



Probing phosphoric acid redistribution and anion migration in polybenzimidazole membranes



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ABSTRACT

Micro platinum electrodes embedded in a laminated phosphoric acid doped polybenzimidazole membrane are employed to monitor the acid migration during hydrogen pump mode operation. Upon application of a constant current, an immediate ohmic resistance decrease of the membrane near the anode is observed, accompanied by a corresponding increase near the cathode side. This is a direct evidence of migration of the acid anions via the vehicle conducting mechanism, resulting in an accumulation of acid at the anode side and depletion at the cathode side. Both resistances reach a steady state value after a prolonged period of measurement, apparently balanced by the back diffusion of the acid molecules. The phenomenon is magnified at higher current densities and with increased thickness of the overall membrane, which is of significance in quantitative understanding of the proton conductivity mechanism e.g. for determination of the anionic transference number. The finding provides a technique to monitor the acid redistribution within the membrane as a basis for an engineering solution to address the long-term durability of fuel cells built around phosphoric acid doped polymer membranes.

1. Introduction

The high temperature polymer electrolyte membrane fuel cell (HT-PEMFC) has been gaining attention during the past decades due to its tolerance to CO and H₂S impurities present in reformat gases and simple auxiliary units [1–3]. The proton transport is mediated by phosphoric acid doped into the membrane [4,5], usually based on polymers in the polybenzimidazole (PBI) family [6,7]. Nominally dry phosphoric acid shows a low proton conductivity of around 0.09 S cm⁻¹ at 50 °C, but it increases up to 0.6 S cm⁻¹ when the temperature is increased to 160 °C [8]. In the acid doped polymer membrane, the conductivity may vary in a range from 0.01 up to 0.2 S cm⁻¹ depending on the membrane fabrication procedure [9] and particularly on the phosphoric acid content of the resulting membranes [10–13] and on the partial pressure of water in the atmosphere [14,15].

A unique characteristic of the proton conductivity of phosphoric acid is the high proton transference number t_{H^+} of 97.5% [16], indicating that Grotthuss-type structure diffusion is the predominating mechanism [17,18]. However, recent comprehensive studies show that the transference number strongly depends on the water content [19] and on the presence of other Brønsted bases, such as *N*-heterocycles [20]. The transference number peaks at 100 wt% H₃PO₄ and tends to decrease as the water content increases, not only resulting in increased

conductivity but also increased contribution from the vehicular charge transport. At higher concentrations of acid (> 100 wt%), the concentration of cationic species (mainly H₄PO₄⁺) and highly charged phosphate anions (e.g. H₂P₂O₇²⁻, H₃P₃O₁₀²⁻ and H₂P₃O₁₀³⁻) increases, which in turn also leads to increased contribution of the vehicle mechanism.

In all cases, the vehicle mechanism of proton conductivity causes migration of the acid [21]. It has been known from the days of phosphoric acid fuel cells that the acid movement due to anion migration poses a crucial problem of acid management [22]. This is apparently also of critical concern for the phosphoric acid doped PBI membrane fuel cells, where it causes dramatic redistribution of the phosphoric acid within the membrane-electrode assembly at high current loads [23]. At temperatures above 160 °C and at higher current loads than 200 mA cm⁻², the phosphoric acid was found to penetrate through the catalyst and gas diffusion layers leading to significant acid leaching [24].

This work is devoted to probing the acid redistribution within the PBI membrane by micro reference electrodes integrated in the membrane electrolytes. The configuration allows for a direct measurement of the ohmic resistance through different segments of the membrane, as an indicator of its acid content change upon a flow of electrical current. Similar methods were also done in Nafion-based PEMFC to characterize

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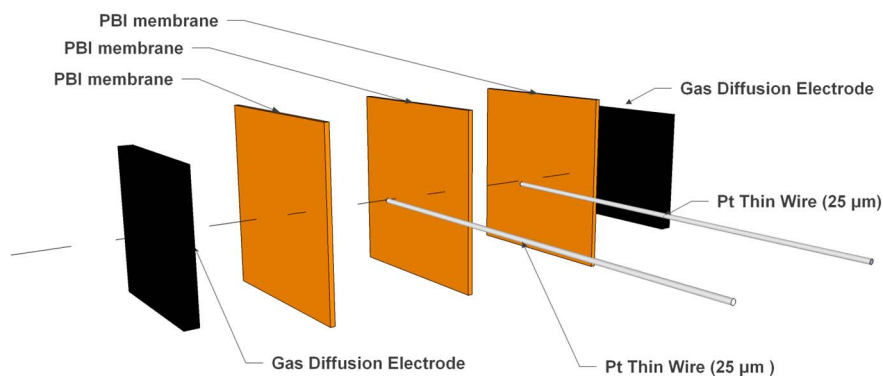


Fig. 1. Schematic drawing of the MEA of multilayered membranes with integrated reference electrodes.

the profile of the water content during operation [25,26]. To simplify the study, the cell is operated in hydrogen pumping mode to exempt the large charge transfer resistance of the oxygen reduction reaction, making the system almost purely ohmic. The presence of hydrogen on both sides of the membrane also enables a stabilized potential of the platinum reference electrodes. This provides a tool for quantitative understanding of the proton conductivity mechanism and evaluation of the acid management issue as a basis for the development of engineering solutions to improve the long-term durability of HT-PEMFC.

2. Experimental

A schematic diagram of the membrane electrode assembly (MEA) is shown in Fig. 1. The poly(2,2'-(*m*-phenylene)-5,5'-bibenzimidazole, PBI) membranes were prepared by solution casting from *N,N*-dimethylacetamide (DMAc), using from the polymer with an inherent viscosity of 1.44 dL g^{-1} (500 mg dL^{-1} in 96% H_2SO_4 at $30.0 \text{ }^\circ\text{C}$) as prepared according to protocols reported in the literature [27]. After extensive washing in demineralized water, the PBI membranes were equilibrated in 85% H_3PO_4 (Sigma-Aldrich) at room temperature for two weeks to give an acid content of around 10 molecules of H_3PO_4 per polymer repeat unit.

The electrodes were prepared by spraying Pt/C (60 wt% Johnson Matthey HiSPEC 9100) dispersed in ethanol on a carbon cloth pre-coated with a microporous layer (Freudenberg H23C2). Platinum loading of 1 mg cm^{-2} was used for both electrodes. The segmented MEAs with integrated reference electrodes were prepared using 3 laminated membrane layers as shown schematically in Fig. 1.

The layers are hereafter referred to as A (anode side), M (middle), and C (cathode side). The thickness of layer A and C was kept constant at $40 \text{ } \mu\text{m}$, while layer M was either 40 or $120 \text{ } \mu\text{m}$. Insulated platinum wires (diameter = $25 \text{ } \mu\text{m}$, $5 \text{ } \mu\text{m}$ polyimide insulation) were placed at the center of the active area and sandwiched between the interfaces of membrane layers, as shown in Fig. 1. The insulation coating at the wire tip located between membranes were burned off beforehand and treated with $5 \text{ } \mu\text{L}$ of 2 wt% PBI in DMAc twice. Excess DMAc was evaporated in a fumehood, leaving a film of the polymer on the Pt to improve the ionic contact. Under a flow of hydrogen on both electrode side, the permeated hydrogen stabilizes the potentials of two platinum reference electrodes (ranges from 0 to 3 mV at open circuit voltage). The MEAs were assembled by sandwiching the laminated membranes between the two electrodes with an area of $3.1 \times 3.1 \text{ cm}^2$. The active area was 8.8 cm^2 , since frames of polysulfone were used as reinforcement around the electrode edges. The electrochemical impedance spectroscopy data were acquired using a VersaStat 4 potentiostat from Princeton Applied Research, at 5 mV amplitude in the frequency range 2500–75 Hz. The ohmic resistance was taken at the intersection with the real axis in the Nyquist plot. Measurements during open circuit voltage (OCV) were taken to calibrate the exact position of Pt wires.

The cell housing consisted of two aluminum end plates with heating elements and current collectors. Clamping was done by tightening four

end corners of endplates using 8 mm nuts and bolts. The MEAs were hot pressed within the cell housing at $120 \text{ }^\circ\text{C}$ at a torque of 1 Nm for 10 min. The cell temperature was subsequently increased to $160 \text{ }^\circ\text{C}$ and left under hydrogen flow overnight before measurement. The hydrogen flow was 100 NmL min^{-1} on both sides and the current was provided by an external power supply.

3. Results and discussion

The polarization data for the cells with different thicknesses of the middle layer are shown in Fig. 2a. Both cells showed an almost linear *i*-*v* relationship, which suggests an ohmic-dominant process throughout the whole current density range [28,29]. Potentiostatic impedance scans of the working cell further showed a very small arc representing the hydrogen oxidation and reduction at the anode and cathode, respectively.

The sum of the potentials across different layers corresponded well with the total cell potential. The area specific resistance of the different layers of the segmented MEAs, as obtained from the electrochemical

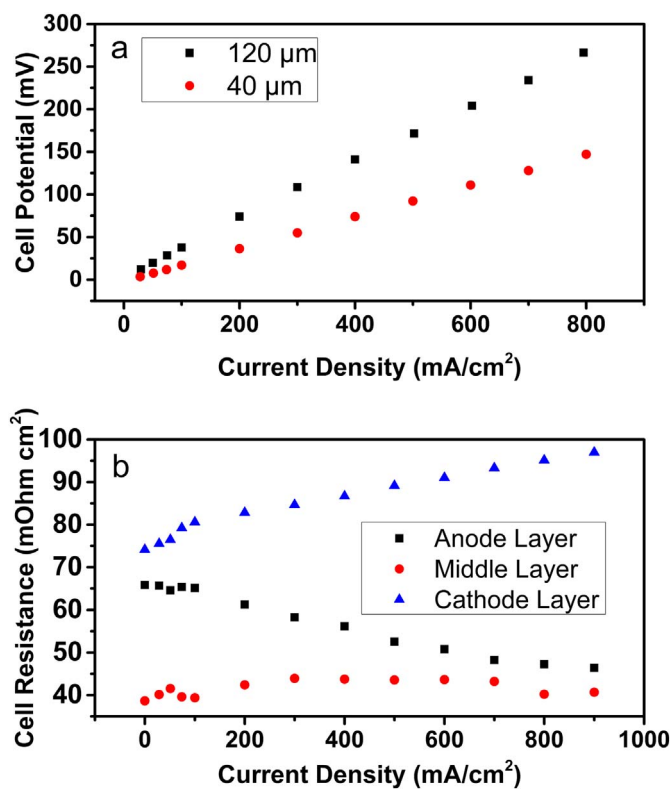


Fig. 2. Polarization curves of the cells equipped with middle layers of 40 and $120 \text{ } \mu\text{m}$ (a) and the corresponding series resistances of different segments at different current densities for the cell with a $40 \text{ } \mu\text{m}$ middle layer (b).

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