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Three-dimensional multiscale analysis of degradation of nano- and micro-structure in direct methanol fuel cell electrodes after methanol starvation

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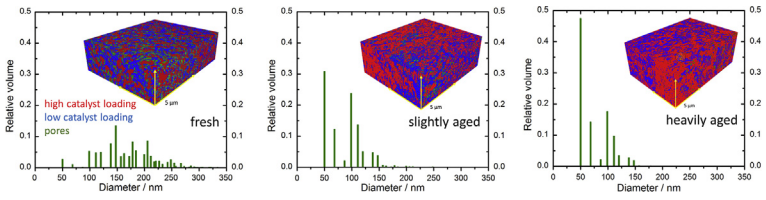
HIGHLIGHTS

- 3D Multiscale analysis of electrode degradation after methanol depletion.
- Combined 3D analysis of nano- and micro-structure.
- Degradation affects mainly anode catalyst layer.
- Methanol depletion leads to a collapse of the anode catalyst pore structure.
- Isolated (cut off from fuel supply) pores and pore channels were found.

GRAPHICAL ABSTRACT



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ABSTRACT

This study investigates the ageing effects on the microstructure of the anode catalyst layer of direct methanol fuel cells (DMFC) after complete methanol starvation. To this end the samples of two methanol-depleted membrane electrode assemblies (MEA) have been compared with a pristine reference sample. A three-dimensional characterization of the anode catalyst layer (ACL) structure on a nanometer scale has been conducted by focused ion beam (FIB)/scanning electron microscope (SEM) tomography. The FIB/SEM tomography allows for a detailed analysis of statistic parameters of microstructured materials, such as porosity, tortuosity and pore size distributions. Furthermore, the SEM images displayed a high material contrast between the heavy catalyst metals (Pt/Ru) and the relatively light carbon support, which made it possible to map the catalyst distribution in the acquired FIB/SEM tomographies. Additional synchrotron X-ray tomographies have been conducted in order to obtain an overview of the structural changes of all the components of a section of the MEAs after methanol depletion.

1. Introduction

Because of the high energy density and the relative easy handling and storage of liquid methanol, direct methanol fuel cells (DMFCs) are perfectly suited for use in mobile and stationary

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applications. One of the key goals in DMFC research is to increase the lifespan of DMFC cells operating in a stack [1–5]. Enhancing the DMFC lifespan would raise the attractiveness of DMFCs and hence facilitate a broad market launch.

In order to better understand and evaluate the impact of the different ageing mechanisms which occur under different operating conditions the analyses of a system run under extreme operating conditions can be helpful. One of the most detrimental failures that can occur in DMFC operation is a partial or even a complete depletion of the methanol supply on the anode side of a single cell operated in a DMFC stack. In real life operation, the anode catalyst layer of an individual cell operated in a stack environment will experience an uneven distribution of the methanol-water solution where the methanol concentration can locally drop to critical values.

Such non-uniformities of the methanol concentration in the ACL can be caused by blockages of transport channels in the anode diffusion layer due to gas bubbles [6]. Furthermore, the operation of a stack at high load causes a gradient in the methanol concentration between the anode in- and outlet of a cell, which can lead to a local depletion of methanol in the region around the anode outlet.

If methanol is no longer available for the oxidation reaction at the anode while the oxygen reduction reaction at the cathode is still being maintained, the local anode potential will rise until water, the carbon support and even the noble catalyst metals Ru and Pt are oxidized in order to maintain the current through the stack. If larger parts of the ACL are depleted of the methanol supply the anode potential can increase to values at which the cell voltage is reversed.

Although local methanol depletions, which emerge during real life operation, have a rather small effect on temporary DMFC performance they do have a noticeable negative impact during long-term operation, lowering the overall stack performance and reducing the DMFC lifespan.

Previous research on methanol-depleted DMFCs has already been conducted by means of SEM, energy dispersive spectroscopy and spatially resolved X-ray absorption spectroscopy [1,7,8]. These investigations showed drastic changes in the ACL after the methanol-depletion procedure, such as a densification of the ACL and a redistribution of the catalyst materials, especially of Ru. These changes were accompanied by a performance loss of up to 84% after complete methanol depletion.

In the past, tomographic imaging techniques were used to study the three-dimensional structure and morphology of fuel cell MEAs [9]. X-ray tomography allows for the investigation of entire electrodes or cells [10–28]. Whereas characterization techniques using electrodes as a probe such as FIB/SEM or electron tomography, are well suited to analyze the local structure of the electrode with special resolutions of a few nanometers [29–40].

This paper will focus on the three-dimensional, structural investigation of the ACL of methanol-depleted DMFCs on a nanometer scale using focused ion beam/scanning electron microscope (FIB/SEM) tomography. In order to obtain an overview of the entire membrane electrode assemblies (MEA) of the investigated samples additional synchrotron X-ray tomographies with a resolution on the micrometer scale have been conducted.

2. Experimental

2.1. Samples

The gas diffusion layers (GDL) consisted of carbon cloth (AvCarb®1701 HCB from Ballard Material Products), which has been hydrophobized by soaking in a PTFE dispersion (TF 5032 from Dyneon™) and subsequently sintered at 350 °C. The micro porous layer (MPL) that consisted of carbon black (VULCAN® XC72 from Cabot) and PTFE (TF 5032) had been applied directly onto the hydrophobized GDL by doctor blading. The catalyst ink was directly dispensed over the dried MPL by means of doctor blade technique. On the anode side, the catalyst ink consisted of a Nafion® dispersion (LQ1115 from Ion Power) and a carbon supported Pt/Ru-catalyst (HiSpec®12100 from Johnson Matthey, Pt:Ru ratio of 50:50 wt%) with an overall catalyst loading of 2.6 mg cm^{-2}. The catalyst ink on the cathode side also consists of the Nafion® dispersion LQ1115 and of a carbon supported Pt catalyst (HiSpec®13100 from Johnson Matthey) with a Pt loading of 1.9 mg cm^{-2}. After drying the catalyst layers of both sides were manually sprayed with the Nafion® dispersion LQ1115 and hot pressed with a Nafion® 115 membrane from DuPont for 5 min applying a pressure of 500 N cm^{-2} at a temperature of 130 °C.

In order to simulate a stack environment, the ageing procedure has been performed in galvanostatic mode with a current density of 150 mA cm^{-2}. Using electrical heating elements at anode and cathode side the operation temperature of the cell was hold at 70 °C. Before substituting the methanol feed with distilled water, the anode was fed with a 1 M aqueous methanol solution. After several minutes of regular cell operation the methanol solution was substituted with distilled water.

Wippermann et al. [1,7] were able to classify the process of methanol depletion into three consecutive phases which are each initialized by a drop in cell voltage and characterized by the faradaic reactions taking place in the potential windows of the respective phase. In the first phase of the methanol depletion the anode potential increases by more than 1 V reaching values between 1.4 V and 2.3 V. In this potential range an oxygen evolution reaction is triggered:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad U_0 = 1.230\ V \tag{1}$$

This reaction is catalyzed by Ru producing hydrated ruthenium oxides in the process.

Phase II of the methanol depletion is dominated by a substantial corrosion of the carbon support enabled by the oxygen evolution reaction:

$$2C + 2H_2O + O_2 \rightarrow 2CO_2 + 4H^+ + 4e^- \; U_0 = 1.230\ V \tag{2}$$

During this phase the anode reaches potentials between 2.3 V and 2.9 V. The direct, although kinetically sluggish carbon corrosion

$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^- U_0 = 0.207\ V \tag{3}$$

and the carbon corrosion catalyzed by Pt

$$Pt + H_2O \rightarrow PtOH_{ad} + H^+ + e^- \tag{4a}$$

$$C + H_2O \rightarrow CO_{ad} + 2H^+ + e^- \tag{4b}$$

$$\Rightarrow Co_{ad} + PtOH_{ad} \rightarrow Pt + CO_2 + H^+ + e^- \tag{4c}$$

also take place.

In phase III the anode potential further increases to values between 2.9 V and 3.5 V. The potential is now high enough to substantially accelerate a direct corrosion of the carbon support according to eq. (3) making it the dominating faradaic reaction of this phase.

Two methanol-depleted samples have been investigated and compared with a pristine reference sample. The first sample has been subjected to the methanol depletion procedure for 60 min completing phase II and reaching an anodic potential of 2.2 V. The second sample has been methanol-depleted for 70 min until the