Three dimensional Reconstruction of PEFC Catalyst Layers

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ABSTRACT

The introduction of hybrid electric vehicles has prepared the complete replacement of gasoline systems by systems based on batteries or polymer-electrolyte fuel cells. One of the main sources for performance losses, degradation problems and cost are the catalyst layers. Therefore there is a great need for detailed insight into catalyst layer materials to exploit their potential. In order to solve this problem we define a threefold aim: The first step is to develop a new method for morphology analysis in order to get a 3D image of the catalyst layer. The second step is finding a means to quantitatively describe the morphology of such a geometry. Finally we intend to calculate an optimum morphology eliminating or at least reducing some of the sources of performance loss. In this paper we present an analytical method for morphology analysis suited for the catalyst layer and the first 3D reconstruction of such a layer of a polymer electrolyte fuel cell. We further present first results on our way to quantitatively describe the morphology.

1. Introduction

The three dimensional reconstruction of polymer electrolyte fuel cell (PEFC) catalyst layers requires a spatial resolution of 10-1000 nm to capture the characteristic length scales of the pore space. Neutron tomography, magnetic resonance imaging (MRI) and x-ray-tomography are inappropriate methods for this task due to their relatively low spatial resolution [1]. Atomic force tomography does not provide element information which is important for investigation of catalyst layers. Compared to scanning electron microscope (SEM) imaging the transmission electron microscope (TEM) has better spatial resolution; the image dimension is small which makes this method suitable for small scale features such as individual catalyst agglomerates. A promising method for direct reconstruction available in materials science is focused ion beam - scanning electron microscope (FIB-SEM)-tomography. The apparatus for this method consists of two cross beams: An electron beam for the SEM and an ion beam for etching having a precision of 20 nm and below [2]. By successively etching slices from the sample and taking images of the surface a 3D dataset can be produced. Reconstruction yields a three-dimensional picture of the nano material. Recently, this method has been shown useful for ceramic fuel cell electrodes [3]. Here we present the direct reconstruction of a PEFC catalyst layer in section two.

Stochastic methods can be used to describe porous, heterogeneous materials [4,5]. Different stochastic descriptors (morphologic functions) correlate with different material properties [6]. These functions can be used to derive a stochastic reconstruction of a material which is called ‘stochastic reconstruction’. For stochastic reconstruction the most established reconstruction method is Simulated Annealing (SA) [7]. The question which group from the set of all stochastic descriptors is sufficient for a reliable material description is still a matter of research [8]. In this paper we present the evaluation of two promising candidates on the quest to find the right set of stochastic descriptors: The Pore-Size Density Function (PSDF) and the cumulative Pore-Size Distribution Function (cPSDF) which are directly calculated from the reconstruction of the PEFC catalyst layer which is presented in section three.

2. Direct reconstruction of a PEFC catalyst layer

The reconstruction procedure can be subdivided into image acquisition, segmentation and visualization of the material (Fig. 1).

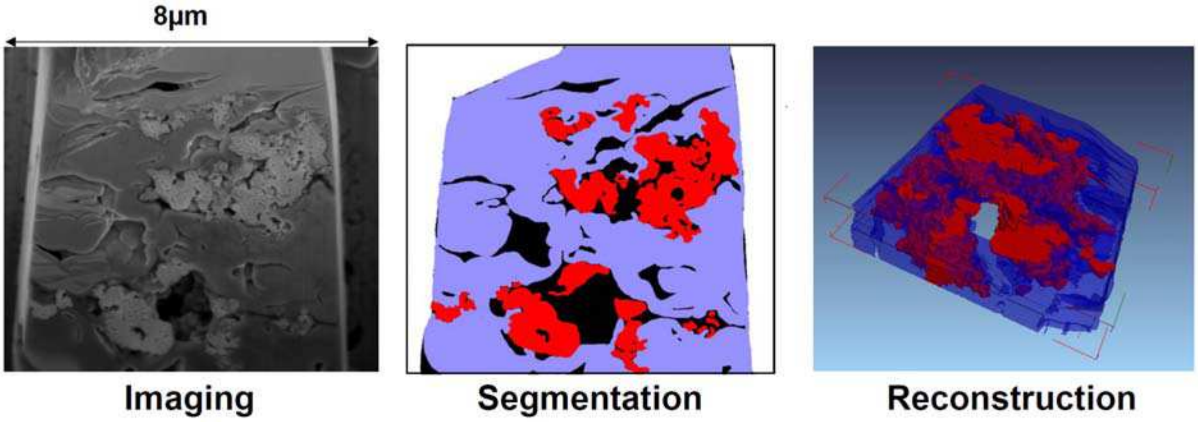

Figure 1: The three basic steps in 3D reconstruction: Image acquisition means actually taking the images. Segmentation is the division of the image into different material types. 3D Reconstruction means producing a 3D geometry from the segmented images.

A Fumapem F-950 membrane, which is a per-fluorinated sulphonic acid/PTFE copolymer, is investigated as example material. The sample was investigated with a dual-beam FIB/SEM instrument. A representative area was chosen to perform the reconstruction. A series of 113 images with a distance of 30 nm was taken where the thickness of the layer was about 2 µm.
Due to the time consumption segmentation being the subdivision of the acquired image is one of the most important steps in tomography. In the present case the image is divided into pore space and solid space. Due to the complexity of the structure a simple segmentation approach like threshold segmentation fails. One way of approaching this challenge is via a manual segmentation which can take between 2-3 hours per image. Therefore we developed a semi-automatic approach. It is based on preselecting with an optimized threshold value in the first step and manually improving the results in the second step. With this approach the manual segmentation time was reduced to about 45 min.
For three-dimensional visualization of porous media it has become a state-of-the-art to use Amira® [9]. The images were cut to 1650x700 pixels. In the z-direction 113 images are taken with a distance of 30 nm. The resolution of the images is 2.5 nm/pixel. Hence the final geometry was 4150x1750x3390 nm³ in x-,y- and z-direction respectively. The final voxel size is 1x1x12 pixels that is 2.5x2.5x30 nm³. A cube of the geometry is shown in Fig. 2.

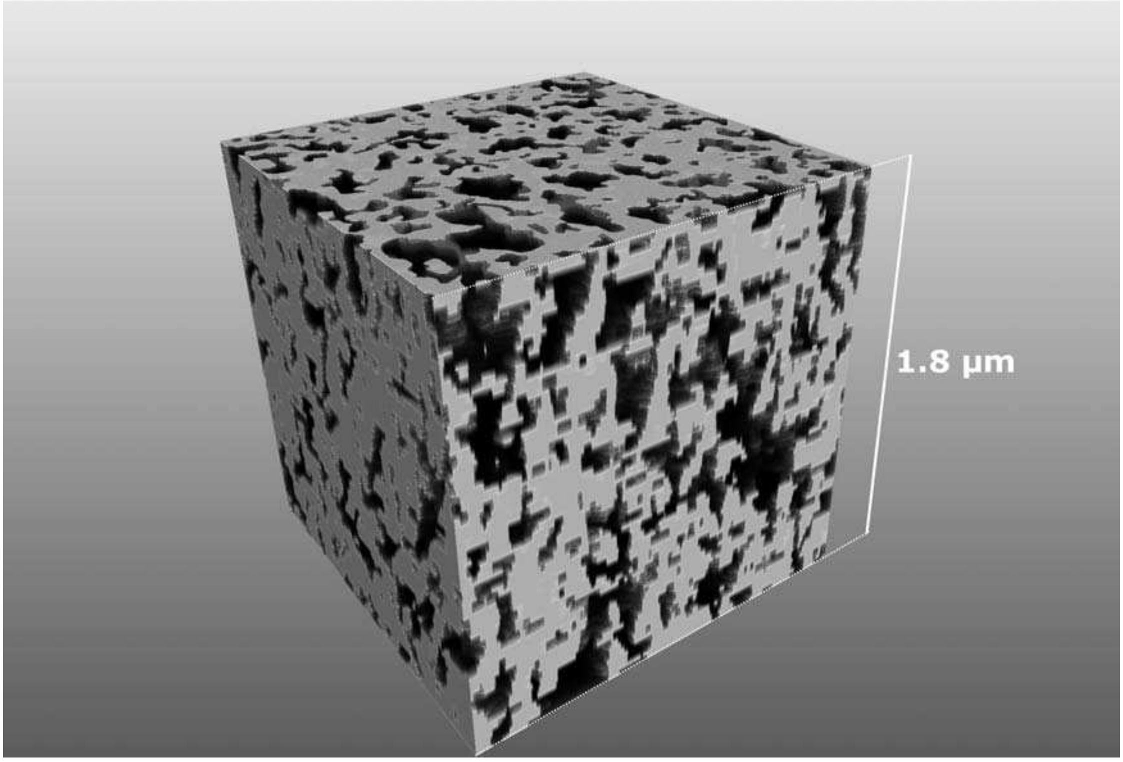

Figure 2: A cube from the 3D reconstruction of a porous polymer-electrolyte fuel cell cathode catalyst layer. The reconstruction is based on 113 SEM images obtained with a separation of 30 nm. The layer is a highly porous carbon network with well-connected pores that form continuous pathways within the layer. The side-length of the cube geometry is 1.8µm.

3. Description of the morphology

The PSDF P(r) of the pore space is defined as the probability that a randomly chosen point of this phase lies at a distance r from the nearest point on the solid-pore interface. It normalizes to unity. The associated cPSDF F(r) is defined as:

$$\boldsymbol{F}(\boldsymbol{r}) = \int_{\boldsymbol{r}}^{\infty} \boldsymbol{P}(\boldsymbol{r}')\boldsymbol{dr}' \qquad (1)$$

Thus F(r) is the fraction of the pore space with a pore radius bigger than r. The F(r) can be imagined as the probability that a randomly inserted sphere of radius r completely lies within the specified phase (e.g. pore space). It therefore contains information about three-dimensional connectivity [5]. The functions were evaluated by creating a distance transform of the geometry (Fig.3). The PSDF was then evaluated by summing up the amount of pixels at a radius value r and dividing it by the overall number of pixels. The cPSDF was calculated from this data.

4. Conclusion and Outlook

On our way to fulfil the threefold aim presented in the introduction we can state that we have reached the first aim: Developing an analytical method for PEFC catalyst layer 3D reconstruction. A full 3D reconstruction by FIB-SEM has been presented. The availability of a real 3D pore-structure model will make it possible to solve the next step in our approach: To quantitatively describe the morphology of this structure. Algorithms for calculating other stochastic descriptors like n-point correlation functions will be implemented in the near future. At the same time an optimized Simulated Annealing algorithm will be implemented.

This will give rise to new model approaches for PEFC catalyst layers which we finally wish to find approaching our final step: Finding better nano geometries for catalyst layers with improved transport properties and catalyst utilization.

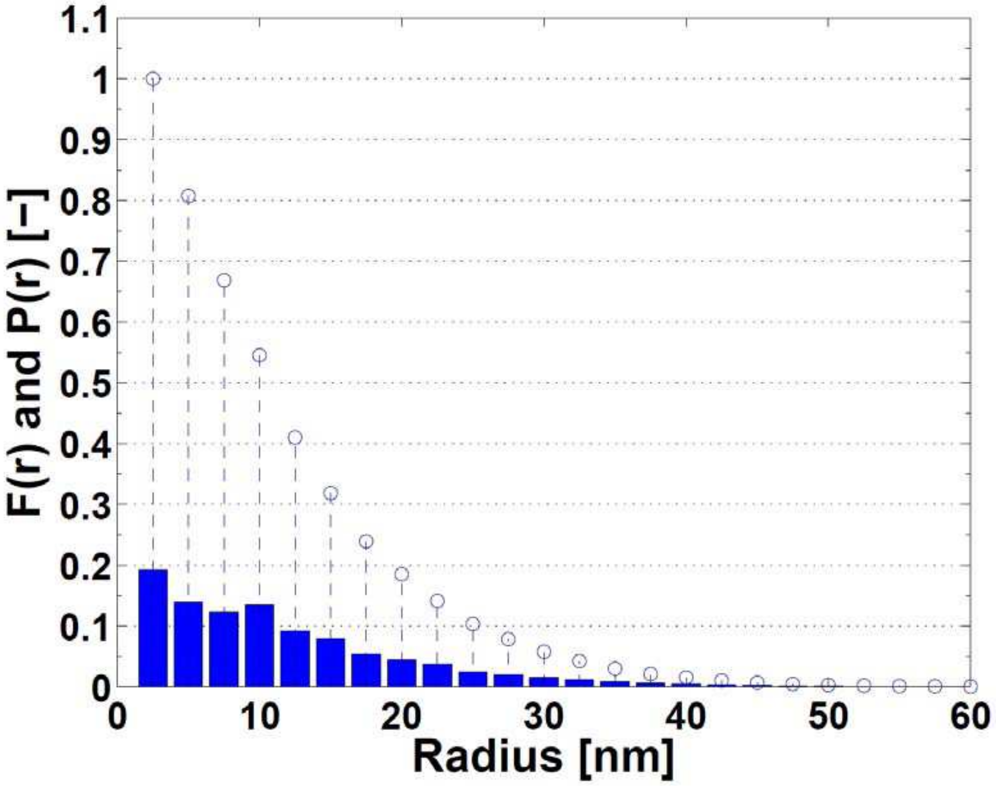

Figure 3: Pore-Size Density Function (PSDF) as a histogramm and the cumulative Pore-Size Distribution Function (cPSDF) as points are shown as a function of the radius. These functions can be used to reconstruct a 3D geometry by using the Simulated Annealing method.

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6. References

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