Enhanced FIB-SEM Reconstruction of PEMFC Catalysts Layers by Filling via Atomic Layer Deposition

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Abstract

The bottleneck of FIB-SEM reconstruction of PEMFC catalyst layers is the segmentation, i.e. the physical interpretation of the raw SEM images. It is either extremely time-consuming when done manually, or incorrect when applying a threshold, as commonly done. We propose filling the catalyst layer via ALD prior to FIB-SEM reconstruction. In combination with threshold segmentation it is significantly faster and yields a more accurate reconstruction than state-of-the-art methods.

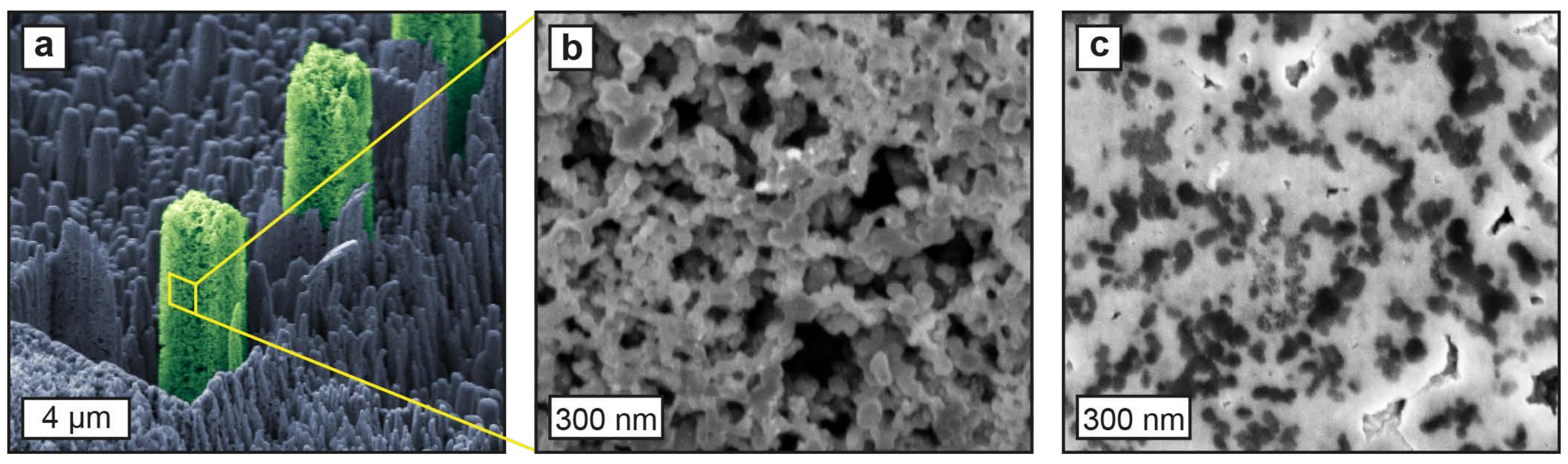


Figure 1: PEM fuel cell catalyst layer. a) FIB milled towers for improved ALD precursor accessibility. b) Catalyst layer before ALD filling. c) Catalyst layer filled by ALD.

Motivation

For the investigation of PEMFC catalyst layer (CL) structures FIB-SEM tomography is a well-established technique. However, a bottleneck of the reconstruction of the CL is the segmentation, i.e. the assignment of each pixel of the SEM images to e.g. pore space or solid phase. As pores are (electron) transparent they do not have a material contrast to the solid phase and therefore cannot be discriminated by threshold algorithms.

A very straightforward approach to yield high contrast between pores and solid is the use of a filling material. However, filling the CL with resins or liquid metal fails due to either insufficient wettability or low contrast in SEM images. [1] To overcome this we suggest **atomic layer deposition (ALD)**: ALD by its nature of depositing a thin film from a gaseous precursor is capable of intruding into smallest pores. Furthermore, ALD offers an enormous variety of materials to be deposited[2] and therefore allows selecting a filling material that exhibits a high contrast.

Methods and Materials

Investigated Catalyst Layer: Gore PRIMEA A510.1 M710.18 C510.4 PEMFC membrane electrode assembly

Atomic Layer Deposition The catalyst layers were coated in a cyclic manner, at 115 °C in a vertical flow type hot wall reactor (OpAL, manufactured by Oxford Instruments). An overall of 500 cycles were performed resulting in an approximate film thickness of 80 nm. (Deposited material will be disclosed in the upcoming publication.)

FIB milling and FIB-SEM Tomography (Zeiss Neon 40EsB). Prior to ALD infiltration, towers of 2 µm edge length were FIB-milled into the CL to provide good accessibility for the precursors and reduce the number of unfilled cavities (Figure 1a). The entire series constists of 170 FIB cuts (30 kV, 5 pA, 5.5 nm cutting distance) and SEM images (in-lens detector, 5 kV, 1.861 nm/px).

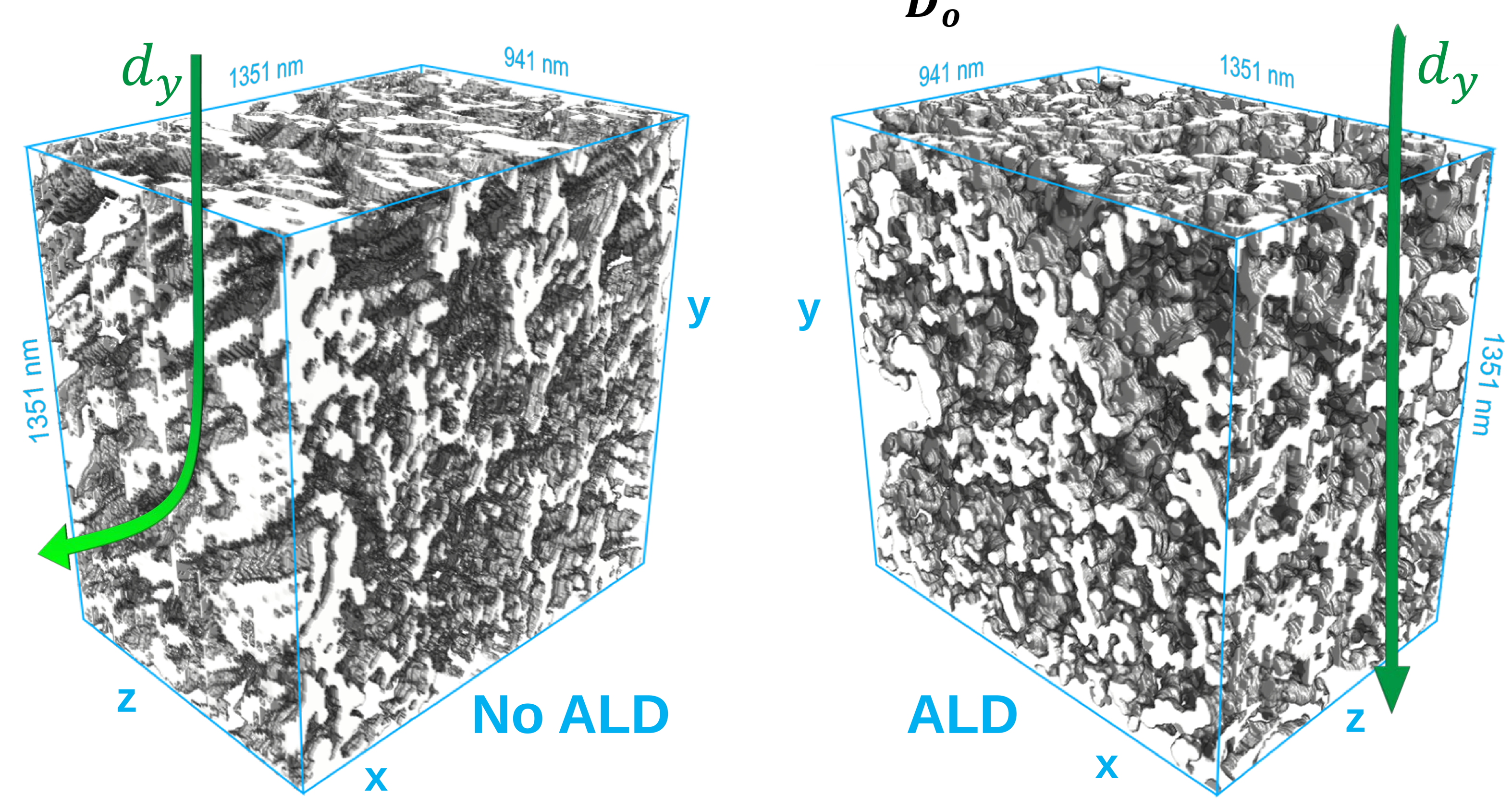
Post-Processing and Diffusivity Calculation: Matlab (image registration, adaptive thresholding), ImageJ (image enhancement), GeoDict (calculation of relative Laplace diffusivities)

Results

As depicted in Figure 1c pore space is well filled (Infiltration depth: approx. 1.5 µm) and only few cavities remain, enabling straightforward and accurate thresholding segmentation.

To illustrate the importance of correct segmentation, the relative Laplace diffusivities of the reconstruction was compared to those of a reconstruction without prior ALD filling. The diffusivities of the non-filled sample revealed a strong anisotropy (Figure 2) caused by incorrect discrimination of pores and solid particles, whereas this artifact could not be found in the ALD filled sample.

Relative Laplace Diffusivities $d = \frac{D_s}{D_o}$



No ALD:

	d_x	d_y	d_z
x	32,169	-0,157	1,094
y	-0,097	39,311	6,821
z	1,110	6,821	50,561

diverted

vs.

straight

ALD:

	d_x	d_y	d_z
x	44,958	0,004	0,992
y	0,043	47,005	0,987
z	1,054	0,854	42,207

Figure 2: Laplace Diffusivities of non-filled and ALD filled reconstructions: d (relative), D_s (in structure), D_o (in empty space)

Outlook

- By filling pores, differences in gray values of the solid particles, are solely material-dependent. In future work, this could allow differentiating between different solid phases, e.g. identifying platinum clusters.
- Broadening the perspective, we propose ALD as a pore space filling method for any carbon-based material (microporous layer, conductive additive of Li-Ion batteries) analyzed by SEM.

Acknowledgements

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References

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