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Short communication

Implications of polymer electrolyte fuel cell exposure to synchrotron radiation on gas diffusion layer water distribution

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HIGHLIGHTS

- In-situ synchrotron based X-ray tomographic microscopy of water in PEFC.
- Studied influence of X-ray irradiation on water saturation.
- Absorption of 3.5 J cm^{-2} X-ray energy clearly distorts current and water distribution.
- Measurement bias difficult to detect as water distribution patterns remain similar.

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ABSTRACT

Synchrotron radiation (SR) based imaging of polymer electrolyte fuel cells (PEFC), both radiography and tomography, is an attractive tool for the visualization of water in the gas diffusion layer as it provides temporal and spatial resolutions one order of magnitude superior to neutron imaging. Here we report on the degradation of cell performance and changes in GDL water saturation after SR irradiation of about 43% of a cell's active area. Fast X-ray tomographic microscopy (XTM) scans of 11 s duration are used to compare the GDL saturation before and after a 5 min irradiation period of the imaged section. The cell voltage and the water saturation decreased clearly during and after the exposure. Estimates of the current density of the SR exposed and non exposed cell domains underline the effect of irradiation.

1. Introduction

X-ray tomographic microscopy (XTM) has proven to be a valuable tool to study the water transport paths in the gas diffusion layers (GDL) of polymer electrolyte fuel cells (PEFC) [1–7] in order to improve the water management and power density.

Though the effects of high energy radiation are well known in the field of radiation chemistry (see e.g. O'Donnell [8]) and Schulze et al. [9] have shown already in 1999 how Nafion degrades during XPS analysis, the consequences of X-ray exposure on PEFC operation remain unclear and are rarely discussed in the electrochemical literature on X-ray imaging [3,7,10–12]. This work intends to show, how X-ray induced PEFC performance degradation biases the water distribution measured via XTM. Additional to the XTM imaging, the cell performance after the imaging experiments is characterized and the sulfate release of ex-situ SR exposed catalyst coated membrane samples is analyzed by liquid ion chromatography to gain understanding of the sources of performance degradation.

2. Experimental

A single channel cell [3] designed for XTM investigations as shown in Fig. 1a was used. The active area of the catalyst coated membrane (CCM, 2-mil Nafion with Pt-loading 0.2/0.4 mg cm^{-2} from Umicore) was limited to 30 mm^2 by a polymer sub-gasket and the GDL (Toray TGP-H060 with MPL from Umicore, 2.3 mm width,

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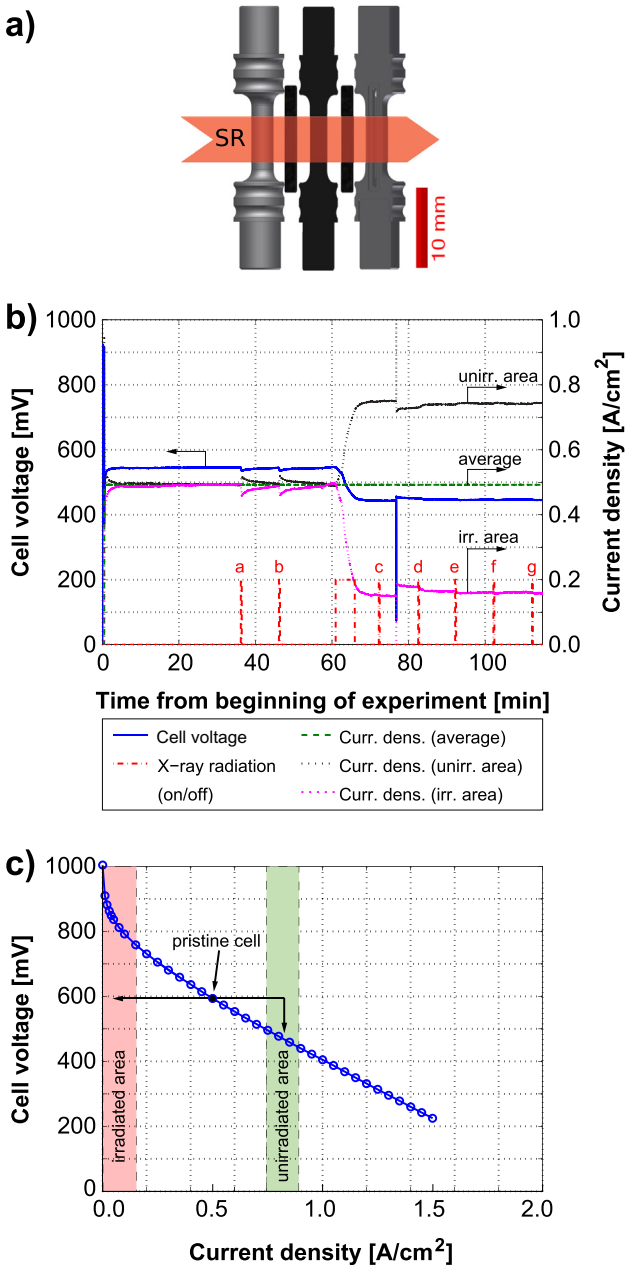

Fig. 1. a) Schematic of XTM-PEFC. Red arrow indicates the SR irradiated domain of the flow field, GDL and CCM (sub-gasket, heater and temperature sensors not shown); b) time series data of cell voltage, X-ray shutter state (zero means shutter closed), average cell current density, as well as current densities of SR irradiated and non-irradiated domains estimated from interpolated polarization curve data c) polarization curve of pristine cell (30 s current holding time); the deviation of 45 mV cell voltage at 0.5 A cm^{-2} before the SR exposure introduces an uncertainty of the current densities for the non-irradiated (light green area) and for the irradiated area (light red area) after the SR exposure. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

13.4 mm length). The cell was operated at a temperature of 35 °C with hydrogen/oxygen feed humidified at room temperature (40% relative humidity) with gas velocities of 0.56 m s^{-1} at the cathode and 1.1 m s^{-1} at the anode (stoichiometries > 10).

XTM imaging experiments were performed at the TOMCAT beamline of the Swiss Light Source (SLS) at Paul Scherrer Institut, Switzerland [13]. A pco.Dimax camera was used for fast tomographic scans (180° sample rotation, 1001 projections, 11 ms exposure time per projection, 11 s total scan time) at 13.5 keV monochromatic beam energy and a beam height of 5.6 mm. The beam photon flux[1] of 6×10^{13} ph (s cm^2)$^{-1}$ at 13.5 keV corresponds to an energy flux of 130 mW cm^{-2}. The maximum magnification of the zoom objective microscope resulted in 2.95 μm pixel edge length.

At the beamline, the cell was operated at a constant current of 150 mA (0.5 A cm^{-2} average) for 60 min before the irradiation experiment, with the cell voltage being stable during operation for the last 30 min. The imaged and SR irradiated center section of the cell consisted of 43% (12.9 mm^2) of the overall active area. During the SR irradiation period of 300 s (5 min) the membrane electrode assembly (MEA) was oriented perpendicular to the beam.

The CCM has an absorbance factor of 0.125 [11]. It accumulates in total an X-ray energy of 3.3 J cm^{-2} (10.9 mW cm^{-2}) during the 300 s irradiation and about 0.1 J cm^{-2} during a single fast XTM scan, taking into account the reduction of the beam intensity due to the cell components between the X-ray source and the CCM.

Before and after the extended SR irradiation period of 300 s, fast XTM scans were taken to study the water distribution in the SR irradiated area. To measure the unbiased water distribution, two XTM scans were performed 25 and 15 min before the SR irradiation, labeled as scan a and b, respectively. 6 min after the SR irradiation the cell was scanned (scan c) and then every 10 min following the water development of the water distribution for 46 min (scans d to g). The degradation of cells at 30 °C from few fast XTM scans, accumulating up to 60 s exposure time at TOMCAT (absorbed X-ray energy of 0.7 J cm^{-2} at the CCM), can be regarded as negligible [7].

Image segmentation was done as described in Ref. [3] but limited to liquid water as in Ref. [7] because the overall solid segmentation was prevented by inhomogeneities of the gray scale values in the MPL domain due to the strong absorption of the catalyst layer.

As the X-ray irradiation of the cell causes a performance degradation of the irradiated domain [10], the current of the irradiated domain (I_{irr}) will decrease. Since the cell is operated in constant current mode, the current of the unirradiated cell area (I_{unirr}) has to increase accordingly to maintain the overall cell current (I_{tot}), as it holds:

$$I_{tot} = I_{irr} + I_{unirr} \quad (1)$$

Under the assumption of a homogeneous cell voltage (E) over the whole MEA area, the current density of the non-SR exposed cell area and I_{unirr} can be estimated using an interpolation of the cells pristine polarization curve data ($i_{prist}(E)$)

$$I_{unirr} = i_{prist}(E) \times A_{unirr} \quad (2)$$

where A_{unirr} is the unirradiated cell area of 17.1 mm^2. Rearranging Eq. (1) and inserting Eq. (2) gives an estimate of I_{irr}, that can be converted into an estimation of the current density of the irradiated cell area (i_{irr}) knowing the irradiated cell area (A_{irr} = 12.9 mm^2)

$$i_{irr} = \frac{I_{tot} - i_{prist}(E) \times A_{unirr}}{A_{irr}} \quad (3)$$

[1] The values of the beam energy flux and of the absorbed X-ray energy reported here are higher than those reported by Roth et al. [11]. This is because in Ref. [11] a more conservative estimate of the beam intensity of 1×10^{13} ph (s cm^2)$^{-1}$ at 13.5 keV was used.