



# The effect of electric field on the oxidative degradation of polybenzimidazole membranes using electro-Fenton test



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## ABSTRACT

The degradation of membranes in proton exchange fuel cells by chemical oxidation is one of the main factors limiting their lifetime. The effect of electric field on the oxidative degradation of poly[2,2'-(*m*-phenylene)-5,5'-bibenzimidazole] (PBI) was investigated using electro-Fenton tests. The degraded PBI was characterized by measuring the sample's intrinsic viscosity ( $\eta_{\text{int}}$ ) and weight loss and using thermal gravimetric analysis (TGA), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR),  $^1\text{H}$  nuclear magnetic resonance spectroscopy ( $^1\text{H}$  NMR), and X-ray photoelectron spectroscopy (XPS). When the intensity of the electric field was increased from 0 V/m to 5000 V/m, the membrane's weight decreased, while the  $\eta_{\text{int}}$  of PBI decreased rapidly. Meanwhile, a larger number of larger pores formed on the PBI membranes, according to SEM images. The thermal stabilities of the degraded PBI membranes decreased significantly when the intensity of the electric field increased. FTIR,  $^1\text{H}$  NMR, and XPS spectra revealed that an electric field accelerated the formation of amide and amino groups after the breakdown of benzimidazole rings in PBI. The amino groups were stabilized by protonation in the acidic Fenton reagent. A possible mechanism for the increased oxidative degradation of PBI in an electric field was proposed.

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## 1. Introduction

Poly[2,2'-(*m*-phenylene)-5,5'-bibenzimidazole] (PBI) is a high-performance polymer with an outstanding thermal and oxidative stability that is attributed to its aromatic structure and the rigid nature of its bonds [1]. PBI membranes doped with phosphoric acid (PA) are promising candidates as electrolytes for intermediate-temperature proton exchange membrane fuel cells (IT-PEMFCs) because of their thermal and chemical stability and ability to conduct protons [2]. Since IT-PEMFCs can be operated at elevated temperatures (up to 200 °C) without humidification [3,4], platinum (Pt) catalysts have improved tolerances to impurities (e.g., CO [5,6], SO<sub>2</sub> [7]) and more rapid kinetics for the oxygen reduction reaction [8,9]. These properties allow IT-PEMFCs to achieve good heat utilizations, while being reasonably integrated with other processing units [10].

However, IT-PEMFCs have low durabilities, limiting their ability to become commercialized as a fuel-cell technology. The

degradation of fuel cell performance is inevitable after long-term operation, and the degradation of fuel cell membranes is a key source of this short operation life. The three main degradation mechanisms for fuel cell membranes include oxidative degradation, mechanical degradation, and thermal degradation [11–15]. For PBI-based IT-PEMFCs, the oxidative degradation of the PBI membranes has been identified as the leading failure mechanism in evaluations of durability.

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is gradually produced during the long-term operation of IT-PEMFCs. H<sub>2</sub>O<sub>2</sub> is an oxidant and is formed either from the crossover of oxygen through the membrane towards the anode compartment that is reduced by hydrogen or from hydrogen crossover towards the cathode compartment to react with oxygen. H<sub>2</sub>O<sub>2</sub> is also produced in the membrane through reactions between permeating oxygen and protons migrating under counter-current conditions [16,17]. H<sub>2</sub>O<sub>2</sub> is continuously decomposed to generate free radicals (e.g., hydroxyl (HO·) and hydroperoxyl (HOO·) radicals) with transition metal ions (e.g. Fe(II)) [18]. These free radicals rapidly attack C–H bonds and eventually lead to the rupture of macromolecular chains in polymer. For this reason, the durability of membranes is often evaluated by treating them with H<sub>2</sub>O<sub>2</sub> [19,20], sometimes with the addition of Fe(II) to form

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Fenton's reagent [21–23], which is used to accelerate the oxidative degradation of PBI membranes in *ex situ* evaluations of durability.

The Fenton test is an *ex situ* method for investigating the oxidative degradation of membrane electrode assembly (MEA) and proton exchange membranes. The Fenton test is beneficial because some factors affecting degradation can be investigated individually [24–26] and degradation can be accelerated. Therefore, much effort has been focused on *ex situ* studies of PBI membranes [27–31]. There are two main mechanisms for the oxidative degradation of PBI. For mechanism I, Zhihong Chang et al. [27] found that the hydrogen atom in the N–H bond of the imidazole ring was oxidized after reacting with HO· or HOO·. Benzene rings were then oxidized into quinone, following by yielding dicarboxylic acid eventually. In contrast, Qingfeng Li et al. [28] proposed mechanism II in which degradation begins when hydroxyl radicals attack the carbon atom linking the imidazole and benzene rings, causing the imidazole ring to eventually open. However, these oxidative degradation studies were carried out using conventional *ex situ* methods without taking into account the effect of electric fields.

The oxidative degradation of PEM fuel cells between anode and cathode occurs in an environment with an electric field when the cells are under normal operating conditions. Ka Hung Wong and Erik Kjeang [32] showed that Fe ions generated in the membrane electrolyte assembly undergo redox cycling, maintaining a relatively high Fe(II) concentration in the membrane. This results in the severe oxidative degradation of these membranes. They also found that the state and distribution of reactive Fe ions inside the PBI membranes were highly sensitive to cell voltage. The extent of redox cycling by Fe ions was significantly reduced at lower cell voltages. Fe ion reduction was suppressed in the anode catalyst layer, and most of the Fe ions accumulated in the cathode catalyst layer where equilibrium between Fe(II) and Fe(III) was attained. The concentration of Fe(II) in the membrane decayed exponentially when the cell voltage was reduced, and the formation of harmful hydroxyl radicals was greatly suppressed, elucidating the mitigating effect of low cell voltages on the oxidative degradation of membranes.

To address the problem described above, electro-Fenton tests were used in this work to understand the effect of electric fields on the chemical degradation of PBI membranes. At different electric field intensities, the intrinsic viscosity and weight of the PBI membranes changed. The cross-sectional morphologies and thermal stabilities of the degraded PBI membranes were investigated using Fourier transform infrared spectroscopy (FTIR), <sup>1</sup>H nuclear magnetic resonance spectroscopy (<sup>1</sup>H NMR) and X-ray photoelectron spectroscopy (XPS). Analysis of the degraded PBI membranes allowed for an improved understanding of possible reactions involved in PBI degradation by HO· or HOO· free radicals in different electric fields.

## 2. Experimental

### 2.1. Materials

3,3-diaminobenzidine (DAB, 99%) was obtained from Shanghai Bangcheng Chemical Co. Isophthalic acid (IPA, 98%), triphenyl phosphate (TPP, 98%), polyphosphoric acid (PPA, 115%), phosphoric anhydride (P<sub>2</sub>O<sub>5</sub>, 98%), N,N-dimethylacetamide (DMAc, 98%), sodium hydroxide (NaOH, AR), ethyl alcohol (C<sub>2</sub>H<sub>5</sub>OH, AR), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 96%), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30%, w/v), and ferrous sulfate (FeSO<sub>4</sub>·7H<sub>2</sub>O, 98%) were obtained from Shanghai Chemical Reagent Co. All chemicals were used without further purification.

### 2.2. Synthesis and membrane preparation of PBI

DAB (3.2141 g, 15.0 mmol) and IPA (2.4920 g, 15.0 mmol) were

added to a mixture of 160.00 g PPA and 0.10 g TPP (TPP/DAB (w/w) ≈ 3%) containing 9.72 g P<sub>2</sub>O<sub>5</sub>. The polycondensation reaction was allowed to proceed for 20 h under an N<sub>2</sub> atmosphere. Details of the synthesis were similar to those of reference [27].

PBI (2.00 g) was dissolved in 100 mL DMAc. After the PBI solution was filtered and poured into a horizontal glass plate, it was heated at 100 °C for 24 h. The membrane was then heated at 180 °C for 2 h to remove DMAc.

### 2.3. Electro-Fenton tests

A new *ex situ* method for evaluating the oxidative stability of PBI membranes was developed in which the Fenton test was performed in the presence of an electric field. This method is called the electro-Fenton test in this work. The setup for the electro-Fenton test is shown in Fig. 1. A direct current (DC) voltage, provided by a Lodestar LP6002D DC Power Supply (China), was applied between two copper plates to create a constant intensity electric field.

PBI membranes (8 cm × 8 cm × 50 μm) were immersed in 75 mL of Fenton reagent, which contained 30 wt% H<sub>2</sub>O<sub>2</sub> and 20 ppm Fe(II) for the formation of HO· and HOO· radicals. The Fenton reagent was prepared immediately before use. The Fenton reagent and the membranes were placed in a crystallizing dish with a flat lid, which was placed in a preheated oven at 68 °C. Every 16 h, the Fenton reagent was replenished. After 16 h, the membranes were collected from the crystallizing dish, either in pieces or as a powder after filtration. The samples were washed thoroughly with distilled water and dried at 120 °C for at least 12 h before characterization.

Using COMSOL Multiphysics 5.0, the electric field intensities of fuel cells were calculated to be 5000 V/m and 2000 V/m at 0.95 V and 0.60 V. In order to obtain a similar electric field in the electro-Fenton test system, the electric field intensity was set to 5000 V/m and 2000 V/m by adjusting the DC voltage, the distance between the two copper plates and the height of the Fenton reagent. The electric field intensity was calculated using COMSOL Multiphysics 5.0 and electric fields of 5000 V/m and 2000 V/m were obtained. The distance between the two copper plates and the height of Fenton reagent were set to 20 mm and 4 mm, respectively. DC voltages of 20 V and 10 V achieved electric fields of 5000 V/m and 2000 V/m. The results of electric field intensity simulations are shown in Fig. 2.

### 2.4. Characterization

The viscosity-averaged molecular weight (M<sub>v</sub>) of PBI was obtained from the intrinsic viscosity (η<sub>int</sub>) of the samples using an Ubbelohde viscometer (Shanghai Chemical Reagent Co., 1.0 mm–1.1 mm). Five different solutions were prepared containing of 0.2 g/dL, 0.4 g/dL, 0.6 g/dL, 0.8 g/dL, and 1.0 g/dL PBI in 96% sulfuric acid. The flow times of each solution and the 96% sulfuric

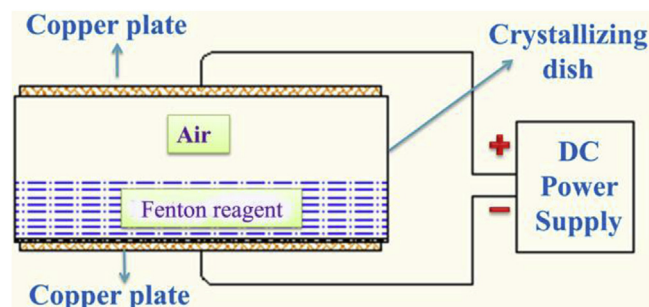


Fig. 1. Setup for the electro-Fenton test system.

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