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Quantification of double-layer Ni/YSZ fuel cell anodes from focused ion beam tomography data

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HIGHLIGHTS

- A new algorithm for the distinction between Ni-, YSZ-, and pore-phase is presented.
- 2 types of Ni/YSZ anodes are reconstructed and compared to each other.
- Microstructure parameters and particle size distributions are evaluated and discussed.
- The anode functional layer (AFL) adjacent to the electrolyte is separately quantified for the first time.
- Differences between both anode types and between AFL and substrates are discussed.

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ABSTRACT

Three-dimensional microstructure reconstructions of Ni–yttria-stabilized zirconia (Ni/YSZ) anodes are presented, all of which are based on focused ion beam tomography data.

The reconstruction procedure, starting from a series of 2D scanning electron micrographs, is investigated step by step and potential sources of error are identified. The distinction between Ni phase, YSZ phase and pore phase is solved by an advanced algorithm, which belongs to the *region-growing* image segmentation methods. This improves the accuracy of automated grayscale segmentation especially for images with low contrast, which is characteristic of both solid phases in Ni/YSZ anodes.

Critical microstructure parameters like material fractions, surface areas, particle size and distribution of Ni, YSZ, and pore phase, as well as phase connectivity and triple-phase boundary density, are evaluated and discussed.

In this contribution, two types of high-performance Ni/YSZ anodes – differing in thickness of both the anode functional layer and the anode substrate – are reconstructed and compared to each other. For the first time, the anode functional layer adjacent to the thin film electrolyte is separately quantified. The presented methods are qualified to quantitatively compare different anode microstructures and relate the result to their electrochemical performance.

1. Introduction

Solid oxide fuel cells (SOFCs) are one of the most promising energy conversion technologies due to their high efficiency, low emissions and fuel flexibility. The electrochemically active part of an SOFC consists of three components: two porous electrodes (anode and cathode), which are separated by a dense electrolyte [1]. Today, the state-of-the-art design is based on an anode-supported cell (ASC) made of Ni and yttria-stabilized-zirconia (Ni/YSZ), developed for operating temperatures T_{op} of between 600 °C and 900 °C. High performance ASCs normally consist of a double-layer anode, (1) a 200–1500 μm thick and highly porous anode substrate – which provides mechanical stability and the transport of fuel, exhaust gases and electrons -, and, (2), a 5–30 μm thin anode functional layer (AFL) – which provides the electro-oxidation of the fuel (or the reduction of H_2O and CO_2 in electrolysis mode) at the triple-phase boundary. Naturally, phase composition and microstructure of both layers have to be customized to the desired functionality. Hence, a separate quantification of the anode substrate and the AFL is a prerequisite for ASC improvement. Nonetheless, to the best of our knowledge, such an analysis using FIB tomography was not yet reported in literature.

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As stated above, the standard SOFC anode is a composite of three phases: (1) an electronic conducting solid (e.g. Ni), (2) an ionic conducting solid (e.g. YSZ) and (3) a pore phase. The oxidation of the fuel gas (e.g. H_2) occurs, according to the following reaction:

$$H_2 + O^{2-} \rightarrow H_2O + 2e^- \quad (1)$$

Thus, the oxidation of the fuel gas requires a triple-phase boundary (TPB), where all three phases coexist. Moreover, an intimate contact between the two solid phases is required, and the electronic conducting phase must percolate with the current collector, the ionic conducting phase with the electrolyte and the pore phase with the gas channel.

This underlines microstructure as a key property [2,3], and improvement requires a quantification of the structural parameters and a correlation to their effects on electrochemical performance. Many groups have studied the subject of 3D reconstruction for SOFC anodes, and Table 1 lists available information (the list is far from exhaustive). Fig. 1 demonstrates, that reconstructed anode volumes start from 75 μm^3 [4] and go as large as 17,400 μm^3 [5], while the resolution can be as low as 4300 voxel per μm^3 [5] or as high as 166,000 voxel per μm^3 [6]. Naturally an appropriate resolution as well as a large enough volume is necessary to obtain reliable results, and hence a trade-off between resolution and volume is of particular importance. Sometimes, however, this high resolution was drastically downsized for the 3D simulation itself [7,8], most probably because of a lack of capable data handling software. This overview reveals, that both focused ion beam/scanning electron microscopy (FIB/SEM) (e.g. Refs. [4–15]) as well as X-ray (e.g. Refs. [16,17]) tomography methods were already applied to (i) quantify the structural parameters of SOFC anodes (e.g. Refs. [4,7,9–11,16]) or (ii) to implement 3D reconstruction data as model geometry in microstructure models (e.g. Refs. [5,6,8,9,18,19]). On the whole, much less information is available on the consecutive image processing steps, which are necessary to obtain reliable results based on high-quality tomography data. For example, the grayscale images, which consist of a voxel grid (voxel = volumetric pixel), have to be partitioned into disjoint regions corresponding to the different phases in a segmentation procedure. This step is highly nontrivial, especially for microstructures with more than two phases, e.g., for solid oxide fuel cell anodes consisting of Ni phase, YSZ phase and pore phase. In the literature given in Table 1 and Fig. 1, the segmentation procedure was either done by hand [7,12] or semi-automatically [9,10], or reported as “grey level-based thresholding” [11] and based on “brightness of image” [13].

Jorgensen et al. [20] as well as Holzer et al. [21] presented advanced segmentation methods, but despite from that, not much is reported on the segmentation of SOFC anodes. In this contribution we introduce a fully automatable and precise multi-step segmentation procedure, which belongs to the *region-growing* image segmentation method [22] and demonstrate that the most common method of segmentation, thresholding [23], is inappropriate.

For this purpose, two different types of Ni/YSZ anodes, originating from high-performance anode-supported cells (ASC), are reconstructed via FIB-tomography. For the first time, both layers (anode substrate and anode functional layer) of an ASC are separately analyzed and compared with each other. For the sake of completeness, reconstruction data of a double-layer anode sintered onto an electrolyte supported (half) cell (ESC) is reported in Ref. [24]. Critical microstructure parameters like material fractions, surface areas, particle size distribution of Ni, YSZ, and pore phase, as well as phase connectivity and triple-phase boundary density, are evaluated and discussed.

2. Experimental

Two different types of anode-supported cells (ASCs) (herein referred to as type A and type B, respectively) are investigated. The ASCs have a double-layer anode, an anode functional layer and an anode substrate, using (1) nickel (Ni) as catalyst and electronic conducting solid, (2) yttria-stabilized zirconia (8YSZ) as ionic conducting solid, and, (3) a pore phase. The AFL has an interface to the thin (~7–10 μm) 8YSZ electrolyte, which then is coated by a thin $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (CGO) interlayer and a mixed ionic–electronic

Table 1
3D reconstructions of solid oxide fuel cell anodes, performed via FIB- and X-ray tomography, published in literature (the list is far from exhaustive).

Name	[Citation]/data set	Volume [μm^3]	Pixel size [nm]	Image dist. [nm]	No. images [–]	No. voxel [×10^6]
FIB tomography:						
Joos (this work)	Type A	1765	30	30	277	~65.36
	Type B	887	30	30	149	~32.85
Shearing	[4]/a	75	19	30	40	~6.9
	[4]/b	722	20	19	175	~95
Kanno	[5]/A	2424	37.2	74.5	n/a	~23.5
	[5]/B	3905	37.2	61.7	n/a	~45.7
	[5]/C	17,399	55.8	74.7	n/a	~74.8
Shearing	[6]	50.6	20	15	100	~8.4
Wilson	[7]	109	13.9	50	82	~12.8
Matsuzaki	[8]	3391	13.7	59.2	228	~305.2
Shikazono,Iwai	[9,10]	972	26	62	100	~23.2
Vivet	[11]	967	10.4–13.2	100	115	~7.0
Cronin	[12]/A	914	25	50	n/a	~29.2
	[12]/B	1121	25	50	n/a	~35.9
Kishimoto	[13]/A	1205	26.6	60	76	~28.4
	[13]/B	1013	26.6	62	100	~23.1
	[13]/C	1664	26.5	72	84	~32.9
Matsui	[14]/Ini	1357	44.67	104.9	96	~6.5
	[14]/A	1402	44.67	103.7	100	~6.8
	[14]/B	1310	44.67	97.2	100	~6.8
Matsui	[15]/1	3368	27.9	~61	213	~71
	[15]/2	3150	27.9	~61	191	~66.6
X-ray tomography:						
Laurencin	[16]	185,220	60	X-ray	X-ray	857.5
Shearing	[17]/200×	37,945	65	X-ray	X-ray	n/a
	[17]/800×	331	32	X-ray	X-ray	~10.1