# Influence of thermal post-curing on the degradation of a cross-linked polybenzimidazole-based membrane for high temperature polymer electrolyte membrane fuel cells

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## HIGHLIGHTS

- Thermal post-curing of cross-linked polybenzimidazole-based HTPEM under air.
- Post-cured membranes showed higher mechanical, thermal and chemical *ex-situ* stability.
- Durability in fuel cell cycled operation was improved by longer post-curing times.
- The occurring degradation mechanisms were determined.
- Longer post-curing period were shown to enhance the resistance against short circuits.

## ARTICLE INFO

## ABSTRACT

The lifetime stability of membranes is one of the main requirements regarding reliability of high temperature polymer electrolyte membrane fuel cells. The present work has improved durability under cycled operation by thermal post-curing of cross-linked polybenzimidazole (PBI)-based membranes. The membranes were dried over 1, 2 and 3 h at 250 °C under air. Ex-situ experiments proved an increase in stability by post-curing. The liquid uptake and swelling in phosphoric acid increased with longer curing periods. The effect of thermal treatments on cycle stability, lifetime and begin-of-life performance of the membrane electrode assemblies (MEAs) was investigated. Longer post-curing periods of the membranes had no influence on the MEAs' begin-of-life performance and constant current behavior over 2300 h. However, the 3 h post-cured MEAs showed enhanced cycle stability. *Post-mortem* analysis was carried out to identify the occurring degradation mechanisms. While a significant loss of phosphoric acid and a reduction of electrochemical surface activity on the cathode were observed for both post-cured MEAs, the 3 h dried membrane sample had a significantly higher resistance against pinhole formation during the long term test. Altogether, this work presents thermal post-curing as a promising method for the reduction of degradation determining effects in fuel cell membranes.

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## 1. Introduction

Within the last years of fuel cell development major attention was given to polymer electrolyte membrane fuel cells because of their promising high efficiency. This technology is often based on perfluorosulfonic acid polymer membranes (e.g. Nafion®) [1]. As the proton conductivity in these membranes is dependent on presence of liquid water, their operation temperature has to be lower than 100 °C. This results in two main limitations. First, a humidification of the reactant gas is required in order to keep the conductivity high enough for fuel cell applications. Second, the catalyst is more sensitive against impurities, especially carbon monoxide, at temperatures less than 100 °C [2,3].

High temperature polymer electrolyte membranes (HTPEM) using phosphoric acid doped polybenzimidazole (PBI) as proton conductor operate at higher working temperatures of 150–200 °C without the necessity of humidification of the reactant gases [4–6]. These temperatures have additional benefits such as faster reaction kinetics on the electrodes, increased catalytic activity and simplified heat management [7–10].

In spite of these advantages, the lifetime of the HTPEM membrane electrode assemblies still remains the major concern. Several achievements have been made in the last years for constant current

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measurements [11,12]. However, the goal of minimal performance losses over long operating periods with a large number of shut downs, remains challenging [13]. In several studies, the lifetime reducing degradation effects have been investigated [11,12,14–16]. However, the detailed mechanisms that occur in the different MEA components and the relative contribution of each material's degradation are not yet completely understood [17].

For HTPEM fuel cells a higher resistant membrane against chemicals, heat and mechanical stress in combination with an enhanced level of proton conductivity is essential [17,18]. Therefore, new membranes should not only show improved stability but also allow a higher phosphoric acid binding capacity [19]. Striving for the goals of performance, lifetime and cost on the membrane side, different approaches have been reported in literature [17–20]. Most of these concepts rely on new combinations of polymers and their additives. In order to build strong covalent linkages with the imidazole groups of the PBI, covalent cross-linkers are in use. The cross-linked PBI has a higher stability than membranes of pure PBI. Various different cross-linkers are in use, such as organic diacids [21], dihalides [22–25], diisocyanates [26,27] and diepoxides [28–30]. Wang et al. reached a better mechanical and chemical stability same as a higher conductivity at higher phosphoric acid doping levels of an epoxy cross-linked PBI membrane [30]. Lin et al. improved the performance of a PBI membrane by producing mechanical stable, cross-linked membranes with lower thicknesses and therefore reduced electrolyte resistance [31]. Aside from these material variations, the fabrication and post-treatment parameters were found to have large influences on the properties of the final membrane [18,32,33]. During membrane formation, the duration and temperature of various drying steps influence the materials' morphology [33–35]. It was found that thermal treatment did positively influence the liquid uptake behavior and acid binding capacity as well as the lifetime and cycle stability [36–38]. Due to thermal post-curing of a pure PBI membrane for 16 h at 350 °C under argon, Aili et al. achieved higher lifetime under constant operation at 0.6 A cm$^{-2}$ [33].

In the present work, the influence of shorter thermal post-treatment under air at 250 °C on PBI-based membranes is analyzed. Systematic examinations of the mechanical, thermal and chemical properties are carried out and the data are compared to electrochemical lifetime behavior of the MEAs under start-stop cycling and 2300 h constant operation. An understanding of the occurring degradation mechanisms of the different samples should give a deeper insight in the benefits of membrane post-curing.

## 2. Experimental

### 2.1. Membrane preparation

The membranes were solution casted from dimethylacetamide (DMAc, synthesis grade, Merck). Therefore, *meta*-PBI powder was dissolved in DMAc under stirring for 3 h at 200 °C under pressure. A solution of bisphenol A diglycidyl ether (synthesis grade, Sigma Aldrich) in DMAc was added. All chemicals were used as purchased without further purification. The membranes were casted by solvent evaporation at 70–100 °C on a carrier foil. Thermal post-treatment in the dryer was done for 1, 2 and 3 h at 250 °C under air. Membranes with longer post-treatment got brittle and were therefore not tested in this work. The cross-linked membranes were referred to as M0 (0 h), M1 (1 h), M2 (2 h) and M3 (3 h). The average thickness variation of the sheets was below 1 μm.

### 2.2. Ex-situ membrane characterization

The thermal stabilities of the membrane samples were determined by thermo gravimetric analysis (TGA) on a *Perkin–Elmer TGA*

*4000*. About 10 mg of the material were filled into the crucible. All measurements were recorded with a heating rate of 10 °C min$^{-1}$ and under nitrogen atmosphere.

The solubility of the membranes was tested by extraction in DMAc. Pieces in the size of 3 cm × 3 cm were dried in the oven over night at 150 °C before their weight was measured. After this, the membrane was put into a round bottom flask and covered with DMAc. The solvent was heated up to 130 °C for one hour. After cooling the solution to room temperature, the extracted samples were dried over night at 150 °C and weighted afterwards. The extraction residue was calculated as the remaining percentage of the membranes' mass.

The swelling behavior and liquid uptake of the membranes were determined by immersing 2.5 cm × 3 cm pieces in phosphoric acid for 30 min at 130 °C. The weight and dimensional changes between the dry and the doped membrane were recorded. Liquid uptake and swelling ratios were calculated as percentage weight increase and dimensional growth.

The mechanical properties of the samples were determined by measuring stress–strain curves on a *BT1 FR0.5TN.D14/500 N Zwicki* from *Zwick*. Membrane pieces (1 cm × 15 cm) were punched out of the membrane. The average thickness of every sample was evaluated with a thickness gauche from *Sylvac*. All measurements were carried out at room temperature.

To investigate a possible change of crystallinity in the membranes, X-ray diffraction (XRD) patterns were taken on a Seifert THETA/THETA-diffractometer (GE Inspection Technologies) equipped with a Meteor OD detector, using Co-K$_\alpha$ radiation ($\lambda = 1.79$ Å). A $2\theta$ detection range of 10–70°, a step size of $2\theta = 0.05°$ and an acquisition time of 10 s/($2\theta$-step) were used.

### 2.3. MEA preparation

The catalyst support (high surface area carbon, HSAC, BET: 250–300 m$^2$ g$^{-1}$) material with PTFE as hydrophobic binder material was applied on a wet proofed carbon based gas diffusion layer from Freudenberg Fuel Cell Technologies (FFCT) via a doctor blade process. The height of the doctor blade was adjusted to 610 μm to get an optimal loading of carbon/PTFE on the gas diffusion layer and dried at 170 °C under constant air flow. The platinum catalysts were deposited on the catalyst support layer via an electroless deposition method by impregnating a solution of H$_2$PtCl$_6$ into the catalyst support layer with subsequent thermal reduction. The platinum to carbon ratio was set to 0.4. The obtained crystallite size of the platinum particles on the HSAC was 2.7 nm, which was determined by XRD measurements. The MEAs were then manufactured by doping the catalyst layer with phosphoric acid and hot pressing them with the membrane. All samples had the same amount of phosphoric acid in the finally obtained MEA.

### 2.4. MEA-testing

The begin-of-life (BOL) polarization curves were determined in a single cell setup with an active area of 50 cm$^2$ and a single serpentine channel flow field structure on anode and cathode. Reactant flow rates were measured and controlled using mass flow controllers. The cell temperature was set to 160 °C controlled by electrical heating cartridges and the gas stoichiometry was kept constant at 1.2 for hydrogen and 2.0 for air.

Start stop cycle tests were done to investigate the stability of the MEAs under fuel cell cycling operation. A 50 cm$^2$ single cell was heated up to 80 °C. At this temperature, the cathode was purged with dry air for five minutes. Then the cell was heated to 120 °C. At this temperature, the anode was purged with nitrogen. Afterwards the hydrogen flow on the anode and the air flow on the cathode