



# A polybenzimidazole/ionic-liquid-graphite-oxide composite membrane for high temperature polymer electrolyte membrane fuel cells



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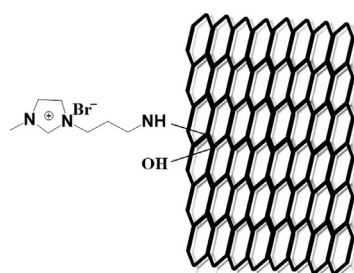
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## HIGHLIGHTS

- 1-(3-Aminopropyl)-3-methylimidazolium groups (ionic liquid) was bonded to the graphite oxide.
- ILGO filler enhanced the proton conductivity of PBI membrane.
- ILGO/PBI membrane showed superior performances in HT-PEMFC.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Graphite oxide is successfully functionalised by 3-aminopropyltriethoxysilane ionic liquid and used as a filler material in a polybenzimidazole (PBI) membrane for high temperature proton exchange membrane fuel cells. The ionic-liquid-graphite-oxide/polybenzimidazole (ILGO/PBI) composite membrane exhibits an appropriate level of proton conductivity when imbibed with phosphoric acid at low phosphoric acid loading, which promotes its use in fuel cells by avoiding acid leakage and materials corrosion. The ionic conductivities of the ILGO/PBI membranes at 175 °C are 0.035 S cm<sup>-1</sup> and 0.025 S cm<sup>-1</sup> at per repeat units of 3.5 and 2.0, respectively. The fuel cell performance of ILGO/PBI membranes exhibits a maximum power density of 320 mW cm<sup>-2</sup> at 175 °C, which is higher than that of a pristine PBI membrane.

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## 1. Introduction

In the last decades, considerable efforts have been made to develop high temperature (>100 °C) proton exchange membrane fuel cells (PEMFCs) using polymer acid complexes (PACs) because it offers significant advantages in this temperature range, such as (1)

improved CO tolerance, (2) enhanced efficiency, (3) avoidance of flooding by water, (4) opportunity to use non-noble metal catalysts, and (5) system simplification [1–5].

Solid-state electrolytes loaded with phosphoric acid provide less corrosion and more immobilisation compared to aqueous phosphoric acid fuel cells (PAFCs) [6–8]. The phosphoric-acid loaded polybenzimidazole (PBI) is the best-known example of a membrane; PBI has been used to produce reasonably successful membranes for fuel cells with excellent thermo-chemical stability and good conductivity [6,7]. However, in many cases, PBI/H<sub>3</sub>PO<sub>4</sub> membranes exhibit high conductivity values only with high acid

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loadings, which are usually at least higher than 5.0H<sub>3</sub>PO<sub>4</sub> molecules per repeat unit (PRU) of PBI [8].

Such a high PA acid content creates problems of mechanical strength reduction and elution problems of electrolytes, as well as catalyst corrosion problems associated with the use of an excess of highly concentrated PA at high temperature [9,10]. One promising idea to reduce the loading level is to fill solid proton conductors into the PBI membrane, such as solid acids, ionic liquid and graphite oxide [10–12].

Graphite oxide (GO) consists of carbon, oxygen and hydrogen and is exfoliated into individual graphite oxide nanoplatelets in water because of the hydrophilic oxygen groups attached to the graphene sheets [13]. The presence of acidic groups of GO, such as carboxylic acid and epoxy oxygen, could facilitate hopping of protons [14–16]. According to our previous work, the sulfonic acid groups functionalised to GO could improve water retention ability and provide hydrogen bond for the conductivity increase [17]. So, the sulphonic GO with PBI exhibited improved performance at low PA loading level. Functionalised graphite oxide (FGO) is also easy to disperse in a solvent, resulting in a homogeneous distribution into polymer matrices; in addition, the functional groups could improve the proton conductivity. Hence, the functionalised GO is a suitable candidate filler material for use in membranes to improve the proton conductivity and avoid excessive content of PA. Recently, functionalised GO was used in composite membranes and has attracted much attention. Functionalised groups, such as 3-mercaptopropyl trimethoxysilane (MPTMS) [15], added into graphite oxide were incorporated with the perfluorinated polymer Nafion<sup>®</sup>. The functionalised graphite controlled the state of water by means of nanoscale manipulation of the physical geometry and the chemical functionality of ionic channels. The confinement of bound water within the reorganised nanochannels of composite membranes enhanced the proton conductivity at high temperature via the low activation energy for ionic conduction [16]. Additionally, the increase of FGO nanofiller loading extended the number of available ion exchange sites per cluster, resulting in the increased proton mobility in the membrane at higher temperature and lower humidity [15]. Ionic liquids (ILs) are organic salts with high ionic conductivity and wide electrochemical potential windows. ILs could improve safety and enable a higher operating temperature range to be used [18,19]; therefore, they were considered as an additive in the proton exchange membrane. According to the oxygen group located in GO, the ILs could be readily bonded to the GO. The combination of GO and IL may enhance the PBI membrane conductivity because both the ILs and GO may provide hydrogen bond as the proton transport route [20].

In this work, the GO sheets were functionalised by an ionic liquid group 1-(3-aminopropyl)-3-methylimidazolium (ILGO) to combine with the PBI membrane loaded with phosphoric acid. The membrane proton conductivity and fuel cell performance were studied, and the results indicated that the performance of the PBI/H<sub>3</sub>PO<sub>4</sub> membrane was enhanced with the addition of ILGO.

## 2. Experimental methods

A graphite oxide (GO) sheet was synthesised from graphite (Shandong Qingdao graphite company, China) by oxidation with KMnO<sub>4</sub> in concentrated H<sub>2</sub>SO<sub>4</sub> according to the Hummers method [21]. A graphite sheet, was placed in cold (0 °C) concentrated H<sub>2</sub>SO<sub>4</sub> (85 wt.%), and KMnO<sub>4</sub> powder was added gradually by stirring and cooling to ensure a temperature below 20 °C. This mixture was stirred at 35 °C for 30 min, and then the temperature was increased to 98 °C, and 150 mL of distilled water was later added slowly. This temperature was maintained for 15 min. The reaction was subsequently terminated by adding a large amount of distilled water and

30% H<sub>2</sub>O<sub>2</sub> solution. Finally, the mixture was filtered and rinsed with 5% aqueous HCl solution until the sulphate could not be detected with BaCl<sub>2</sub>, and then the mixture was dried under a vacuum at 50 °C [21].

1-(3-aminopropyl)-3-methylimidazolium bromide (IL-NH<sub>2</sub>) was prepared through 1-methylimidazole (0.395 mL, 5 mmol) and 3-bromopropylamine hydrobromide (1.1000 g, 5 mmol) in 12.5 mL ethanol under nitrogen for 24 h. The resulting turbid mixture was re-crystallised by ethyl acetate as an anti-solvent. Finally, the resulting white powder was dried under vacuum at 60 °C overnight.

The ionic liquid graphite oxide (ILGO) was later synthesised by an epoxide ring-opening reaction between graphite oxide (GO) and IL-NH<sub>2</sub> [22]. First, 0.05 g of GO was homogeneously dispersed in 50 mL of deionised water, and then 0.05 g (8.9 × 10<sup>-4</sup> mol) of KOH was added into in the mixture, followed by 30 min of ultrasonication. Second, IL-NH<sub>2</sub> (0.05 g) was then added into the mixture and ultrasonicated for another 1.0 h. The turbid mixture was then transferred into a three neck bottle and vigorously stirred at 80 °C for 24 h. The resulting ILGO was subsequently washed with ethanol and water, and then air-dried [22]. ILGO was dispersed in a poly (2,2'-m-(phenylene)-5,5'-bibenzimidazole (PBI)/N,N-dimethylacetamide (DMAc)) solution with a mass ratio of 5 wt.%, and the membrane was loaded with phosphoric acid of 2 mol L<sup>-1</sup> and 4 mol L<sup>-1</sup> for three days each.

The membrane in-plane conductivity was measured using a four-point probe with a frequency response analyser (Voltech TF2000, UK). The four-point probe method involves four equally spaced probes in contact with the membrane: two of the probes were used to source current whilst the other two were used to measure the voltage drop. The membranes were cut into 10 mm × 50 mm strips and placed across four platinum foils with equal spacing of 5 mm. The AC impedance values were measured between frequencies of 1–20 kHz. To ensure the membrane reached a steady state, the membranes were held at the each desired conditions for 30 min before performing the measurements. The crystal structures of different membranes were analysed by X-ray diffraction (XRD, PANalytical X'Pert Pro Diffractometer), with a 2θ range of 5–70°. The membrane morphologies were measured by a JSM-5300LV (Japan) Scanning Electron Microscope (SEM). Fourier transform infrared (FTIR) spectroscopy was performed on a Varian 800 FT-IR spectrometer system between 4000 cm<sup>-1</sup> and 400 cm<sup>-1</sup>.

Catalyst inks were prepared by blending carbon supported catalysts (50 wt.% Pt/C, Alfa Aesar) and polytetrafluoro-ethylene (PTFE, 60 wt.% Aldrich) in a water–ethanol mixture under ultrasonic vibration for 10 min [23,24]. Gas diffusion electrodes (carbon paper) incorporated with wet proofed micro-porous layer (H2315 T10AC1) obtained from Freudenberg (FFCCT, Germany) were used as substrates to deposit the catalyst layer for both the anode and the cathode. The catalyst inks were sprayed onto carbon substrates at 100 °C, and the electrodes were held at 150 °C for 2 h to allow any liquid evaporation. The Pt loadings on the cathode and the anode were 0.9 mg cm<sup>-2</sup> and 0.5 mg cm<sup>-2</sup>, respectively. A 4 mol L<sup>-3</sup> H<sub>3</sub>PO<sub>4</sub> solution in a water/ethanol mixture was added onto the surface of the electrodes with a micropipette, and the electrodes were kept at 80 °C to remove the residue water and ethanol [24]. The MEA was finally obtained by hot pressing the electrodes onto phosphoric acid loaded composite membranes at 150 °C for 10 min with a load of 40 kg cm<sup>-2</sup>.

The MEA was fixed between two high-density graphite blocks (impregnated with phenolic resin) with parallel gas flow channels, and the active electrode area was 1 cm<sup>2</sup>. Electric cartridge heaters were mounted at the rear of the graphite blocks to maintain the desired temperature, which was monitored using imbedded

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