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Ongoing Efforts Addressing Degradation of High Temperature PEMFC

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1 High Temperature PEM Fuel Cells

Proton exchange membrane fuel cells (PEMFC) for operation at temperatures above 100 °C have in recent years attracted increased attention as an alternative to conventional PEMFC based on humidified perfluorosulphonic acid membranes [1]. The reasons for aiming at a higher working temperature are increased tolerance to fuel impurities like carbon monoxide [2], the absence of liquid water, higher value of excess heat [3] and higher temperature gradients for cooling, which all lead to simpler and less costly system architecture. In order to operate the cell at temperatures over 100 °C electrolyte membranes less dependent of high water content must be developed and applied. There have been many attempts to develop such high temperature membrane materials (as reviewed [4]) and the most successful one is the phosphoric acid doped polybenzimidazole (PBI) membrane originally invented in the nineties at Case Western Reserve University [5]. There are many variants of PBI and the most common is poly (2,2´-*m*-(phenylene)-5,5´-bibenzimidazole) also called *meta*-PBI, *m*-PBI or often simply PBI (see Figure 1). The polymer itself is not a proton conductor, but when doped with a significant amount of phosphoric acid it gains conductivity comparable to the perfluorosulphonic acids traditionally used in PEMFC. However, one important difference is that the conductivity is still high if the cell is operated without humidification and the cells can be operated at higher temperature.

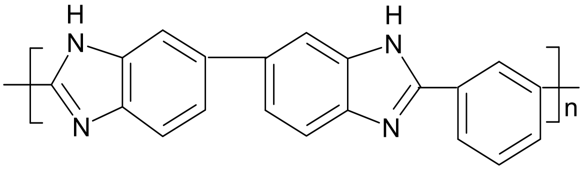

Figure 1: PBI, poly (2,2´-*m*-(phenylene)-5,5´-bibenzimidazole).

2 State-of-the-art for Lifetime and Degradation of High Temperature PEMFC

The high temperature PEMFC (HT-PEMFC) system has reached a state of development where durability becomes a key issue. The PBI based PEMFC can be seen as a hybrid between the conventional PEMFC and the phosphoric acid fuel cell (PAFC) because it has a membrane as well as phosphoric acid in the electrolyte. The electrodes are similar in all three cases with the catalysts being platinum on carbon. It can therefore be expected that many of the degradation mechanisms known from both PEMFC and PAFC will be found with the PBI based HT-PEMFC. The literature on HT-PEMFC degradation is still limited but growing. The authors group published early durability results at different temperatures in 2003 [6]. The experiments (Figure 2) indicated that performance was most stable at temperatures of 150 °C or lower while a fast performance decay was seen at temperatures of 180 and 200 °C. Selected durability results reported are collected in Table 1. It shows that the longest lifetimes are demonstrated at 150 – 160 °C.

Different lifetime targets are set for different applications and by different authorities or stakeholders, but it is normally considered fair to say that for stationary applications like combined heat and power production it is over 40,000 hours at constant load with only few start-ups. For vehicles, only 5,000 hours should do, but at dynamic load and with multiple start-ups.

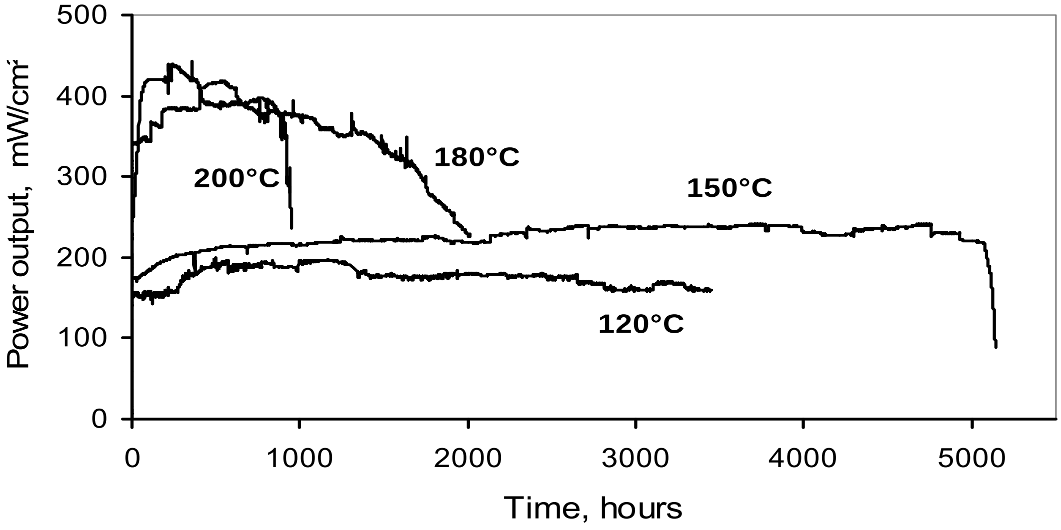

Figure 2: **Early durability results. Constant voltage: 0.5 V, Pt loading: 0.5 mg cm^{-2}, reactants: H_2/O_2 at 1/1 bara, electrode area: 4 cm^2. Re-plotted after [6].**

Table 1: **Selected single cell lifetime results from the literature. Some experiments proceeded after the hours listed. Most reported experiments have been carried out at 150 – 160 °C, and the most commonly used cell is Celtec-P 1000 from BASF.**

Temperature	Lifetime	Degradation	Cell from
80 °C	1,000-1,500 h	14-45 µVh^{-1}	Benicewich, modified PBI
120 °C	3,500-13,000 h	6.3-? µVh^{-1}	DTU, BASF (longest)
150 °C	5,000-10,000 h	n.a.	Fumatech, ABPBI (longest)
160 °C	5,000-18,000 h	5-25 µVh^{-1}	Jülich or BASF (longest)
180 °C	2,000 h	26-? µVh^{-1}	BASF or DTU
200 °C	1,000 h	n.a.	DTU

3 Failure Modes

A PEMFC is a complex structure with multiple internal functionalities and it is obvious that many things can go wrong. A substantial review is given by Borup et al. [7]. Degradation is often described externally as a voltage decay rate (μVh^{-1}) at constant current load. From this, extrapolations to lifetimes are sometimes made, but in many case another failure mode like membrane collapse becomes the limiting factor. The gradual decay is often assigned to catalyst coarsening or corrosion and catalyst substrate corrosion. Membrane failure can be due to mechanical stress or chemical attack in the form of oxidation. In the HT-PEM system acid loss seems not to be as big a problem as in PAFC. This is probably because the long term experiments are carried out at 150 – 160 °C which is significantly lower than for PAFC (~200 °C). In the following examples of results with membrane oxidation and catalyst degradation from the authors group are given.

4 Oxidative Degradation of the PBI Membrane

A well known test for oxidative stability of polymers is the Fenton test in which the membrane is kept in a solution of H_2O_2 and Fe^{2+}/Fe^{3+} ions. It is debated to which extent the test is relevant or too harsh. In this work it is seen as an accelerated test that will show relative stability of selected polymers. The Figures 3 to 6 show oxidation results of different polymers as explained in the figure texts. Nafion is included for comparison. It is common knowledge that hydrocarbon polymers are more sensitive to oxidation than per-fluorinated polymers.

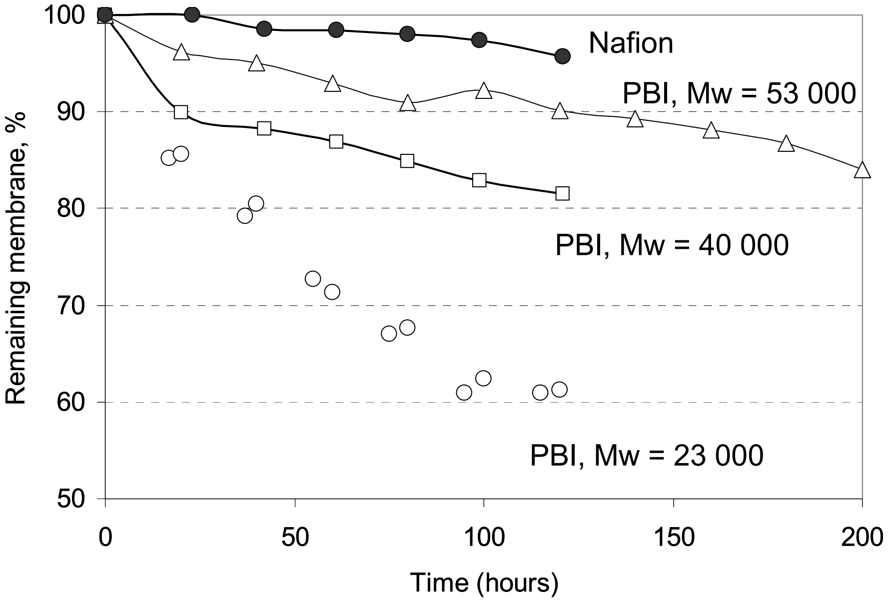

Figure 3: Fenton oxidative testing of Nafion and PBI with different molecular weights as indicated. The experiment indicates a strong dependency on molecular weights.

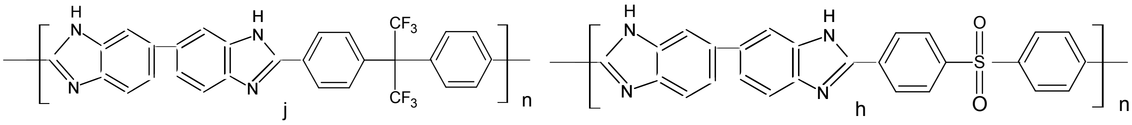

Figure 4: **Structures of F_6-PBI (left) and SO_2-PBI (right) [8].**

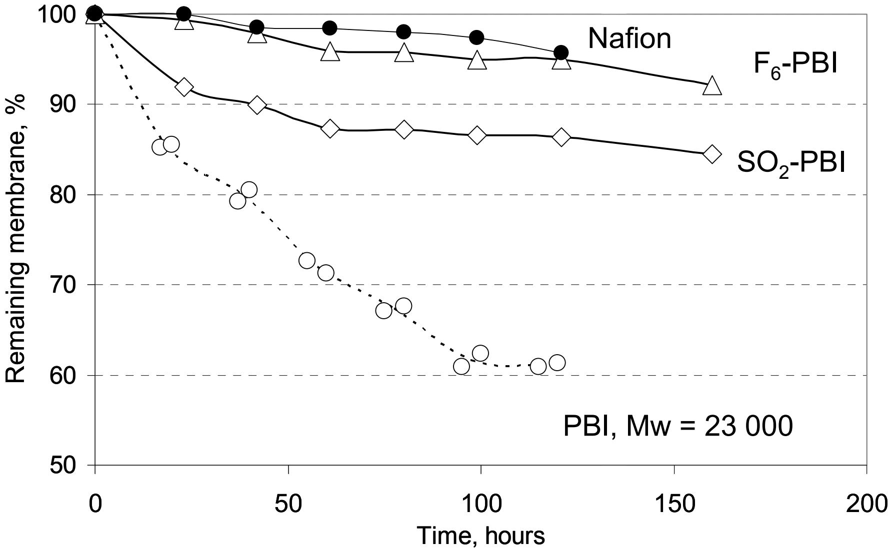

Figure 5: **Fenton oxidative testing of Nafion, F_6-PBI and SO_2-PBI (see Figure 4).**

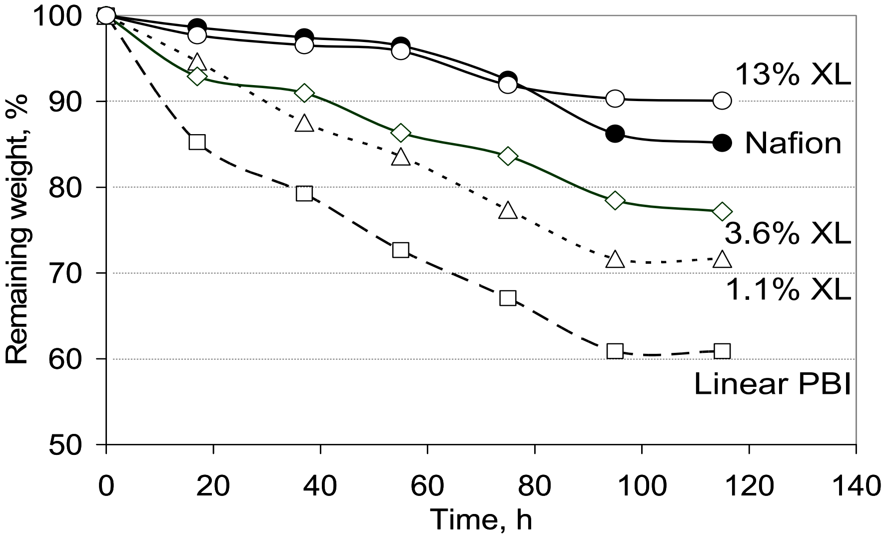

Figure 6: **Fenton oxidative testing of PBI cross-linked to different extents by *p*-xylene dibromide [9].**

It can be concluded that it is possible to increase the lifetime of the polymers in H_2O_2. However, the dependency on molecular weight seen in Figure 3 was somewhat unexpected since the chemistry of the polymer is unchanged. It points in the direction of endpoint attack, but there is no solid conclusion yet. A spectroscopic study is in progress by the authors group. The results on modified PBI are also promising, but they don't show whether the improvement is due to the chemical modification or simply the molecular weight.

5 Carbon Support Oxidation

A series of accelerated carbon oxidation tests were performed on the carbon supported catalyst by voltage cycling. The voltage was cycled between 0.9 and 1.2 V, 3 min per cycle for 17 hours. After a rest period of 6 – 7 hours at 0.5 V a polarization curve was measured. In Figure 7 the performance at 0.5 V is plotted as a function of potential cycles. It can be seen that the standard catalyst support materials, Vulcan XC 72R and Ketjen black as well as HISPEC and Ensaco are most seriously affected, while the graphitized Vulcan XC 72R degrade much slower. The longest lasting candidate is a special corrosion resistant catalyst from Johnson Matthey. There was no detailed information on it available. In all cases the degradation was understood as a loss of active area. This can be caused by detachment due to the support corrosion, but platinum particle growth was also seen by line broadening in X-ray diffraction.

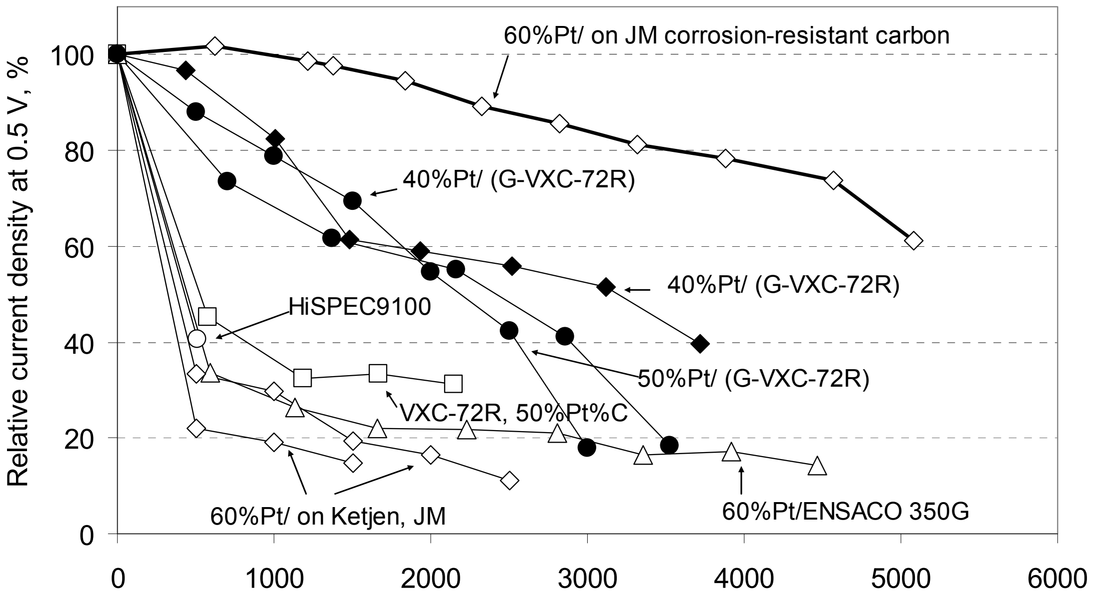

Figure 7: **Results of potential cycling of Pt catalysts on different carbon supports. Open markers refer to standard supports (Vulcan XC 72R, Ketjen black and trademarks). Filled markers are Pt on partially graphitized Vulcan XC 72R. The uppermost curve with thick line is for a special Johnson-Matthey product.**

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