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Short communication

Enhancing the quality of the tomography of nanoporous materials for better understanding of polymer electrolyte fuel cell materials

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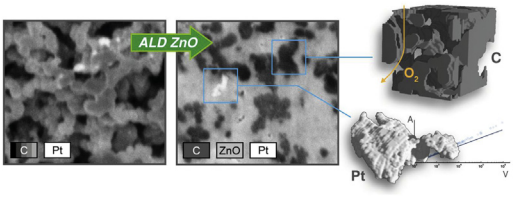
HIGHLIGHTS

- A 3D reconstruction of a PEFC catalyst layer is obtained by FIB-SEM tomography.
- Pores of the catalyst layer are filled with ZnO by atomic layer deposition.
- Filled pores yield high contrast images, enabling more accurate reconstruction.
- Diffusivities are compared for ALD-filled and non-filled reconstructions.
- The distribution of large Pt clusters in the catalyst layer is investigated.

GRAPHICAL ABSTRACT



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ABSTRACT

To investigate the nanostructure of polymer electrolyte fuel cell catalyst layers, focused ion beam – scanning electron microscopy (FIB-SEM) tomography is a common technique. However, as FIB-SEM tomography lacks of image contrast between the catalyst layer and its pores, state-of-the-art reconstruction methods by threshold cannot accurately distinguish between these two phases. We show that this inability leads to an underestimation of the porosity by a factor of nearly two, a reconstruction with channel-like artifacts and that these artifacts make it impossible to calculate reliable diffusivities. To overcome this problem, we fill the pores of the catalyst layer with ZnO via atomic layer deposition prior to tomography. By using atomic layer deposition, even smallest pores can be filled with ZnO, which exhibits a good contrast to the catalyst layer in SEM images. As a result, we present the porosity of the catalyst layer (65%) and its three-dimensional representation without typical reconstruction artifacts. Calculated O_2 diffusivities ($23.05–25.40 \times 10^{-7}$ m^2 s^{-1}) inside the catalyst layer are in good agreement with experimental values from the literature. Furthermore, filling with ZnO permits the identification of large Pt clusters inside the catalyst layer, which were estimated to reduce the catalyst surface area by 9%.

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1. Introduction

Focused ion beam – scanning electron microscopy (FIB-SEM) tomography is a popular technique for the investigation of polymer electrolyte fuel cell (PEFC) catalyst layers due to its ability to resolve the nanoporosity [1–6]. In FIB-SEM tomography, a three-dimensional reconstruction of the porous material is obtained by successive FIB milling and SEM imaging. However, a major drawback of this method is the lack of image contrast between solid particles and the pore space of nanoporous materials such as the PEFC catalyst layer (Fig. 1b). Therefore, segmentation of the catalyst layer, i.e. accurate discrimination of these phases, is highly challenging [1,3,4,7]. However, correct segmentation is essential for the calculation of morphology and transport parameters, which can then be used to better understand the investigated material and develop improved materials.

Tomographic data sets of catalyst layers are commonly segmented by one of the following three approaches: manually [1–3], automated via threshold [4–6] or automated by applying a complex algorithm [8–10]. Pixel-wise segmentation by hand takes a very large amount of time and also depends on the very interpretation of the images by the operator. Hence, automatizing segmentation is inevitable to investigate larger areas, e.g. for better representativeness. However, the common automatization by threshold segmentation assigns pixels to a phase exclusively according to their gray value. It is thus not capable of distinguishing a solid particle from a pore with solid particles in the background, if they possess the same gray value. Only deep pores appear darker than the rest of the catalyst layer due to SEM shadowing effects and thus can be identified by their gray value. However, such discrimination is not possible for most of the catalyst layer. As a consequence, elaborate algorithms have been published, which compare successive SEM images to detect whether a pixel is affected by the FIB milling, and thus lies in the cutting plane and belongs to the solid phase [8–10]. However, due to insufficient accuracy, further research is necessary.

The most straightforward approach to circumvent the segmentation challenge is the use of a filling material in order to obtain a contrast between pores and solid particles that is high enough for accurate automated segmentation. Filling materials range from resins, epoxy [11] or silicone [12] to liquid metals [13]. However, finding a filling material that facilitates good discrimination between pores and solid materials is not trivial: Firstly, the wettability of the porous material for the filling material must be high so that all pores of the porous material can be filled. Otherwise small pores remain empty or pressure must be applied which, however, could potentially alter the porous material's structure. In addition, homogeneous filling of even nano-sized pores should be achieved without any change in the pore shape. It should be noted that the solidification of a resin could be accompanied by shrinking or outgassing. As the second major requirement, the filling material must have a good SEM material contrast to the porous material to be superior to other contrast mechanisms. As the SEM material contrast strongly depends on the atomic number [14], the filling material must consist of elements that are significantly heavier or lighter than the elements of the porous material. This is especially difficult when the sample of interest is a composite of several materials (e.g. the PEFC catalyst layers consisting of carbon, platinum and ionomer [15]). For these reasons, filling the catalyst layer with resins or Wood's metal normally fails to give a reliable structural representation of the pores in tomographic imaging [1].

In the approach presented here, we suggest atomic layer deposition (ALD) as a new pore filling method for fuel cell materials. ALD is capable of intruding into even the smallest pores [16]. Furthermore, an enormous variety of materials can be deposited using ALD [17]. This allows a filling material to be selected that exhibits a high contrast to the elements of the porous material at hand. Güder et al. successfully applied ALD for 3D visualization of nanopores in porous silicon produced by metal-assisted chemical etching and demonstrated the capabilities of this strategy [18]. In this study, we demonstrate the impact of ALD as a filling method for FIB-SEM tomography by filling the catalyst layer with ZnO using ALD. In the following, we first present the preparation of the catalyst layer for ALD infiltration, then the ZnO infiltration by ALD itself, the FIB-SEM tomography process and finally the post-processing to yield a 3D reconstruction. As a result, we are able to represent the diffusivities of the catalyst layer without any of the artifacts of state-of-the-art segmentation. We will then discuss new insights on the distribution of Pt inside the catalyst layer in detail.

2. Experimental

The investigated catalyst layer was the cathode side of a commercial Gore PRIMEA A510.1 M710.18 C510.4 PEMFC membrane electrode assembly. The Pt volume fraction (1.6 ± 0.2 vol%.) in the sample was calculated using the layer thickness (11.4 ± 0.8 μm) as determined by Thiele et al. [2], the Pt loading (0.4 mg cm^{-2}) according to the manufacturer, and the Pt density (21.45 g cm^{-3}).

2.1. Preparatory FIB milling

As ALD applies atoms layer-by-layer, homogeneously, onto the surface of the porous structure, clogging of the pores might block precursor diffusion into the inner sections, leaving unfilled cavities. Hence, to minimize the number of cavities, good accessibility for the precursors has to be ensured. In an initial ALD infiltration of the

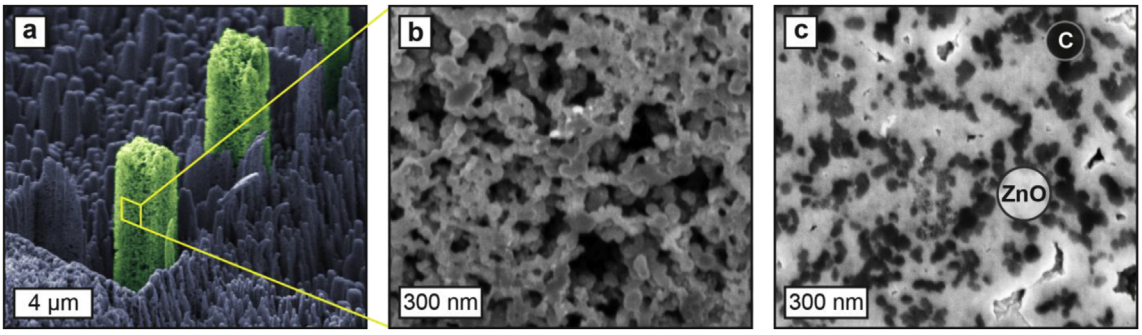

Fig. 1. PEFC catalyst layer a) FIB-milled towers for improved ALD precursor accessibility. b) FIB section of the catalyst layer before ALD filling. c) FIB section of the catalyst layer (dark) filled with ZnO by ALD (bright) taken in the middle of the tower. Contrast enhancement of pore space is clearly visible.