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Short communication

Monitoring the hydrogen distribution in poly(2,5-benzimidazole)-based (ABPBI) membranes in operating high-temperature polymer electrolyte fuel cells by using H-D contrast neutron imaging

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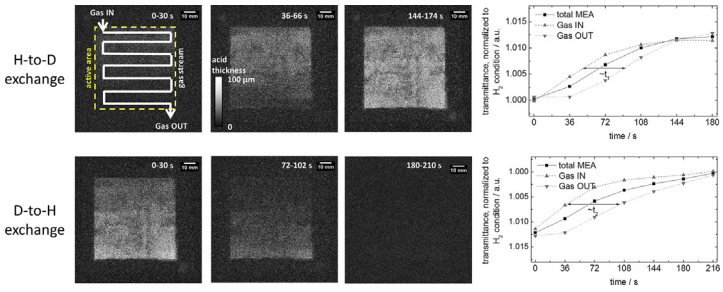
HIGHLIGHTS

- Hydrogen/deuterium exchange processes were analyzed in-operando in a HT-PEFC.
- Neutron radiography was applied to tracking of phosphoric acid in the membrane.
- Different gas exchange times between gas inlet and gas outlet were observed.
- Exchange characteristics were found to be different for H-to-D and D-to-H exchange.

GRAPHICAL ABSTRACT



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ABSTRACT

Neutron imaging in combination with the deuterium contrast method was used to analyze the hydrogen distribution and exchange processes in a high-temperature polymer electrolyte fuel cell in-operando. While operating the cell at steady state conditions at 200 mA cm^{-2} and $\lambda_{an/ca} = 2/2$, changeovers of the anode feed gases between hydrogen (H_2) and deuterium were analyzed by neutron radiography. Proton–deuterium exchange times and progresses were studied in-operando. The exchange of protons by deuterons proceeds much faster (approx. 108–138 s) than the exchange of deuterons by protons (approx. 144–174 s), whereby the exchange takes place first near the gas inlet while a delayed onset was observed near the outlet. We can explain this effect by the different diffusion coefficients and atomic masses of deuterium and hydrogen and the operating conditions of the cell.

1. Introduction

Poisoning of electrochemical catalysts in low-temperature polymer electrolyte fuel cells by carbon monoxide is still an issue. To overcome this deficiency higher operating temperatures can be

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chosen. In a high-temperature polymer electrolyte fuel cell (HT-PEFC) typical operating temperatures range up to 160 °C and a phosphoric acid-doped polybenzimidazole-type membrane is used. Since typical operation conditions in HT-PEFCs imply both acidic and hot environment, most of the commonly available methods to observe proton transport processes in-operando cannot be used [1–3].

Neutron and X-ray imaging are well-established, mostly non-invasive methods for characterizing fuel cells in-operando [4,5]. Degradation processes during start-up and shutdown of cells have been investigated in-situ with high spatial resolution [6], while the morphology of electrodes has been studied ex-situ [7]. Several in-situ studies of HT-PEFCs have been performed using X-ray radiographic techniques [8,9]. Neutron imaging is especially suitable for proton detection since neutrons interact strongly with hydrogen. Moreover, high contrast between hydrogen (H) and deuterium (D) is obtained due to their markedly different neutron attenuation coefficients [10]. On the other hand, both isotopes have very similar physical and chemical properties and can both be used as anode gases in fuel cells behaving in an almost identical way.

2. Set-up

2.1. Test cell

A cell was equipped with a membrane electrode assembly (MEA) composed of a phosphoric acid-doped AM-55 membrane (FuMA-Tech, poly(2,5-benzimidazole)-based, doping level = 470 wt.%, thickness of doped membrane = 85 μm) and two Pt/C-electrodes (platinum loading = 0.94 mg cm^{-2}) coated on non-woven carbon gas diffusion layers (GDLs, Freudenberg H2315 CX165) by a doctor blade technique. Detailed information about electrode fabrication can be found elsewhere [11]. For all analyzed fuel cells the active cell area was 49 cm^2. The flow field used exhibited five meander-shaped channels (width × height = 1.5 mm × 2.5 mm). The cell was operated at constant $\lambda_{an/ca} = 2/2$ and a current density of 200 mA cm^{-2}. The temperature of operation was 160 °C. Not intentionally humidified (dew point at −40 °C) gases were used, i.e. (H_2) and (D_2) at the anode and air at the cathode.

2.2. Imaging

Radiographic measurements were performed on the CONRAD2 beamline at the neutron source BER2 of the Helmholtz-Zentrum Berlin, Germany [12]. An Andor 436 camera combined with a 100-μm thick LiF scintillator allowed for the investigation of the whole cell with a spatial resolution of 53 μm. Detailed information about this equipment can be found elsewhere [13,14]. An aperture of 3 cm resulted in a L/D ratio of 300. Radiographs were taken every 36 s (30 s exposure time plus 6 s read out; each radiograph averages all information occurring during exposure time), perpendicular to the membrane plane while changing between D_2 and H_2 supply during fuel cell operation.

3. Results

During a measurement cycle, the anode supply was switched between D_2 and H_2 supply ten times. This implies that phosphoric acid changes to deuterated phosphoric acid when switching the anodic gas supply from H_2 to D_2 and vice versa. The corresponding exchange processes are shown for various times in Figs. 1 and 2. All radiographs depicted here were normalized with respect to cell operation with H_2. Consequently, the D_2 distribution is visible.

Due to the lower attenuation coefficient of D_2, the cell transmittance increases when using D_2 as anode gas. Using Beer's law with attenuation coefficients of 2.628 cm^{-1} for natural ortho-phosphoric acid (H_3PO_4), 0.068 cm^{-1} for deuterated ortho-phosphoric acid (D_3PO_4), 2.073 cm^{-1} for natural pyro-phosphoric acid ($H_4P_2O_7$) and 0.056 cm^{-1} for deuterated pyro-phosphoric acid ($D_4P_2O_7$) [15], acid thicknesses can be calculated, assuming that H-to-D and D-to-H exchange processes have been (almost) completed at the moment of measurement. This appears realistic since a few minutes after switching gases no further change due to exchange processes were observable in the images (see Figs. 1f and 2f). Considering the changes of transmittances over the analyzed cell area due to H_2 or D_2 operation and the difference of the attenuation coefficients of neutral phosphoric acid and deuterated phosphoric acid, the thickness of the phosphoric acid layer can be determined. Acid thicknesses up to 70 μm were obtained (see Figs. 1

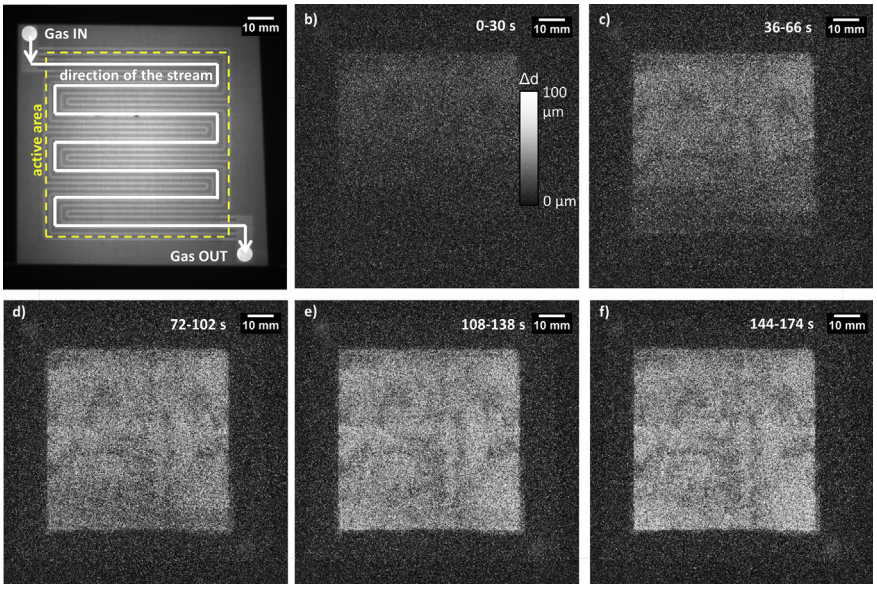

Fig. 1. a) Radiograph of the cell (broken yellow line: active area, white line: flow direction). b–f) Change from H_2 operation to D_2 operation. Each radiograph represents the average of 10 radiographs in equivalent stages. All radiographs were normalized with respect to radiograph obtained under operation with H_2 (radiograph is not shown here). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)