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# Influence of membrane type and molecular weight distribution on the degradation of PBI-based HTPEM fuel cells



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## ABSTRACT

The degradation of high-temperature proton exchange membrane fuel cells with phosphoric acid-doped polybenzimidazole (PBI) based membranes is one of the key challenges for early commercialization. The aim of this work is to analyze the influence of different reinforcement strategies on the performance and degradation of PBI-based membranes. The effects on the membranes were analyzed by polarization curves, long term operation under constant load, electrochemical impedance spectroscopy, *in-situ* cyclic voltammetry and electron microscopy techniques. The results show that the molecular weight distribution of the PBI and the different types of reinforcement have a distinct influence on the poisoning of the cathode layer and the mass transport resistance of the cathode microporous layer. The reasons are discussed in detail and a new degradation mechanism is proposed. A significant reduction of the degradation was obtained by enhancing the interactions between the PBI polymer chains via cross-linking.

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## 1. Introduction

Proton exchange membrane fuel cells (PEMFC) have gained considerable attention in fuel cell research over the last years [1]. The limitation of low temperature PEMFCs, e.g. complex water management, low reaction kinetics and sensitivity to gas impurities, has resulted in an increasing interest in fuel cells which are operated at temperatures above 100 °C [2,3]. Phosphoric acid doped polybenzimidazole (PBI) was established for fuel cell operation from 150 °C to 200 °C without humidification [4–7]. These high temperature PEMFCs (HT-PEMFC) benefit from faster kinetics of the oxygen-reduction-reaction [8,9], simplified heat management and higher carbon monoxide-tolerance [10–12]. In spite of these advantages, the lifetime of HT-PEMFC still remains the major concern [13–15]. In HTPEM fuel cells a more resistant membrane regarding chemical degradation, heat and mechanical stress in combination with enhanced proton conductivity is essential. Different approaches for highly resistant membranes have been reported in literature [16–19]. Most of these concepts rely on new

combinations of polymers and appropriate additives. Kim et al. recently presented cross-linked benzoxazine-benzimidazole copolymer membranes with enhanced durability and performance [20]. Flexible polymer networks with varying properties were achieved by Kerres et al. via ionic cross-linking in acid-base blend membranes [21]. In order to form strong covalent linkages with the imidazole groups of the PBI, covalent cross-linkers are used. The cross-linked PBI has a higher stability than membranes of pure PBI. Various cross-linkers are in use, such as organic diacids [22], dihalides [23–26], diisocyanates [27,28] and diepoxides [29–31]. Wang et al. reached a better mechanical and chemical stability as well as higher conductivity at higher phosphoric acid doping levels of a 1,3-di(2,3-epoxypropoxy)-2,2'-dimethylpropane cross-linked PBI membrane [31]. Lin et al. improved the proton conductivity of a PBI membrane by producing mechanically stable, cross-linked membranes with lower thicknesses and therefore reduced electrolyte resistance [32]. This membrane was tested in a membrane electrode assembly (MEA) over 600 h at stationary operation in hydrogen. The general concept of organic-inorganic composite membranes addresses the weaknesses of PBI-based membranes by improving the mechanical stability in doped status and reducing the phosphoric acid loss during operation [33]. Silica nanoparticles where incorporated in PBI-membranes for HTPEM-FC [19,34,35].

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Wang et al. recently reported an enhancement of the chemical and mechanical stability by silane-cross-linking the PBI chains [36]. Due to the higher acid uptake capacity of the membranes, they showed higher proton conductivity than the pure PBI. In the last years, substrate strengthened membranes were mainly developed for low temperature PEM. Incorporation of porous matrices of polytetrafluorethylene [37,38], nonwoven fabrics of polyimide [39], polyphenylsulfone [40] and inorganic fibers [41] same as meshes of polytetrafluorethylene [42,43] in different polymer solutions enhanced dimensional and mechanical stability of the resulting membranes [42,44]. These strengthening concepts are expected to also have a positive impact on phosphoric acid doped PBI-based membranes. In the described studies, the improvement achieved by new membrane concepts is typically shown by analyzing *ex-situ* properties. Some of the research work include *in-situ* performance tests but only few prove lifetime durability under real fuel cell operation. In some studies, the lifetime reducing degradation effects in HTPEM-FC have been investigated [45–49]. However, the detailed mechanisms that occur in the different MEA components and the contribution of membrane degradation are not yet completely understood [18,45,49].

Even though the influence of molecular weight and distribution on the properties of technical polymers is known from literature, only few efforts were made to use this knowledge for HTPEM-FC development [50–52]. *Ex-situ* testing on Nafion<sup>®</sup> membranes proved a molecular weight dependent degradation [53]. For HTPEM an influence of molecular weight and the molecular weight distribution on the *ex-situ* mechanical stability was observed, whereas the proton conductivity of the phosphoric acid treated membranes remained unchanged [54]. Liao et al. found a significant reduction in molecular weight of the PBI beneath the oxidative conditions of the *ex-situ* Fenton test [55] and Su et al. enhanced the performance and active platinum surface by incorporating lower molecular weight PBI in the electrode layers [56]. Yang et al. showed recently, that higher molecular weight PBI materials possess lower degradation rates in HTPEM fuel cell tests compared to lower molecular weight PBI materials [57]. The influence of the molecular weight distribution on the occurring degradation mechanisms of phosphoric acid doped PBI-based MEAs in fuel cell operation were not yet discussed before.

In the present work, MEAs containing membranes with two different molecular weight distributions of PBI and three reported strengthening concepts were compared before and after 1300 h testing in HTPEM stack operation with reformat gas under constant load. In order to unravel degradation phenomena in phosphoric acid doped PBI-based membranes, the MEAs were analyzed with *in-situ* and *ex-situ* methods after testing. The occurring degradation mechanisms were investigated based on the DC resistances and hydrogen crossover rates, *in-situ* cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), electron microscopy and determination of phosphoric acid content of the MEAs before and after long term tests.

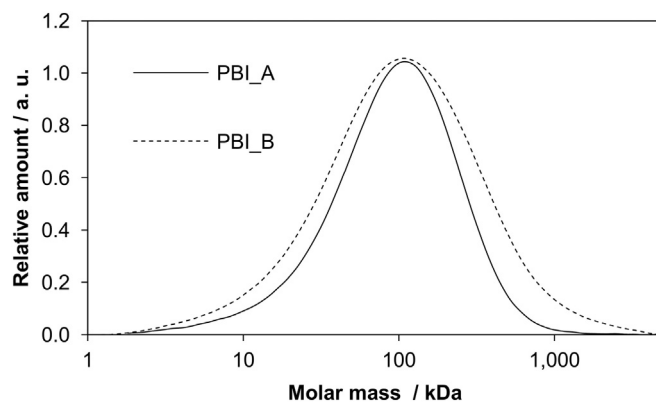
## 2. Experimental

### 2.1. Materials

The measurements were carried out with four poly(2,2'-m-phenylene-5,5'-bibenzimidazole) membranes (Type 1A, 1B, 2A and 3A, Table 1). The polymers of type A and B have different molecular weight distributions (for details see Fig. 1 and Table 2 below). In order to obtain the covalent cross-linked membrane type 1, the PBI polymer chains were bound together with 2% of an organic epoxy cross-linker. Membrane type 2 formed an organic-inorganic composite by cross-linking the PBI organically with silica particles,

**Table 1**  
Overview of the four different membrane concepts and their PBI materials.

Type	Membrane concept	PBI
1A	Covalent cross-linking	A
1B	Covalent cross-linking	B
2A	Organic-inorganic composite	A
3A	Substrate-strengthening	A



**Fig. 1.** GPC measurements of two PBI batches with different MWD.

**Table 2**  
Average molar weights and their distribution of different PBI batches resulting from GPC measurements, Mark Houwink molar mass and viscosity gained by viscometry.

Batch	$M_{MH}/kDa$	$M_n/kDa$	$M_w/kDa$	MWD	$\nu/mm^2 s^{-1}$
PBI A	48.4	50.5	139	2.7	2.04
PBI B	64.2	46.8	198	4.2	2.37

whereas in the substrate-strengthened membrane type 3 the PBI was enforced by a mesh out of polyetheretherketone.

The catalyst support (high surface area carbon, BET: 250–300 m<sup>2</sup> g<sup>-1</sup>) material bounded with polytetrafluoroethylene was applied on a carbon based gas diffusion layer via a doctor blade process and dried at 170 °C under constant air flow. The platinum catalyst was deposited on the catalyst support layer by impregnating a solution of H<sub>2</sub>PtCl<sub>6</sub> and subsequent thermal reduction. The platinum to carbon ratio was set to 0.4. The MEAs were then manufactured by doping the catalyst layers with phosphoric acid and hot pressing them with the membrane.

### 2.2. Characterization methods

#### 2.2.1. Gel permeation chromatography (GPC)

Gel permeation chromatography (GPC) was used to characterize the molecular weight distribution (MWD), the mass and number average molar weight. The PBI samples were diluted to 1% in DMAc and fractionated in an Agilent Technologies 1200 Series. A differential refractometer Shodex RI 71 was used for detection.

#### 2.2.2. Viscometry

1% PBI solutions in DMAc were measured in a capillary viscometer type 532 10 by Schott. After equilibration at 30 °C in the thermostat CT 52 of SI Analytics GmbH, an average of five measurements was taken.

#### 2.2.3. Polarization Curves

A single cell setup with an active area of 50 cm<sup>2</sup> and a single serpentine channel flow field structure on anode and cathode was used. Reactants flow rates were measured and controlled using

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