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Three-dimensional microstructure analysis of a polymer electrolyte membrane water electrolyzer anode

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HIGHLIGHTS

- A FIB-SEM tomography of a PEM water electrolyzer anode catalyst layer is presented.
- Pores are contrasted versus catalyst particles by silicone infiltration.
- Modeling different ionomer contents reveals its influence on transport parameters.
- The study confirms an ideal ionomer content of 40–50% of the pore volume.

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ABSTRACT

The anode catalyst layer of a PEM water electrolyzer is reconstructed using a combination of FIB-SEM tomography and ionomer modeling. The pore space is infiltrated with silicone, enabling good discrimination between pores and IrRuOx catalyst material, while the ionomer cannot be imaged. The reconstructed volume of 29 µm × 24 µm x 7 µm contains catalyst particles with a median size of 0.5 µm and has a porosity of 55%. By modeling different ionomer contents inside the pore space, the impact on microstructural and transport parameters is investigated. At an ionomer content of 40–50% of the pore volume, all transport parameters are in a reasonable range, confirming experimental results from literature. At an ionomer content of 48% the catalyst layer has a porosity of 29%, a median pore size of 0.94 µm, a permeability of the pore space of 1.8 mD and a mean ionomer film thickness of 0.4 µm. The tortuosities of the ionomer and the pore space are calculated to 3.5 and 6.7 at the corresponding phase fractions of 26% and 29% respectively. The electrochemically active surface area estimated from the tomography (1.0 $m^2 g^{-1}$) is considerably lower than literature values, indicating a roughness below FIB-SEM resolution.

1. Introduction

Hydrogen is not only a medium for energy storage with high energy density, but also an important precursor for the production of different chemical products such as ammonia or methanol [1]. Hence, water electrolysis represents a seminal technology, which can link the electricity sector with e.g. the mobility sector or the chemical industry [2]. This enables a flexible utilization of growing intermediate overproduction by renewable energy sources. Polymer electrolyte membrane water electrolyzers (PEMWEs) are still too expensive to achieve high market penetration [3]. Besides saving resources and lowering operational expenditures, higher conversion efficiencies (high current densities at low voltages) result in a more efficient material use and thus reduced capital expenditures. Therefore, optimizing the design with the aim of achieving the highest possible conversion efficiency plays a key role for the future of PEMWE technology.

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PEMWEs comprise an anode at which the oxygen evolution reaction (OER) takes place, a polymer electrolyte membrane (PEM) for proton conduction as well as selective inhibition of gas or electron cross-over and a cathode at which the hydrogen evolution reaction (HER) occurs. Porous transport layers (PTL) enable two phase transport of water and produced oxygen at the anode and hydrogen at the cathode. These are located between the so called flow fields and the catalyst layers. At the cathode usually a carbon supported platinum catalyst is used, enabling fast HER kinetics. In contrast, the reaction kinetics of the OER are sluggish and account for a major part of the conversion losses [4]. Therefore, much effort has been put into optimizing the material composition of the anode in order to improve the catalytic activity [5–7]. State-of-the-art anodes are porous structures comprising Iridium (Ir), Iridiumoxide (IrOx) or Iridumrutheniumoxide (IrRuOx) as catalyst, which are sometimes supported by Titaniumoxide (TiOx) and typically bound by an ionomer [4]. The metallic catalyst material has to provide both active sites and pathways for the electrons. Pores serve as pathways for water access to reaction sites and as escape channels for produced oxygen. Water filled pore space furthermore enables proton conduction over short distances [8]. The proton conduction is increased by the ionomer binder. Thus a complex interplay of different interfaces and transport phases occurs in a working catalyst layer. Consequently, besides the material composition, the microstructure of the anode has a significant impact on the electrolyzer's performance as it determines catalyst accessibility and species transport [9]. Hence, optimizing the anode microstructure is crucial for obtaining higher efficiency and reducing the catalyst loading. Investigating the microstructure by tomographic methods is an important step towards a successful optimization process. Tomographic methods have been well established in other electrochemical cell technologies such as polymer electrolyte membrane fuel cells [10]. For PEMWEs a small number of publications exist, which investigate the structure of the PTL using X-ray tomography [11–13]. However, to our knowledge no work on a tomographic reconstruction of the anode microstructure of a PEMWE has been published yet.

In this paper we analyze the anode microstructure of a commercially available catalyst coated membrane (CCM) of a PEMWE. Focused ion beam scanning electron microscope (FIB-SEM) tomography is used, as its resolution and field of view is suitable for the investigated anode microstructure [14]. Prior to the tomography the pore space was infiltrated with silicone in order to improve the contrast between pores and catalyst material. The ionomer phase was modeled inside the pore space, since it cannot be captured in the silicone-contrasted tomography. Based on the reconstruction and several modeled ionomer contents, we calculate pore size distributions, grain size distributions, transport parameters and the electrochemical active surface area of the anode.

2. Methods and experimental

2.1. PEMWE anode sample

The investigated sample is the anode catalyst of the commercially available FuelCellsEtc EZ CCM with a loading of 3 mg cm^{-2}. The catalyst material is $Ir_{0.5}Ru_{0.5}Ox$ and contains no supporting material, as determined by Energy-Dispersive X-ray Spectroscopy (EDX). In order to facilitate the segmentation of the microstructure reconstruction, the phase contrast between solid material and the pore space was enhanced by infiltrating the sample with silicone as proposed by Ender et al. [15]. Silicone yields a good contrast to the catalyst material. For good penetration of the pore space, a low viscosity silicone was used (Wacker Elastosil RT 604) following Liu et al. [16]. To further improve penetration, the sample was constantly kept under vacuum atmosphere, starting 1 h before infiltration until 30 min after. Excess silicone was removed and the sample was cured for 24 h at room temperature. In order to mitigate charging effects and sample drifting during SEM imaging, a gold layer was sputtered on top of the sample.

2.2. FIB-SEM reconstruction and ionomer modeling

After sample preparation, a cubical volume was reconstructed using a Zeiss Neon 40 EsB FIB-SEM. Therefore, a trench of a few µm depth around a peninsula of app. 34 µm × 28 µm x 20 µm was milled into the sample with a FIB current of 2 nA and 30 kV accelerating voltage. From this, 650 FIB-SEM cross sections were generated with a SEM image resolution of 20 nm at 5 kV SEM accelerating voltage, using secondary electron (SE) and backscattered electron (BSE) detectors and a FIB cutting distance of 35 nm at 1 nA FIB current. From this image series a cubical volume of 29 µm × 24 µm x 7 µm was reconstructed in MATLAB and Fiji [17] following the steps: image registration, geometric correction, cropping and segmentation. SE images showed a high material contrast but poor image quality, while BSE images featured better image resolution, especially at the edges of the IrRuOx phase but a worse material contrast and distortions due to charging effects of the silicone. Therefore, images from both detectors were combined. First, a threshold was applied to the SE images to yield the regions with catalyst material. These regions were then dilated and served as a mask in the BSE images. The masked BSE images were then segmented using the trainable WEKA segmentation plugin of Fiji.

With the reconstruction of the catalyst material and the pores as a basis, the ionomer was modeled inside the pore space with the “add binder” function of the ProcessGeo module of GeoDict [18]. The algorithm is based on the assumption that the binder behaves like a wetting fluid. Thus, small pores are filled first and larger pores are filled gradually with increasing ionomer content of the catalyst layer [19].

2.3. Transport and geometric parameter calculation

The mean anode layer thickness l was determined with MATLAB by averaging the cord length distribution from the membrane to the top of the reconstructed volume. The following modules of GeoDict were used for calculations: PoroDict for size distributions and surface area as described by Wiegmann and Glatt [20], FlowDict for permeabilities and ConductoDict for tortuosities. The mean ionomer thickness d was determined by calculating the shortest distance through the ionomer from each catalyst surface voxel to the open pore space d_{min}^{pore} or to the PTL interface d_{min}^{PTL} (see Fig. 3b). Taking the mean of all calculated distances yields d. For this calculation the reconstructed volume of 7 µm height was extended by mirroring to match the catalyst layer thickness.

2.4. Electrochemical measurements

The polarization measurements of the FuelCellsEtc EZ CCM (based on a Nafion N115 membrane) were performed with a Scribner 857 Redox Flow potentiostat at atmospheric pressure conditions and 80 °C cell temperature. A 5 cm^2 PEMWE electrolyzer cell was used with a 1 mm Mott sintered titanium PTL on anode side and a Freudenberg H23I2 PTL on cathode side. Anode and cathode deionized water feed was adjusted to 40 ml/min. The high frequency resistance (HFR) free voltage was obtained by measuring the HFR at each measurement point at 1 kHz.

3. Results

3.1. Microstructure of the catalyst layer

From the catalyst layer a volume of 29 µm × 24 µm x 7 µm was reconstructed using FIB-SEM tomography. In order to enable discrimination between pores and the catalyst material, silicone was introduced into the pore space. However, the silicone has a low contrast to the ionomer. For this reason, the reconstruction contains only the