Supporting Information

# Elevated-temperature $H_2$ separation using a dense electron and proton mixed conducting polybenzimidazole-based membrane with 2D sulfonated graphene

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## 1. Experimental

### 1.1 Materials and reagents

3,3′-diaminobenzidine (DAB, 99 wt.%) and triglycidylisocyanurate (TGIC, 98 wt.%) were purchased from Shanghai Fangruida Chemical Reagent Co., Ltd. Isophthalic acid (IPA, 99 wt.%) was purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. These chemicals were used without further purification.

Flake graphite was purchased from Qingdao Tianheda Co., Ltd., P.R. China. Sulphuric acid (98.0% purity), potassium permanganate (99.5% purity), hydrogen peroxide (98.0% purity) and sodium dodecyl benzene sulfonate (99.5% purity) were purchased from Sinopharm Chemical Reagent Co., Ltd., P. R. China. Analytic sodium borohydride, sulfanilic acid, sodium nitrite, and hydrazine were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. The catalyst Pt/C (5 wt.% Pt, <80 wt.% $H_2O$) was purchased from Aladdin Reagent Shanghai Co., Ltd.

### 1.2 PBI synthesis

The polymer, polybenzimidazole (PBI) was synthesized *via* molten state polymerization of DAB and IPA. The DAB (4.0 g) and IPA (3.1 g) were mixed together and ground into fine powder before purged under high-purity $N_2$ for 1 h. After that, the obtained mixture was heated under $N_2$ atmosphere to 225 °C for 3 h and then 270 °C for 3 h in an electric oven. The resultant polymer was then continuously heated to a certain temperature (>300$^{o}$ C) to form PBI. The mixture was poured into deionized water, and then filtered and ground from a brown to black powder, which was named

PBI polymer. Before using, the resultant polymer was repeatedly washed using deionized water and ethanol. The relative molecular weight of PBI was measured by Ubbelohde viscosity method as previously reported [1]. The molecular weight of the obtained PBI was about 18,505–22,492 g $mol^{-1}$ (20,325 g $mol^{-1}$ on average).

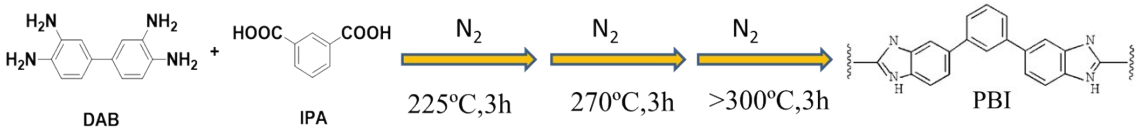


**Figure S1.** Synthesis route of PBI.

### 1.3 GO synthesis

Graphite oxide was pretreated using a typical procedure whereby 75 mg graphite oxide was dispersed in 75 g water. After sonication for 1 h with a Fisher Scientific FSH20H ultrasonic bath cleaner, a clear and brown dispersion of graphite oxide was obtained.

GO dispersion was prepared as the following processes. The graphite oxide was prepared by a modified Hummers method [2, 3]. The major procedure can be briefly described as follows: 2 g of flake graphite was introduced into 96 mL of the concentrated $H_2SO_4$ under stirring and then cooled down to 0 °C, followed by the slow addition of 12 g of $KMnO_4$. The mixture was stirred at 0, 35, 90 °C for 90, 120 and 60 min, respectively. Distilled water (80 mL) was slowly dropped into the resulting solution over a period of around 30 min. After that, deionized water (200 mL) and $H_2O_2$ (10 mL, 30%) were added to the above solution under stirring for additional 10 min to form the graphite oxide after washing using deionized water until pH of 6-7 was

obtained. To exfoliate graphene oxide (GO) flakes, the above graphite oxide slurry was diluted with water in a volume ratio of 1:5 and was mildly sonicated for 10 min. Then, the dispersion was centrifuged. The supernatant was collected until the visible particles were completely removed. The concentration of the obtained GO solution was controlled at 2 g $L^{-1}$.

### 1.4 SG preparation

Sulfonated graphene (SG) was synthesized using the following three steps: (i) pre-reduction of graphene oxide with sodium borohydride; (ii) sulfonation with the aryl diazonium salt of sulfanilic acid; and (iii) post-reduction with hydrazine. In the pre-reduction step, 600 mg sodium borohydride in 15 g water was added into the graphene oxide dispersion after its pH was adjusted to 9-10 with 5 wt.% sodium carbonate solution. The mixture was then kept at 80 °C for 1 h under continuous stirring. During reduction, the dispersion turned from dark brown to black accompanied by out-gassing. Aggregation was observed at the end of the first reduction step. After centrifuging and rinsing with water several times, the partially reduced graphene oxide was redispersed in 75 g water *via* mild sonication. The aryl diazonium salt used for sulfonation was prepared from the reaction of 46 mg sulfanilic acid and 18 mg sodium nitrite in 10 g water and 0.5 g HCl (1 N) solution in an ice bath. The diazonium salt solution was added to the dispersion of partially reduced graphene oxide in an ice bath under stirring, and was kept in ice bath for 2 h. Bubbles were expelled from the reaction mixture and aggregation was observed on the addition of the diazonium salt solution. After

centrifuging and rinsing with water for several times, sulfonated graphene oxide was redispersed in 75 g of water. In the post-reduction step, 2 g of hydrazine in 5 g of water was added into the dispersion and the reaction mixture was kept at 100 °C for 24 h under stirring. After washing with deionized water until neutral and drying at room temperature, the sulfonated grapheme (SG) formed. The degree of sulfonation on graphene from XPS (Figure S2) is about ~8.2 % (mol). In addition, it is found that the content of oxygen is higher than that in terms of $-SO_3H$ group, indicating a few containing-oxygen groups in SG. The conductivities of SG bar are about 502 S $cm^{-1}$ in air at room temperature according to four-probe method, which is thought as the electronic one due to no hydrogen hopping. When hydrogen atmosphere is employed, the conductivities of pure SG bar is ~502.2 S $cm^{-1}$, which is generally assigned to the mixed conducting.

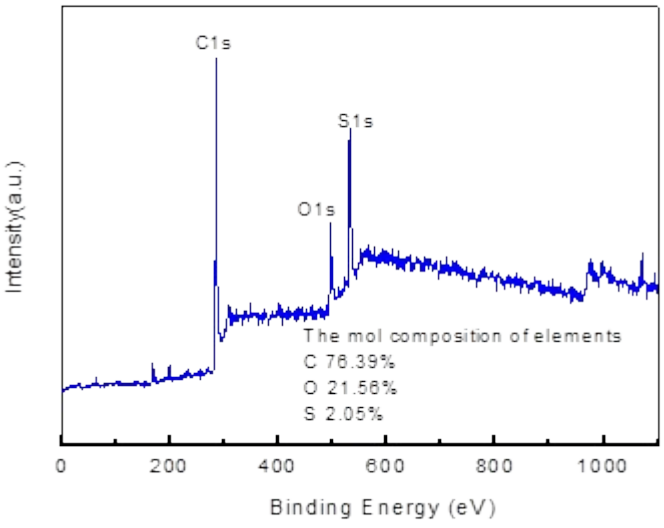


Figure S2 XPS of SG

**1.5 Preparation of the cross-linked PBI-TGIC composite membranes**

The preparation route of cross-linked PBI-TGIC membrane was illustrated in **Figure S3**. In brief, 1.0 g of PBI was added into 10 mL of N,N-dimethyl acetamide (DMAC) solvent and was magnetically stirred at 120 °C for 6 h to fully dissolve PBI. After cooling down to 60 °C, 0.25 g of TGIC (20 wt.% in the mixture of PBI and TGIC) was added to the solution as the cross-linked agent and plasticizer. The solution was further stirred for 3 h until TGIC was fully dissolved. The mixture was then ultrasonicated to remove the bubbles. After that, it was poured onto a glass plate and then heated to 60 °C for 6 h to evaporate water. To further accomplish cross-linking, the membrane was heated to 160 °C for 6 h to form cross-linked PBI-TGIC membrane.

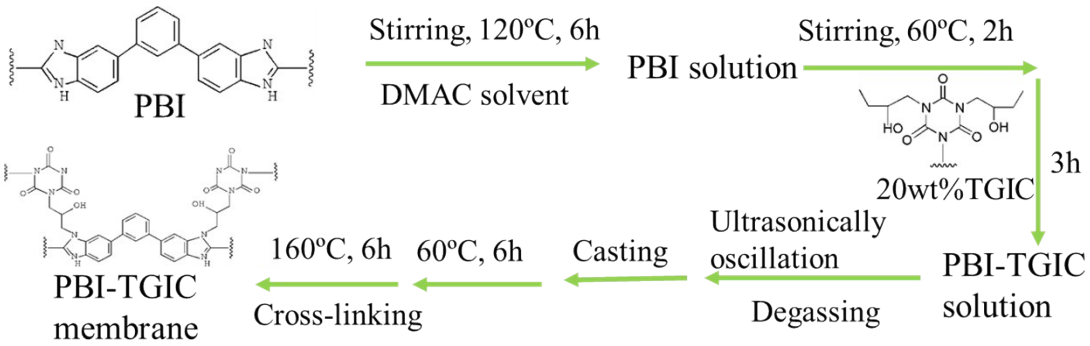


**Figure S3.** Preparation route of the cross-linked PBI-TGIC membrane.

### 1.6 Preparation of the cross-linked PBI-TGIC/SG composite membranes

The cross-linked PBI-TGIC/SG membrane was prepared by a casting method as described in **Figure S4**.

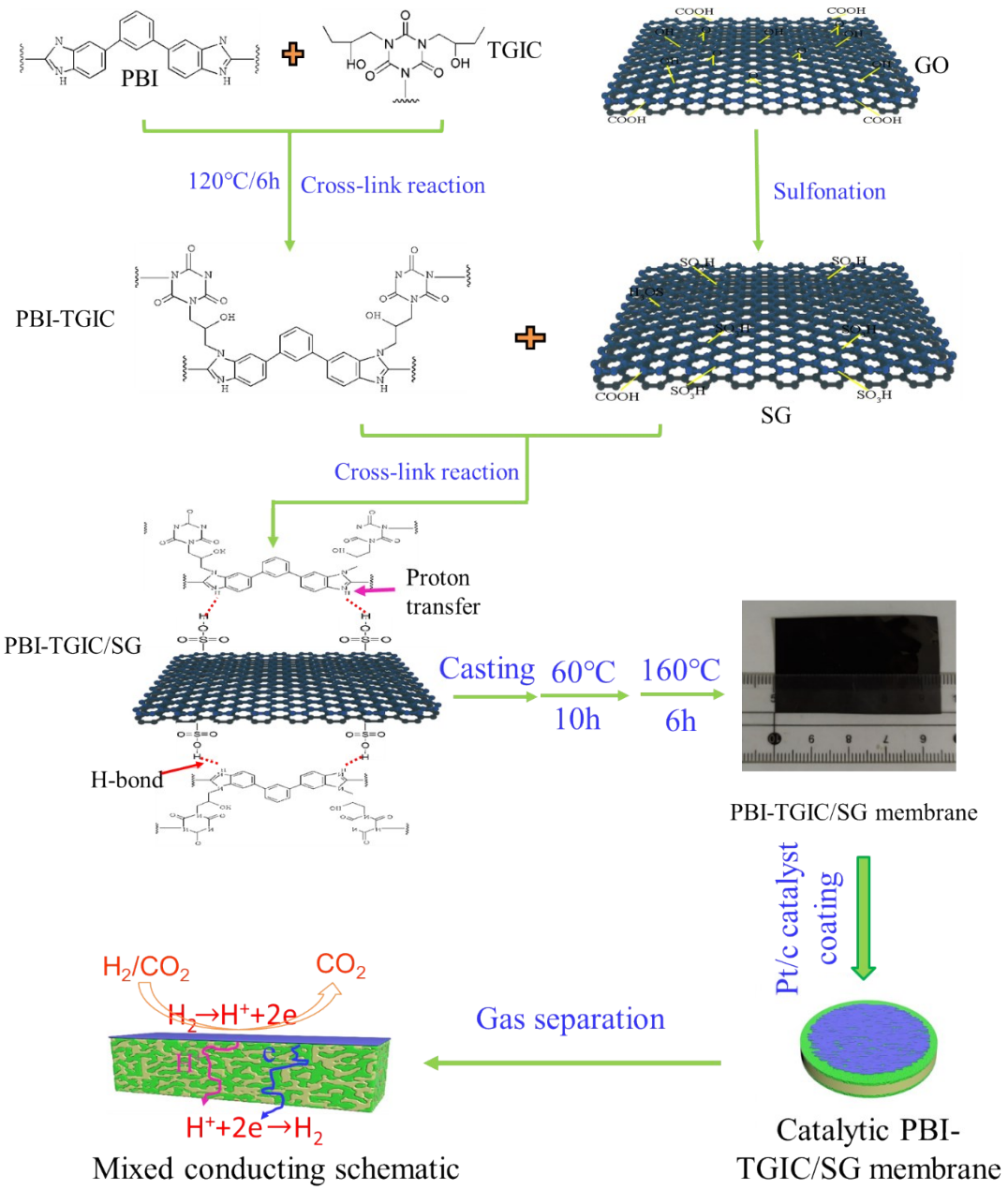


**Figure S4.** Preparation route of the cross-linked PBI-TGIC/SG membrane and gas separation.

## 2. Figures and Tables

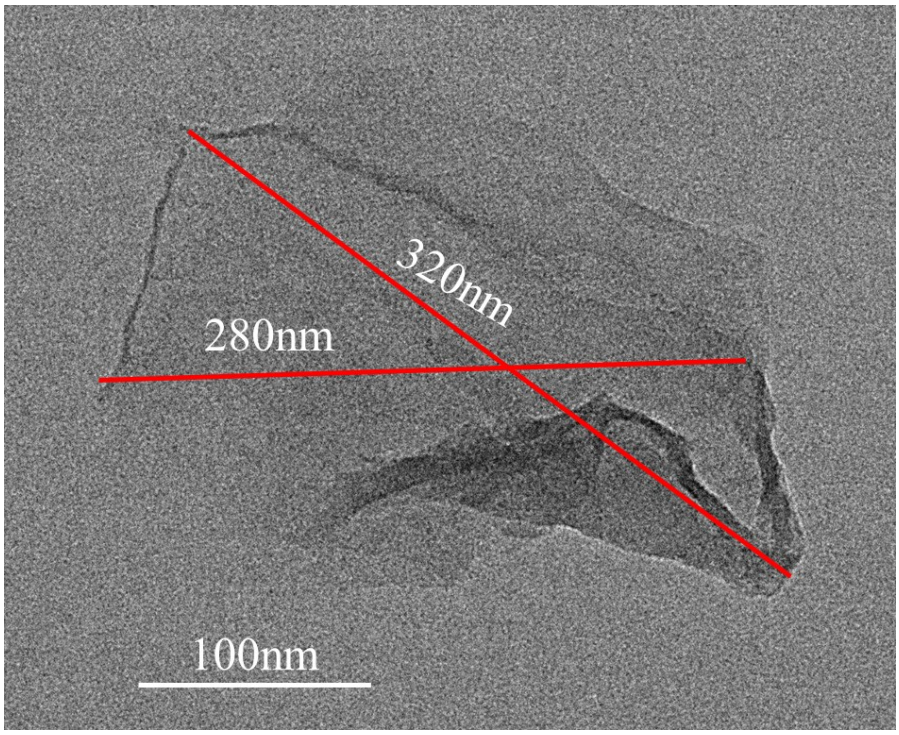


**Figure S5** TEM of SG

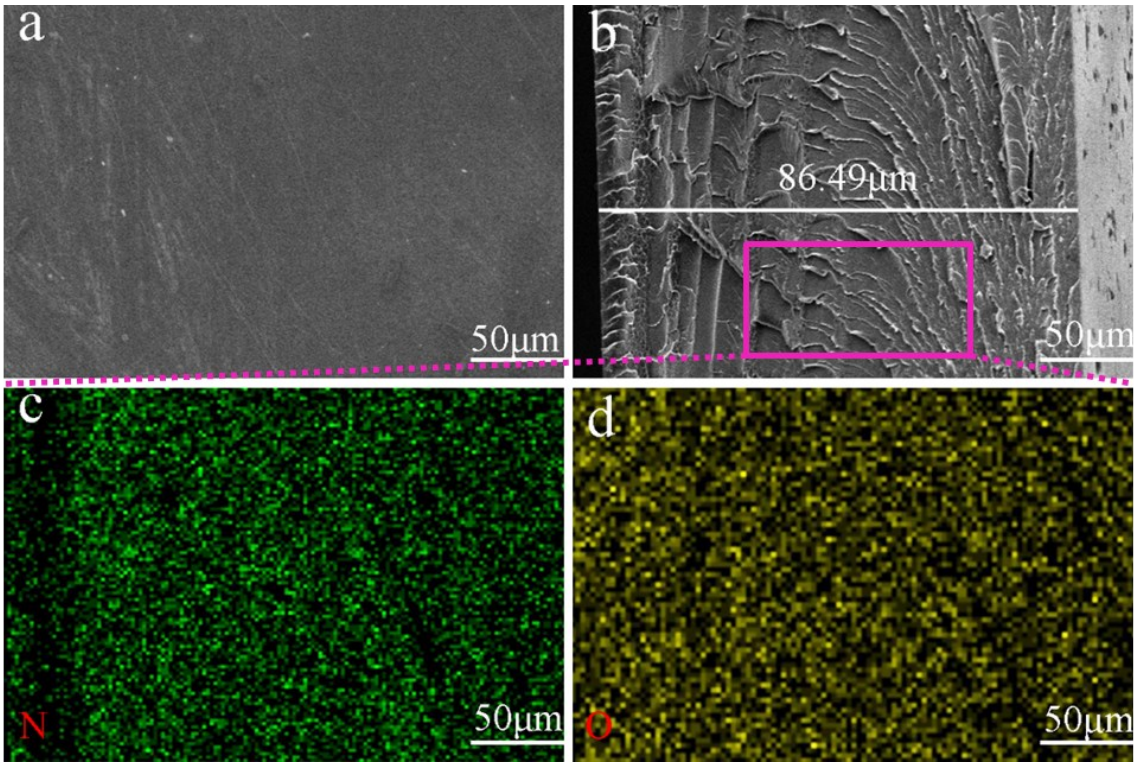


**Figure S6.** Characterization results of PBI-TGIC membrane. Scanning electron microscopy images of membrane **(a)** surface; and **(b)** cross-section; and energy dispersive X-ray spectroscopy elemental map of **(c)** N; and **(d)** O.

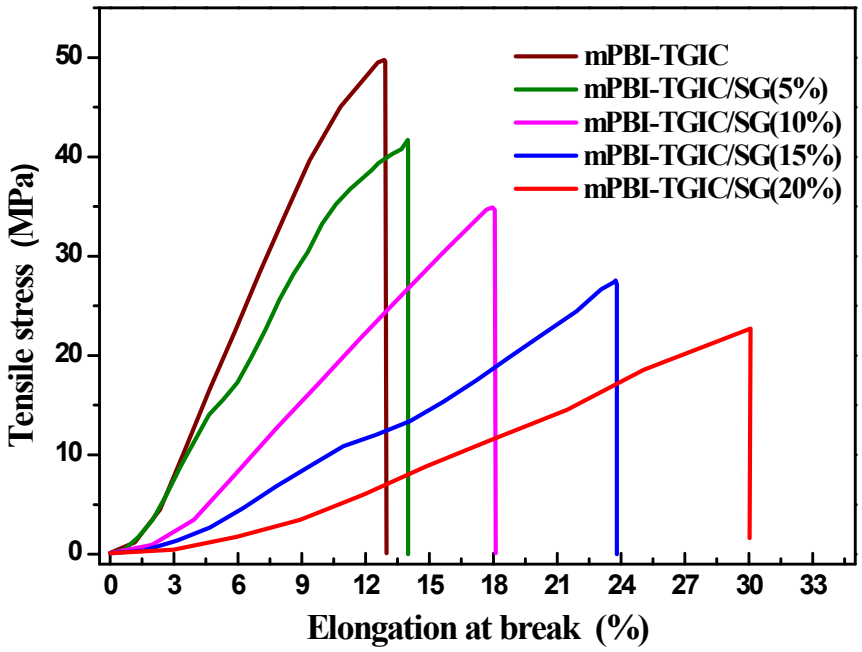


**Figure S7** the tensile stress of PBI-TGIG/SG membranes.

**Table S1.** Comparison of tensile strengths of several PBI-based membranes.

| Material | Tensile strength (MPa) | Cross-linking degree, % | Reference |
|---|---|---|---|
| PBI-TGIC/SG | 49.62-22.67 | 0-20 | This work |
| PBI-TGIC/SPAN | 41.5-21 | 20-50 | [4] |
| PBI-TMBP/PA | 5.2-12.9 | 5-20 | [5] |
| PBI-TMBP/PA | 10.89-28.47 | 4.42-19.84 | [6] |
| PBI/SPEEK | 40.84-59.90 | 0-20 | [7] |
| PBI-BMPAEK/PA | 8.8-10.05 | 2.5-20 | [8] |

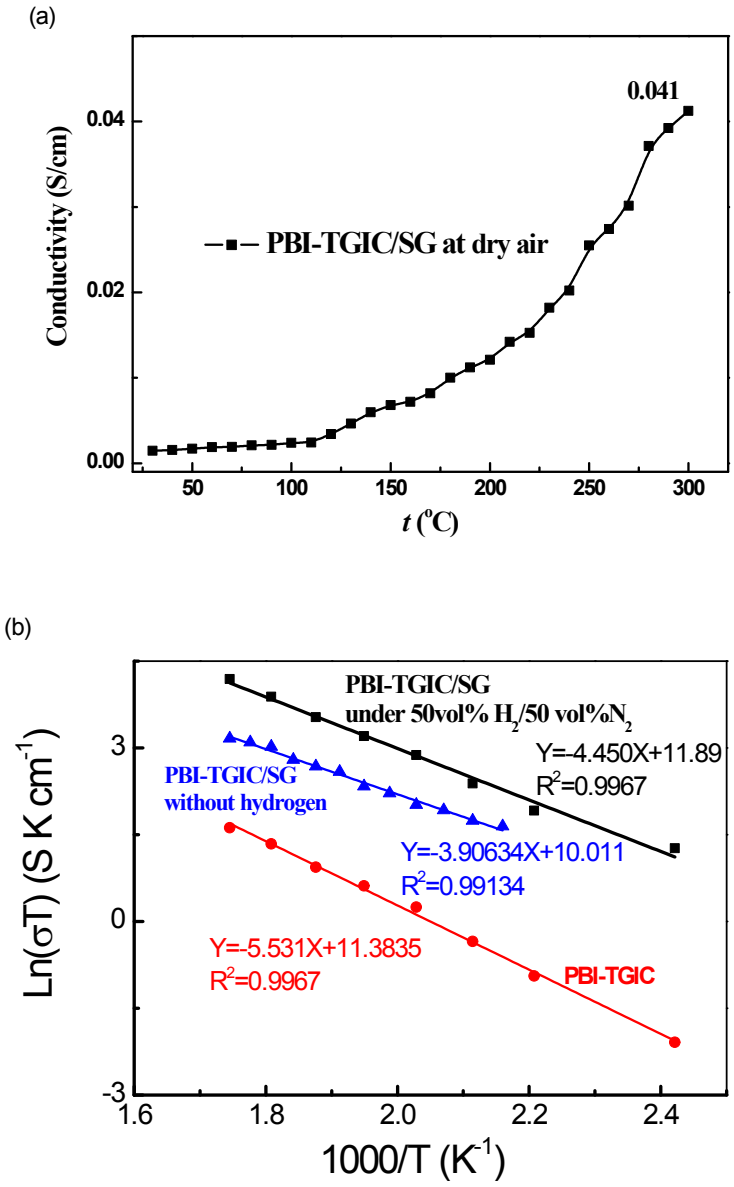


**Figure S8.** Arrhenius plot of conductivities. (a)the conductivities of PBI-TGIC/SG membrane in air; (b) the Arrhenius plot of PBI-TGIC/SG membrane.

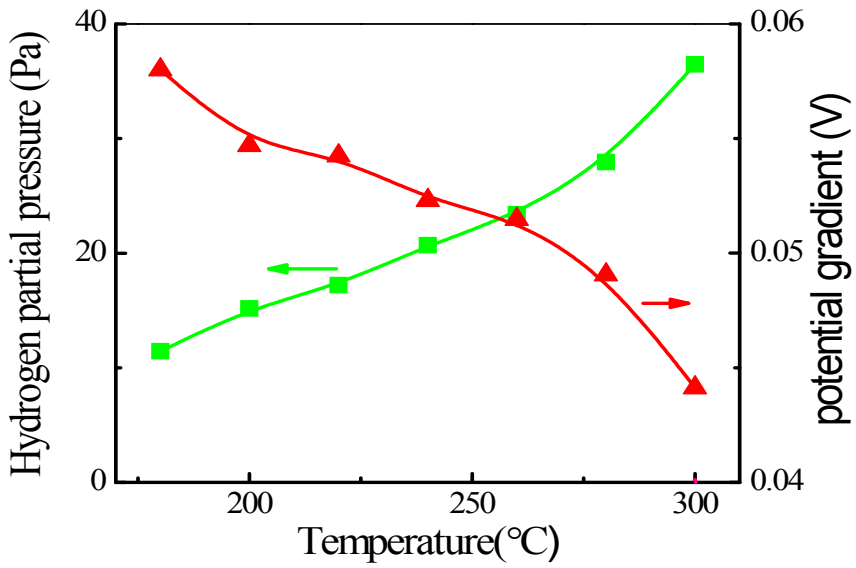


**Figure S9** The testing hydrogen partial pressure on the permeated side and potential gradient based on the *Nerst* equation ($H_2$(feed side)→$H_2$(permeated side)) under 4atm at the feed side.

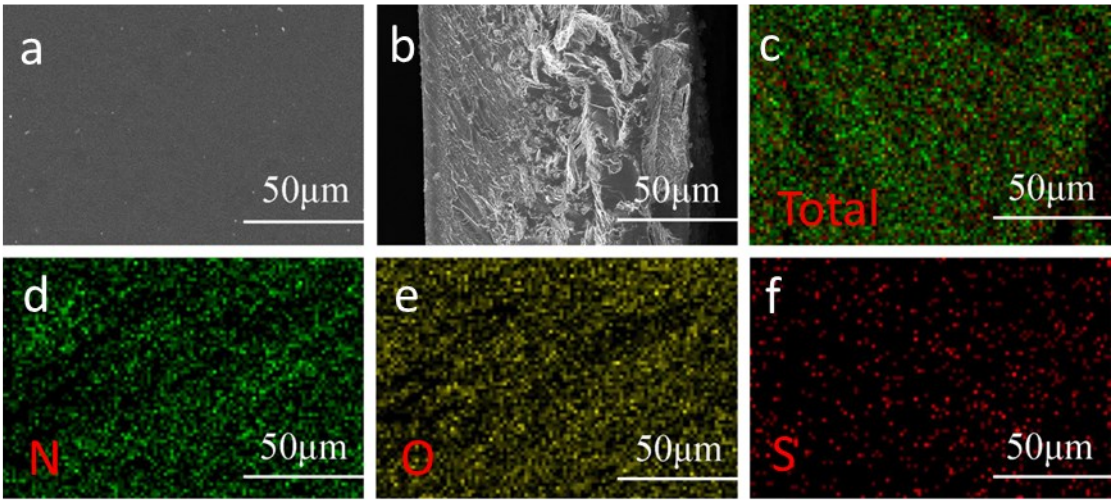


**Figure S10.** Characterization results of PBI-TGIC/SG membrane after 160-h test. Scanning electron microscopy images of membrane **(a)** surface; and **(b)** cross-section; **(c)** Combined N, O, and S energy dispersive X-ray spectroscopy elemental map; and the respective elemental map of **(d)** N; **(e)** O; and **(f)** S.

## References


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