Poly(2,5-benzimidazole) Based Polymer Electrolyte Membranes for High Temperature Fuel Cell Applications

Xujin Bao and Qingting Liu

Department of Materials, Loughborough University, UK, X.Bao@lboro.ac.uk

ABSTRACT

The synthesis and characterizations of novel organic-inorganic composite membrane materials formed by poly(2,5-benzimidazole)/OctaAmmonium POSS® (ABPBI/OA-POSS) are reported. An uniform dispersion of nanoparticles in the membrane with excellent mechanical properties was obtained from ABPBI containing 3% OA-POSS membranes (ABPBI/3OA). Upon impregnation with phosphoric acid, the composite membranes presented higher phosphoric acid uptakes and proton conductivities than that of the pristine ABPBI membranes. The highest proton conductivity of 0.25S/cm was achieved from ABPBI/3OA membrane with 241% of phosphoric acid uptake at $160^{o}C$ without humidification. These properties make them very good candidates as the membranes for polymer electrolyte membrane fuel cells (PEMFCs) at temperatures up to $160^{o}C$.

Keywords: poly(2,5-benzimidazole); OctaAmmonium POSS; polymer electrolyte membranes; high temperature PEMFC

1 INTRODUCTION

For most commercial PEMFCs the proton exchange membranes (PEMs) are based on perfluorosulphonic acid (PFSA) material, e.g. Nafion®, owing to its high conductivity, excellent chemical stability, mechanical properties and potentially long-term durability. High temperature PEMFCs (normally above $120^{o}C$) are considered as the next generation of fuel cell because they offer many benefits including faster electrochemical kinetics, improved and simplified water management, effective thermal management and improved carbon monoxide tolerance etc.[1]

However, the biggest challenge for high temperature PEMFCs is proton exchange membrane materials. Due to the limitation of their glass transition ($\approx130^{o}C$)[2] and reliance of a saturated condition, PFSA based membranes only can be operated under $100^{o}C$. Great efforts have been and are being made to develop PEM materials for high temperatures.[3,4] Polybenzimidazoles (PBIs) are one of these interesting membrane materials because of their excellent chemical and thermal stabilities. When doped with strong acid, i.e. phosphoric acid, the obtained acid based PBIs membranes possess good proton conductivities at high temperatures with low humidity. However, the major drawbacks are the possible acid drawing off during the fuel

cell operation and the low ionic conductivity at low temperature ($<60^{o}C$) [5]. To enhance acid and water retention, composite membranes of PBIs containing inorganic/organic fillers are considered as an effective approach and have been studied by many groups.[6,7]

In this work, OctaAmmonium POSS was used in the synthesis of poly(2,5-benzimidazole)/OA composite in-situ. The presence of POSS cages and Si-O functional groups could enhance the water and acid absorbility and retention at high temperatures with low humidity.
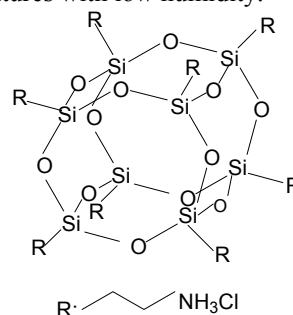

Figure 1. Structure of OctaAmmonium POSS

2 EXPERIMENTAL

2.1 Preparation of membranes

ABPBI membrane: ABPBI was synthesized from 3,4-diaminobenzoic acid (DABA, Sigma-Aldrich UK) in methanesulfonic acid (MSA, Fisher Scientific Co., UK) and P_2O_5 (Fisher Scientific Co., UK) media under nitrogen atmosphere. The synthesis conditions and membrane preparation procedures referred to the literatures[8].

ABPBI/OA-POSS composite membrane: OctaAmmonium POSS (OA-POSS, AM0285 POSS, Hybrid Plastic, Inc., USA) was added into MSA followed by ultrasonication until a homogeneous transparent solution was obtained. Subsequently, P_2O_5 and DABA were added for in-situ synthesis. The rest procedures were the same as that of the ABPBI membrane.

2.2 Characterizations

Tensile strengths of the membranes were measured according to ASTM D638 by a universal testing machines (Model LR50K Plus, Lloyd Instrument, UK). The X-ray diffraction (XRD) patterns of membrane samples were collected from a Cu Kα radiation source at the range of 5-75°. The surface morphology of membranes was observed by a scanning electron microscopy (SEM, LEO 1530VP

FEG SEM). The thermal stability was measured by a simultaneous TGA/DSC (2960 SDT V3.0F, TA Instruments Inc., USA) with a heating rate of $10^{\circ}C/min$ from room temperature to $650^{\circ}C$.

For the measurement of water and phosphoric acid uptakes, the membrane samples immersed in water for 3 days and in different concentrations of phosphoric acid (PA, Fisher Scientific Co., UK) solutions for 7 days, respectively. The water and phosphoric acid uptakes were calculated by following equations

$$Water\ uptake,\ \% = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \qquad (1)$$

$$PA\ uptake,\ \% = \frac{W_{doped} - W_{undoped}}{W_{undoped}} \times 100\% \qquad (2)$$

where W_{wet} and W_{dry} are the weight of wet and dry membrane, W_{doped} and $W_{undoped}$ are the weight of dried membrane after and before doped in phosphoric acid, respectively.

The measurement of proton conductivities of membrane samples was performed with a two-probe ac impedance method by using an electrochemical measurement (1280 EMU, Solartron Analytical Ltd.) over a range of 100Hz to 20kHz. The temperature was varied from $110{\sim}160^{\circ}C$ with $10^{\circ}C$ intervals for anhydrous membranes. The membrane sample was sandwiched between two vertical cylindrical platinum rods (diameter: 2.0mm) with an appropriate pressure. A two-component model with an ohmic resistance in parallel with a capacitor was employed to fit the experimental curve of the membrane resistance across the frequency range (the Nyquist plot). The conductivities of membranes at different temperatures were calculated from the ohmic resistance of the model simulation by the following equation

$$\sigma = d/(R \times A) \qquad (3)$$

where d is the distance between two electrodes, i.e. the thickness of a sample membrane, A is the testing area of a sample membrane and R is the ohmic resistance of the sample simulated from the model.

3 RESULTS AND DISCUSSIONS
3.1 Mechanical properties

The mechanical properties of pristine ABPBI and ABPBI/OA-POSS composite membranes were measured at a fully hydrated and dry state, respectively (Figure 2). The tensile strength and Young's modulus of ABPBI/OA-POSS composite membranes increased compared to that of a pristine ABPBI membrane. The ABPBI/3% OA-POSS (ABPBI/3OA) composite membrane has the highest value of tensile strength and Young's modulus (258.6 and 4577MPa in a dry state, 131.5 and 2395MPa in a saturated state, respectively), owing to the nanoscale distribution of OA-POSS in ABPBI membranes. The elongation values of membranes in a saturated state were larger than that in a dry

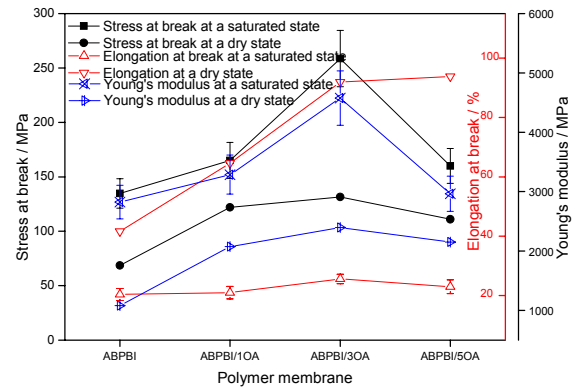state which should be attributed to the plasticization effect from absorbed water.

Figure 2. Mechanical properties of the pristine ABPBI and ABPBI/OA-POSS composite membranes

3.2 Thermal stabilities

The thermal stabilities of ABPBI/OA-POSS composite membranes and pristine ABPBI were investigated by TGA/DSC under air atmosphere (Figure 3). For the ABPBI membrane, the gradual weight loss ($\approx$5.2%) before $350^{\circ}C$ is due to the release of absorbed moisture. The decomposition of ABPBI polymer started from $500^{\circ}C$. At the range of $425{\sim}500^{\circ}C$ there is almost no weight loss but an endothermal peak appears in the DSC curve, which is assigned to the glass transition of ABPBI polymer.[9]
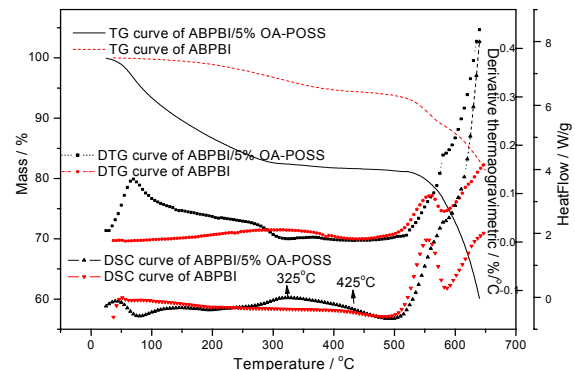

Figure 3. TGA/DTG/DSC curves of ABPBI and ABPBI/5%OA-POSS membranes

For the ABPBI/5OA composite membrane, the weight loss after $500^{\circ}C$ is due to the decomposition of ABPBI polymer and OA-POSS particles. The weight loss before $100^{\circ}C$ in the TG curve and the relative peak appeared in the derivative thermogravimetric (DTG) curve owes to the evaporation of absorbed 'free' water. The Si-O groups in POSS and N-H groups in ABPBI can absorb water via hydrogen bonding. Therefore, the subsequently gradual

weight loss after 100°C is attributed to the release of hydrogen bonded water. The decomposition of OA-POSS structure happens after 500°C[12] and its DTG curve is overlapped by that of ABPBI polymer. However, the clear peak appeared at 325°C in the DSC curve and no weight loss during near temperature range, which indicate the glass transition of the composite membrane. Because the insertion of OA-POSS in ABPBI molecule chains, the movements of ABPBI chains become relatively free, resulting decrease of Tg.

3.3 Membrane morphologies

The XRD patterns of ABPBI and ABPBI/OA-POSS composites in a wide range of 2θ degree were illustrated in Figure 4. The XRD peak at 2θ≈26° is corresponding to a *d* spacing between two parallel benzimidazole chains of 3.3Å, which was due to the stacking of ABPBI chains[10]. With the content of OA-POSS increased from 1% to 5%, a broad peak approximately at 2θ≈15~24° raised indicates a trend of the semicrystalline to amorphous structure.
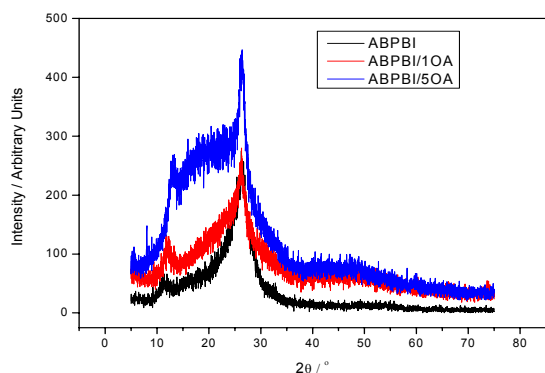

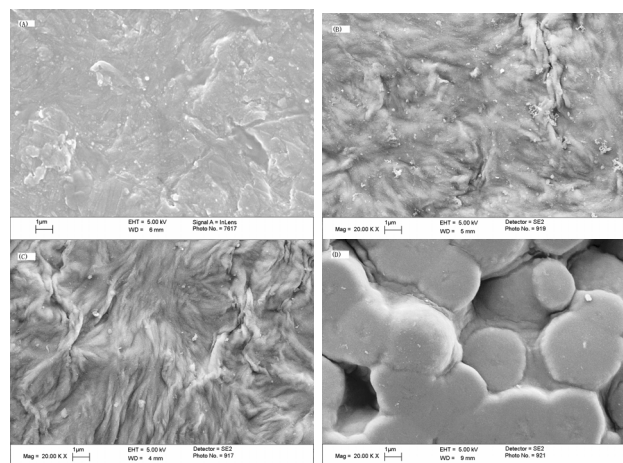**Figure 4. XRD patterns of ABPBI and ABPBI/OA-POSS composites**

Figure 5. SEM images of (A) ABPBI membrane, (B) ABPBI/1OA, (C) ABPBI/3OA and (D) ABPBI/5OA

The surface morphology of ABPBI membrane and composite membranes were studied by SEM (Figure 5).

Compared to ABPBI membrane in Figure 5 (A), the ABPBI/1% OA-POSS and ABPBI/3% OA-POSS composite membranes exhibit uniform morphology owing to the OA-POSS particles uniformly dispersed. However, the holes and irregular shapes appeared in ABPBI/5OA which might be due to the agglomeration of OA-POSS particles, which also indicates the content of OA-POSS in the composite membrane should be less than 5%.

3.4 Water and phosphoric acid uptakes

As shown in Table 1, water uptakes of ABPBI/OA-POSS composite membranes at the ambient atmosphere (50±5%R.H.) and saturate state both are improved compared to that of ABPBI membranes. The excess values of water uptakes in these composite membranes owe to the absorbance by hydrogen bond forms, i.e. Si-O···H-O-H. The lower values of water uptake of all membranes at ambient atmosphere (50±5%R.H.) indicated the 'free' water would be easy to evaporate at low relative humidity (R.H.). The values of phosphoric acid uptake of ABPBI/OA-POSS composite membranes also are bigger than that of pristine ABPBI membrane, which might be due to the reaction via the form of $-NH_3^+H_2PO_4^-$ between OA-POSS and H_3PO_4.

Table 1. Water and phosphoric acid uptakes of ABPBI and ABPBI/OA-POSS composite membranes

Membrane	H_2O uptake, % (Error: ±5%)		PA uptake, % (Error: ±10%)		
	Amb. atm.	Satur.	4M PA	8M PA	12M PA
ABPBI	23.2	31.6	41.4	51.2	64.1
ABPBI/1OA	32.0	61.2	74.9	90.0	95.8
ABPBI/3OA	32.3	106.2	88.7	153	241
ABPBI/5OA	33.1	90.8	85.4	53.1	70.8

The best performance on water and phosphoric acid uptakes from ABPBI/3OA composite membrane was mainly because of the nanoscale dispersion of OA-POSS particles in ABPBI which resulted in the maximum surface area. The values of water and acid uptakes of ABPBI/5OA lower than that of ABPBI/3OA is probably due to the agglomeration of POSS particles resulting a reduction of surface area of POSS particles. Additionally, the decrease of PA uptake of ABPBI/5OA-POSS in 8 and 12M PA solutions compared to that in 4M PA solution suggested that the phosphoric acid would accelerate the aggregation process.

3.5 Membrane proton conductivities

The proton conductivities of dry ABPBI and ABPBI/OA composite membranes doped with different amounts of phosphoric acid are shown in Figure 6. The form of ABPBI-64PA represented an absorbance of 64% phosphoric acid in the ABPBI membrane. The conductivities of PA doped ABPBI and composite

membranes increased with the increasing temperatures and phosphoric acid uptakes. The highest conductivity of 0.25S/cm was obtained from the ABPBI/3OA-241PA at 160°C, which was two orders of magnitude higher than that of ABPBI-64PA (0.0027S/cm). Compared with the ABPBI-64PA membrane, the ABPBI/5OA-63PA had a similar PA uptake but lower conductivity by 40~60%, indicating that the agglomerated OA-POSS particles retard the mobility of protons in the membranes.
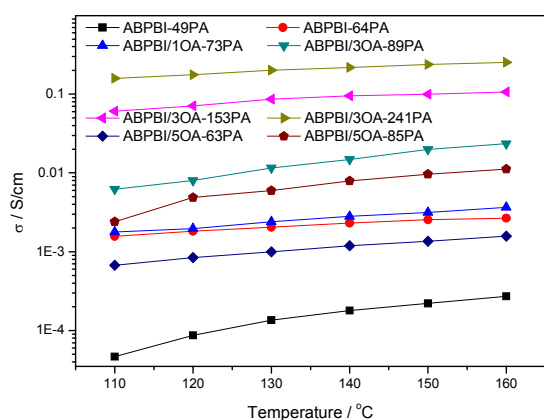

Figure 6. Proton conductivity of dry ABPBI and ABPBI/OA-POSS composite membranes doped with different amounts of phosphoric acid at 110~160°C

4   CONCLUSIONS

ABPBI/OA-POSS composite membranes were successfully prepared via in-situ synthesis followed by membrane casting and phosphoric acid doping procedures. The thermal stable temperature of composite membranes is above 300°C. The mechanical properties of composite membranes by uniformly dispersion of 3% OA-POSS in ABPBI polymer were greatly enhanced. SEM images showed that the suitable contents of OA-POSS were less than 5% to avoid the agglomeration of POSS particles. The increased water uptake in the saturated and dry conditions and improved phosphoric acid absorbility indicated composite membranes should have better performance at low temperatures than the pristine ABPBI membrane. The best mechanical properties, highest water and acid uptakes and conductivities from 110 to 160°C in the anhydrous condition indicated that 3% AO-POSS hybrid ABPBI membrane should be the optical choice for use as polymer electrolyte membranes in high temperature PEMFCs.

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