



A boron phosphate-phosphoric acid composite membrane for medium temperature proton exchange membrane fuel cells



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HIGHLIGHTS

- A composite membrane based on BPO₄ with excess of PO₄.
- Platinum micro electrode was used to study the electrolyte ORR compatibility.
- Conductivity of the self-supported electrolyte was $7.9 \times 10^{-2} \text{ S cm}^{-1}$ at 150 °C/5%RH.
- Fuel cell tests showed a major enhancement in performance of BPO_x over H₃PO₄-PBI.
- Current densities at 0.6 V were 706 for BPO_x and 425 mA cm⁻² for 5.6H₃PO₄-PBI.

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ABSTRACT

A composite membrane based on a non-stoichiometric composition of BPO₄ with excess of PO₄ (BPO_x) was synthesised and characterised for medium temperature fuel cell use (120–180 °C). The electrolyte was characterised by FTIR, SS-NMR, TGA and XRD and showed that the B–O is tetrahedral, in agreement with reports in the literature that boron phosphorus oxide compounds at B:P < 1 are exclusively built of borate and phosphate tetrahedra. Platinum micro electrodes were used to study the electrolyte compatibility and stability towards oxygen reduction at 150 °C and to obtain kinetic and mass transport parameters. The conductivities of the pure BPO_x membrane electrolyte and a Polybenzimidazole (PBI)-4BPO_x composite membrane were $7.9 \times 10^{-2} \text{ S cm}^{-1}$ and $4.5 \times 10^{-2} \text{ S cm}^{-1}$ respectively at 150 °C, 5%RH.

Fuel cell tests showed a significant enhancement in performance of BPO_x over that of typical 5.6H₃PO₄-PBI membrane electrolyte. The enhancement is due to the improved ionic conductivity (3×), a higher exchange current density of the oxygen reduction (30×) and a lower membrane gas permeability (10×). Fuel cell current densities at 0.6 V were 706 and 425 mA cm⁻² for BPO_x and 5.6H₃PO₄-PBI, respectively, at 150 °C with O₂ (atm).

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1. Introduction

Increasing the operating temperature of polymer electrolyte membranes fuel cell above 100 °C is highly desirable [1]. This will result in several advantages: faster reaction rates at both electrodes, anode and cathode, an improved CO tolerance leading to a simplified fuel pre-treatment [2–4], higher ionic conductivity can be achieved and improved heat and power cogeneration [5].

Research on proton exchange membranes for medium temperature (120–180 °C) PEMFCs operating under low humidity is usually focused on polybenzimidazole based membranes. PBI is

typically doped with phosphoric acid to provide proton conductivity [3,6]. Sulphuric acid [7] and ionic liquids [8] have been used to replace phosphoric acid; however these resulted in poorer performances. Phosphoric acid has specific properties making it a desirable candidate for medium temperature electrolytes: excellent thermal, chemical and electrochemical stability at fuel cells' conditions and low vapour pressure at temperatures above 150 °C [9].

However, limitations include deactivation via phosphate anion adsorption at positive potentials [6,10] and acid leaching.

Other approaches have utilised organic/inorganic membrane composites using phosphoric acid as an electrolyte with 1H-1,2,3-triazole grafted alkoxy silanes and tetraethoxy silane (TEOS) [11], 3-glycidoxypropyltrimethoxysilane (GPTMS) and 3-amino-propyltriethoxysilane (APTMS) [12] or zirconia and zeolite [13] to produce self-supporting membranes.

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While research often focuses on the ionic conductivity of the developed membranes, the compatibility of the electrolyte for fuel cell application is of utmost importance, and includes factors such as: conductivity, thermal stability, electrochemical stability and compatibility with the catalyst under reducing and oxidizing potentials and O₂/H₂ permeability. Electrolyte permeability to gases also strongly influences mass transport of electro-active species and hence influences electrode reaction kinetics [14]. While pristine PBI is considered a good candidate for membrane materials due to its low gas permeability, addition of PBI to the catalyst layer for proton conduction could impose mass transport limitation on anode and cathode performances, depending on the thickness of the polymer film formed on the catalyst sites and the amount of phosphoric acid doped in the PBI required to facilitate proton conduction. The higher the doping level used, the higher the conductivity would be, but mechanical properties, such as tensile stress of PBI deteriorate dramatically due to increased swelling. High swelling will also cause a significant increase in permeability and hydrogen cross-over of around 5 mA cm⁻² [15] and produce an open circuit voltage of around 0.85 V [16]. A balance between conductivity and mechanical properties was achieved at doping level of c.a. 5.6 acid per repeat PBI unit (PRU) [17]. Doping level will also affect significantly the electrode performance due to acid mobility from the membrane to the electrodes.

At doping level of 5.6 PRU the ionic conductivity is ca 4.5 × 10⁻² S cm⁻¹ (150 °C, 3%RH) [18]. There is a need to improve the membrane conductivity to around 8 × 10⁻² to minimise IR losses and obtain membrane conductivities similar to Nafion[®]. This can be accomplished by a larger phosphoric acid content in the membrane but without increase in permeability and swelling. One way to achieve this is via composite membranes.

PBI membranes with high acid doping of 6 PRU means that there is a large quantity of free mobile acid available to flood the catalyst layer. To resolve this changes in the anode and cathode structures is required. These include the use of thicker catalyst layer, utilising lower Pt/C ratio (20–30% wt) and increased de-wetting by increasing the Teflon content to 40% wt [19]. Another limitation is the chemical stability of the PBI membranes which degrades at temperature above 150 °C due to dehydration of phosphoric acid and other environmental issues [20].

In boron phosphate BPO₄ both P⁺⁵ and B⁺³ are tetrahedrally coordinated by oxygen. The structure of stoichiometric boron phosphate is similar to that of cristobalite, containing alternate PO₄ and BO₄ tetrahedrally linked by shared oxygen atoms forming a three dimensional network [21,22]. While BPO₄ is only partially soluble or insoluble in water (depending on preparation temperature), its conduction mechanism at low temperatures is significantly dependant on humidity, i.e. liquid phase conduction involving H₃PO₄ molecules [23] (10⁻⁷ S cm⁻¹ at 0%RH to 4.8 × 10⁻² S cm⁻¹ at 100%RH) where the surface layers of the solid BPO₄ are rendered mobile by the hydrolysis and dissolution in water resulting in several species including phosphoric acid [24]. Composites of organic/inorganic membranes with BPO₄ and sulphonated polyetheretherketone (SPEEK) up to 40% wt lead to improved membrane properties [25,26], composite of BPO₄ and PBI-SPEEK gave maximum conductivity at 20% wt BPO₄ of 6 × 10⁻³ S cm⁻¹ [26].

The non-stoichiometric composition of BPO₄ with excess of PO₄ units (B/P 0.8) increases its conductivity [23]. We propose a composite membrane (BPO_x) based on non-stoichiometric composition of BPO₄ with significant excess of PO₄ (B/P: 0.25). The excess phosphoric acid will facilitate proton conduction in the temperature range of 100–200 °C in the absence of water, while BPO₄ will provide a three dimensional network with PO₄ resulting in a composite membrane.

2. Experimental

2.1. Materials and BPO_x

Boric acid (>99.5%, Sigma), ortho phosphoric acid (reagent grade, Fisher) and dimethyl sulfoxide DMSO (>99.5%, Sigma) were used as received.

BPO_x samples with B/P atomic ratios 0.25 have been prepared from ortho-phosphoric acid and boric acid. Applicable amounts of the acids (4 mol H₃PO₄:1 mol H₃BO₃) were stirred continuously in a ceramic pan at 250 °C in air until a thick white slurry was obtained. The obtained slurry was then kept at the same temperature without stirring for 6 h. The samples were then transferred to sealed glass bottles to prevent humidity adsorption from the atmosphere. After cooling, the samples solidified and were ground and pressed using a 32 mm stainless steel pellet die (Fluxana, Germany) at 10 tonnes, producing 150 μm composite membrane discs.

2.2. Preparation of PBI/PBO_x hybrid membranes

Poly(2,2'-m-(phenylene)-5,5'-bibenzimidazole) PBI powder was dissolved in DMSO. The composite membranes were fabricated using a solution casting method [8]. An appropriate amount of BPO_x was added to the PBI/DMSO solution (3 wt%) to produce 3 and 4 PRU [moles BPO_x per mole PBI], resulting in a viscous gel-like solution after stirring, due to the interaction between PBI and PBO_x. The mixture was sonicated for several hours and placed in a water bath at 75 °C for 12 h. The obtained viscous solutions were cast on a Petri dish in an open oven at 80 °C for 12 h. The uniform composite hybrid membranes were peeled from the Petri dish and dried further in an oven at 110 °C for 4 h before starting the measurements. Attempts to prepare membranes with higher BPO_x content were not successful as the filler content become too high with respect to the polymer (PBI) and cracked membranes were obtained.

Impregnation method was also investigated to prepare PBI/BPO_x membranes. PBI membranes obtained from PBI/DMSO solution 3 wt%, were immersed in saturated solution of the prepared BPO_x in DMSO, DMAc, H₂O and methanol at 60 °C for one week. The resulting membranes had very low electrolyte uptake (max 0.9 PRU) and therefore low conductivity, which is mainly due to the low solubility of the prepared BPO_x in the studied solvents. BPO₄ prepared at temperature of 250 °C has ca 50% soluble part when 1 wt% slurry in water was tested for 15 h [23].

2.3. BPO_x characterisation

FTIR spectra of the membranes samples were measured with a Varian 800 FT-IR spectrometer system in the range of 4000–600 cm⁻¹ with a resolution of 2 cm⁻¹. The KBr pellet method was employed for solid samples.

¹¹B and ³¹P Solid state MAS NMR spectra were obtained using Varian VNMRs spectrometer (EPSRC UK National Solid-state NMR Service at Durham). Direct excitation: frequency and acquisition time of 128.3 Hz, 30 ms and 161.9 Hz, 50 ms, respectively. References: BF₃/OEt₂ and 85% H₃PO₄.

XRD pattern was collected using the PANalytical X'Pert Pro diffractometer using the X'Celerator area detector, Cu K X-rays were used.

Thermal stability of the prepared PBO_x samples was investigated by thermogravimetric analysis (Perkin Elmer, TGA 4000). The samples were heated from room temperature to 500 °C with a heating rate of 5 °C/min under nitrogen atmosphere. Weight loss was measured and reported as a function of temperature.

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