

ALTERNATIVE SUPPORT MATERIALS AND THE ROLE OF THE SUPPORT MORPHOLOGY FOR THE ELECTRODE STRUCTURE

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Introduction

Among the major issues hindering a commercial market launch of low-temperature polymer electrolyte membrane fuel cells (PEMFC), the poor durability of the carbon-supported catalysts appears to be the most critical. In particular in the harsh conditions at the cathode side, severe corrosion of the carbon support takes place. This leads to an almost complete collapse of the 3D porous electrode structure and thus to severe mass transport limitations. Alternative support materials for low temperature fuel cells have to meet different demands like good electronic conductivity, high surface area as well as high oxidation resistance. Recent research focuses on novel, non-carbon support materials, using either electron conductive oxides or polymers.

The optimization of the electrode structure is a key issue for its functional capability. An optimized electrode structure has to guarantee good electronic and ionic contact of the catalytically active sites, while the porous structure should maintain the unhindered transport of reactants and products. Moreover, the porous structure has to be guaranteed also after long-term operation. In this context, it is getting more and more important to not only find stable materials, but also consider these materials under the aspect of a structure forming component in the final electrode structure as well as the materials' "processibility". This means that in addition to purely chemical considerations also Materials Science aspects have to be taken into account.

In order to test the suitability of novel support materials, the development of new analysis techniques is indispensable. In recent years, various methods have been used to study the electrode structure of PEMFC MEAs in detail. Most of the previous studies were based on electron microscopy, although Hg porosimetry renders information about the electrode's porosity as well. Rolison et al. [1] analyzed the advantages of catalytic nano-architectures by a combination of scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Both methods are fully capable of displaying the 2D structure of the samples under investigation. 3D properties, such as pore elongation

or information on the open porosity, however, cannot be determined by any of these techniques. In 2001, Inkson et al. [2] published the 3D characterization of a metallic nanocomposite by Focused Ion Beam (FIB) tomography. Starting from there, FIB tomography was developed further and first results in 3D reconstruction concerning PEMFCs were published by Ostadi et al. [3] in 2010.

Experimental

Membrane electrode assembly preparation

MEAs were manufactured using different fabrication processes depending on the material. The standard method is a slightly modified airbrush technique, which was first published by Wilson et al. [4]. But also the novel layer-by-layer approach [5] and the DECAL technique [6] were used where appropriate.

Characterization

FIB nanotomography was performed using a Zeiss 1540EsB CrossBeam[®]. A FIB serial sectioning and SEM imaging sequence based on the work of Holzer et al. [7] was used for obtaining slices of approx. 15 nm thickness. Alignment of the image stacks was obtained via a recursive method using the software ImageJ with StackReg Plugin [8]. A representative subvolume was defined and binarized using the Otsu thresholding algorithm [9]. For the 3D visualization of the 2D binarized image datasets, the commercial visualization software package VGStudioMax 2.0 was employed.

The supported catalysts were characterized using X-ray diffraction (XRD) and transmission electron microscopy (TEM) to obtain the particle size and dispersion. Electrochemical testing was either done by cyclic voltammetry (CV) or in single cell tests (E-i curves).

Results and Discussion

After alignment and reconstruction of the images, a 3D visualization of an MEA prepared by the layer-by-layer process was obtained (Figure 1). The z-direction indicates the FIB milling direction, whereas Figure 2 displays the exact position of the 3D reconstruction within the MEA. The MEA prepared by the standard airbrush process (not shown) contains a high number of large, elongated

pores. These can be explained by the specifics of the preparation. Since the ink (catalyst powder plus ionomer) is applied in successive thin layers, the drying process of each layer leads to surface cracks, which are covered with ink in the next airbrushing step. The 3D reconstruction of the MEA prepared by the layer-by-layer technique, however, features a more homogeneous porosity with smaller and more uniform pores and a higher total pore volume [7].

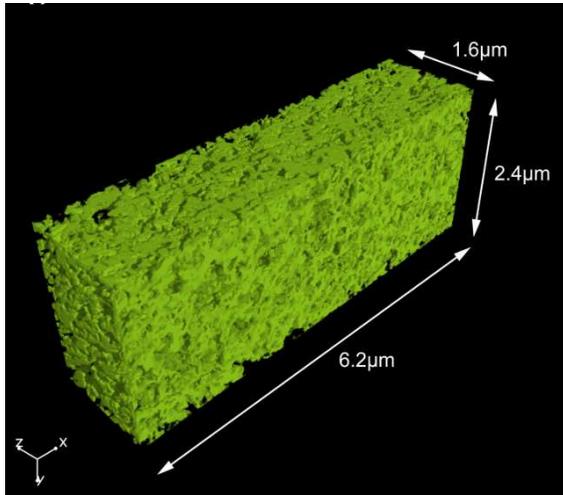


Figure 1: 3D visualization of an MEA prepared by the layer-by-layer technique.

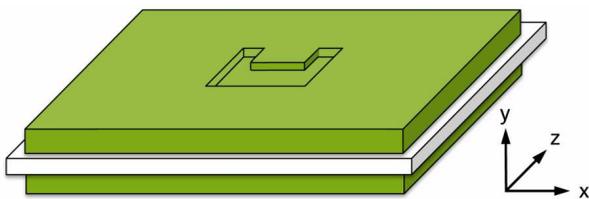


Figure 2: Position of the 3D reconstructions within the MEA.

A false colour image of the porous electrode structure of a standard MEA with carbon-supported catalyst is shown in Figure 3. The morphology of typical carbon agglomerates can be easily identified in the image (black and lilac colour). It is observed that the support morphology controls the 3D electrode architecture to a large extent. However, in the design of novel materials this aspect is often neglected.

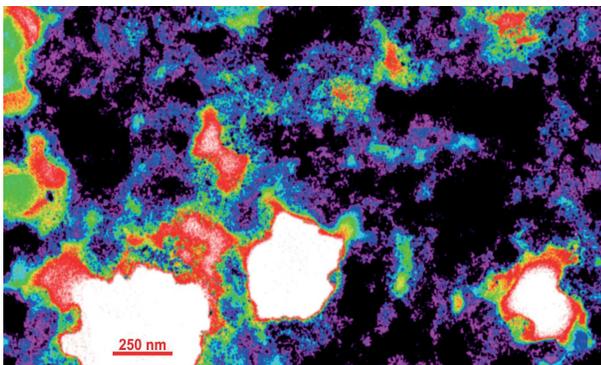


Figure 3: False color image of a porous electrode structure.

Conclusion

Different types of non-carbon support materials have been synthesized and investigated with respect to their structure, dispersion and particle size using transmission electron microscopy and X-ray diffraction. The support materials were either commercially available or synthesized in our group and then decorated with small and uniform Pt nanoparticles by a wet-chemical process, the so-called polyol method. Preliminary electrochemical characterization by cyclic voltammetry and in fuel cell tests, however, showed only mediocre performances as compared to the standard carbon-supported Pt catalysts.

This is most probably due to the following reasons:

- standard electrode preparation procedures used nowadays are optimized for carbon-supported materials. There is only limited experience in the preparation of electrodes made of new non-carbon supported materials.
- The electron conductivity in most of the oxide supports is obtained by suitable dopants, which are not yet optimized.
- Most oxidic supports tend to form very dense electrode layers, which hinder facile mass transport and efficient water management.

Acknowledgements

The kind support of M. Timpel, T. Arlt and I. Manke from HZB Berlin is gratefully acknowledged. Parts of the project were funded by the Deutsche Forschungsgemeinschaft (DFG) and the German Federal Ministry of Education and Research (BMBF) under Grant No. 03SF0324.

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