [42], on the other hand, the aggregation of POSS in the ABPBI-2.0POSS sample leads to a negative effect on the mechanical properties by generating discontinuities in the polymer phase.

For the effective operation of PA-PBI in HT-PEM fuel cells, it is necessary to achieve high proton conductivity while avoiding the disadvantages of free PA. Therefore, the PA-doped membranes were boiled in hot water to remove the free PA as much as possible. As shown in **Fig. 4b**, the ABPBI-POSS membranes present higher WU and PA DL values than the pure ABPBI membrane. It is clear that the hydrophilic groups including the benzimidazole groups in the ABPBI chains and the hydroxyl groups generated by the epoxy ring opening as well as the basic benzimidazole groups can contribute the water and acid absorbilities, respectively. As mentioned above, the star copolymer increased the distance between the ABPBI chains and the molecular-level free volume. More water and PA molecules are present in the enlarged space, resulting in the strong enhancement of water absorbilities and acid retentivities. However, for the 2.0 wt% POSS content, the ABPBI-2.0POSS sample dissolved in the 70% PA solution, most likely due to its poor mechanical properties.

The PA–PBI PEMs often exhibit excessive swelling that degrades the performance of PEMFCs. In **Fig. 4c**, except for the ABPBI-2.0POSS membrane dissolved in PA solution, the swelling ratios of the remaining ABPBI-POSS membranes increased with the POSS content increasing to 1.5 wt%. As discussed above, the introduction of the star copolymer gave rise to more free space and reduced entanglement of the polymer chains in the composite membranes, resulting in the increased swelling ratio.

The oxidative stability of a PEM is an extremely important parameter for assessing the long-term durability of a cell because the $\cdot\text{OH}$ and $\cdot\text{OOH}$ radicals generated during the cell operation attack the polymer chains, resulting in the degradation of the polymer matrix [18]. As shown in **Fig. 4d**, the ABPBI-0.5POSS and ABPBI-1.0POSS membranes exhibit better oxidative stability than the pristine ABPBI membrane, while the ABPBI-1.5POSS and ABPBI-2.0POSS samples show poorer oxidative stability. A PBI chain has two types of end groups, namely $-\text{COOH}$ and $-\text{NH}_2$. The $-\text{NH}_2$ end group is easily oxidizable compared to $-\text{COOH}$ and the inserted $-\text{NH}-$ group, and is mainly responsible for the oxidative and thermal stability of the whole polymer chain. The amount of the $-\text{NH}_2$ end groups should be greatly reduced by the epoxy-ring opening reaction, and therefore the star copolymer (ABPBI-0.5POSS and ABPBI-1.0POSS) shows better oxidative stability than the pristine ABPBI polymer. However, for the ABPBI-1.5POSS and ABPBI-2.0POSS samples, the shortened polymer chains and enlarged free spaces imply that the polymer chains are more easily attacked by radicals. Based on these results combined with the above analysis of mechanical stabilities and

film-forming properties, it was concluded that ABPBI-1.0POSS was the most suitable material for PEM fabrication.

Proton conductivity and single cell performance: The proton conductivity results for the PA-doped membranes based on ABPBI and ABPBI-POSS membranes with similar PA DLs are shown in **Fig. 5A**, and it is observed that the proton conductivities of the ABPBI-POSS composite membranes were higher than that of the ABPBI membrane at the temperature range of 120-180 °C, with the best conductivity obtained for ABPBI-1.0POSS. Generally, the higher PA DL indicates higher proton conductivity. Since these PEMs had similar PA DLs, the improvement of proton conductivities from ABPBI-POSS composite membranes should be attributed to the enhanced ability of PA molecule movement, which is also consistent with the relative E_a values shown in **Fig. 5A**. The E_a value indicates the ease of proton hopping and rotation of both donor and acceptor, and a larger value implies that a higher enthalpy is required for the proton transfer. As reported in [2], due to the lower E_a of proton migration, the proton conduction through H₂O, PA, and ionic- or H-bonds is more effective than that through the PA-imidazole link in the PA-PBIs membranes. Therefore, the lower E_a values obtained using the ABPBI-POSS membranes imply that the enhanced absorptilities of water and PA contribute to the improvement in the proton conductivities. Comparison to the proton conductivities reported in the literature (**Table S2**) shows that the proton conductivity values of ABPBI-1.0POSS in the anhydrous conditions such as 0.019 S/cm at 160°C and 0.022 S/cm at 180 °C are higher than those of the other

ABPBI/POSS hybrid membranes, and are also comparable to those of the ABPBI and PBI membranes with embedded inorganic particles [3, 11, 16].

Fig. 5 (A) Proton conductivities and activation energy (E_a) values of the PA-doped ABPBI and ABPBI-POSS membranes in the temperature range of 120-180 °C under anhydrous atmosphere; (B) Polarization and power density curves from the single cell tests conducted under non-humidified H₂/O₂ at 170 °C; (C) EIS measurements of ABPBI and ABPBI-1.0POSS membranes based single cells at 0.6 V after activation; (D) Stability test of the ABPBI-1.0POSS based single cell at a constant current load of 0.2 A/cm².

The single cell performance characteristics of the ABPBI (thickness of 120 μ m) and ABPBI-1.0POSS (thickness of 110 μ m) membranes were investigated at 130 °C

(Fig. S6) and 170 °C (Fig. 5B), respectively. As shown in both figures, the open circuit voltages of both ABPBI and ABPBI-1.0POSS membranes were above 0.9 V, indicating that the membranes effectively prevent the undesirable gas permeation. The ABPBI-1.0POSS membrane achieved peak power values of approximately 300 mW/cm² at 130 °C and 570 mW/cm² at 170 °C, nearly 1.3 and 1.2 times greater than those obtained with the ABPBI membrane. These power density values are comparable to those of the Sn-PA embedded ABPBI membranes [43] and are even higher than those of the clay-embedding ABPBI and PBI membranes [16, 44]. The resistances of the two MEAs were determined in the single cell setup at 0.6 V by in situ impedance measurements, as shown in Fig. 5C. Previous work has shown that R_{ct} (charge transfer resistance) is strongly related to the methods used for the MEA fabrication [45]. Thus, the R_{ct} values of the ABPBI-1.0POSS (0.28 $\Omega \cdot \text{cm}^2$) and the ABPBI (0.27 $\Omega \cdot \text{cm}^2$) membranes are almost identical because the same method was used for the preparation of both of these MEAs. Meanwhile, the R_{Ω} (cell resistances) value of the ABPBI-1.0POSS (0.17 $\Omega \cdot \text{cm}^2$) is obviously lower than the ABPBI membrane (0.28 $\Omega \cdot \text{cm}^2$), implying that ABPBI-1.0POSS membrane has a higher proton conductivity, which is consistent with the results presented in Fig. 5A.

The stability of the single cell based on the ABPBI-1.0POSS membrane was tested under constant current conditions at 160 °C for 100 h. As is shown in Fig. 5D, in the first 5 h, the single cell voltage continued to rise because the PA on the membrane diffuses to the catalytic layer and increases the electrochemically active area [34]. Then, the voltage dropped slightly due to the loss of some free PA in the membrane and the

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4 decrease in the mass transfer [46]. The stabilized voltage with less than 2.0% voltage
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6 loss after 60 h indicates that the ABPBI-1.0POSS membrane has excellent durability
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8 and can be used in HT-PEMFCs. Generally, the star copolymer membrane-based MEA
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10 exhibits superior single cell performance under high temperatures and anhydrous
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12 conditions, suggesting that this approach is an efficient method for optimizing PA-PBI
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14 membranes for use as high-temperature PEMs.
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19 4. Conclusions

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21 The ABPBI-POSS star copolymers were successfully prepared via an *in-situ*
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23 synthesis procedure for high-temperature PEMs. The beneficial effects of the star
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25 copolymer resulted in the reduced intrinsic viscosity and enlarged free volume as well
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27 as the reinforcement of POSS nanoparticles in the obtained composites, and the
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29 composite membranes showed improved film-forming property, water absorptivities,
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31 acid retentivities, and mechanical properties. For the composite membrane with the
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33 optimal G-POSS content (1.0 wt%) with the removal of free PA to the extent possible,
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35 the ABPBI-1.0POSS based single cell achieved the power density of 570 mW/cm²
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37 under non-humidified H₂/O₂ at 170 °C, which was not only 1.3 times higher than that
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39 of the pristine ABPBI sample in this work but also comparable to the values obtained
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41 for the other ABPBI composite membranes reported in the literature. Thus, this study
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43 provides a simple method for the preparation of PA-PBI-based HT-PEMs with a good
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45 balance between mechanical and film-forming properties.
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55 Acknowledgments

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Scheme 1

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5