



Phosphoric acid distribution and its impact on the performance of polybenzimidazole membranes



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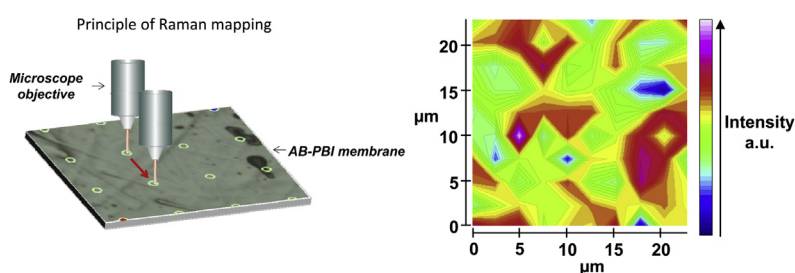
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HIGHLIGHTS

- Not only doping degree but also doping time defines the conductivity of the membrane.
- Prolonged doping time achieves uniform phosphoric acid distribution in the membrane.
- Confocal Raman microscopy visualizes acid distribution depending on the doping time.
- Homogenous phosphoric acid distribution reduces acid migration out of the membrane.
- Doping time and temperature have to be optimised for each type of polymer membrane.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 10 February 2014

Received in revised form

4 June 2014

Accepted 5 June 2014

Available online 1 August 2014

Keywords:

HT-PEM

PBI doped with phosphoric acid

Confocal Raman microscopy

Membrane conductivity

Phosphoric acid distribution

PBI – phosphoric acid interaction

ABSTRACT

Phosphoric acid doped polybenzimidazole (PBI) is the most common membrane material for high-temperature polymer electrolyte membrane fuel cells (HT-PEMFC). The PBI membrane is usually doped in hot phosphoric acid. Immersion time and acid temperature affect the doping level of the membrane. In this work we studied the influence of doping time and temperature on the ex-situ and in-situ proton conductivities of poly (2, 5-benzimidazole) (AB-PBI) membranes as well as the fuel cell performance. Confocal Raman microscopy was employed to spatially resolve the acid distribution within the AB-PBI membranes. Therefore the interactions between the basic nitrogen-sides of the AB-PBI polymer and the phosphoric acid protons were investigated. We found that membranes with a 6 h doping time had significantly higher proton conductivity than those doped for only 3 h. In terms of absolute acid up-take, however, the difference was rather small. This result shows that the doping level alone does not define the conductivity of the membrane. The conductivity is also influenced by the micro acid distribution within the membrane. Highest membrane conductivity and fuel cell performance with fumapem AM cross-linked membranes were achieved with a doping time of 6 h and a doping temperature of 120 °C.

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1. Introduction

The HT-PEMFC operates at temperatures from 140 °C to 200 °C and requires high membrane conductivity in this temperature range. The HT-PEMFC performance benefits from high working

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temperatures due to faster electrode kinetics and a higher tolerance to impurities like carbon monoxide (CO) [1,2]. Perfluorosulfonic acid polymers like Nafion, the most common membrane material for low-temperature PEMFCs, rely on hydration of the membrane to ensure high proton conductivity at elevated temperatures [3,4]. Many hydrocarbon polymers were investigated as alternatives to Nafion for HT-PEMFC applications [5] and one of the most promising candidates is phosphoric acid doped Poly[2,2-(*m*-phenylene)-5,5-benzimidazole] (PBI) [6,7].

PBI is an aromatic heterocyclic polymer with good chemical resistance and high mechanical strength [8]. To achieve adequate proton conductivity for fuel cell operation, however, PBI needs to be doped with acid because of its low intrinsic conductivity. The doped membranes show high conductivity at low humidified conditions [9] and low gas crossover [10]. A promising PBI derivative is AB-PBI [11–13] which can be easily synthesized from a single cheap monomer [14].

Usually phosphoric acid is used as the doping agent for PBI membranes due to the high conductivity of phosphoric acid doped membranes compared with other acids as doping agents [15]. Membrane conductivity strongly depends on the amount of acid inside the membrane [16], which depends on the acid concentration [17] and the doping time [18]. The membrane conductivity plays a key role for the fuel cell performance and therefore a high amount of acid in the membrane (doping level) is preferred. However, apart from the total amount of phosphoric acid inside the membrane, the interactions between the acid molecules and the N-sides of the AB-PBI are important to prevent acid leakage from the membrane into the electrodes and gas diffusion layers (GDL) during fuel cell operation.

These interactions can be observed with Raman spectroscopy [18]. There are only a limited number of studies on PBI with Raman spectroscopy despite the fact that Raman measurements are fast and non-destructive [19], which further enables confocal Raman imaging with a fairly high in-plane spatial resolution [20]. Recently, AB-PBI membranes doped with different amounts of phosphoric acid were investigated with Raman spectroscopy and the characteristic bands were assigned [21]. Several PBI derivatives were studied with this method [22], [23]. However, to our knowledge, spatially resolved confocal Raman microscopy had not been used to study phosphoric acid doped AB-PBI membranes before.

In this study, we report the effects of the doping time and acid temperature on the ex-situ membrane conductivity, the fuel cell performance, and the cell resistance (which is mainly determined by the in-situ membrane conductivity). The interactions between phosphoric acid and the AB-PBI membrane were visualized with confocal Raman microscopy.

2. Experimental

2.1. Membrane doping and gas diffusion electrode preparation

AB-PBI membranes (fumapem AM cross-linked, Fuma-Tech) were doped with phosphoric acid by immersion in concentrated phosphoric acid (85%, Carl Roth) at different temperatures in the range of 80–140 °C for up to 7 h to achieve various doping levels (Fig. 2). The temperature was controlled by a dry bath thermostat (Boekel scientific) and the amount of acid in the membrane was determined gravimetrically. The surface of the membranes was carefully blotted with paper to remove phosphoric acid on the surface. The estimated error of this measurement is less than 10%.

For the gas diffusion electrode (GDE) catalyst suspensions (“catalyst inks”) containing water (Millipore), isopropanol, PTFE solution (60%, 3 M), and 20% Pt/C catalyst (Heraeus) were used. The catalyst ink was sprayed in multiple layers directly onto the

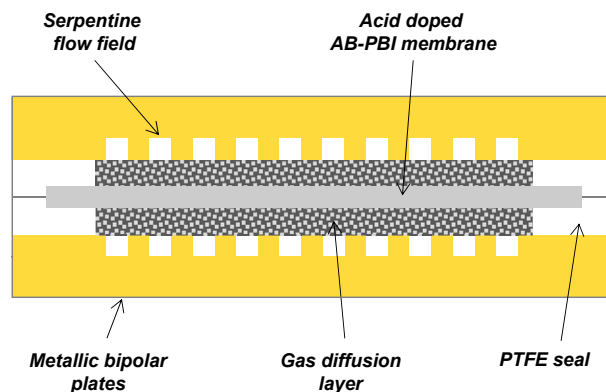


Fig. 1. Full cell setup layout for impedance measurements.

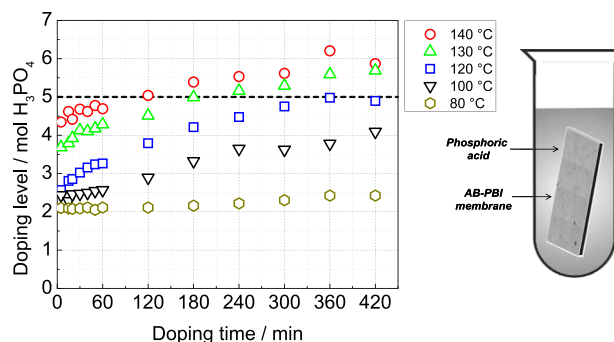


Fig. 2. Doping process of an AB-PBI membrane in hot phosphoric acid at various temperatures. The weight increase of AB-PBI membranes correlates with the sojourn time in the phosphoric acid (left). Illustration of an AB-PBI membrane immersed in acid (right).

microporous layer of the GDL (H2315 C2, Freudenberg) at a substrate temperature of 80 °C. For this study, the catalyst loading was kept constant at 1 mg cm⁻², which was gravimetrically determined and the GDEs had a PTFE content of 10% by weight. A detailed description of the GDE preparation was described in Ref. [24].

2.2. Electrochemical characterization

The membrane electrode assemblies (MEAs) were prepared by placing the GDEs in direct contact with the doped AB-PBI membranes in single cells without hot-pressing (Fig. 1). The single cells with an active area of 4 cm² included gaskets (PTFE from Bohler), sub-gaskets (PEEK from Victrex), metallic bipolar plates with single serpentine flow-fields (1 mm × 1 mm in dimension), and aluminum plates equipped with heating cartridges. The MEAs were compressed by circa 30% of the total thickness of individual components to maintain a constant contact pressure. The cell performance was studied at 160 °C and ambient pressure using dry hydrogen and air as reactants. Stoichiometric mass flows of hydrogen ($\lambda = 1.4$) and air ($\lambda = 2$) were used for current densities equal to or above 200 mA cm⁻². Gas flows were fixed for current densities below 200 mA cm⁻². Polarization curves were recorded by increasing the current density stepwise from zero (open circuit) up to 800 mA cm⁻² or until the cell voltage dropped below 300 mV. Cell internal resistances were determined by measuring AC impedances at 1 kHz with an MR 2212 W impedance meter (Schuetz Meßtechnik).

The membrane ex-situ conductivity was measured with the same hardware except that the cell was not supplied with reactant

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