Proposal 20171538

Title
Fundamental understanding of dominating water transport mode in PEFC gas diffusion layers

Abstract
Water management is the major limiting factor in PEFC for further increase of power density of polymer electrolyte fuel cells (PEFC). The dominating water transport mode in the gas diffusion layer (GDL) of PEFCs is unclear. Operando X-ray tomographic microscopy with 1-2 s acquisition time is required to capture the water distribution in the opague GDL structures dynamically and to conclude on the dominating water transport mode.

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Experiment Category	
Experiment Type	Normal
Research Area	Catalytic Materials/Surface Science

Experiment Requirements	
Eligible for EU Support	No
Number of Shifts Required	6
Schedule Preferences	Mai or June
Beamline/Station	TOMCAT

Links to related proposals of relevance to the current proposal		
Proposal	Title/Proposer/Infos given by the proposer about the relation	Report
20170876	Title: Water feature detectability in subsecond XTM of gas diffusion layer of PEFC Proposer: Dr. Jens Eller Infos: During this campaign, water feature detectability under different imaging parameters will be quantified and guide the imaging conditions for operando experiments proposed in this proposal.	Available

A Goal of the experiment

The goal of the proposed experiment is to identify the dominating water transport mode in the gas diffusion layer (GDL) of polymer electrolyte fuel cells (PEFCs). After years of different neutron and X-ray imaging studies it remains still unclear, if the produced water is transported dominantly by either capillary pressure [1] or root-like merging of condensation clusters [2,3] mechanism (see Fig. 1). It is of paramount importance to know which process is dominating and should be considered most of all during future material development. Previous with XTM at static PEFC operation conditions were not able reveal the dominating water transport mode so far. Thanks to the development of dynamic PEFC XTM in second scan time regime ([4], see Fig. 2), the verification of it's imaging capabilities (exp. report 20170876) and the development of water cluster classification algorithms ([5], Fig. 3), it will be possible follow the dynamics of water accumulation in the GDL and identify the driving process.

B Background

Hydrogen fed polymer electrolyte fuel cells (PEFC) are expected to play a major role in a future decarbonized energy system [6], in particular in the mobility sector. Water management is the major limiting factor in PEFC for further increasing power density [7]. Inside the PEFC, the water management is complex: on one hand, the membrane needs a certain hydration state in order to ensure sufficient proton conductivity; on the other hand, excessive water leads to blocked gas pathways in the porous structures with increased mass transport losses (see Fig. 4). These flooding effects can dramatically decrease the accessibility of oxygen, resulting in mass transport limitations ([8], so-called flooding) that prevents high current density operation that is necessary for high power automotive applications.

The dynamic operando XTM setup and image processing knowhow of the proposers was recently used to guide PEFC development in collaboration with a major car manufacturer in during industry beam time at TOMCAT in July 2017.

C Experimental method; specific requirements

Synchrotron radiation based X-ray tomographic microscopy is required due to the fine and opaque fiber structure of the GDL (~7 um fiber diameter) and the transient water transport processes in PEFCs. The fuel cell set-up for operando XTM (see Fig. 5) was developed and exploited during previous campaigns (20090986, 20100287, 20100818, 20110297, 20120161) will be used. It allows precise control of fuel cell operation conditions, eg. in-let gas humidity and cell temperature.

XTM scans with 13.5 keV monochromatic beam energy with voxel size of 3 μm and scan times around 1-2 s is needed to capture of the dynamics of liquid water during operando XTM experiments with a detectability of small water features (>95% detectability for most of the water droplets above diameter of 15 um, see exp. report 20170876). Upcoming microscope upgrade is expected to increase detectability and to reduce scan time, and thereby dose to the cell per scan, further. XTM scans will be acquired during fuel cell operation at different temperature (30^oC, 60^oC), low and high current density (0.5A/cm^2, 1.0A/cm^2) and in-let gas relative humidity varying from 0% (dry gas) to 110% (oversaturated gas) in order to screen for the different water transport modes. Two GDL samples with different pore structures from two different manufacturers (SGL, Toray) will be examined.

D Results expected

With an XTM image acquisition time between 1 - 2 s and feed gas humidity increasing operation conditions, whether a water cluster built up from the catalyst layer towards the GDL-channel/rib interface (capillary pressure driven flow) or growth and aggregation of various independent condensation spots favorable in the GDL domain under the rib (root-like condensation clusters merging), will be clarified. GDL samples from two different manufacturers (SGL, Toray) will be depicted to better understand the influence of the underlying pore structure over a wide range of PEFC operation conditions. These insights into the fundamental water transport mode will potentially guide fuel cell design and material modifications to foster the dominating water transport regime.

E Estimate and justification of the beamtime

Sequences imaging of fuel cells with 2 different GDL samples (SGL, Toray) operating at 2 temperature levels (60^oC, 80^oC) and 2 current densities (0.5A/cm^2, 1.0A/cm^2) with increasing gas relative humidity from 0 to 110% will be acquired for 8 cells (2 materials, two repetitions). The estimated average test-time for one cell is 10 h in total (incl. mounting, PEFC operation and XTM acquisition at different conditions with intermediate drying of the cell). Together with fuel cell test bench set-up (4 h per campaign) and beamline setup (2 h) for 4 cells tested at 8 different conditions, a total time of 46 h (4 h +2 h + 4 *10 h) is estimated. Therefore, we apply for a total of 6 shifts (48 h).

F References relevant to the experiment description

[1] S. Litster, D. Sinton, N. Djilali, J. Power Sources, 154(1), 95-105 (2006).
[2] J. H. Nam, M. Kaviany, Int. J. Heat & Mass Transfer, 46(24), 4595-4611 (2003).
[3] U. Pasaogullari, C. Y. Wang, J. Electrochem. Soc., 151(3), A399-A406 (2004).
[4] J. Eller, F. Marone, F. N. Büchi, ECS Trans. 69(17), 523–531 (2015).
[5] J. Eller, J. Roth, F. Marone, M. Stampanoni, F.N. Buechi, J. Electrochem. Soc. 164 (2), F115-F126 (2017).
[6] IEA; Advanced Fuel Cells Implementing Agreement Annual Report (2009).
[7] D. Hayashi, A. Ida, S. Magome, T. Suzuki, S. Yamaguchi, R. Hori, SAE Technical Paper 01-1188 (2017).
[8] J. Eller, T. Rosén, F. Marone, M. Stampanoni, A. Wokaun, F. N. Büchi, J. Electrochemical Society, 158 (8), B963-B970 (2011).

SLS related publications of the proposers (within the last 18 months)
[1] K. B. Hatzell, J. Eller, S. L. Morelly, M. H. Tang, N. J. Alvarez, Y. Gogotsi; Direct observation of active material interactions in flowable electrodes using X-ray tomography; Faraday Discuss., 199, 511-524 (2017).
[2] M. A. Safi, N. I. Prasianakis, J. Mantzaras, A. Lamibrac. F. N. Buechi; Experimental and pore-level numerical investigation of water evaporation in gas diffusion layers of polymer electrolyte fuel cells; Int. J. Heat. Mass Transfer, 115 (A), P238-P249 (2017).
[3] J. Eller, J. Roth, F. Marone, M. Stampanoni, F.N. Buechi; Operando properties of gas diffusion layers: Saturation and liquid permeability; J. Electrochem. Soc. 164 (2), F115-F126 (2017).
[4] A. Forner-Cuenca, J. Biesdorf, A. Lamibrac, V. Manzi-Orezzoli, F.N. Büchi, L. Gubler, T.J. Schmidt, P. Boillat; Advanced water management in PEFCs: Diffusion layers with patterned wettability: II. Measurement of capillary pressure characteristic with neutron and synchrotron imaging; J. Electrochem. Soc. 163 (9), F1038-F1048 (2016).
[5] I. V. Zenyuk, A. Lamibrac, J. Eller, D. Y. Parkinson, F. Marone, F. N. Buechi and Adam Z. Weber; Investigating Evaporation in Gas Diffusion Layers for Fuel Cells with X-ray Computed Tomography; J. Phys. Chem. C, 120 (50), F28701–F28711 (2016).
[6] T. Agaesse, A. Lamibrac, F. N. Buechi, J. Pauchet, M. Prat; Validation of pore network simulations of ex-situ water distributions in a gas diffusion layer of proton exchange membrane fuel cells with X-ray tomographic images; J. Power Sources, 331, F462-F474 (2016).
[7] A. Lamibrac, J. Roth, M. Toulec, F. Marone, M. Stampanoni and F. N. Buechi; Characterization of Liquid Water Saturation in Gas Diffusion Layers by X-Ray Tomographic Microscopy; J. Electrochem. Soc. 163(3), F202-F209 (2016).
[8] S. H. Eberhardt, F. Marone, M. Stampanoni, F. N. Buechi and T. J. Schmidt; Operando Xray Tomographic Microscopy Imaging of HT-PEFC: A Comparative Study of Phosphoric Acid Electrolyte Migration; J. Electrochem. Soc. 163(8), F842-F847 (2016).
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Other publications of the proposers (within the last 18 months)
[1] M. Suermann, K. Takanohashi, A. Lamibrac, T. J. Schmidt, F. N. Buechi; Influence of Operating Conditions and Material Properties on the Mass Transport Losses of Polymer Electrolyte Water Electrolysis; J. Electrochem. Soc. 164 (9), F973-F980 (2017).
[2] M. Suermann, T. Kiupel, T. J. Schmidt, F. N. Buechi; Electrochemical Hydrogen Compression: Efficient Pressurization Concept Derived from an Energetic Evaluation; J. Electrochem. Soc., 164 (12), F1187-F1195 (2017).
[3] M. Suermann, A. Patru, T. J. Schmidt, F. N. Buechi; High pressure polymer electrolyte water electrolysis: Test bench development and electrochemical analysis; Int. J. Hydrogen Energy, 42(17), P12076-P12086 (2017).
[4] U. Babic, M. Suermann, F. N. Buechi, L. Gubler, T. J. Schmidt; Critical Review—Identifying Critical Gaps for Polymer Electrolyte Water Electrolysis Development; J. Electrochem. Soc. 164 (4), F387-F399 (2017).
[5] L. Holzer, O. Pecho, J. Schumacher, Ph. Marmet, O. Stenzel, F.N. Buechi, A. Lamibrac, B. Muench; Microstructure-property relationships in a gas diffusion layer (GDL) for Polymer Electrolyte Fuel Cells, Part I: effect of compression and anisotropy of dry GDL; Electrochimica Acta, 227 F419-434 (2017).
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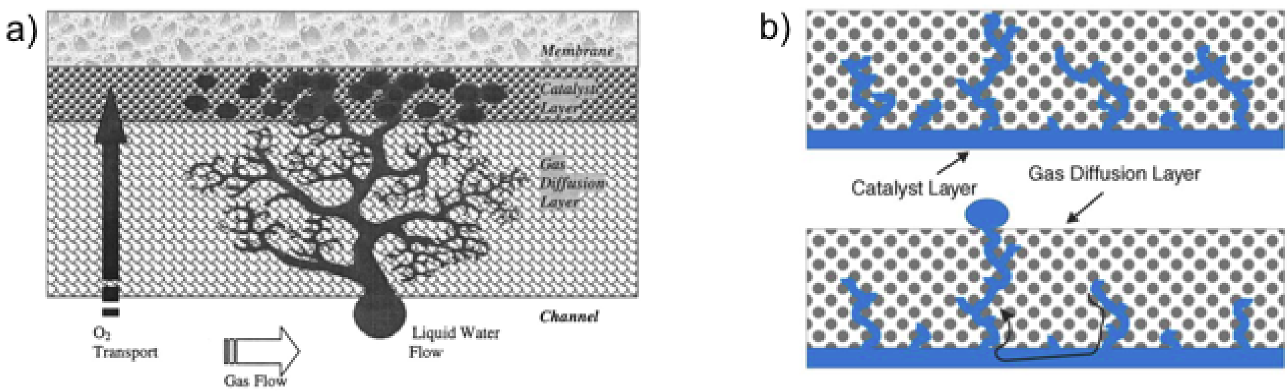
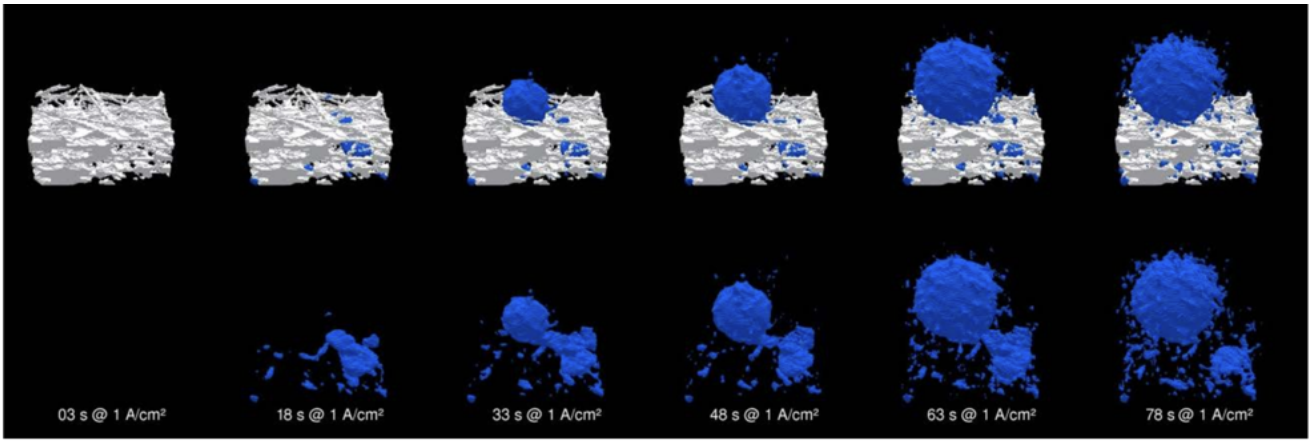
[7] P. Pietsch, M. Hess, W. Ludwig, J. Eller, and V. Wooda; Combining operando synchrotron X-ray tomographic microscopy and scanning X-ray diffraction to study lithium ion batteries; Sci Rep. 6, F27994 (2016).



a) Root like merging of condensation clusters.
Nam & Kaviany, Int. J. Heat Mass Trans. ***46*** *(2003)*
Pasaogullari & Wang, J. Elec. Soc. ***151*** *(2004)*

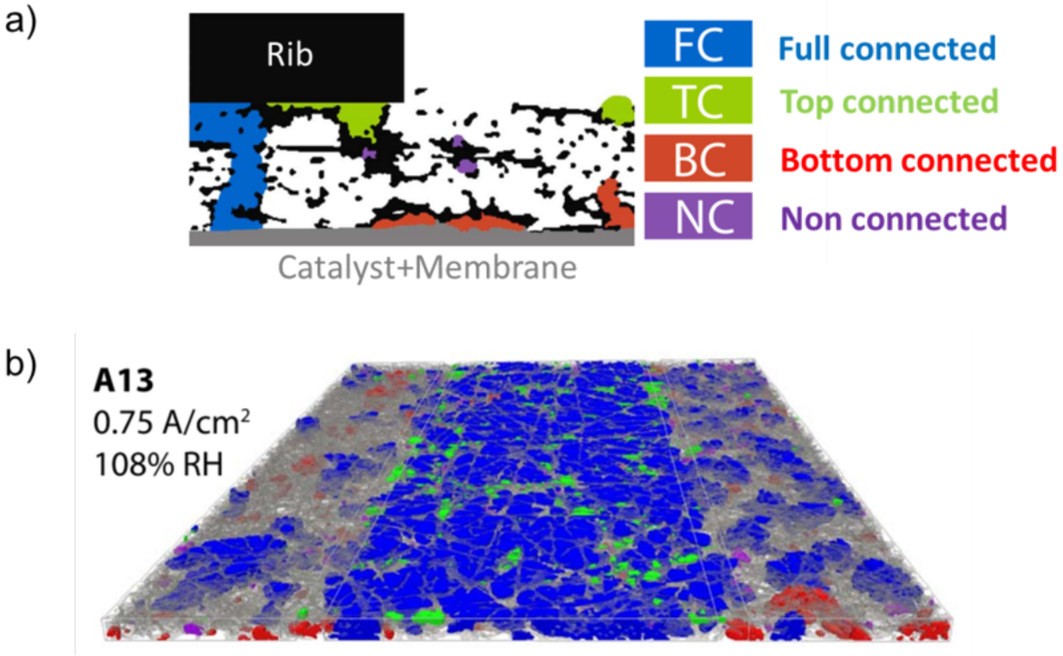
b) Capillary pressure driven liquid flow.
Litster, Sinton, Dijlali, J. Pow. Sources ***154*** *(2006)*

Figure 1: Two fundamental water transport modes in gas diffusion layer (GDL).



- Surface rendering of the liquid water for selected scans. In the top row, the liquid water is shown together with the solid GDL, while the GDL is not shown in the bottom row; droplet is not removed due to low gas speed (approx. 0.8 m/s).

Figure 2: Subsecond XTM 3D renderings



a) Sketch of the different cluster types that can be found in the GDL domain; b) Cluster connectivity analysis of static PEFC scan (scan time 10s)

Figure 3:

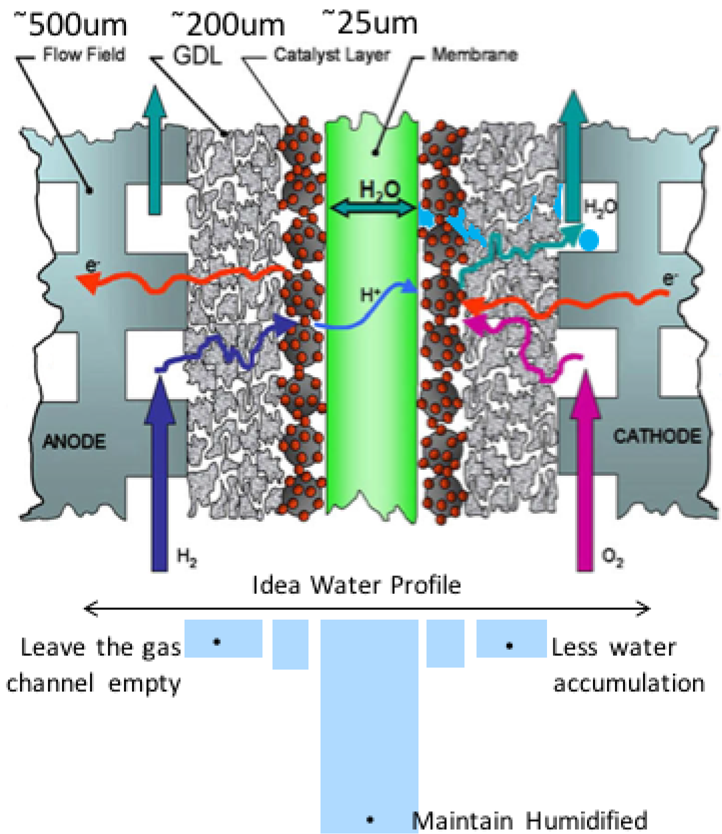
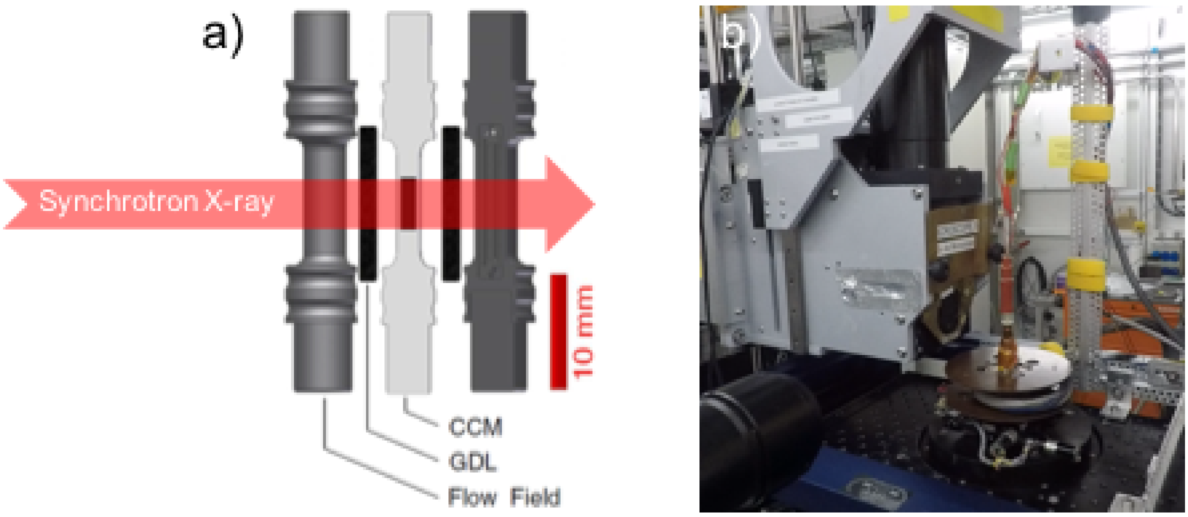


Figure 4: PEFC Scheme and the water profile



a) Schematic of XTM PEFC components.

b) Operando fuel cell set-up at the beamline in front of the scintillator (X-ray beam coming from the right side).

Figure 5: Image of Setup at beamline

Sample

Sample #1

Sample and chemical substance to be used in this experiment	
Substance	Carbon Fiber; Platinum contained catalyst
Chemical formula	Carbon fiber paper surface-treated with PTFE or FEP; Platnium contained catalyst.
Structure	Multilayer
Size X	5
Size Y	5
Size Z	0.2
Mass	1.6
Container	Vespel cell
High purity	No
After the experiment the sample will be	Removed by user
No ethical issues declared on this sample.	

Sample environment	
Cryojet [K]	270-370
Hotair blower	No
High voltage	No
High pressure	No
High temperature	No
Magnetic field	No
Cryogenic liquid	No
Be window	No

Safety aspects	
Chemical hazards	
Chemical hazards	Burnable chemicals and solvents Gases (CO, H2, N2, O2, CO2, noble gases, others) Reactive chemicals
Specification of chemical hazards	In the setup for running the fuel cell, the sample is overflowed with synthetic air and hydrogen with low gas flow up to 200ml/min
Exhaust disposal conditions	The exhausted gas (air and H2) will be first diluted with N2 and then disposal through TOMCAT exhaust gas pipeline. The disposal gas-diluting set-up has been developed in previous beamtime.

Experimental report	
Proposal ID	20170876
Last modified	15.Sep.2017 21:12:57

Title: Water feature detectability in subsecond XTM of gas diffusion layer of PEFC

A) Overview

This report will be updated as soon as the scheduled experiment on 18th Sept 2017 is finished. Thanks!

B) Quality of measurement/data

N/A

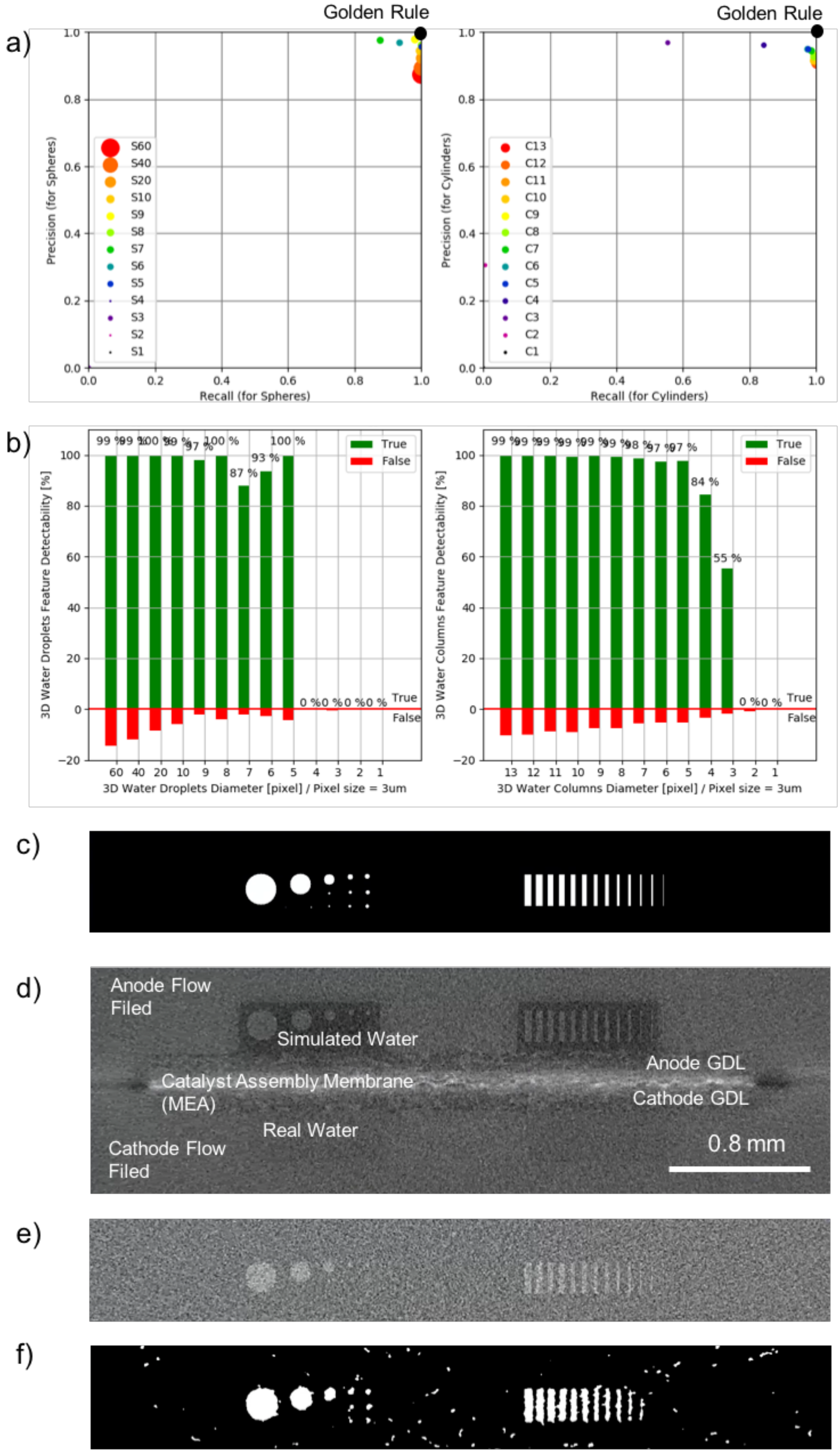
C) Status and progress of evaluation

N/A

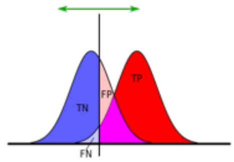
D) Results

N/A

Experimental report attachment



- Receiver operation characterization (ROC) plot for ground truth in c)



$$Recall = TP/(TP+FN)$$
$$Precision = TP/(TP+FP)$$

- 3D Feature detectability bar plot for ground truth in c)
- Green bar is True Positive (TP)
- Red bar is False Positive (FP)

- 2D representation of 3D ground truth: different size of water droplets structure (left), water columns structure (right)
- Add ground truth mask to dry scan to simulate artificial water structures

- Subtraction of d) with another dry scan with the same imaging condition

- Filtered and thresholded e)
- Pixel comparison with c) to define the feature detectability

- Filters: 3D Median (d=3), 3D Anisotropic Diffusion (Iter=3)
- 16bit Mapping Threshold (value=35800)

Figure 1: Feature detectability analysis for a 1.6 s scan of XTM fuel cell.