



meta-PBI/methylated PBI-OO blend membranes for acid doped HT PEMFC



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ABSTRACT

Methylation of polybenzimidazole leads to positively charged polymer backbones, and moveable anions. Ion exchange of methylated PBI-OO in phosphoric acid (PA) shows that the resulting polymers dissolve. *meta*-PBI, however, absorbs about 400 wt% PA while remaining a self supported membrane. We investigate the properties of blend membranes, employing *meta*-PBI for mechanical integrity and methylated PBI-OO for high PA uptake and resulting proton conductivity. While small additions of PBI-OO decrease the tensile strength of blend membranes (58 MPa for 10% PBI-OO), further addition leads to an increase, and 50% blend membranes show again a tensile strength of 74 MPa, just 3 MPa lower than pure *meta*-PBI membranes. Thermal stability of iodide exchanged blend membranes appears to be remarkably high, probably because cleaved iodomethane does not evaporate but methylates *meta*-PBI. PA concentration in doped membranes of 60–63% is reached by doping in 60% PA (blend; 6.3 PA/repeat unit) and 70% PA (*meta*-PBI; 4.6 PA/r.u.). This suggests that blends absorb PA more strongly. Both membranes show similar conductivity between rt and 140 °C, indicating that PA concentration describes these membranes better than PA/r.u. In the fuel cell, blend membranes show similar or better performance than *meta*-PBI. In the TGA, blends doped in 20% PA showed a stable plateau between 115 and 180 °C, while *meta*-PBI lost weight continuously.

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1. Introduction

Phosphoric acid (PA) doped polybenzimidazole membranes were shown to be proton conductive by Savinell

and Wainright [1] and are especially useful for high temperature polymer electrolyte membrane fuel cells (HT PEMFC). Typical operating conditions are temperatures around 160 °C without humidification of the fuel and oxidant gas streams [2]. One of the most investigated problems is the trade-off relation between the PA doping level, which correlates with the proton conductivity, and the inversely correlated mechanical stability (tensile strength and resistance to indentation). The most common way to increase the membrane stability is crosslinking [3,4].

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Methylation of polybenzimidazoles leads to 1,3-dimethylated polybenzimidazolium electrolytes [5]. Recently, we and others reinvestigated into methylated polybenzimidazoles in the search for alkaline stable anion exchange membranes [6–8]. It turned out that the 2-position is sensitive towards hydrolysis under alkaline conditions. However, bulky groups can sterically protect the 2-position [9]. The thermal stability is usually in the range of over 180 °C (iodide exchanged membranes) and increases with decreasing anion nucleophilicity (over 220 °C for carbonate exchanged membranes) [10]. It was observed that fully methylated polybenzimidazole (PBI-OO with 95% degree of methylation) dissolves in 85% phosphoric acid. Also after ion exchange in 0.5 M K_3PO_4 for 48 h, the polymer was found to dissolve in water within 5 days. This observation inspired us to prepare blend membranes of *meta*-PBI (providing mechanical stability) and methylated PBI-OO (providing an easier pathway for protons when fully swollen by phosphoric acid). It should also be noted that all phosphoric acid can be leached out from PBI, but that 2 dihydrogenphosphate ions per repeat unit are inseparable part of phosphate exchanged methylated PBI-OO (Fig. 1).

Structurally, alkylated PBI can be understood as a polymeric ionic liquid (PIL). For phosphoric acid doped PBI containing a protic ionic liquid (1-methyl-3-propylimidazolium dihydrogenphosphate), Ye et al. reported that the IL acts as a proton transfer bridge, plasticizes PBI, balances the strength of hydrogen bonding in the membrane and helps to absorb and retain water [11]. To our knowledge, we are the first to report a polymeric ionic liquid (e.g. polybenzimidazolium) blended with PBI.

2. Experimental

2.1. Materials

meta-PBI was provided by Danish Power Systems (Dapozol, $M_w = 45,000$ g/mol, calculated from the viscosity measurement in concentrated sulphuric acid at 30 °C according to [2]). Poly[(2-(4,4'-diphenylether)-5-oxybenzimidazole)-2,5-benzimidazole] (PBI-OO) was commercially obtained from Fumatech (Germany), and has a M_w of >40,000 g/mol according to the specification. Methylated PBI-OO was prepared according to the literature, by

dissolving PBI-OO in NMP, adding sodium hydride and iodomethane, and, after complete reaction, precipitation of the methylated product in acetone [12]. DMSO was obtained from Daejung, all other chemicals were obtained from Sigma and used without further purification.

2.2. Membrane fabrication

5 wt% solutions were obtained by dissolving PBI-OO in DMSO at room temperature and *meta*-PBI in DMAc at 160 °C. After cooling to room temperature, the solutions were mixed in the required ratio and cast on a glass plate with a doctor blade (400 μ m gap). The solvents were removed at 60 °C, first under ambient pressure for 5 h, later under vacuum.

2.3. Water uptake

1 cm $\times$ 4 cm sized membrane samples were dried for 1 day at 60 °C in the vacuum, weighed (dry weight; WD) and immersed in water for one day. The membranes were quickly wiped with tissue to remove surface water, and weighed again to obtain the wet weight (WW). The water uptake was calculated according to

$$\text{Water uptake}[\%] = 100 \cdot (\text{WW} - \text{WD}) / \text{WD}.$$

2.4. Mechanical testing

Stress–strain curves were obtained with a Cometest QC-508E universal testing machine. The sample size was 1 cm $\times$ 4 cm, and the elongation speed was 10 mm/min. Humidity and temperature were not controlled but registered for every measurement. The maximum stress was taken as the tensile strength. For each material, 4–6 samples were cut from one membrane and measured.

2.5. Thermogravimetric analysis

Thermal stability of membranes was measured with a TA instruments TGA Q50 in air or nitrogen. Sample weights were around 20 mg, and the temperature was increased 10 °C/min from room temperature to 800 °C in air if not mentioned differently.

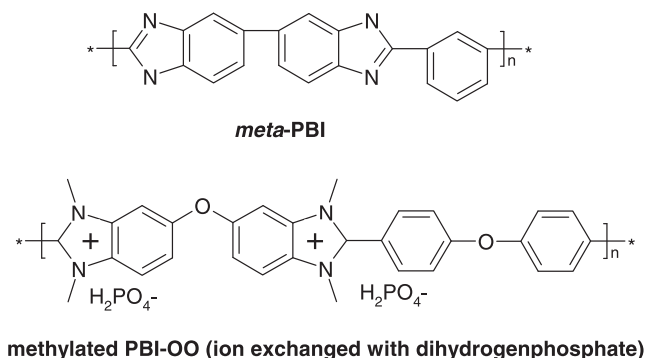


Fig. 1. Structures of *meta*-PBI and methylated PBI-OO.

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