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Coating Distribution Analysis on Gas Diffusion Layers for Polymer Electrolyte Fuel Cells by Neutron and X-ray High-Resolution Tomography

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ABSTRACT: Coating load and distribution in gas diffusion layers (GDLs) for polymer electrolyte fuel cells (PEFCs) have a major influence on mass transport losses. To be able to optimize the coating distribution and get more accurate data about the influence of the coating on the PEFC performance, better characterization techniques are necessary. Common analysis techniques are limited to selected sections of the material, or they are not sensitive to small amounts of coating. We propose a new methodology to get a complete description of the coating distribution and the GDL structure by combining high-resolution X-ray tomography with high-resolution neutron tomography. Using an isotopic gadolinium staining method to enhance the neutron and X-ray absorption contrast, lower quantities of coating can be detected. The combination of both imaging techniques allows for a more detailed analysis of the coating distribution.

INTRODUCTION
Polymer electrolyte fuel cells (PEFCs) are among the technologies expected to have an important role in the energy transition toward renewable energy. They operate by generating electricity through an electrochemical reaction. In the anodic electrode, hydrogen is oxidized, producing protons, and in the cathodic electrode, oxygen is reduced, consuming protons and producing water. Due to the sluggish kinetics of the reaction, in particular the oxygen reduction reaction, a catalyst is required to improve the cell performance; in the large majority of cases, a layer composed of platinum nanoparticles supported in carbon is used.1

The reactant gasses are brought into the cell through a series of channels in a flow field and are transported through the gas diffusion layer (GDL) to the catalyst layer of each electrode where the reaction takes place. The two cell compartments are separated by a polymer electrolyte membrane (PEM), which conducts the protons, avoids the gas cross over, and acts as an electrical insulator. The water produced at the cathode is transported through the GDL in the opposite direction to the reactant and exits the cell through the same gas channels in the flow field.

Water management is one of the main challenges to maximize the power output of PEFCs. On the one hand, the PEM needs to be hydrated to be a proton conductor and to avoid degradation. On the other hand, an accumulation of water in the GDL layer can hinder the reactant access to the catalyst generating mass transport losses. These losses become particularly important when the cell operates at high current densities because the reactant consumption rate is larger and the water production is higher.2

The most commonly used water management strategies comprise modifying the GDL in order to improve water removal.3 GDLs are usually papers, fleece, or cloths made out of carbon fibers with a fiber diameter of approximately 10 μm. In the majority of cases, the GDLs have thicknesses between 100 and 400 μm with the most common thickness around 200 μm and a mean pore size of 20 μm2 and are chosen because of their good electrical and thermal conductivities, high gas permeabilities, and sufficient chemical and mechanical resistances. State-of-the-art GDLs undergo hydrophobic treatment and feature an additional layer, facing the PEM, with small pores (<1 μm) called microporous layer.4,5 The hydrophobization is achieved by coating the carbon fibers with a fluoropolymer, generally poly(tetrafluoroethylene) (PTFE) or fluorinated ethylene propylene (FEP). The most common coating methodology is to imbibe the GDL in an aqueous solution containing the fluoropolymer and drying the
material, after which the fluoropolymer particles are then sintered by heat treatment. An optimal amount of hydrophobic coating reduces the wettability of the GDL, limiting water accumulation and thus improving the PEFC performance. However, the addition of coating can also decrease the electric and heat conductivity and reduce the effective diffusivity. Thus, an excess of coating is detrimental to performance, and improved application methods are highly desired. Since the contact angle is a surface property, an ideal coating would be a thin layer well covering the substrate and the conditions used for the analysis. This disparity shows that coating load is not a sufficient criterion to analyze the effect of coating on performance. Nevertheless, it is the main parameter used to compare coatings, as it is straightforward to measure, unlike other more precise criteria such as the coating distribution. Yet, this distribution is of high importance, and a homogeneous distribution is not trivial to obtain.

Mathias et al.3 studied the through-plane distribution of coating and found that coating tends to accumulate in the surface regions of the GDL, leaving the bulk with a lower coating load. The authors determined that this disparity in distribution was generated during the drying step of the coating. Later, Rofaiel et al.15 associated this inhomogeneous distribution with water retention in the GDL during operation. Hiramitsu et al.16 studied the effect of coating distribution in the GDL on performance and degradation. They compared two different types of fluoropolymers: PTFE and polyperfluoro(4-vinylxy-1-butene) (Cytop). They used an atomic force microscope to screen a small section of the fiber and reported that the PTFE yields an inhomogeneous fiber coating and Cytop yields a more homogeneous coverage, though the distribution of the coating throughout the GDL was not specified. They analyzed the GDL properties after long-term performance experiments and concluded that a homogeneous coating can help prevent GDL degradation since it limits the oxidation of the carbon fibers.

More recently, Thomas et al.17 have proposed a different application method for hydrophobic coatings based on electrochemical grafting, and Van Nguyen et al.18 have also proposed a new methodology based on direct fluorination. Both studies reported some improvement on fuel cell performance in comparison to classical coating application methods. These examples show that a deeper understanding of the coating distribution is needed to explain some of the experimental discrepancies that can be seen in the literature, helping researchers to better comprehend water transport in the GDL and manufacturers to optimize their coating procedures.

The complexity of the material limits the techniques available for determining coating distribution. Hiramitsu et al.16 used atomic force microscope surface analysis to distinguish the fiber coverage of the GDL. Nevertheless, the area of analysis includes only a few fibers, and the information of the coating distribution on a representative area of the GDL cannot be achieved with this technique since due to the inhomogeneous morphology of the GDL a larger area including several pores should be analyzed to be representative. Rofaiel et al.,15 Mathias et al.,3 and Ito et al.13 employed a combination of scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS). The coating distribution was obtained from the SEM image of the GDL cross section combined with the elemental mapping provided by EDS. These techniques are accessible in many research institutes, but the results must be interpreted carefully. EDS is a macroscopic surface technique, and due to the porous aspect of the sample, only the surfaces directly facing the exterior will be accessed. Another drawback related to the porosity of the material is that cross sections where the coating has not been damaged or deformed are extremely challenging to obtain and the measurement is limited to one section of the GDL. Depending on the morphology of the material, this section may not be fully representative of the bulk material. The main drawback, however, is that, due to border effects and the low molecular weight of fluorine, small amounts of coating are difficult to be detected by SEM or EDS. Mendoza et al.19 improved the technique slightly by taking a similar approach but combining SEM with Raman spectroscopy. The surface planes of the GDL can be analyzed with this technique obtaining a better spatial resolution and a lower detection limit, as low as 5.4% coating load. Nevertheless, only coating accumulations, not fiber coverage, can be detected, and the bulk information is lost.

To get a more accurate idea of the 3D distribution of the coating in the GDL, Fishman and Bazylik20 and Khajeh-Hosseini-Dalam et al.21 used X-ray tomographic microscopy (XTM). With this technique, the coating cannot be directly distinguished from the fibers due to a similar cross section of the interaction of X-rays with carbon and fluorine and small amounts of coating cannot be detected. However, it is a powerful method to visualize the pore structure in three dimensions, and transport properties such as the relative diffusivities and permeabilities can be computed from this information.22,23

To summarize, the main limitation of the current methods is that they are either only applicable to small fractions of the sample or unable to distinguish between the carbon fibers and the hydrophobic coating. Here, we propose to combine XTM with neutron tomographic microscopy (NTM) to obtain a detailed insight into the coating distribution in GDLs. Using radiation grafting, we incorporate an isotopically enriched contrast enhancement agent specifically to the coating (see Figure 1). The main interest of using neutron imaging lies in the fact that one isotope of gadolinium, 157Gd, has a very strong interaction with thermal neutrons: The total cross section of 239800 barns24 is more than 4 orders of magnitude higher than that of carbon (5.5 barns). In consequence, the carbon fibers are invisible to NTM and the coating distribution could be obtained without any disturbance from the edge of the fibers, provided that a sufficient spatial resolution is available. The recent advances in the available neutron imaging instrumentation led to enhancement of the spatial resolution capabilities of NTM to the sub-10 μm domain.25 Combining the information of the coating provided by NTM with the detailed structural information provided by XTM, we obtain a precise description of the three-dimensional coating distribution throughout the entire GDL on volumes large enough to be representative of the corresponding material.

### RESULTS AND DISCUSSION

#### Sensitivity of the NTM Method

In Figure 2, an in-plane slice from the NTM measurement of a sample stained only
locally (in bands with a width of 500 μm) is represented. The attenuation coefficient provided by the stained coating is very high (10–100 cm\(^{-1}\)) due to the large cross section of \(^{157}\)Gd. In comparison, the neutron attenuation coefficient is 0.3 cm\(^{-1}\) for carbon with a density of 2.0 g·cm\(^{-3}\). Correspondingly, a negligible signal is measured in the unstained areas, which confirms our assumption that the NTM method is able to measure the coating distribution with high contrast and without any disturbance from the GDL structure.

**Local Coating Distribution and Fiber Coverage.** The pore structure, mean pore size, fiber morphology, and distribution and the presence and characteristics of the binder may alter significantly the coating coverage of the GDL. One of the most common materials used in fuel cell research, the SGL Sigracet 24 series (simply called “SGL” hereinafter), has a very heterogeneous pore diameter distribution with low fiber density. In their production process, the carbon fibers are impregnated with carbonizable resins\(^{26}\) that act as binders, which are afterward graphitized. The binder forms porous structures that accumulate mainly at the intersections of the fibers. These small binder pores, combined with the large fiber pores, result in a broad pore size distribution. The binder can hardly be distinguished from the coating, as intensity fluctuations (Figure 3b) may either stem from the contrast agent or from density variations. Some groups have managed to segregate the binder from the carbon fiber structure, yet they were not able to discern a binder from a fluoropolymer.\(^{27}\) These characteristics make SGL an interesting material to test the newly proposed technique with low coating loads since the coating detection is more complex than for other GDL materials.

*Figure 1.* (a) Representation of a coated GDL including a cross section. Fibers are represented in black, coating in green. (b) Scheme of the \(^{157}\)Gd staining method. (c) Illustration of the chemical composition. The process includes copolymer grafting and immersion in \(^{157}\)GdCl\(_3\), for ionic exchange of the protons in the acid groups, finally resulting in a material with \(^{157}\)Gd stained coating.

*Figure 2.* GDL locally stained with \(^{157}\)Gd. (a) Neutron tomography slice and (b) schematic representation. The GDL was stained in 500 μm wide areas separated by 1000 μm. The areas without staining are not visible in the neutron radiography.

*Figure 3.* In-plane tomography slices for an SGL Sigracet 24AA sample coated with 9% FEP. (a) Neutron microtomography, (b) X-ray microtomography, and (c) 3D reconstruction rendering of the XTM data from the neighboring area of the selected slice, highlighted by the orange rectangle and the orange arrow, two isolated fibers with thin coating coverage.
In Figure 3, the imaging results for a SGL 24 AA with 9% coating load are presented. The three different components are hardly distinguishable in the XTM slice (Figure 3b). With our methodology, only the coating is stained since the graphitized binder and the carbon fibers will not be altered by the treatment. In the NTM slice (Figure 3a), the bright white spots correspond to the Gd stained coating. As expected, coating accumulates mainly at the fiber intersection, but single fiber coating coverage can also be detected. In this type of material, the coating seems to distribute in three different ways: at the fiber intersection, finely spread over the binder, or covering specific isolated fibers, as highlighted with arrows in Figure 3. In Figure 3c, segmented data from the XTM measurements is presented, and this reconstruction helps visualize the immediate surroundings of the fiber. To do the 3D rendering the program, VGSTUDIO was used, and for all cases, 11 slices were used, showing information from 5 slices before and 5 slices after of the selected slice as a center, in this case Figure 3b. The absence of crossing fibers in front or behind the highlighted fibers confirms that the coating identified in these positions do cover single, isolated fibers.

A fleece-like substrate such as the Freudenberg H23 presents a different type of challenge. This substrate has no binder, so the coating interacts directly with the carbon fibers. The pore size distribution of a Freudenberg GDL is much narrower, and the fibers are more frequently grouped in bundles. These characteristics make it an interesting sample for studying the coating coverage of fibers since the FEP interacts directly with the fiber instead of the binder, but the material has a very high fiber density, which makes the coating more likely to accumulate in the multiple fiber intersections. In order to improve the homogeneity, we used a vacuum coating application, and since the detectability limits of the technique were being tested, low coating loads were also employed.

In Figures 4 and 5, slices of the NTM and XTM and the 3D reconstruction of the selected area are shown for the Freudenberg H23 sample coated in vacuum with 9% FEP. (a) Neutron microtomography, (b) X-ray microtomography, and (c) 3D reconstruction rendering of the XTM data from the neighboring area of the selected slice; fibers are colored gray, and coating is colored green. (d) Enlarged view of the XTM slice mark in panel (b) by an orange rectangle showing the edge effects. (e) Profile across a single fiber showing the edge effects.

Figure 4. In-plane tomography slices for the surface region of a Freudenberg H23 sample coated in vacuum with 9% FEP. (a) Neutron microtomography, (b) X-ray microtomography, and (c) 3D reconstruction rendering of the XTM data from the neighboring area of the selected slice; fibers are colored gray, and coating is colored green. (d) Enlarged view of the XTM slice mark in panel (b) by an orange rectangle showing the edge effects. (e) Profile across a single fiber showing the edge effects.

Through-Plane Coating Distribution. Besides the local coating distribution, an important information for GDL coating procedures is the evenness of coating through the material thickness. Figure 6 shows a single slice projection of the cross section of the Freudenberg H23 sample with 9% coating under vacuum (same sample as used for Figures 4 and 5). Similar to the previous analysis, coating can only be identified from XTM (Figure 6b) in the form of large agglomerations near the surface region. In the NTM data set (Figure 6a), these large coating accumulations appear as an intense white signal, as expected from the higher concentration of the contrast agent, but the presence of smaller amounts of coating is visible across the entire GDL.

This strongly inhomogeneous distribution across the material thickness does not appear for all coating application procedures. Figure 7 displays the average coating distribution of four different samples. To obtain this data, the registered NTM 3D data sets were averaged along the width of the whole material. Since each sample contains a different amount of coating, the contrast of each image was individually adjusted to maximize the visibility. Nevertheless, the absolute values of the corresponding attenuation coefficients allow a quantitative sample-to-sample comparison.

As can be seen in Figure 7, different distributions can occur, including a flat and homogeneous distribution through the
material (Figure 7c), a slightly asymmetric distribution (Figure 7b), and configuration where the coating is minimal in the center (Figure 7a, corresponding to the sample analyzed previously) or in the borders (Figure 7d). This methodology allows the analysis of the whole sample and is therefore more representative of the material compared to the single cross sections, which can be obtained by SEM-EDS or SEM-Raman techniques. It must be noted that, although the average data was extracted here out of a the high-resolution data set acquired for the purpose of the local distribution analysis, the extraction of coating distribution profiles could be obtained by keeping the same $^{157}$Gd staining methodology but using a lower resolution setup, for example, an anisotropic setup with a high resolution only in the direction across the sample and/or using two-dimensional imaging instead of computed tomography. Doing so would allow measurement of a higher number of samples and analysis of the reproducibility of the coating procedures. This technique has been applied for in-house FEP coated samples, but the same methodology is applicable for commercially available PTFE coated samples as well as most available fluoropolymers.

**CONCLUSIONS**

Using a combination of X-ray and neutron tomographic microscopy, we demonstrated novel possibilities for three-dimensional, high-resolution analysis of the coating distribution in fuel cell GDLs. The coating is made specifically visible to neutrons by incorporating a strong contrast agent, $^{157}$Gd, which also provides additional contrast for X-rays. Analysis of different samples has shown that X-rays allow the high-resolution imaging of the material structure and of important
coating accumulations, while the high selectivity of neutrons to the contrast agent provides the complementary information of the distribution of smaller amounts of coating not detectable by X-rays. For a given material substrate (SGL Sigraet 24AA), the combined analysis evidenced that the coating is also found around single, isolated fibers, while for the second substrate (Freudenberg H23) the coating mostly accumulates at the intersections and in the spaces between parallel fibers. The developed methodology will be an invaluable asset for the characterization of coating methods and thus the development of an “ideal” coating providing optimal coverage of the carbon surface with a minimal obstruction of the pores.

■ EXPERIMENTAL SECTION

Coating Application Procedure. Commercial GDLs were coated and irradiated following a procedure similar to the one previously reported by Forner-Cuenca et al.\(^29\) For this experiment, carbon flocs (Freudenberg H23) and carbon papers (SGL Sigraet 24AA) were used. The coating was applied using two different methodologies. The standard coating procedure was to dip the GDL into an aqueous solution of FEP (FEPD121, 55% (w/w) solids, DuPont) for 1 min. The initial solution concentration determines the final coating load, and the relation between initial concentration and final coating load can be found elsewhere.\(^30\) The second methodology consisted of employing the same type solution containing FEP but submerging the GDL in solution under vacuum. For the coating under vacuum, the sample was placed in a sealed reactor and the pressure was reduced to approximately 0.6 bar. Under these conditions, the coating solution was transferred to the reactor and the sample was submerged for 1 min. After this time, the reactor was opened to ambient pressure and the sample was removed from the solution. In both cases, after imbibition, the samples were placed in a vacuum oven and dried for half an hour at room temperature. Afterward, the temperature was raised to 70 °C at a rate of 0.5 °C/min and held for an hour. The samples are then left to slowly cool down. The complete drying process was carried out under vacuum. The coated GDLs were subsequently sintered by heating them under air at 250 °C for 20 min followed by another 20 min at 280 °C. After this, they were let to cool down slowly.

Staining Procedure. The coated GDLs were activated using an electron beam (E怎么能Lab 200 sealed laboratory emitter system, Comet AG, Switzerland). The samples were exposed to a dose of 50 kGy under nitrogen (<200 ppm oxygen), employing an acceleration voltage of 200 keV.

For testing the sensitivity of the method, a radiation mask was used to partially block the radiation. For testing the sensitivity of the method, a radiation mask was used to partially block the radiation. For the coating analysis, after activation, the samples were exposed to a dose of 50 kGy under nitrogen (<200 ppm oxygen), employing an acceleration voltage of 200 keV.

Micro X-ray computed tomography (XTM). XTM was performed using a Nanotom-m Lab-CT scanner (GE Measurements & Control) at PSI. The samples were imaged using an acceleration voltage of 60 kV and a current of 250 μA. For each scan, 800 projections were recorded during the 360° sample rotation. Each projection consists of two averaged images with an exposure time of 5 s each. An 83-fold magnification was used, which results in a final voxel size of 1.2 μm. The linear attenuation coefficients obtained out of the X-ray tomographic reconstruction were validated by measuring the value obtained for the aluminum foil used to separate the samples. An exact theoretical value cannot be calculated due to uncertainties in the X-ray energy spectrum, but a measured attenuation coefficient of 0.5 cm\(^{-1}\) corresponds an X-ray energy of 23 keV, well within the expected range for the X-ray spectrum.

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All authors discussed the results and contributed to the neutron tomography. J.H. performed the X-ray experiments, and A.M. prepared the samples, performed the experiments, analyzed the data, and wrote the manuscript. All authors discussed the results and contributed to the final manuscript.

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**REFERENCES**


