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Title: Long-term Durability of HT-PEM Fuel Cells Based on Thermally Cross-linked Polybenzimidazole

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Keywords: durability, polymer electrolyte membrane, fuel cell, polybenzimidazole, cross-linking, thermally cured

S1 EIS experimental details

Though there should be little to no difference between results measured by galvanostatic- as opposed to potentiostatic EIS, it was determined that galvanostatic EIS was the more favourable mode as is often the case for devices with low impedance [1, 2]. The interference from inductance at high frequency was mitigated by ensuring that the applied cable and its positioning were fixed throughout each measurement. Also, the applied cable was shielded and its length was kept

relatively short (≈ 2 m) [1, 3, 4]. Magnetic coupling as a result of mutual inductance was minimised by twisting together the current leads. This reduces the magnetic field because that which is generated by current flowing in one direction is compensated by that which is generated from current flowing in the opposite direction. Furthermore, the effect of the residual magnetic field was minimised by also twisting together the potential leads. Ideally, residual interference should then affect both the sense- and reference electrode leads with an equal magnitude of inverse polarity – effectively generating a common mode signal that does not affect the EIS measurement. Finally, the current leads were separated from the potential leads as much as possible since the intensity of the magnetic field is reduced with distance.

The choice of what amplitude to apply was made by trial and error before starting the experiment and with the use of other MEAs that had been manufactured in a similar manner. First, a low amplitude was applied which yielded very noisy results. By repeated iteration, increase of the amplitude led to noise reduction. However, at a certain point the recorded EIS spectra became different from that recorded using lower amplitudes; usually a change in the low frequency region was observed. Such a change signifies that the amplitude is too high, and a reduction was made accordingly.

Prior to start-up of each cell, a short circuit impedance measurement was made for the empty cell hardware at the operating temperature of the cells, i.e. including everything but the PTFE gas sealings and the MEA itself. This was done to estimate which part of the EIS response from an operating fuel cell could not be attributed to the MEA in question. These measurements were carried out by applying an alternating current signal of approximately 280 mA (200 mA_{RMS}), and the resulting resistance of the cell hardware accounted for approximately 5-8 % of the series resistance measured for MEAs at BoL. The short circuit series resistance measurements are only indicative and have not been corrected for in the presented data because they include contribution

from an unrelated contact resistance, namely that between two flow plates. Furthermore, the stability of this resistance has not been verified, though it is reasonable to assume that it does not change much over the course of the experiment.

Small amounts of water could condense in the exhaust tubes during operation since they were not isolated. The amount of water that would be condensed at any given time was less than 0.5 mL and was solely observed in the tube for the cathode exhaust. This had discernible impact neither on the steady state performance nor on the polarisation curve behaviour. Though indiscernible from direct current measurements, this water condensation did result in noise during EIS measurements at frequencies that were characteristic to each individual cell. Therefore, the exhaust tubes were disconnected from the cell immediately before an EIS measurement and then reconnected once the measurement had been carried out.

It is clear from the EIS measurements that there are additional arcs at low frequency for sample PBI-4k4 and X-1k which indicates slight mass transport problems already from BoL. In turn, by transitorily increasing the gas flows of air and hydrogen by just a few NmL min⁻¹, the low frequency arc for these cells was identified as being due to mass transport limitation on the anode side; the low frequency arc decreased as the anode gas flow was increased. For sample PBI-4k4, the mass transport resistance increased slightly right up until the EoT, whereas the maximum mass transport limitation for sample X-1k seems to have occurred after about one week of operation. Seeing that the hydrogen gas flow is quite small to begin with, it is possible that a leak from the anode gas chamber can be the cause of the observed mass transport resistance during the current increase of EIS sampling. The phenomenon cannot necessarily be ascribed as being due to a significant difference in the MEAs.

S2 Supplementary figures and tables

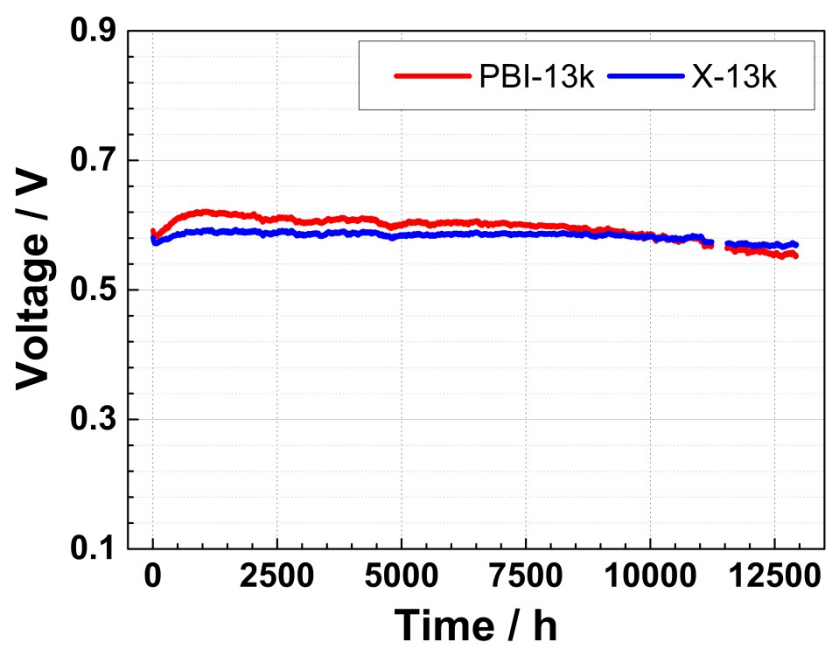


Figure S1 Steady state lifetime curves for MEAs based on linear *m*-PBI and cross-linked *m*-PBI operated at 160 °C, 200 mA cm⁻², $\lambda_{\text{air}}=4$, and $\lambda_{\text{H}_2}=2$. **This figure is intended for view in colour.**

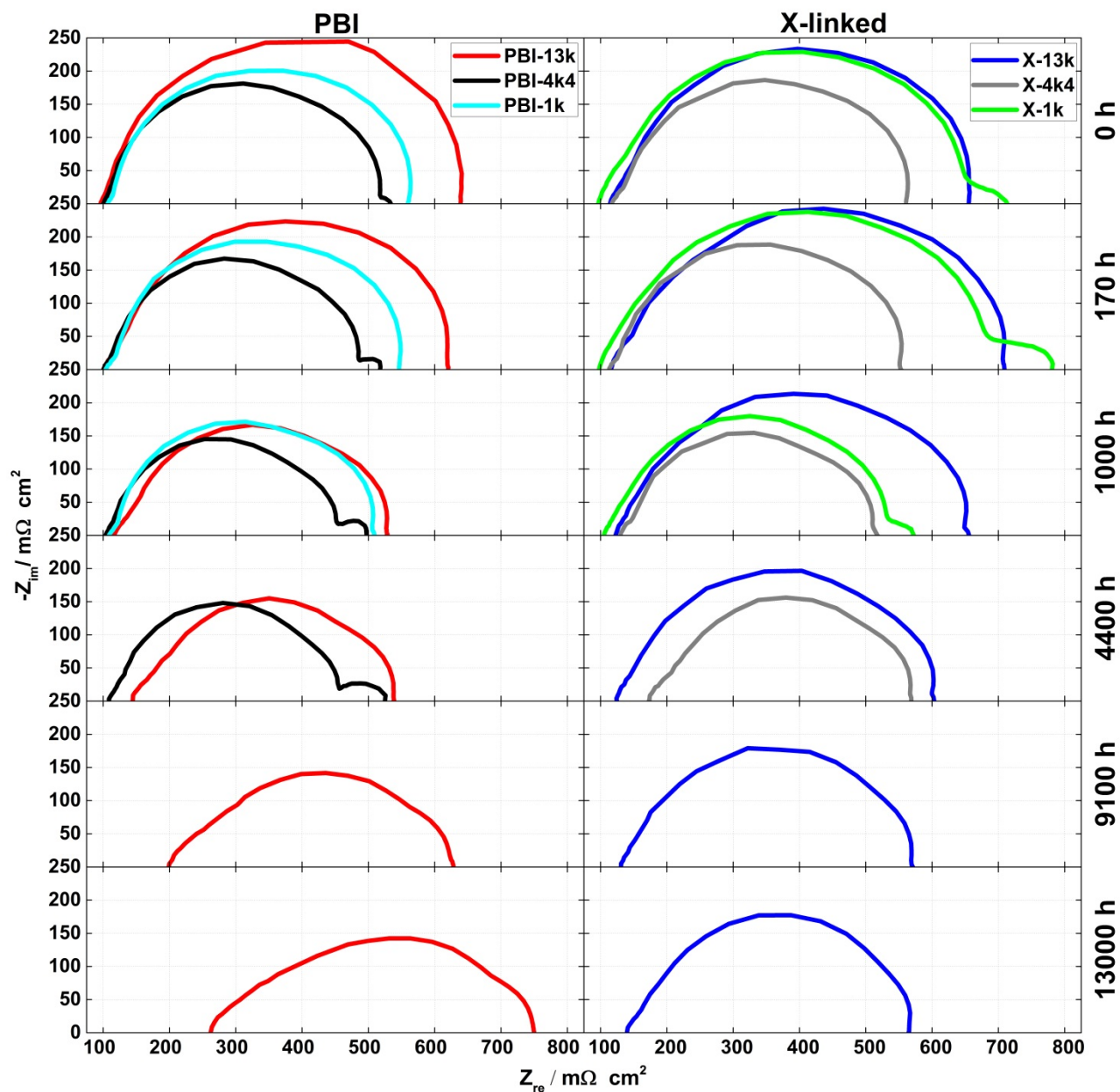


Figure S2 Comparison of EIS measurements over time for three MEAs based on linear *m*-PBI membranes (left) and for three MEAs based on cross-linked *m*-PBI membranes (right).

Interferences caused by noise have been masked. **This figure is intended for view in colour.**

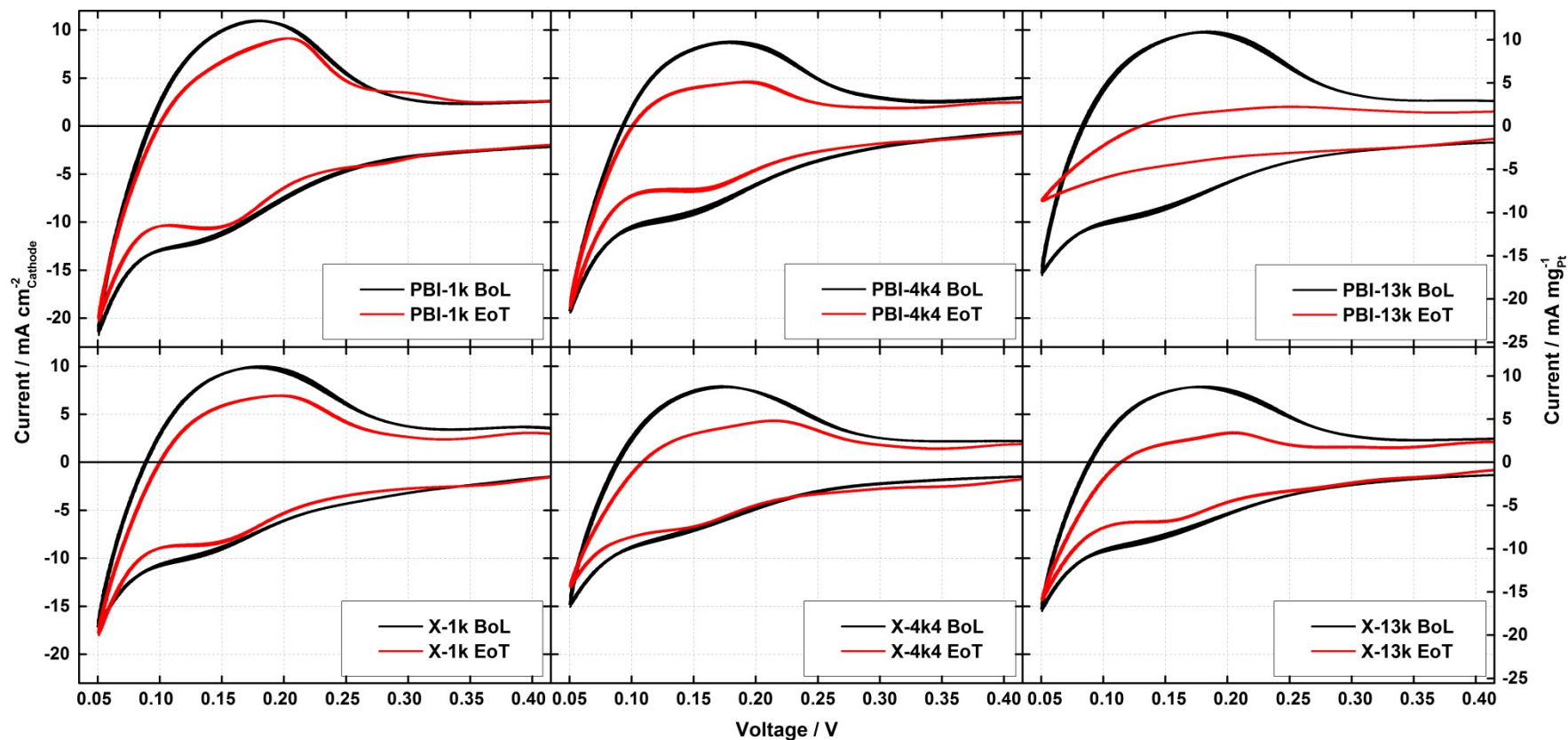


Figure S3 Average of 20 cyclic voltammograms at BoL (black) and EoT (red) of three MEAs based on linear *m*-PBI membranes as compared to three MEAs based on cross-linked *m*-PBI membranes. The thickness of the curve relative to that of the legend is indicative of the measurement stability as it represents the standard deviation in current and voltage between each set of 20 cycles. The maximum coefficient of variation is less than 3 % of the average for each point. **This figure is intended for view in colour.**

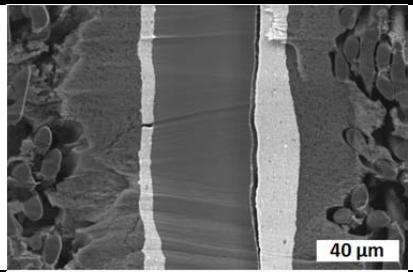
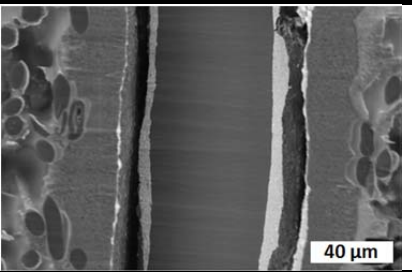
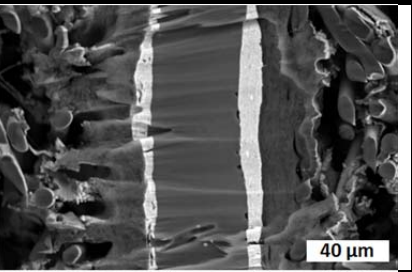
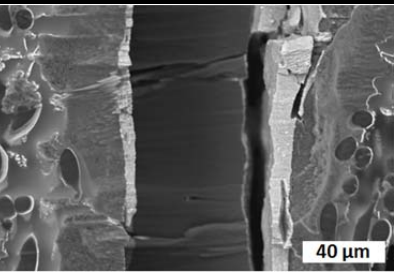
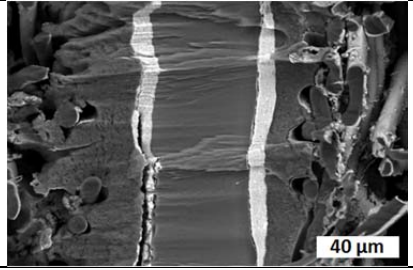
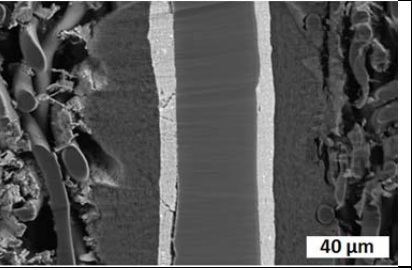
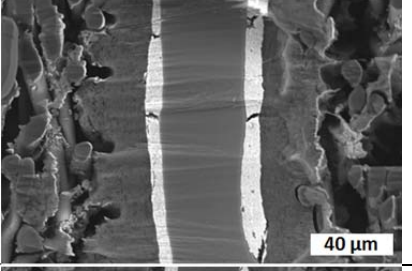
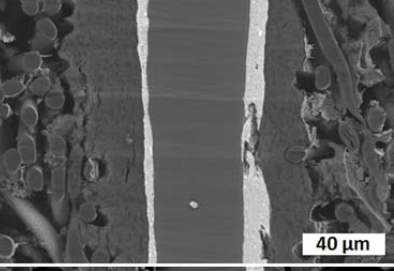
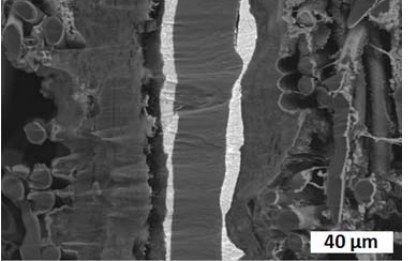
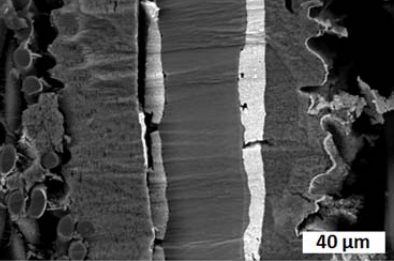
	Linear <i>m</i> -PBI		Cross-linked <i>m</i> -PBI	
	Batch #1	Batch #2	Batch #3	Batch #4
As prepared				
1000 h		-		-
4400 h	-		-	
13000 h	-		-	

Figure S4 Cross-sectional backscatter electron images of MEAs based on linear *m*-PBI membranes (left) as compared to MEAs based on cross-linked *m*-PBI membranes (right) after the indicated duration of steady state operation, cf. sample names in Table 1. All scale bars are 40 μm and the cathode faces right in every case.

1 References

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