

Supporting information to the short communication:

CROSS-LINKED POLYBENZIMIDAZOLE MEMBRANES FOR FUEL CELLS

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1. Polybenzimidazole synthesis

The linear polybenzimidazole (poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole, PBI) was first synthesized from 3,3'-diaminobenzidine tetrahydrochloride (DAB, Aldrich) and isophthalic acid (Aldrich) by condensation polymerization in polyphosphoric acid (PPA) at 200°C. Into a 1 L round bottom flask equipped with a stirrer and nitrogen inlet was added 300 g of polyphosphoric acid was added and the temperature was increased to 140°C under stirring. 10 g of 3, 3' - diaminobenzidine tetrahydrochloride was added gradually. It should be remarked that DAB is harmful by inhalation, ingestion or absorbing through skin and may act as a carcinogen. Safety glasses, gloves, adequate ventilation are required for operation with it. Hydrogen chloride gas was eliminated under a stream of nitrogen. To this solution, 4.2 g of isophthalic acid was added and the temperature was increased to 200°C and kept for 20 hours. At the end of the synthesis, the polymer in polyphosphoric acid was poured into 5 L of water to isolate the polymer. The polymer was afterwards washed with water by decantation. To neutralize the excess acid contained in the polymer, a sodium bicarbonate solution was used to the successive washing until pH = 7. The polymer was finally filtered and washed thoroughly with water and then methanol. After drying at 90°C under vacuum overnight, about 7.6 g of a brown powder was obtained.

The polymer was first characterized with viscosity measurement using an Ubbelohde viscometer. 0.5 g of the polymer was dissolved in 100 ml 96% H₂SO₄ under stirring at

room temperature. The inherent viscosity of the polymer was found to be 0.52, corresponding to an average molecular weight of 21,500.

For membrane casting, the polymer was dissolved in N,N-dimethylacetamide (DMAc, Aldrich) at 80°C under stirring. The resulting solution was then filtered to remove any undissolved polymer and diluted to a 5% solution.

2. Membrane casting

The used cross-linker is α,α' -dibromo-p-xylene (DBpX), which is dissolved also in DMAc. A mixture of 5% PBI solution and 5% DBpX solution was then prepared. The ratio of the PBI solution and the DBpX solution was selected according to the degree of cross-linking that is desired. One mole of DBpX with two functional groups is added for each two equivalents of PBI amine hydrogen that are desired to be cross-linked. Membranes were cast using Petri dishes. Thickness and size of the membranes were varied by altering the volume of solution and the diameter of the dishes. The majority of the solvent was evaporated in a ventilated oven in a temperature range from 60 to 120°C. The membranes were further heat-treated at temperatures ranging from 160 to 300°C.

3. Acid doping

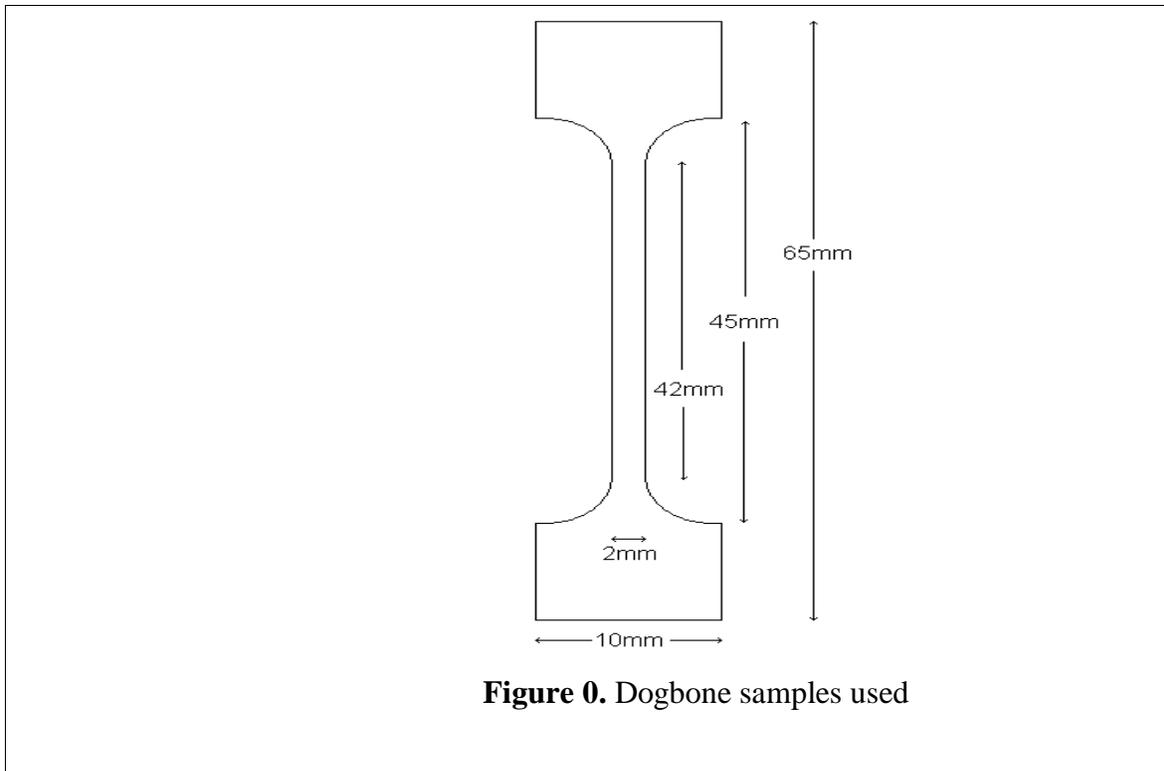
Linear PBI membranes was acid-doped in 75% phosphoric acid at room temperature for a few days, giving an acid doping level of around 6 mol H₃PO₄ per PBI repeat unit. For the cross-linked PBI membranes the acid doping took place in 75-85% phosphoric acid at temperatures of 120-160°C for 15-20 hours. The weight changes before and after the acid doping were measured and used for the acid doping level calculation. The weight gain was due to both water and phosphoric acid, however, the water uptake is assumed to remain unchanged in the presence and absence of phosphoric acid.

4. Solubility test in DMAc

The cross-linking was characterized by measuring the solubility of the membranes in DMAc. Due to its low molecular weight, the linear PBI used was found to be completely dissolved in DMAc at 80°C after about an hour. The cross-linked PBI membrane samples were immersed in DMAc (1% of the polymer solution would be obtained upon a complete dissolution) at 80°C under stirring. At time intervals of 1, 4, and 18 hours, respectively, the remaining membrane samples were taken out of the solution, dried at 180°C for 2 hours, and weighed. The solubility of the membranes was then obtained from the weight losses.

5. Tensile measurement

The equipment used for measuring mechanical properties was a modified universal materials strength testing machine (Testometric Micro 350). A dog bone sample (see figure 1) was held by two grips and the test procedure of ASTM D638 was adapted. The upper grip together with a load cell was mounted on a movable sled, which was driven by a motor upwards at a constant rate (10 mm/min) to elongate the membrane sample. Grip separation and axial force were recorded as a function of time using an A/D converter.



The membrane sample, together with both grips and the sled, was contained in a metallic chamber, which were equipped with attached heating elements and inlet and outlet of the humidified air. For controlling the relative humidity, water was pumped into a steam generator by means of an infusion pump (kdS 101, KD Scientific, USA). The accuracy of the pump was $< \pm 1\%$ within the flow rate range of 0.001-0.351 ml/min. The steam was produced and converged with an air flow and directed into the chamber through PTFE tubes. The tubes were heated to 20°C above the measuring temperatures inside the chamber, in order to avoid the steam from condensing before it entered the chamber. The relative humidity was calculated from the air flow and water pumping rate at different temperatures, and calibrated by using a relative humidity transmitter (operational at up to 180°C).

6. Conductivity measurement

Conductivity measurements were carried out by using a four-probe conductivity cell, as schematically represented in Fig.2. The membrane was fixed on a glass plate as the upper sample holder. Two measuring probes made of platinum were fixed through the sample holder and in contact with the membrane sample at a distance of 1.0 cm apart. The glass plate with the membrane sample was then assembled onto a Teflon holder, on which 2 platinum foils were attached as the current supply terminals. The assembly was then placed in a glass tube with openings for the humidified air inlet and outlet. The whole cell was kept in an oven for high temperature measurements. The relative humidity was controlled in the same way as in the tensile measurement, described above. The symmetric square wave current was supplied through the platinum foils in a frequency range from 6 to 10 kHz. The voltage drop through the membrane was measured via the platinum probes.

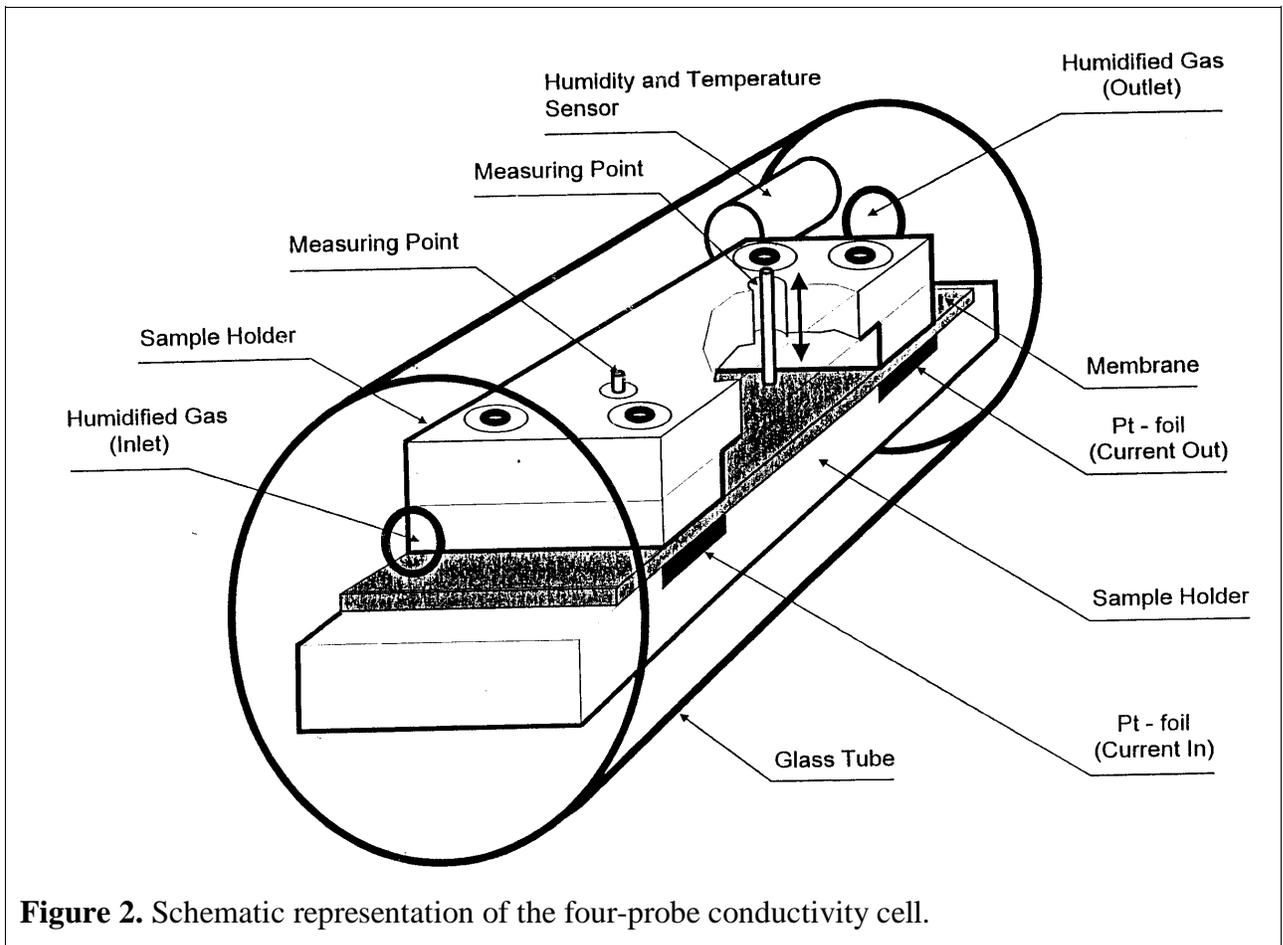


Figure 2. Schematic representation of the four-probe conductivity cell.

7. Fenton test

For testing the membrane degradation by oxidative radicals, a Fenton solution of 3% H_2O_2 containing 4 ppm Fe^{2+} was used. Fe^{2+} was added as $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ for accelerating the effect to produce hydroxide radicals. Membrane samples were immersed in the Fenton solution at 68°C . After a certain period of time, the membrane samples (as whole or in pieces) were collected by filtering, dried at 120°C for 2 hours, and weighed to measure the weight loss. For the successive measurements, the fresh Fenton solution was prepared and preheated, into which the dried membrane samples were placed for continuation.