

# A Novel Rigid Cross-linked Polymer of Intrinsic Microporous Anion Exchange Membrane

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## ABSTRACT

In this study, a rigid diazide cross-linker, 2, 6-bis (4-azobenzylidene)-4-methylcyclohexanone, was introduced into a quaternary ammonium modified polymer of intrinsic microporous (PIM) anion exchange membrane (AEM), QPIM-1, by impregnation, which was then cross-linked by thermal initiation to prepare a rigid cross-linked microporous anion exchange membrane cQPIM-1. The effects of crosslinking on the structures and performances of membrane are investigated. The presence of cross-linker and incomplete reaction are observed by the results of Fourier-transformed infrared (FT-IR). The cross-linked AEM shows significantly enhanced the tensile strength of the membrane is obviously increased through dynamic tensile test. Notably, the swelling ratio (SR) and water uptake (WU) are only 6.08% and 11.93% at 80 °C, which are only 42.8% and 26.8% lower than that of QPIM-1 before cross-linking. In addition, a desirable OH<sup>-</sup> conductivity of 39.10 mS/cm at 80 °C can be obtained, owing to the inter-chain microporous structure of PIM alleviating the blocking effect of cross-linking reaction on ion conductivity.

**Keywords:** anion exchange membrane fuel cell, cross-linked anion exchange membrane, azide crosslinker, swelling resistance

## 1. INTRODUCTION

AEM as the core component affects the performance and lifetime of anion exchange membrane fuel cell (AEMFC), so the preparation of AEM with high ionic conductivity (IC) and low SR has become a research focus [1]. Guiver [2] et al, introduced quaternary ammonium ion groups into a rigid, twisted polymer of intrinsic microporous (PIM-1) membrane [3][4] by post-

modification process to prepare QPIM-1 AEM, which has good mechanical properties and ion conductivity. But the WU of QPIM-1 was as high as 40.4% and the SR was 9.0% when ion exchange capacity (IEC) is 1.35 mmol/g, and when IEC increased to 2.1 mmol/g, the WU and SR rise to 68.9% and 16.7%, respectively. To alleviate the mutual constraint between the IC and the SR of QPIM-1 and to meet the requirement of high swelling resistance of AEM for AEMFC application. In this study, a rigid cross-linking process is developed for laboratory-prepared QPIM-1 AEM, and a new rigid cross-linked microporous QPIM-1 AEM is prepared by introducing the rigid diazide cross-linker, 2, 6-bis (4-azobenzylidene)-4-methylcyclohexanone, into QPIM-1 by impregnation method, and the cross-linking reaction is initiated by high temperature under N<sub>2</sub>-protected environment. The chemical structures, mechanical properties and ionic conductivity properties of cross-linked PIM AEMs are characterized and evaluated.

## 2. EXPERIMENTAL

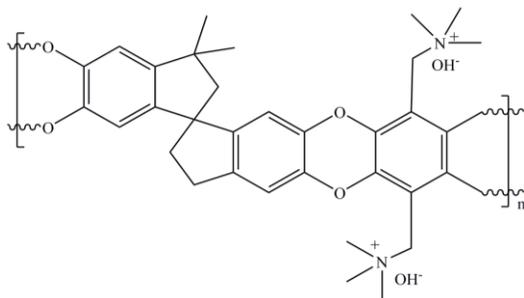
### 2.1 Material and methods

The AEM used in this work was a prepared QPIM-1 with a thickness of approximately 50 ± 5 μm. Its chemical structure is shown in Figure 1(a) and synthesis preparation process is referred to previous work [2]. The cross-linking agent is a diazide (2, 6-bis (4-azobenzylidene)-4-methylcyclohexanone (85%) brought from TCI showed in Figure 1(b). Methanol (MeOH, 99.0%) and Tetrahydrofuran (THF, 99.9%) were purchased from Energy Chemical and used as received. Sodium Hydroxide (NaOH, 97.0%) was purchased from Sigma Aldrich and used as received.

The cross-linker in THF solutions with 0.5 wt%, 2.5 wt% and 5.0 wt% concentrations were prepared, and the QPIM-1 in Cl<sup>-</sup> form membranes are immersed in 20 mL of

the solution for 12 h (avoid light), removed and immersed in THF to clean the residual cross-linker on the membrane surface. THF liquid on the membrane surface was wiped off after removal to obtain AEMs impregnated with different concentrations of cross-linker. These AEMs were spread and sandwiched into two glass plates wrapped in tinfoil, quickly placed in a N<sub>2</sub> reflux environment protected from light, and the cross-linking reaction was thermally initiated at a high temperature of 160 °C for 12 h. After the reaction, the residual unreacted cross-linking agent was washed by repeated immersion in methanol, then washed repeatedly with deionized water and stored in deionized water. The AEMs obtained from the cross-linking reaction at different concentrations were recorded as cQPIM-1 (X). The OH-AEMs were obtained by ion replacement, immersed in 1 mol/L NaOH solution for 12 h at room temperature, and then stored in deionized water with deionized water after repeated washing until neutral.

(a)



(b)

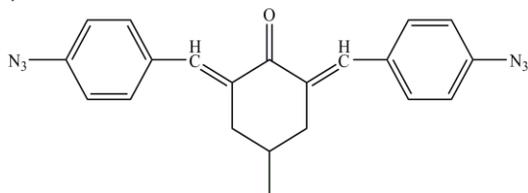


Fig.1 Chemical structure of materials

## 2.2 Characterization

The Fourier transformed infrared tests (FT-IR) of the membrane samples are recorded on Bruker Tensor 27 in total reflection mode. The mechanical property is test on an electric stretching apparatus Instron E1000 at speed of 1mm/min under atmospheric condition.

The SR and WU (%) are measured by dry and wet film method and calculated by its length expansion between the dry membrane and membrane equilibrated in liquid water at different temperature, and is calculated as follows:

$$WU = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (1)$$

$$SR = \frac{L_{\text{wet}} - L_{\text{dry}}}{L_{\text{dry}}} \times 100\% \quad (2)$$

$W_{\text{wet}}$  and  $L_{\text{wet}}$  are the mass and length of the membrane in the wet state, and  $W_{\text{dry}}$  and  $L_{\text{dry}}$  are the mass and length of the membrane in the dry state, respectively. The result is obtained by repeating the measurement data three times and taking the average value.

The IEC (mmol/g) is calculated from the Molar titration measurements using the Cl<sup>-</sup> form membrane.

$$IEC = \frac{0.01 \times V_{\text{titr}}}{m_{\text{dry}}} \quad (3)$$

Where  $V_{\text{titr}}$  (mL) is the volume of AgNO<sub>3</sub> solution consumed and  $m_{\text{dry}}$  (g) is the mass of the dry film used for the test, three measurements were repeated and the average value was taken as the final value.

The ionic conductivity of membrane in IC<sup>-</sup> and OH<sup>-</sup> form is calculated by measuring the AC impedance measured using a two-probe AC impedance spectroscopy method using an electrochemical workstation on Metrohm Autolab. The IC ( $\sigma$ , mS/cm) is calculated as follows:

$$\sigma = \frac{l}{A \times R} \quad (4)$$

$A$  (cm<sup>2</sup>) is the cross-sectional area of membrane, and  $l$  (cm) is the distance between the electrodes.

## 3. RESULTS AND DISCUSSION

### 3.1 Synthesis results

FT-IR spectral data of AEM before and after crosslinking are shown in Fig 2, where 1600 cm<sup>-1</sup> corresponds to the absorption peak of the C-C stretching vibrational bond in the benzene ring, and the characteristic peak at 2100 cm<sup>-1</sup> is the characteristic peak of the azide group generated by the introduced diazide cross-linker [5], and the appearance of this characteristic peak indicates that the diazide cross-linker was effectively introduced into QPIM-1. The analysis also reveal that it is known that the intensity of the characteristic peak of the azide group increased significantly and sequentially with the increase of the impregnated cross-linking agent concentration, indicating that there is a significant increase in the

degree of cross-linking of AEM as the concentration of the impregnated cross-linking agent increased.

The color images of cQPIM-1(X) also support this conclusion. As shown in Figure 3, where (a) is QPIM-1 with bright yellow color; (b) is cQPIM-1 (0.5 wt%), the comparison reveals that the membrane color changes to light orange after the reaction of the introduced cross-linker; (c) is cQPIM-1 (2.5 wt%), and (d) is cQPIM-1 (5.0 wt%), it can be seen that the membrane color gradually darkens with the increase of the concentration, from light orange to orange-red to close to blood red.

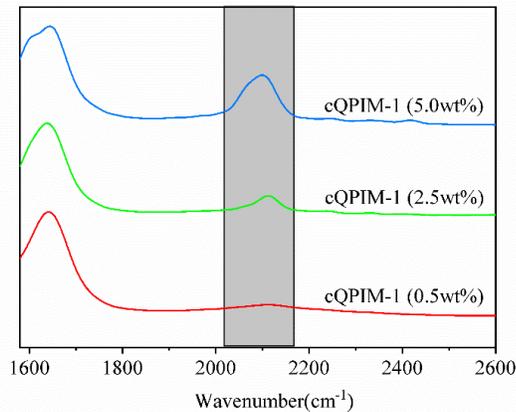


Fig.2 FT-IR spectra of cQPIM-1(X)

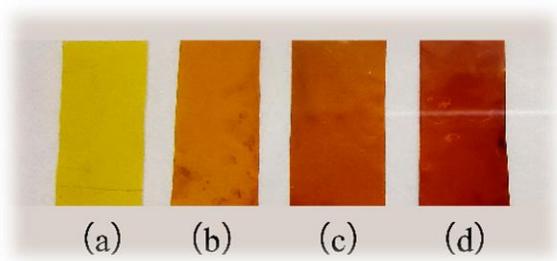


Fig.3 Images of cQPIM-1 and QPIM-1

### 3.2 Mechanical property

Table 2 shows the mechanical property data of AEM. Under the same test conditions, the mechanical tensile strength and Young's modulus of cQPIM-1 are significantly improved compared with QPIM-1. The tensile strength of QPIM-1 was 15.6 MPa, and the tensile strength of cQPIM-1 (5.0 wt%) increases to 19.2 MPa, while the Young's modulus increased about three times to 1.5 GPa. This is because the polymer chains formed a cross-linked network through the cross-linking reaction of the azide groups, forming tighter connections through strong covalent bonds and increased inter-chain interactions.

Tab.1 Mechanical properties of cQPIM-1(X) and QPIM-1

Membrane	Tensile strength [MPa]	Young's modulus [GPa]	Elongation at break [mm/mm]
QPIM-1	15.6	0.5	5.3
cQPIM-1 (0.5wt%)	16.1	1.0	3.8
cQPIM-1 (2.5wt%)	18.2	1.4	3.4
cQPIM-1 (5.0wt%)	19.2	1.5	3.1

Figure 4 shows the bending of cQPIM-1 (5.0 wt%) in the dry state. cQPIM-1 (5.0 wt%) has the lowest elongation at break, but it can still bend in the dry state, which shows that the AEM obtained still has good flexibility after cross-linking.



Fig.4 Flexible cQPIM-1(5.0 wt%) that can be bent easily in the dry state

### 3.3 Water uptake and swelling ratio

Table 3 shows the data of water absorption and swelling rate, ion exchange capacity, and ionic conductivity. As the concentration of cross-linker increases, the degree of covalent network increases and the connectivity of water molecule transport channels within the membrane decreases, thus the swelling resistance of the membrane is continuously enhanced. Experimentally measured IEC has a slight decrease with increasing concentration of impregnated cross-linking agent, indicating that the introduction of cross-linking agent causes little change in the number of moles of ionic groups contained per unit mass of membrane. The swelling and water uptake of the membranes before and after cross-linking were measured and compared. The swelling and water uptake of AEM decreases significantly after cross-linking, from 14.2% of QPIM-1 to 6.1% of cQPIM-1 (5.0 wt%), while the water uptake decreases from 44.85% to 11.9%. cQPIM-1 have much better anti-swelling performance than the original QPIM-1. It is also showed that cQPIM-1 shows little change in water absorption swelling rate measured at 20 °C and 80 °C, so

cQPIM-1 has a better thermal dimensional stability, which may be due to the lack of motility of its rigid trapezoidal backbone itself.

Tab.3 Properties of cQPIM-1 and QPIM-1.

Membrane	IEC <sup>a</sup> [mmol/g]	SR <sup>a</sup> [%]	WU <sup>a</sup> [%]	$\sigma$ (Cl <sup>-</sup> ) <sup>b</sup> [mS/cm]	$\sigma$ (OH <sup>-</sup> ) <sup>b</sup> [mS/cm]
QPIM-1	1.30	14.2	44.4	15.2	46.2
cQPIM-1 (0.5wt%)	1.28	10.4	15.7	12.4	34.1
cQPIM-1 (2.5wt%)	1.26	8.2	12.9	11.4	32.8
cQPIM-1 (5.0wt%)	1.25	6.1	11.9	10.5	29.4

a: Measurement at room temperature

b: Measured at 60 °C

### 3.4 Ion conductivity

The Cl<sup>-</sup> conductivity decreases after cross-linking occurred. cQPIM-1 (0.5 wt%) had a Cl<sup>-</sup> conductivity of 12.4 mS/cm at 60 °C, which is lower than that of QPIM-1 with a Cl<sup>-</sup> conductivity of 15.2 mS/cm, higher than the one of 11.4 mS/cm for cQPIM-1 (2.5 wt%) and 10.5 mS/cm for cQPIM-1 (5.0 wt%).

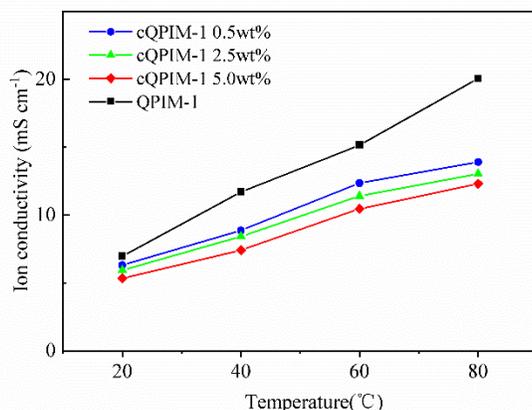


Fig.5 Ion conductivity of the cQPIM-1(X) and QPIM-1

The results shows that after the cross-linking reaction of the polymer backbone, the pore structure formed changes making the ion channels formed more distorted and the connectivity of the ion conduction channels decreases or even channel blockage occurs, while the IEC of AEM after the cross-linking reaction does not change much, but the water absorption rate decreases significantly, weakening the migration ability of ions in the membrane, indicating that the cross-linking

reaction hinders the ion conduction in the membrane to some extent and affects the ion conductivity of AEM<sup>[4]</sup>.

### 4. CONCLUSION

In this study, a new cross-linked microporous polymeric anion-exchange membrane cQPIM-1 AEM was prepared by introducing the rigid cross-linker azide 2,6-Wcyclohexanone into QPIM-1 AEM by impregnation, and the cross-linking reaction was thermally initiated under N<sub>2</sub> protection.

In terms of membrane structure, FT-IR test shows that the cross-linking agent was effectively introduced into the QPIM-1 membrane and a partial cross-linking reaction took place. The tensile strength of the cross-linked membranes is enhanced based on the analysis of mechanical tensile results. In addition, the swelling and water absorption of the cross-linked membrane are only 6.08% and 11.93% at 80 °C, which are 42.8% and 26.8% lower than those of the uncross-linked QPIM-1, respectively, with significantly enhanced swelling resistance.

The rigid azide based cross-linked microporous polymeric anion exchange membrane cQPIM-1 prepared in this work has excellent anti-swelling ability while retaining good ionic conductivity, and thus is expected to be widely used in alkaline anion exchange membrane fuel cells and other fields.

### ACKNOWLEDGEMENT

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