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Engineered Water Highways in Fuel Cells: Radiation Grafting of Gas Diffusion Layers

*Antoni Forner-Cuenca**, Johannes Biesdorf, Lorenz Gubler, Per Magnus Kristiansen, Thomas Justus Schmidt, Pierre Boillat

A. Forner-Cuenca, J. Biesdorf, Dr. L. Gubler

Electrochemistry Laboratory, Paul Scherrer Institute (PSI), 5232 Villigen, Switzerland

E-mail: antoni.forner@psi.ch

Prof. Dr. P. M. Kristiansen

Institute of Polymer Nanotechnology, University of Applied Sciences and Arts Northwestern Switzerland (FHNW), 5210 Windisch, Switzerland

Prof. Dr. T.J. Schmidt

Electrochemistry Laboratory, Paul Scherrer Institute (PSI), 5232 Villigen, Switzerland, and Laboratory of Physical Chemistry, ETH Zurich, 8093 Zurich, Switzerland

Dr. P. Boillat

Electrochemistry Laboratory, Paul Scherrer Institute (PSI), 5232 Villigen, Switzerland and Neutron Imaging and Activation Group, Paul Scherrer Institut (PSI), 5232 Villigen, Switzerland

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Polymer electrolyte fuel cells (PEFCs) have become a promising candidate for replacing fossil fuel fed engines in both stationary and mobile power sources, owing to their zero-emission characteristics, high efficiency and power density. Years of intensive research (from around 800 publications in 2000 to about 3000 in 2014, patents from 500 in 2000 to nearly 3000 in 2012)^[1] brought the technology to a status where commercialization appears realistic, with first systems recently appearing on the market for both stationary and mobile applications,^[2] specifically the latter at elevated price (47 \$/KW_{system} in 2012, 30 \$/KW_{system} being the target for 2017).^[3]

Nevertheless, some technical issues remain, which require special attention, such as cost and durability, in which an important role is played by water management. The water management is not a trivial issue in PEFCs and needs to be carefully controlled. On the one hand, the

membrane needs to be sufficiently hydrated to ensure practical proton conductivity (~0.1 S/cm). On the other hand, excessive amounts of water in the gas diffusion layer and flow field channels can hamper the access of reactant gases to the catalyst layer, leading to increased mass transport losses.^[4] Consequently, power density is reduced if the delicate balance between these two requirements is not fulfilled, resulting in an increased stack size – and cost – for a specified output power. Furthermore, some degradation mechanisms (e.g. starvation) are thought to be related to water flooding.^[5]

State of the art PEFCs include a gas diffusion layer (GDL), a porous layer made of carbon fibers responsible not only for the fine distribution of reactant gases, but also for the transport of product water, heat and electrical current. These functions imply a triple set of contradictory requirements: high diffusivity of the gas phase, high permeability of the water phase and high thermal and electrical conductivity of the solid phase. On the cathode, liquid water flows from the catalyst layer towards the gas flow channels through the GDL, in opposite direction to oxygen diffusion. Capillary pressure is the driving force for water transport,^[6] which depends both on the pore size and the internal contact angle between water and the porous medium, showing the importance of the microstructure and the surface energy of the material at the local level.^[7] In order to prevent excessive water accumulation in the GDL, a hydrophobic coating, usually polytetrafluoroethylene (PTFE), is applied. The portion of the GDL filled with water is determined by the lowest resistance pathways in terms of capillary pressure, which are tortuous and sometimes dead-ended, resulting in a non-optimal relationship between the water and gas transport characteristics (**Figure 1**). In a recent study of our group, we have shown that even though a high PTFE loading results in lower water content, the impact of this water is much higher than for materials with a moderate PTFE loading and higher water accumulation.^[8] This emphasized the fact that not only the *amount* of water in the porous structure is important, but that its *distribution* is crucial and has to be controlled. The fundamental interest of GDLs with patterned wettability was highlighted by

Utaka et al. using a stacked arrangement of alternating hydrophobic and hydrophilic gas diffusion layers and measuring the oxygen diffusivity through this arrangement.^[9] The impact of water saturation on diffusivity was shown to be clearly lower for this hybrid arrangement compared to experiments made with either purely hydrophobic or purely hydrophilic layers. While the benefit of GDLs with defined water removal pathways is clearly established, none of the previous studies found in the literature proposed a method to produce such materials in a way compatible with mass production. In the broad sense, previous approaches can be categorized into three groups: first, the “perforation approach” was initially published by Gerteisen et al. and continued by other groups.^[10-12] This method consists of locally increasing the pore size within the GDL by either laser or mechanical perforation, which resulted in reduced mass transport losses when cylindrical holes were introduced into the GDL underneath the flow channels. A major drawback of this approach is the very limited design flexibility, in particular the impossibility of generating patterns for the improvement of in-plane transport properties. Second, the approach of “local coating” is based on the application of a hydrophobic coating to defined regions, leaving the remaining (carbon fibers) uncoated. Although this method was shown to be successful on small samples in terms of oxygen diffusivity improvement, it appears to have a rather limited scale-up potential.^[13,14] Third, the “surface and physical interaction” approach has only been reported in patented literature and is based on plasma induced surface modification of the GDL using patterns and deposition of solid hydrophilic particles (metal oxides).^[15] Surface modifications in the range of 1 μm can preferentially relocate the water on the surface but the bulk properties remain unmodified.^[16] Deposition of solid oxide nanoparticles into the inner porosity appears difficult to implement and the lack of covalent bond chemistry may affect the durability.

We propose a material design consisting of defined patterned hydrophobic regions providing a dry, non-mass transport limited pathway (decreased tortuosity) for reactant gases to reach the catalyst layer. Intermittent hydrophilic regions of the proposed material provide a separate

pathway for product water to leave the cell (Figure 1). A minimum feature size of 100 μm seems to be the reasonable target since for most carbon fiber papers this dimension corresponds to the size of 2-3 pores.

Here, we report a new fabrication method (Figure 2) based on radiation grafting for preparing novel GDL materials with patterned wettability properties. First, commercial GDLs are coated with a hydrophobic fluoropolymer. Then, they are locally exposed to an electron beam (using masks for pattern creation) in order to create radicals in the polymeric coating. Finally, they are immersed into solutions of hydrophilic monomers and graft co-polymerization occurs only in the regions previously exposed to the electron beam. One of the main advantages of the method lies in the realistic scale-up possibilities. Furthermore, modifications throughout the bulk of the GDL and tunable wettability offer significant advantages compared to previous approaches.^[17]

Fluorinated ethylene propylene (FEP) was chosen as hydrophobizing agent. Contrary to the commonly used PTFE, FEP offers higher resistance to radiation as well as stronger hydrophobicity and better reaction kinetics towards graft co-polymerization.^[18] We used N-vinylformamide (NVF) as a hydrophilic monomer leading to the graft-copolymer system FEP-g-NVF. Kinetic studies performed on flat FEP foils (25 μm) allowed finding synthetic conditions to lower the contact angle to values of $20\pm 3^\circ$ from initially $105\pm 3^\circ$. Additionally, experiments were carried out with FEP foils in order to validate the pattern sizes and their spatial resolution. A high accuracy of pattern reproduction on the modified substrate was obtained (Figure S1).

These conditions were then applied to the grafting reaction of NVF into the porous medium. A GDL modified using the procedure described above is shown in Figure 3a, after imbibing the material with water. The hydrophilic slits are clearly visible as water tends to accumulate in these regions. Elemental mapping with energy dispersive x-ray (EDX) spectroscopy was performed from the top (Figure 3b) and bottom surfaces of the modified GDL. In spite of the

irregular nature of the intensity signal due to the material roughness, it was found that the modified area (visualized by the presence of chlorine after forming the quaternary ammonium salt, see experimental section) is a sharp band on both surfaces (Figure 3c), confirming that the electrons effectively activate the material throughout its thickness, and that their scattering does not result in an important loss of resolution.

As of now, EDX has been employed to indicate the presence of chemical modifications leading to hydrophilic regions, however the penetration depth of the technique is limited to several micrometers (on top and bottom surfaces). Similarly, optical visualization confirmed the preferential location of water on the surface of the material, but did not give information about the distribution in the inner pores of the material. For that reason, a setup was designed in order to precisely control the capillary pressure while measuring the local saturation of the porous material. Broadly speaking, water is pushed against the GDL and the response in terms of water redistribution is quantified using neutron radiography. This technique represents one of the most complete ex-situ characterization methods available because it contains information about the inner properties (pore size distribution and internal wettability).^[19]

In the absence of capillary pressure (Figure 4a, 0 mbar radiograph) no liquid water is present in the porous medium, except in the region adjacent to the injection channel. At 10 mbar (Figure 4b) the hydrophilic lines appear partially filled. Larger pores in the low contact angle region are preferentially filled at lower pressures. At slightly increased pressure, 20 mbar (Figure 4c), the lines seem totally filled with saturation values of around 80% in the hydrophilic region and 20% in the hydrophobic domain. Lateral spreading is detected at 40 mbar (Figure 4d), reaching saturation of around 100%, while the line broadens to around 400 μm width. Complete saturation of the material and therefore loss of structuring happens at around 50 mbar (Figure 4e). The observed behavior already suggests a potential improved water removal within an operating fuel cell: liquid water will flow through the predefined

hydrophilic regions towards the flow channels (and subsequently leave the cell) when low capillary pressures form, leaving dry hydrophobic regions for high gas diffusivity.

In order to investigate the performance achieved during operation using the modified materials, in-situ testing was carried out. The fuel cell setup used permits for simultaneous operation of 6 cells, having identical humidified inlet gases and precise thermal management. Thanks to these features, materials comparison (cathodic GDLs) can be done in a highly reliable way. Polarization curves of three different materials are shown in Figure 5. As can be seen, in-house coated and commercially available PTFE treated GDLs exhibited quite similar performance. This was done in order to validate our coating procedure and to provide a baseline with a commercial product. The use of FEP instead of PTFE, a higher coating load and different methods for applying the coating could explain the small differences observed. Interestingly, a substantial performance increase was observed for the GDLs with patterned wettability. Samples with 500 μm wide hydrophilic lines and 950 μm separation were used, with the direction of the hydrophilic lines perpendicular to that of the flow channels. A clear improvement in the region of the curve limited by mass transport (at current densities, $i > 0.6 \text{ A/cm}^2$) was observed for the modified samples. This result highlights the potential of the new proposed material to significantly improve the performance and reduce the flooding without the addition of a microporous layer (MPL).

In summary, we presented here a novel method for producing GDLs with patterned wettability that improve fuel cell performance. Synthetic details were reported together with ex-situ chemical characterization technique (EDX) and capillary pressure studies combined with neutron radiography. The synthetic process confers the material with a tunable gradient of hydrophilic and hydrophobic properties depending on the polymer chemistry used (monomer and synthetic conditions). Additionally, full design flexibility is permitted while the modification takes place throughout the bulk (or any pre-selected depth by adjusting the electron energy) of the porous structure without affecting the mechanical properties of the

material. One of the main advantages of this approach is that it could be realistically scaled up into a roll-to-roll production process.^[20]

Porous structures such as GDLs, microporous layers (MPLs) and catalyst layers are of high relevance to the fuel cell community and can benefit from the presented approach. Beside of fuel cell application, other fields such as microfluidics, ink jet printing and water-oil separation face similar problems and could benefit from the presented technology in the future.^[21-24]

Experimental Section

Coating procedure: Commercially available carbon fiber papers (Toray TGP-H-060, 190 μm thickness) were coated with FEP. A dispersion of FEP (FEPD121 DuPont 55% solids) was diluted (1 part per 5 parts of water) and samples were slowly dipped into the coating solution for 60 seconds. Afterwards, they were placed horizontally on a needle-point holder to avoid gravitational effects and wicking coming from interfaces.^[25] Holders were placed in a vacuum oven and kept at room temperature for 60 min, afterwards the temperature was increased to 100°C and maintained for 60 min. This first thermal process allows for evaporation of water and traces of other solvents present. The heater was then switched off to allow for gentle cooling down of the sample. Samples were taken out and placed in a muffle oven at atmospheric pressure and two new temperature ramps were set: the first up to 260°C allows for evaporation of the surfactant (50 min ramp, 10 min plateau) and the second one up to 280°C allows for sintering of the polymer (20 min ramp, 20 min plateau). Coating loads of around 30% by weight were obtained and this process was proved to provide a homogenous distribution of the coating throughout the bulk of the GDL (Figure S4).

Irradiation: Low-energy electron beam treatment was carried out in an EBLab 200 sealed laboratory emitter system from Comet AG (Flamatt, Switzerland). Samples were subjected to

a dose of 50 kGy under nitrogen (<200ppm oxygen), employing an acceleration voltage of 200 kV at a conveyor speed of 12 m/min and an air gap of 10 mm.

For the patterned materials, 2 mm thick stainless steel masks were prepared with water jet (Waterjet AG, Aarwangen) with a pattern of 500 μm spaced 950 μm . The thinner lines were machined into 0.5 mm thick stainless steel sheets using a combination of laser and water jet (Synova, Lausanne) with a pattern of 100 μm spaced 500 μm . After electron beam treatment, samples were rapidly stored at -80°C to minimize radical recombination prior to grafting.

Grafting reaction: N-vinylformamide (NVF) was used as grafting monomer. Pure monomer (Sigma Aldrich 98%) was used as received. Cylindrical glass reactors (60 mL) were used at atmospheric pressure. The reactor chamber was deoxygenated by flushing with nitrogen (8mL/min) for 60 min. Afterwards, reactors were placed into a water bath at 70°C to start the radical polymerization. The materials were then rinsed under vacuum by flowing 300 mL of ethanol, isopropanol and water in three consecutive cycles.

Hydrolysis and ion exchange with Cl⁻: This step is not part of the normal synthesis and was applied, for visualization purposes, only to the samples measured by energy dispersive X-ray. Samples were placed in a solution of 2M NaOH at 70°C during 5 hours for the hydrolysis of NVF to N-vinylamine (NVA). Afterwards, samples were placed in a solution of 0.1M HCl at room temperature overnight for forming the ammonium salt.

Microscopy: The scanning electron micrographs were recorded using a FE-SEM Ultra 55 (Carl Zeiss, Oberkochen, Germany). Energy dispersive X-ray analysis was performed using a compatible accessory (EDAX TSL, AMETEK). The elemental mappings presented here were taken with an acceleration voltage of 10 keV, an aperture of 60 μm and a gun-to-sample distance of 8 mm.

Capillary pressure experiment: The cell design is the same as the ones used for the in-situ characterization, except that only one central channel is used for water injection (1 mm width).

The modified GDL was located with the hydrophilic lines perpendicular to the channel. A porous hydrophobic membrane (HVHP04700, Durapore) of 125 μm thickness was used as a separator. This allows having the gas equilibrated at atmospheric pressure; meanwhile it is impermeable for liquid water. Water pressure was controlled by regulating the height of a 30 L water vessel with a precision motor. A time of 10 minutes was allowed for equilibration. Neutron radiographs in through-plane configuration were taken during the whole duration of the imbibition. Experiments were carried out at 25°C.

Neutron imaging: Images were recorded at the ICON beamline of the SINQ spallation source at the Paul Scherrer Institute.^[26] Measurements were performed with a 20 μm $\text{Gd}_2\text{O}_2\text{S}$ scintillator. The pixel pitch was 13.5 μm and the effective resolution (10% amplitude of the modulation transfer function), taking into account the blurring induced by the beam divergence combined to the sample-detector distance of 30 mm, was 9.1 line pairs per mm corresponding to a spatial resolution of 55 μm . A CCD camera (Andor DV436, 2048x2048 pixels) was used, with an exposure time of 30 s and a readout time of 8 s. All radiograms underwent noise filtering (3x3 median filter), correction of the beam and detector inhomogeneities, correction of the background contributions (detector background, neutrons scattered by the setup) and correction of beam intensity fluctuations. According to the Lambert-Beer law,^[27] the water thickness can be calculated using a known attenuation coefficient of 4.5 cm^{-1} for the setup used. More details about the image processing can be found in the reference.^[28]

In-situ testing: The multicell setup described elsewhere^[29] was used. Cells were machine into aluminum and nickel-gold coated. Flow fields have 5 parallel channels (0.55 mm depth and 1 mm width). The temperature was set to 50°C and the relative humidity (RH) of both anode and cathode was set to 100%. Fixed gas flow rates of 0.4 NL/min and 1.0 NL/min were used

for the anode and cathode, respectively, translating to very high stoichiometries (> 60 at a current density of 1 A/cm^2) corresponding to the “differential cell” concept.^[8]

A catalyst coated membrane (CCM) (Primer 5710, W.L. Gore & Associates, Inc., USA) was used with Pt-loadings of $0.1 \text{ mg}_{\text{Pt}}/\text{cm}^2$ and $0.4 \text{ mg}_{\text{Pt}}/\text{cm}^2$ on anode and cathode, respectively. Three cells were built with Toray 30%FEP pattern-grafted (cathode) and Toray 30% plain (anode); two cells contained Toray 30% plain (cathode) and Toray 30% plain (anode); and one cell contained Toray TPG-H-060T commercial (anode and cathode). The GDL compression rate was set to 20%. The Toray 30% FEP plain and Toray 30% FEP grafted are both obtained from the same batch of in-house coated materials.

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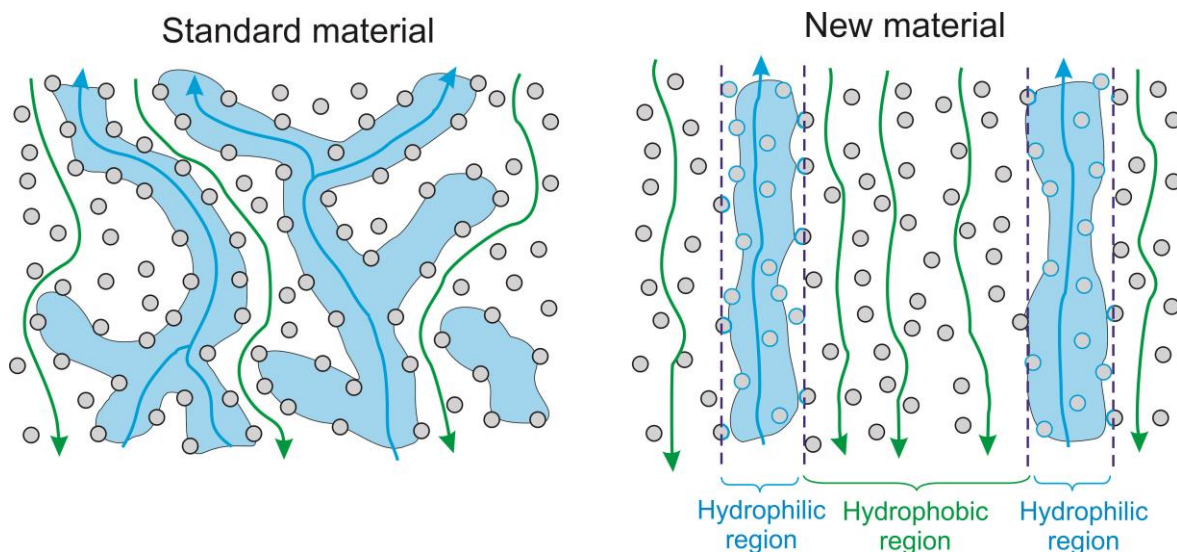


Figure 1. Illustration of the relation between the pathways for liquid water (blue) and for reactant gases (green) in porous materials. Left: in standard hydrophobic materials. Right: in the new proposed material.

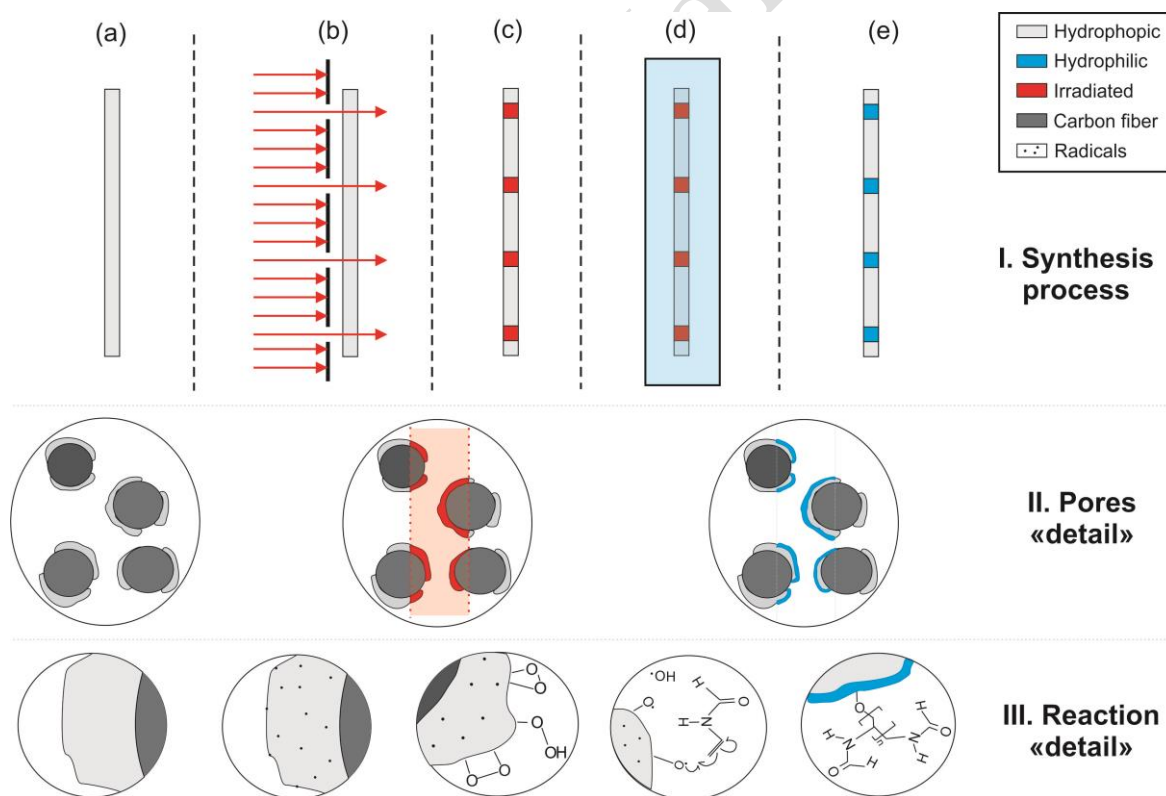


Figure 2. I. Synthesis method for the porous material with patterned wettability. (a): base porous material (hydrophobized). (b): irradiation using a mask. (c): locally irradiated base material. (d): imbibition with grafting solution. (e): resulting material with patterned wettability. II. Illustrations of the pore “detail” to show the modification occurring on the coating of the carbon fibers. III. Illustration of the reaction “detail”.

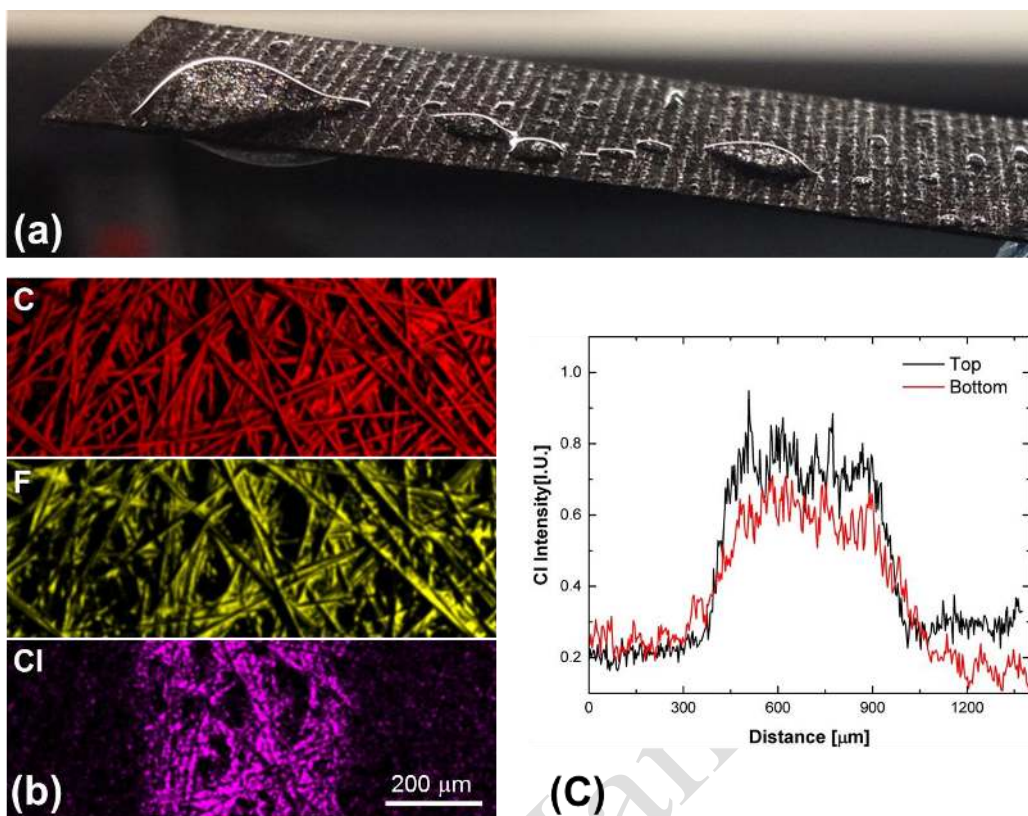


Figure 3. (a) Image of a modified Toray GDL with a pattern of 100 μm (hydrophilic) – 500 μm (hydrophobic) after imbibition in water; (b) EDX elemental mapping of a modified region of 500 μm showing three elements: carbon (representative of carbon fibers and coating), fluorine (representative of coating) and chlorine (representative of the grafted modification and ion exchange); (c) EDX intensity profile for chlorine measured from top (black curve) and bottom (red curve) over one hydrophilic line.

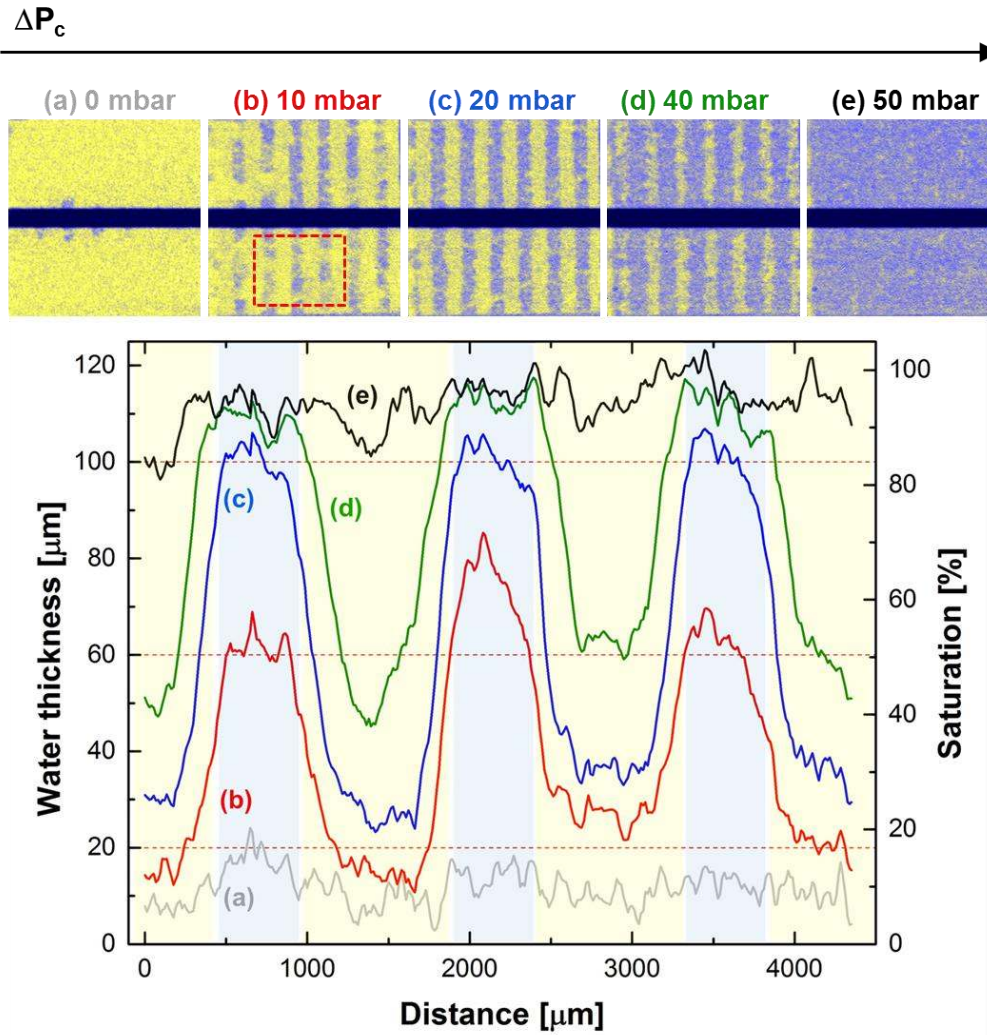


Figure 4. Capillary pressure experiment of a modified GDL (Toray 30%FEP 500-930 μm with NVF) measured with neutron radiography. The radiographs on top show water locations within the GDL with increasing capillary pressure: (a) 0 mbar, (b) 10 mbar, (c) 20 mbar, (d) 40 mbar and (e) 50 mbar. The graph below shows the quantified water thickness and saturation in a selected region for the different capillary pressures applied.

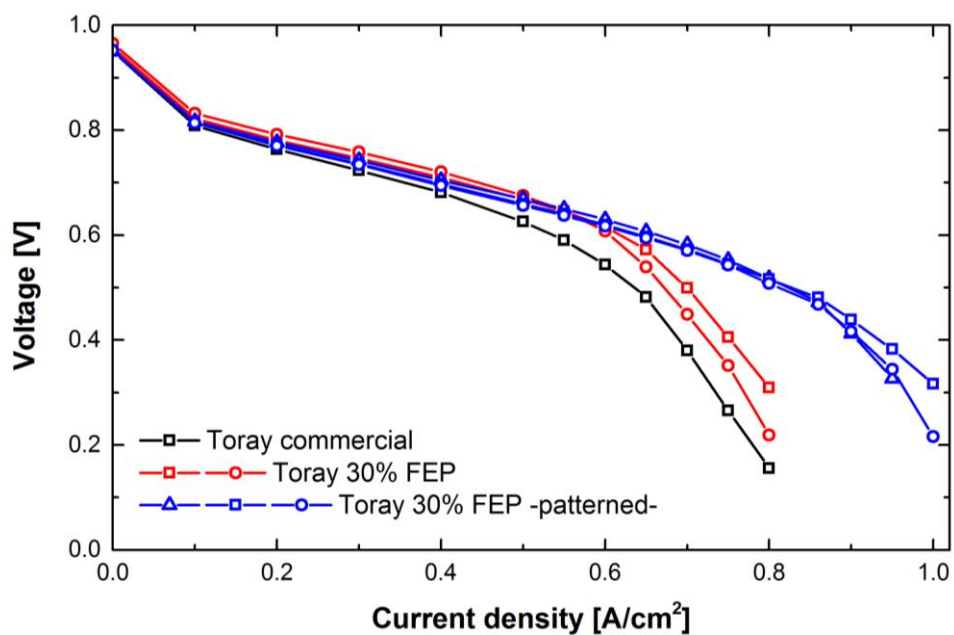


Figure 5. Polarization curves at 50°C, 100%RH anode and cathode of the following three materials: Toray TPG-H-060T commercial (*Toray commercial*) -1 cell-, Toray TPG-H-060 coated in-house with 30%wt. FEP (*Toray 30% FEP*) -2 cells- and Toray TPG-H-060 coated in-house with 30%wt. FEP and pattern-grafted (500 μm hydrophilic slits with 950 μm separation) with NVF (*Toray 30% FEP -patterned-*) -3 cells-.