



# The influence of phosphoric acid migration on the performance of high temperature polymer electrolyte fuel cells

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## HIGHLIGHTS

- Electrochemical impedance spectroscopy can monitor phosphoric acid redistribution.
- Changes in low frequency regime of the EIS spectra are observed.
- Time constants for PA flooding (8.1 min) and PA de-flooding (5.8 min) were obtained.
- First method to monitor phosphoric acid redistribution electrochemically.
- No impact on cell performance is observed; likely due to improved kinetics.

## ARTICLE INFO

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## ABSTRACT

In high temperature polymer electrolyte fuel cells, phosphoric acid migration induces flooding of the anode gas diffusion layer at high current densities. The present study focuses on determining the influence of phosphoric acid flooding of the anode GDL on hydrogen mass transport limitations. Two methods for quantifying the performance losses at high current densities, related to acid migration, are discussed: anodic limiting current density measurements and electrochemical impedance spectroscopy. It is demonstrated that the limiting current measurements, the common method for determining transport resistances, is unable to detect the changes induced by acid migration, due to the transient time required when switching to the required low hydrogen concentrations, while EIS is able to capture the changes induced by acid migration because it is faster and less invasive. For diluted hydrogen, an increase of the transport resistance is measured, however the effect on the cell performance is negligible. The time constants for anode GDL flooding and de-flooding are determined based on the EIS data and found to be  $8.1 \pm 0.1$  min for flooding and about  $5.8 \pm 0.9$  min for de-flooding under the applied conditions.

## 1. Introduction

High temperature polymer electrolyte fuel cells (HT-PEFC) operate at temperatures between 160 °C - 180 °C. This allows for easier heat recovery and increases the tolerance towards impurities in the fuel. It also has advantages in reduced complexities with the balance of plant like gas humidification or reformer when natural gas is used as the fuel, which are generally associated with low temperature polymer electrolyte fuel cells (LT-PEFC) [1–3].

The unique feature of HT-PEFCs is their membrane chemistry based on polybenzimidazole, which is doped with phosphoric acid as the

electrolyte [1,4]. Unlike in the perfluoro-sulfonic acid polymers of LT-PEFCs, the electrolyte is not chemically bound to the membrane polymer and only a fraction of the electrolyte is interacting with it [5]. As demonstrated by Eberhardt et al. [6,7] and by Becker et al. [8] the bulk of the electrolyte is mobile and able to migrate within the membrane and can also invade the gas diffusion layer (GDL) or even the flow field channels. This can lead to a loss of electrolyte, which makes phosphoric acid redistribution a major limitation for the lifetime of HT-PEFC [9,10].

As found by Eberhardt et al. [6,7], a crucial parameter for phosphoric acid migration in HT-PEFCs is the current density. At high

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current density, phosphoric acid migrates towards the anode, thereby flooding the anode GDL, and in the worst case even the flow-field channels. The reason for this is that since the electrolyte is not covalently bound to the base polymer, a fraction of the ionic current is carried by migration of hydrogen phosphate anions towards the anode, i.e. the transport number for the proton is less than unity. This effect is also known from phosphoric acid fuel cells (PAFCs) [11], where phosphoric acid is confined in a silicon carbide matrix. The flooding of the anode GDL and flow field channels with phosphoric acid is not only a concern for the durability of HT-PEFCs, but is expected to also affect the hydrogen transport through the GDL and therefore, the performance of HT-PEFCs. This is of special importance when operating the cell with reformat gas as the fuel, where hydrogen is diluted and the hydrogen partial pressure is lower compared to operation with pure hydrogen. Also, the hydrogen partial pressure further decreases from channel inlets to outlets. The reduced hydrogen partial pressure in the channel leads to a smaller concentration gradient between channel and catalyst layer and therefore, amplifies the increasing transport resistance in the GDL.

This effect is well known from LT-PEFCs, where water can flood the cathode GDL at high current densities and/or high cathode gas humidity and the water saturation in the GDL introduces oxygen transport limitations [12–14].

The goal of the study is to quantify the transport losses induced by phosphoric acid migration into the anode GDL. Two methods were adapted: the first one utilizes anodic limiting current measurements while the second method is based on electrochemical impedance spectroscopy (EIS). The advantages and disadvantages of each method are discussed and the influence of phosphoric acid migration on the fuel cell performance is analyzed. To the best of the authors' knowledge, this is the first time that these methods were used in the context of phosphoric acid migration in HT-PEFC.

## 2. Experimental setup and procedures

### 2.1. Test setup

All experiments were performed with a so-called differential cell setup, minimizing all gradients in the direction of the gas flows. The MEA used was assembled in-house using BASF Celtec<sup>®</sup> membranes with an acid loading of 34–36 mg<sub>PA</sub>cm<sup>-2</sup> and a ratio of phosphoric acid (PA) to PBI units of  $n_{PA}/n_{PBI} = 33 \pm 2$  [15]. The membrane area was 10\*10 cm<sup>2</sup>. The catalyst layer consisted of Pt/Vulcan XC-72 supported platinum catalyst, with 1 mg<sub>Pt</sub>cm<sup>-2</sup>, coated onto the microporous layer of an SGL-38 carbon paper and an area of 7\*7 cm<sup>2</sup> for both anode and cathode. To achieve a differential cell operation, the cell area was reduced to 2 cm<sup>2</sup> by a kapton sheet of 25 μm thickness with a window (near the cathode outlet) of 1.1 × 1.8 cm<sup>2</sup> placed between the cathode GDL and the membrane. The resulting MEA was placed between two 45 cm<sup>2</sup> flow fields made from pyrolytically surface treated and sealed graphite (proprietary surface treatment by POCO Graphite, USA). The anode plate had a two-channel serpentine flow geometry while the cathode consisted of three channel serpentine flow geometry. The channels had 1.2 mm width and 2 mm depth. A hard-stop perfluoroalkoxy alkane (PFA) gasket of thickness 320 μm was used on both sides; resulting in a MEA compression of about 30%. The compressed total MEA thickness was 830 μm.

The control and data acquisition of the test parameters was carried out using LabVIEW software. There were two thermocouples to sense and control the anode and the cathode temperatures. A Biologic SP-300 potentiostat was used for controlling the electric parameters.

The break-in of the cell was carried out for 80–100 h at 160 °C with a fixed flow of 833 mL min<sup>-1</sup> of hydrogen and air. All j/E curves were measured from open circuit voltage (OCV) down to 0.1 V with a ramp rate of 10 mV/s. All gases were humidified at room temperature and fed with constant flows on both anode (H<sub>2</sub> or H<sub>2</sub> diluted in N<sub>2</sub>,

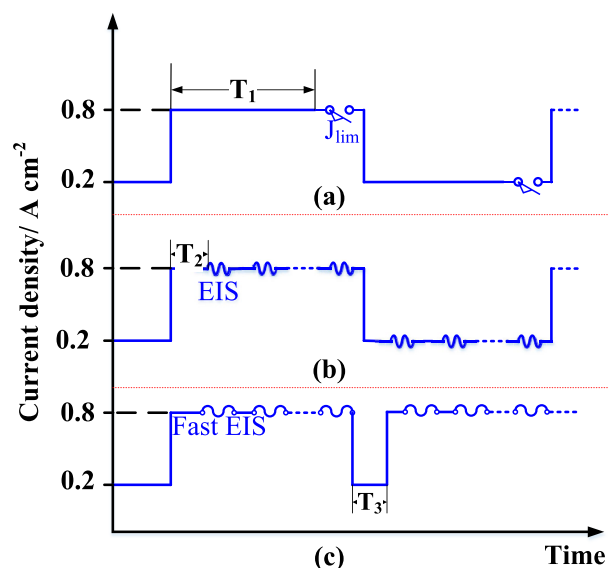


Fig. 1. Test sequences with change between low ( $0.2 \text{ A cm}^{-2}$ ) and high current density ( $0.8 \text{ A cm}^{-2}$ ) for a) for anodic limiting current method, (b) for EIS method to measure flooding and de-flooding kinetics and (c) for fast EIS to investigate the first 2 min of flooding and de-flooding kinetics.

$1667 \text{ mL min}^{-1}$ ) and the cathode (oxygen,  $833 \text{ mL min}^{-1}$ ). This corresponds to a stoichiometry of about 598 for the anode (with pure hydrogen) and the cathode at a current density of  $0.2 \text{ A cm}^{-2}$  respectively. The cell temperature was 160 °C for all experiments.

### 2.2. Anodic limiting current measurement

For determination of the anodic limiting current, two current density sequences were used as shown in Fig. 1a, where the time duration 'T<sub>1</sub>' was 1440 min (24 h) for slow cycling and 30 min for fast cycling. The limiting current experiments were carried out with hydrogen concentrations between 0.05 and 1.0 mol%, with the balance being nitrogen in all cases.

The limiting current measurement sequence at the end of the high and low current density periods was as follows:

Operation was changed from constant current to constant voltage at 0.75 V before changing the gas mixture from pure hydrogen to 1%. This was to avoid a surge in the current density when going to limiting current conditions. Then a constant voltage of 0.2 V was maintained for the different hydrogen dilutions, with the 1st dilution at 1% for 15 min and other dilutions for 2 min each. The long step in the beginning was necessary to reach constant conditions due to the time taken by the gases to reach a uniform concentration in the humidifier and cell.

### 2.3. Electrochemical impedance spectroscopy

For the EIS analysis and its interpretation the concept of the differential cell is particularly useful as disturbance of along-the channel artifacts are avoided [16]. The test protocol (cf. Fig. 1b) was used to trigger phosphoric acid flooding and de-flooding with a holding time of 4 h at each current density. After a change in current density, a relaxation time of 2 min, denoted 'T<sub>2</sub>' was waited for the cell voltage to stabilize before EIS measurements. EIS spectra were recorded by scanning the frequency from 100 kHz to 100 mHz with 5 points per decade; resulting in a measurement time of ca. 50 s per spectrum. The AC signal applied was 5% of the DC load.

Unless otherwise stated, impedance spectra were measured every 2 min for 60 min after a current step. Impedance spectra were measured at standard conditions at 160 °C with standard flows of  $1666 \text{ mL min}^{-1}$  for the anode (10% H<sub>2</sub> in N<sub>2</sub>) and  $833 \text{ mL min}^{-1}$  for the cathode (pure

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