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PEM water electrolysis: preliminary investigations using neutron radiography

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Abstract

The quasi-dynamic water distribution and performance of a proton exchange membrane (PEM) electrolyzer at both a small fuel cell's anode and cathode was observed and quantitatively measured in the in-plane imaging geometry direction(neutron beam parallel to membrane and with channels parallel to the beam) by applyingthe neutron radiographyprinciple at the neutron imaging facility (NIF) of NIST, Gaithersburg, USA. The test section had 6 parallel channels with an active area of 5 cm^2 and in-situ neutron radiography observation entails the liquid water content along the total length of each of the channels.The acquisition was made with a neutron cMOS-camera system with performance of 10 sec per frame to achieve a relatively good pixel dynamic range and at a pixel resolution of 10 x 10 μm^2.A relatively high S/N ratio was achieved in the radiographs to observe in quasi real time the water management as well as quantification of water / gas within the channels. The water management has been observed at increased steps (0.2A/cm^2) of current densities until 2V potential has been achieved. These observations were made at 2 different water flow rates, at 3 temperatures for each flow rate and repeated for both the vertical and horizontal electrolyzer orientation geometries. It is observed that there is water crossover from the anode through the membrane to the cathode. A first order quantification (neutron scattering correction not included) shows that the physical vertical and horizontal orientation of the fuel cell as well as the temperature of the system up to 80°C has no significant influence on the percentage water (~18%) that crossed over into the cathode. Additionally,a higher water content was observed in the Gas Diffusion Layer at the position of the channels with respect to the lands.

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*Keywords:*Electrolysis; Neutron Radiography; NIST-NCNR; PEM Fuel Cell

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1. Introduction

Recently hydrogenProton-Exchange-Membrane (PEM) fuel cells (FC) made significant progress in several countries with roadmaps toward commercialization[USDOE, 2016; Prasad, 2016], causing eventuallya growing interest in technologies for also high quality hydrogen generation. Thus, the use of PEM water electrolysis for hydrogen fuel production became a vector of interest for fuel cell deployment opportunities in sectors such as sustainable mobility, material handling, and back-up power. Hydrogen is the only energy storage concept to address energy storage in range > 100 GWh[Waidhas, 2016]. PEM water electrolysis (PEMEL) is also considered as one of the most favorable technologies for hydrogen generation with many advantages over other available technologies such as simplicity, high current densities, solid electrolyte and high working pressures.

Wateris decomposed by passing an electric current through the waterinto hydrogen and oxygen in the presence of suitable substances, called electrolytes. The operating principle of PEMELs is often referred to as the reversed operation of a fuel cell whereby the water is oxidized at the anode (oxygen production) to produce oxygen electrons and protons (eq-1), however, the materials and configuration thereof are typically different from PEM-FC. Optimized electrolysis plants usually operate at electrolyte temperature of 70-90^{o}C and cell voltage of 1.85-2.05 V (Zouliaset.al., 2006).

$$H_2O\ (l) \rightarrow 4H^+(aq) + 4e^- +\ O_2\ (aq) \tag{1}$$

The protons pass directly through the membrane to the cathode were they recombine and form hydrogen (eq-2).

$$2H^+ + 2e^- \rightarrow H_2 \tag{2}$$

Water electrolysis yield no side reactions that could generate undesired byproducts, therefore the net balance is (eq-3):

$$2H_2O\ \rightarrow (4e^-) \rightarrow O_2 + 2H_2 \tag{3}$$

Unfortunately, gas crossover occurs when either hydrogen or oxygen cross through the membrane to the other side and thus pose safety issues such as explosive gas mixtures but also lowers the efficiency of the electrolyzer and enhances degradation of the membranes. (See Fig. 1.)

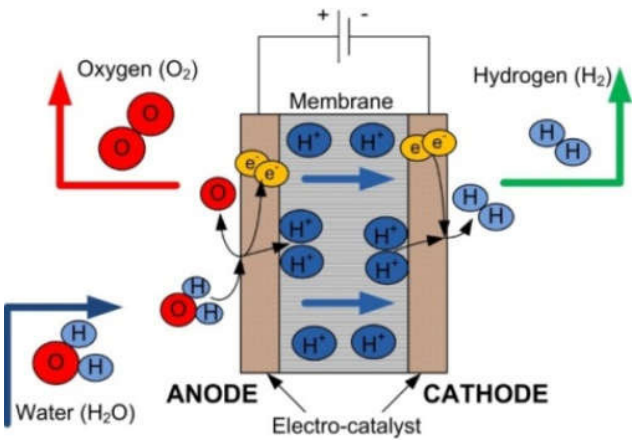

Fig. 1.Schematic of a PEM electrolyser setup [1].

Jacobson, 2004 indicated that the water balance in a normal operating fuel cell is critical to the operation of the cell and that proper humidification of the membranes will allow optimum conduction of protons. Water entering the electrolysis system which is not transformed into ions, and water that has crossed over into the cathode and is not

being removed quickly, could jeopardize the optimal functionality of the system. This is where neutrons can play a role in analyzing the effectiveness of the gas diffusion layer and water channels in removing water from the electrolyzer fuel cell.

This paper focusses on most recent preliminary studies where neutron radiography has been applied in the detection of hydrogen compounds in a working hydrogen fuel cell during the process of electrolysis. The concentration of the H2-gas being produced is actually too low to be detected via neutron radiography and all results show the water (black), which has a relatively higher neutron attenuation coefficient than the other materials in the experiment and detected within the channel areas of the electrolyser (See figure 4).

In an earlierbothpublication on the application of neutron radiography as analytic method on an electrolyser using PEM fuel cells, Murakawa et.al [2015] focused only on the water-accumulation process in the gas diffusion layer (GDL) under the lands and channels. He concludes that the water accumulation in the GDL under the lands was larger than that under the channels during the period of early PEFC operation. However, this study focuses only on the detection and quantification of the liquid water and subsequent gas within the channels at the cathode and anode during the in-situ electrolysis process of a single working and experimental PEM fuel cell and specifically in the in-plane direction.

2. Experimental setup

The neutron imaging facility (NIF) at the National Institute for Standards and Technology (NIST), USA and located in the NIST Center for Neutron research (NCNR) was utilized. A thermal neutron beam with intensity of 1.38×10^7neutrons.cm^{-2}.sec^{-1} (maximum for the facility) at an L/D of 450 was applied. The full size of the beam waschoked down by a beam limiter to a size of 2.2 cm ×2.2 cm to avoid unnecessary activation of the Fuel Cell and to expose only the area of interest (AOI) which is mainly the channels on both the anode and cathode side.

The electrolyzer fuel cell was aligned in its in-plane direction facing the radiation beam (Fig. 2a) in front of the camera box and as close as possible to the scintillator screen (Fig.2b). The electrolyzer was coupled with all the necessary utilities on the anode side of the cell such as the water inlet and access water – Oxygen removal outlet from and to the reservoir. On the cathode side the cell was equipped with an outlet for hydrogen to the outside of the NIF facility for safe release thereof into the beam port hall. The fuel cell base material has been fitted on both the anode and cathode side with 2 heating elements and an electrical DC potential (both operational from outside the NIF chamber during neutron exposure). A digitally controlled water pump was used for precise regulation of the flow of water into the anode of the electrolyzer.

The neutron radiographs were captured via a 7.9mg/cm^{2}Gadox scintillator (P43) from Lexel Imaging using a ANDOR CCD camera in 16 bit mode and cooled to -30°C for high resolution and electronic noise free imaging. A 85mmNIKON lens focused the image onto the 6.5micrometer pixel size sensor to obtain an effective pixel pitch of 10 micrometer. [Physics NIST, Camera accessed Jan 2017]

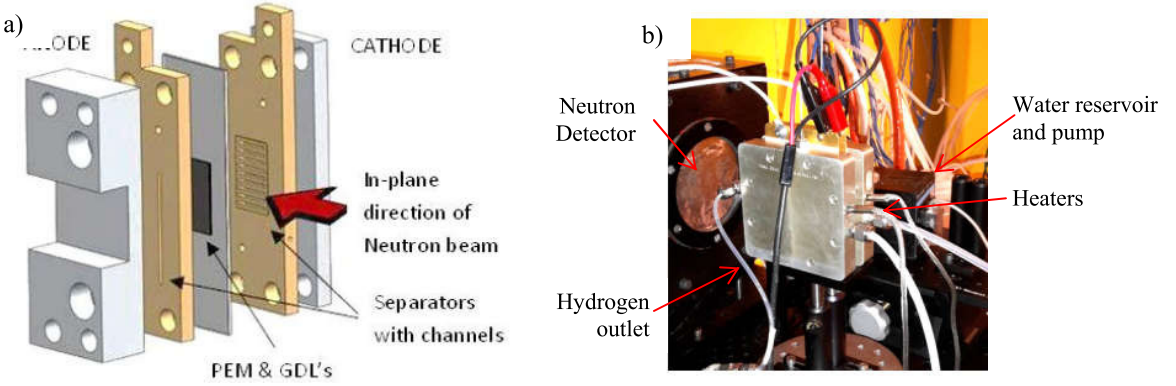

Fig. 2. a) Schematic illustration of the experimental setup and in-plane direction of the neutron beam [1]. b) Experimental set up of the electrolizer fuel cell in the NI chamber at NIST.

The sets of experiments were conducted with the electrolyzer fuel cell orientated in a vertical (see Fig.2b) and then thereafter in a horizontal position. At each orientation, three (3)sets of experiments were conducted with the fuel cell basis materials heated to Ambient = 27°C, 60°C and 80°C temperatures respectively. At each temperature setting, two (2) sets of experiments were conducted with the water flow rate at 11ml/min and 37ml/min. Neutron radiographs were acquired for each of these conditions described above at a rate of 1 integrated frame per 10 sec for duration of 300 sec, starting at a current density of 0A. Similar sets of neutron radiographs were acquired thereafter with the increase of the current density in steps of 0.2A until the potential difference of the cell reached approximately 2V. See Fig.3. for the polarization curves for the operation of the electrolyzer at different water flow rates and fuel cell temperatures achieved in both the vertical and horizontal orientation of the cell.From these curves it is evident that the electrolyzer functions normally as expected.However, the sudden change in the slopes can be explained that in our experiments, novel and experimental catalyst-coated membranes (CCMs) based on 3M NSTF technology were used. The anode catalyst loading was considerably smaller than in conventional CCMs [Bessarabov 2015]. Due to the fact that the loading of anode catalyst was lower than that of commercial CCMs for water electrolysis, as well as that the gas diffusional layer was not optimised, the over-potential at lower current densities was higher than in conventional PEM water electrolysis systems.

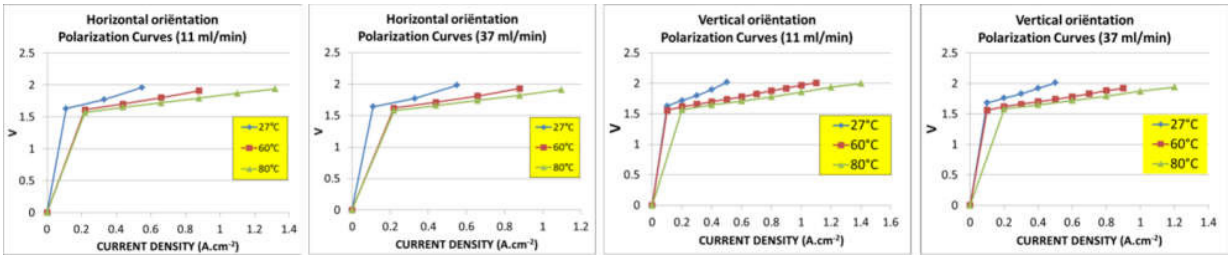

Fig. 3.Polarization curves for all the experiments conducted in a specific orientation, water flow and current density.

The illustration in Fig.4.showsthe vertical and horizontal orientations of the experimental electrolyzer fuel cell, the dimensions of the channels as well as the channels as area-of-interest (AOI) for neutron radiography.

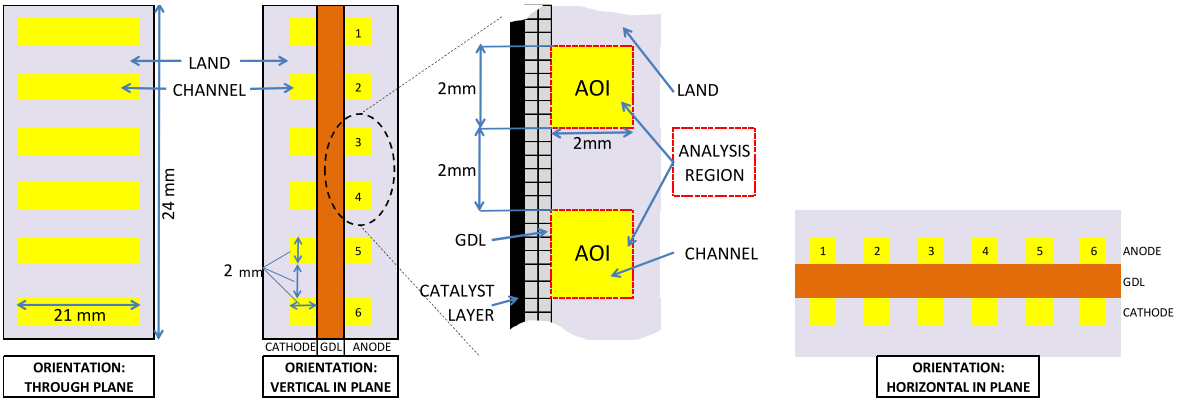

Fig. 4.Schematic diagram of the detail of the dimensions of the PEM electrolyser fuel cell. Experiments were performed only in both the in-plane orientations (vertical & horizontal) with the channels (yellow) as main areas-of-interest.

3. Analysis Method

Qualitative:

Neutron radiographs provide a visual observation for qualitative analysis of the channels at the anode and cathode.An assessmentof the water and gas content during operation at the different parameters mentioned in Section 2were made. Each radiograph present is an accumulation of multiple radiographs being captured every 10sec for a period of 300sec.This visual assessment indicates the integrated information obtained in one radiograph along

the 21mm length of each of the channels.Fig.5 shows these time-resolved radiographs (a pair) each per orientation and at different time intervals T_i.

Regular water flow patterns were observed in the vertical orientation experiments when the water was fed from the bottom of the electrolyser into the anode [A]as shown in Fig.5 as irregular flow was observed with no established channel water pattern when the water was fed into the system from the top.The black areas in channels represent the water (Scale bar or RIGHT indicating the percentage water in the channels in grey scale).

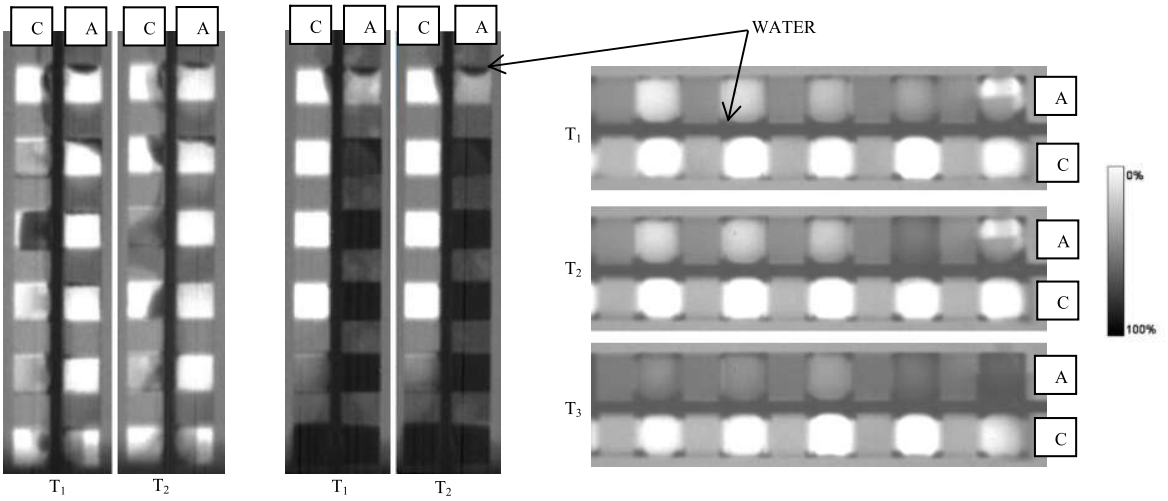

Fig. 5.LEFT: Vertical top initiated flow ; MIDDLE: Vertical Bottom initiated flow ; RIGHT: Horizontal flow with Anode at top.

Observation at the horizontal orientated cells shows a higher concentration of water,as expected, in the anode (the input) as the cathode [C]. Unexpectedly, water has crossed over through the membrane into the cathode which could hinder H-production and the transport thereof outwards from the system. The cathode maintains a regular pattern of water continuously over time. Interestingly the water has accumulated (was not expected) in the corners of the channels at both the anode and cathode. The oxygen and hydrogen production in the anode and cathode respectively are located in the center of the channels while more water, as expected, is located near the membranes.

Quantitiative:

Calibration calculations for the correct determination of the neutron attenuation of Ti(base material of the fuel cell) and water are necessary for the accurate determination of the water content within the channels of the electrolyzer. This calibration process followed here is a first order process and does not include corrections for neutron scattering or beam hardening.From basic principles of neutron attenuation with matter it can be shown that the attenuation for water and Ti can be expressed in general asshown in eq-4:

$$\ln\left[(I_0 - I_{DC})/(I - I_{DC})\right] = \Sigma_{Ti} x_{Ti} \tag{4}$$

With I_0 the intensity with no sample, I the intensity at a certain thickness x_{Ti} of the Ti-material, I_{DC} the dark current electronic noise of the detection system and Σ_{Ti} the linear attenuation coefficient of the medium under investigation which is an unknown for the Ti body and water within the channels.

To determination the neutron attenuation of Ti from a single radiograph (See fig.6.), the electrolyzer is in a non-operational state and thus without any water. The various thickness of the Ti are known to be A: 31.2mm, B: 27.2mm and C: 10mm respectively. The corresponding different average pixel grey scale values (with a $SD_{pixel} = 3$) are displayed in a histogram. The application of eq-4 results in the graph (Fig.6) with the slope the Σ_{Ti}.

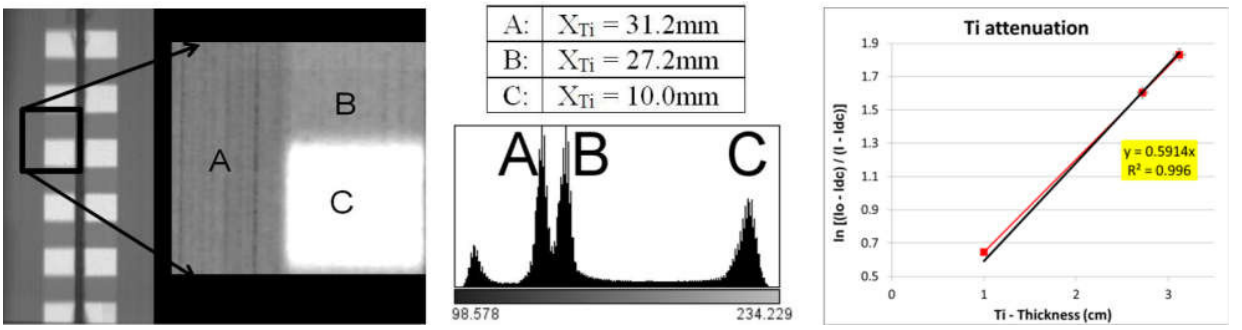

Fig. 6.Determination of the Ti neutron attenuation: LEFT: Neutron radiograph with system at dry state showingzoomed in viewwith the areas A,B and C. MIDDLE: Histogram with pixel values for 3 individual regions. RIGHT: Utilisation of eq-4 in a graph to determine the Σ_{Ti}

Using Eg-4 to determine the thermal neutron attenuation of Ti and generating Fig.6 RIGHT for this experiment, it is found that $\Sigma_{Ti} = 0.592_{avg} \pm 0.017$ (3% error) cm^{-1}.

For water calibration to obtain the neutron attenuation coefficient for water the operating condition of the cell at 0V and 0A was used. At this condition the anode and cathode is in a dry (0%) and fully wet (100%) condition respectively knowing that the channels are either completely dryor fully filled with water. As the water is located within the channels, the attenuation of water has an offset of $0.5914cm^{-1}$ for the contribution of the Ti-material of the channel – for this experiment a wall thickness of 1cm. The neutron attenuation for H_20 for this experimental setup was found to be $\Sigma_{water} = 2.51\ cm^{-1}$ using eq-5:

$$\ln\left[(I_0 - I_{DC})/(I - I_{DC})\right] = \Sigma_{Water} x_{Water} + \Sigma_{Ti} x_{Ti} \quad (5)$$

The schematic illustration as in Fig.1 shows an ideal situation with all the water, being fed into the anode, are "used or split". One should therefor expect constant water content at the anode present, equally distributed through all the channels and with no residual water left at the anode.

4. Results and Discussion

The initialpurpose of this study was to observe qualitatively the movement and behavior of the water as well as the production and movement of oxygen and hydrogen in the anode and cathode respectively. Observation of both the anode and cathode was planned to view the behavior of the electrolysis process. However, data being made available through neutron radiography can be used for either qualitative as well as quantitative analysis once the detector has a linear response characteristic. Table-1 presents the percentage water in the anode and cathode at all the different experimental parameters.

Although the membranes of the electrolyzer in the Gas-Diffusion-Layer (GDL) ishydrophilic of nature, the observation of water crossed over into the cathode is being confirmed as~18% percent water are present in both the vertical and horizontal orientations. As expected, the percentage water in the anode, the entrance of water into the system, is high and found to be ~ 44%. At the higher water flow rate of 37ml/min, no significant difference in the amount of cross over water in the cathode for both orientations of the electrolyzer is being observed and was calculated to be in the order of ~ 19%. The experiment did not focus on the water transport process as such and thus does not reveal the tempo of the water transport through the membrane.

Additionally, the water concentration of the GDL could be observed at a low pixel resolution and found to be different within the area of the channel and the glands during operation. The background radiograph (no water as shown in fig.6) is being subtracted from the radiograph at any given time during the electrolysis process (those in fig. 5) to reveal only the change in pixel grey scale value at the time caused by the water. As no water calibration was performed for this material, only a qualitative observation could be made that indicates higher water content in the GDL at the position of the channels rather than at the position of the lands. See Fig. 7 with water visualized as white in the resultant radiograph. Line profiles (RED at the Anode and YELLOW at the GDL) show a larger arbitrary grey scale value at the channel region indicating thus more water than the lands region. This

observationconfirms the research of Murakawaet.al, 2015 who made an in depth study of the water content of the GDL.

Table-1: Results of the experimental electrolysis process. The percentage water found in the Anode and Cathode channels for 2 x orientations of the cell:V = Vertical orientation; H = Horizontal orientation, 2 different water flow tempo of 11 and 37ml/min, at ambient pressure and at three different temperatures (27°C, 60°C and 80°C). The standard deviation of all results is ~ 2%. A = Anode; C = Cathode

VERTICAL ORIENTATION

	11 ml / min	
TEMP (°C)	A	C
27	37.4%	17.3%
60	35.0%	18.9%
80	40.3%	19.9%
AVG	37.5%	18.7%

V

VERTICAL ORIENTATION

	37 ml / min	
TEMP (°C)	A	C
27	45.1%	16.2%
60	44.3%	19.8%
80	44.2%	20.2%
AVG	44.6%	18.6%

11 ml/min 37 ml/min

HORIZONTAL ORIENTATION

	11 ml / min	
TEMP (°C)	A	C
27	32.9%	15.8%
60	33.2%	20.4%
80	32.2%	19.6%
AVG	32.8%	18.5%

H

HORIZONTAL ORIENTATION

	37 ml / min	
TEMP (°C)	A	C
27	46.0%	22.5%
60	40.7%	19.4%
80	43.0%	21.6%
AVG	43.1%	21.1%

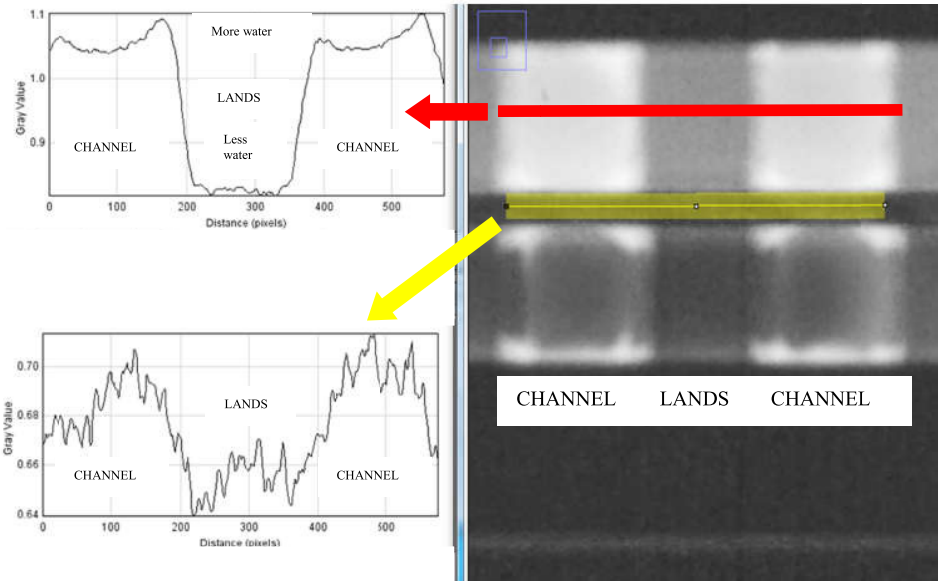

Fig. 7.TOP LEFT: A line profile at the position of the channels and land at the anode within the Ti-body of the electrolyzer. BOTTOM LEFT: A line profile at the position of the GDL spanning across the channels and land. RIGHT: Neutron radiograph at the horizontal orientation of the electrolyzer of 2 channels and 1 land indicating the positions of the line profiles.

5. Conclusion and Future

The water behavior and management of the electrolysis process in a working fuel cell has been investigated using neutron radiography at a spatial resolution of 10 micron. Valuable insight and additional information were obtained

in the internal working of the electrolyzer. No attempt was made to quantify the H production in the cathode as it is difficult to detect or quantify the different gases via neutron radiography due to their low neutron attenuation. However, a first order estimate (without correction of neutron scatter) of 19% ± 2% water in the anode and cathode for each experimental condition could be achieved. Higher water content in the GDL at the position of the channels w.r.t. the lands were observed.Future experiments will aim to quantify the H-production rate and to look deeply into the water cross over mechanism within the membranes.

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References

Ajay K. Prasad, A.K., Opportunities and Challenges for Commercialization of Fuel Cells, http://www.energy.udel.edu/symposium2014/7-Prasad.pdf Accessed on 5 June 2016

Dmitri Bessarabov, Haijiang Wang, Hui Li, Nana Zhao (ed), PEM Electrolysis for Hydrogen Production: Principles and Applications., 2016, CRC Press.

Dimitrios Tsiplakides, 2012, PEM water electrolysis fundamentals. Accessed on 16 August 2016, http://research.ncl.ac.uk/sushgen/docs/summerschool_2012/PEM_water_electrolysis-Fundamentals_Prof._Tsiplakides.pdf

Emmanuel Zoulias, Elli Varkaraki, Nicolaos Lymberopoulos, 2006, A REVIEW ON WATER ELECTROLYSIS, Accessed on 16 Aug 2016, http://www.cres.gr/kape/publications/papers/dimosieyseis/ydrogen/A%20REVIEW%20ON%20WATER%20ELECTROLYSIS.pdf

Physics NIST, http://physics.nist.gov/MajResFac/NIF/camera.html. Accessed in Jan 2017.

Jacobson, D. 2004, Neutron Imaging facility: PEM Fuel Cells. Accessed on 18 Aug 2016, http://physics.nist.gov/MajResFac/NIF/pemFuelCells.html

Manfred Waidhas, Siemens AG,https://www.iea.org/media/workshops/2013/hydrogenroadmap/Session4.2WaidhasSiemens.pdfAccessed on 10 Aug 2016.

MurakawaHideki, Katsumi Sugimoto, Nobuki Kitamura, Masataka Sawada, Hitoshi Asano, Nobuyuki Takenaka, Yasushi Saito, Visualization of water accumulation process in polymer electrolyte fuel cell using neutron radiography. Physics Procedia 69, (2015), 607 – 611.

US Department of Energy (DOE), https://www.hydrogen.energy.gov/roadmaps.html, Accessed on 10 June 2016