Cross-linked high acid doping level polybenzimidazole membranes with high conductivity and improved mechanical properties

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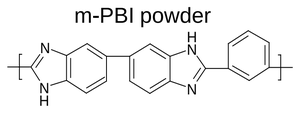
Introduction: This work shows the elaboration of high temperature fuel cell membranes (PEM). The polyphosphoric acid (PPA) process is used to get a high acid doping level PBI membrane. The acid doping level is the number of phophoric acid molecules in one repeat unit of polybenzimidazole. The higher this value is, the higher the conductity is. However the mechanical properties become lower. In this work differents ways are used to improve the membrane mechanical properties while keeping high electronic properties. A cross-linker is incorporated before the membrane casting, thermical and plasma treatment are realised to raise the cross-linking. Membranes caracteristics are shown in this poster and the fuel cell test peformances also.

1- Membrane elaboration

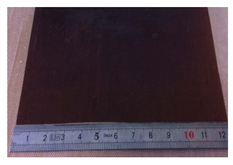
m-PBI powder



PPA 160°C, 3h

Solubilisation

Cross-linker addition



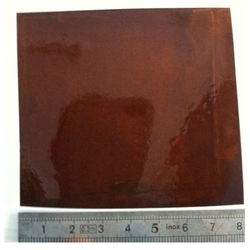
Casting

Thermal treatment (160°C 2h)

Plasma (Ar, 100 W)

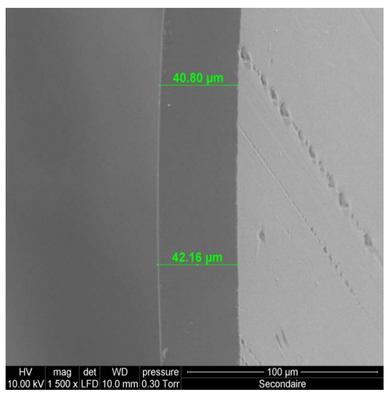
Cross-linking

Cross-linked m-PBI/H_3PO_4 membrane



2- Characterisation

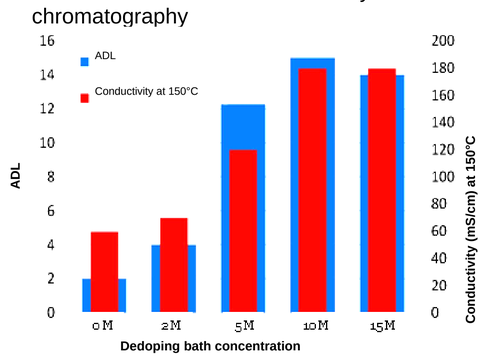
o *Microscopy :*



SEM picture:
-Dense, homogeneous membrane
-Thickness ~ 60 µm

o *Acid doping Level :*

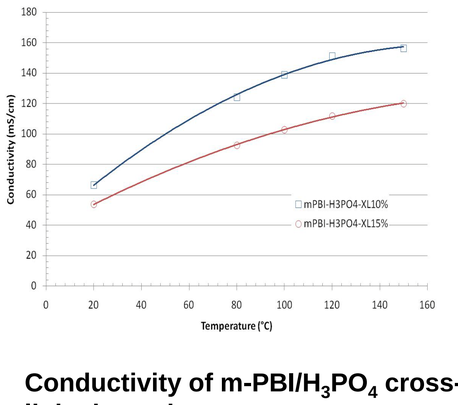
The ADL has been determinated by ionic chromatography



-Conductivity and ADL connection :
De-doping : membranes are de-doped by immersing in controlled concentration phosphoric acid solution
The higher ADL is, the higher is the conductivity.

o *Conductivity :*

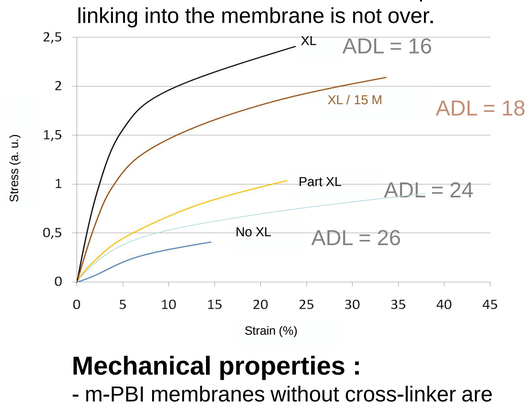
The conductivity measurements have been realised through the plane from 20°C to 150°C



Conductivity of m-PBI/H_3PO_4 cross-linked membrane :
-The conductivity is close to **160 mS/cm at 150°C**
- σ decreases when the quantity of cross-linker increases. The cross-linkage rate is an important parameter on the conductivity

o *Mechanical properties :*

Mechanical properties experiments have been determined by traction test. “XL” means cross-linked. “Part XL” membranes haven’t been plasmed, so cross-linking into the membrane is not over.

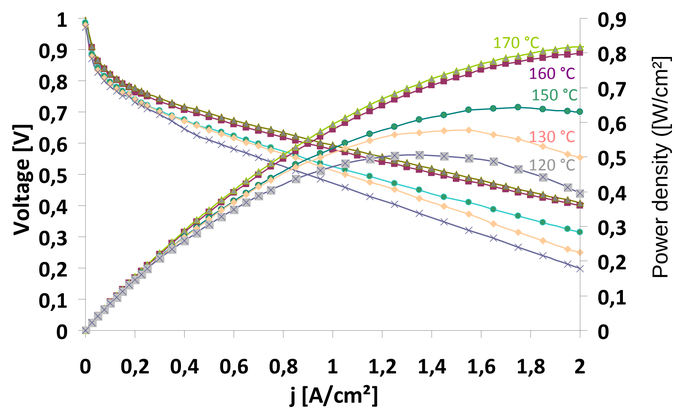


Mechanical properties :
- m-PBI membranes without cross-linker are fragile.
-The plasma is an important step, it completes the reticulation.
- The mechanical properties are also connected to the ADL. High acid contain membrane has low mechanical properties

3- Fuel cell test

o *H_2/O_2 test :*

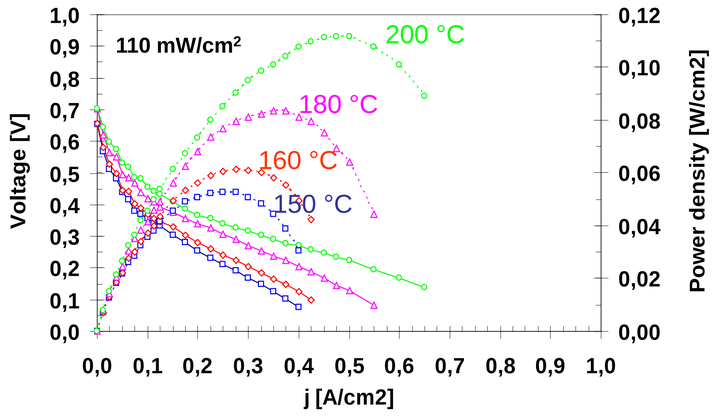
Cross-linked m-PBI/H_3PO_4 membranes: 1 bar abs pressure, temperature 120 – 170 °C



Polarisation curves with cross-linked m-PBI/H_3PO_4 membrane. Temperature effect with H_2/O_2. Baltic Fuel Cell electrodes.

o *Ethanol test :*

Cross-linked m-PBI/H_3PO_4 membranes: Vapour feed, 1 bar abs pressure, temperature 150 – 200 °C



Polarisation curves with cross-linked m-PBI/H_3PO_4 membrane. Temperature effect with ethanol/water [4.2M] gas mixture/Oxygen. Baltic Fuel Cell electrodes.

Conclusion : In this poster, the elaboration of high acid doping level PBI membrane has been shown. The high acid contain leads to high conductivity but poor mechanical properties. However, by adding a cross-linker agent into the membrane, cross-linked m-PBI/H_3PO_4 membranes are obtained and lead to an signicative improvement of the mechanical properties (from 0.4 to 2.5 GPa). Their conductivity are still high (σ ~ 160 mS/cm) and allow the fuel cell test application. Indeed, in fuel cell tests, the highest power density get is close to 900 mW/cm² at 170 °C for the H_2/O_2 fuel cell and 120 mW/cm² for the DEFC test.