Quantitative analysis methods for three-dimensional microstructure of the solid-oxide fuel cell anode

X Song,[1] Y Guan,[1] G Liu,[1*] L Chen,[1] Y Xiong,[1] X Zhang,[1] and Y Tian[1*]
[1] National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, People's Republic of China
[*] E-mail：liugang@ustc.edu.cn; ychtian@ustc.edu.cn

Abstract. The electrochemical performance is closely related to three-dimensional microstructure of the Ni-YSZ anode. X-ray nano-tomography combined with quantitative analysis methods has been applied to non-destructively study the internal microstructure of the porous Ni-YSZ anode. In this paper, the methods for calculating some critical structural parameters, such as phase volume fraction, connectivity and active triple phase boundary (TPB) density were demonstrated. These structural parameters help us to optimize electrodes and improve the performance.

1. Introduction

Solid-oxide fuel cells (SOFCs) have gained great interest among scientists for its clean, economic and environmentally friendly features. The porous composite material of nickel (Ni) and yttria-stabilized zirconia (YSZ) is widely used as the SOFC anode because of its strong electronic conductivity and high catalytic activity. The oxygen (air) flows through the cathode pore channel and reacts with electrons to form oxygen anions. Electrons participating in the reactions must be supplied by the cathode electronic conductor. Oxygen anions are transported to anode by the electrolyte and react with fuel (H2) to produce electrons [1-3]. The electrochemical reactions are active at the TPB where all the three phases coexist [2, 4]. So the TPB length affects the SOFC performance, which indicates that the electrochemical properties of SOFC depend on the electrode microstructure. The reactants are unable to be transported to the reactive sites by isolated phase networks. Therefore, only the TPBs consisting of three connected phases (active TPBs) can keep the electrochemical reaction going on.

Non-destructive imaging method based on X-ray computed tomography with synchrotron radiation (SR-XCT) is a powerful tool to study the porous electrodes [5-8]. Due to the tunable photon energy, a specific element can be identified by spectroscopic imaging which can indicate the presence of a particular atomic species by taking two imaging below and above the element absorption edge [9, 10]. Moreover, SR-XCT is capable of imaging large volume materials due to its large depth of focus and high penetrating power [11-13]. The quantitative analysis of the 3D microstructure is critical for illustrating how and where the triple phases interconnect based on the detailed 3D microstructure information. So quantitative analysis methods were developed for computing the microstructure parameters, such as volume fraction, connectivity of special phase and active TPB density.

2. Experiment

Imaging experiments were performed using Xradia nanoXCT-S100 system on the beamline U7A at National Synchrotron Radiation Laboratory (NSRL) in Hefei, China [14]. The sample was fetched from the used SOFC anode and polished to several tens of microns, then mounted on the tungsten tip holder that was rotated from -90^o to 90^o at 1^o intervals. A position adjacent to the top of specimen (less than twenty microns) was chosen to image. A series of 181 X-ray transmission radiographs was collected and reconstructed as a 3D volume using reconstruction software of Xradia. Ni, YSZ and pore phase can be identified from the images by comparing Ni absorbing contrast in the two imagings taken at photon energy 8.3 keV (below the Ni edge) and 8.38 keV (above the Ni edge) [15]. Since the focal length of a Fresnel zone plate is proportional to the incident X-ray energy [16]. The focal length is 24.101 mm for 8.3 keV and 24.333 mm for 8.38 keV in the imaging system, respectively. We only change the object distance by moving the sample stage for the different photon energy imaging to meet the thin lens formula [17]. The imaging magnification ratio of 8.3 keV to 8.38 keV is about 1.0098 due to object distance changed, which can be negligible in the experiments. According to their different grey levels in two volume data, the individual virtual slices were allowed to be segmented into Ni, YSZ and pore phase.

3. Computational method

A method applied to calculate the phase connectivity and active TPB density is described briefly in this section. Each voxel of the saved 3D volume data was labelled as 1 (Ni), 2 (YSZ) or 3 (Pore). The connectivity of each phase can be estimated in the same implementation procedure. Here take the Ni phase for example. One side of the image is defined as input and the opposite is defined as output. Ni voxels in the input side are chosen as start points and assigned a mark ‘CI’.

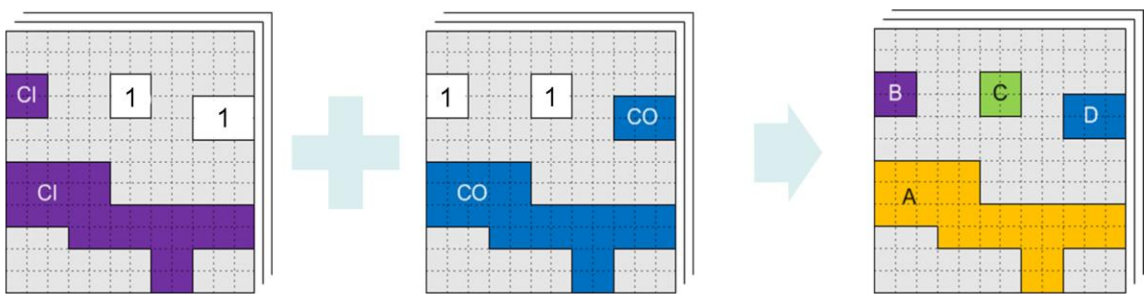

Figure 1. Schematic diagram of the ‘burning’ method for Ni phase.

Ni voxels adjacent to these marked voxels will be assigned the same mark (see Fig. 1), which is so-called the ‘burning’ method [18]. All voxels with this mark ‘CI’ are considered to form a spanning cluster from the input to the output side. Similarly, another spanning cluster assigned another mark ‘CO’ is found from the output to the input side. By comparing these two spanning clusters, the overlapped regions could be identified as the connected phase (area ‘A’ in Fig. 1). The remained regions in two spanning clusters are identified as dead-end phase (area 'B' and 'D' in Fig. 1). Ni voxels not in spanning cluster are identified as isolated phase (area 'C' in Fig. 1).

If the neighbouring four voxels in 3D structure contain three labels, 1 (Ni), 2 (YSZ) and 3 (Pore), the common edge of these three voxels is labelled as TPB. The above labels ('connected', 'dead-end' and 'isolated') is applied to identify whether the TPB components are touching the connected networks of each phase. If the TPB lies on connected networks of each phase (Ni, YSZ, pore), it is labelled 'active'. Total active TPBs are obtained via inspecting the whole volume in three directions x, y and z.

4. Results and discussion

A cuboid volume was cropped from the total reconstructed 3D volume and every virtual slice was segmented into three phases (Ni, YSZ and pore) by their gray levels. Figure 2 shows a 3D visual representation of the cropped volume, with Ni phase in red, YSZ phase in yellow and pore phase in blue. The cuboid volume is 8.1×7.4×8.1 μm^3 and the voxel size was 58.3×58.3×58.3 nm^3.

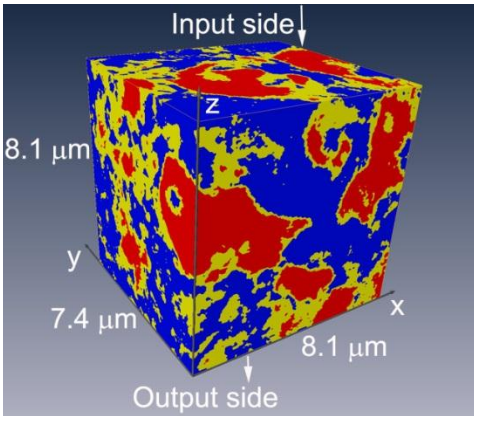

Figure 2. The 3D image view of the anode volume with Ni shown in red, YSZ in yellow, pore in blue. Both input and output sides are perpendicular to the z axis.

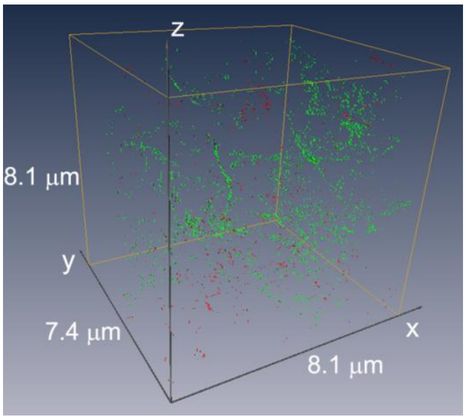

Figure 3. The 3D view of electrochemically active TPBs (green) and other TPBs (red).

The connectivity of each phase plays an important role in the electrochemical reaction of H_2 with O^{2-} to produce electrons. It is expected that only the TPBs that lie on connected networks of each phase (Ni, YSZ and pore) are electrochemically active. Thus, analysing the connectivity of each phase is an indispensable step to obtain the quantity of electrochemically active TPBs. As shown in Table 1, the volume fraction and connectivity of special phase are calculated.

Table 1. Percentages of the different compositions.

	Ni	YSZ	Pore
Volume fraction (%)	23.13	34.87	42.00
Connectivity (%)	92.53	98.49	98.98
Dead-End rate (%)	1.96	0.11	0.21
Isolated rate (%)	5.51	1.40	0.81

The volume fraction is calculated via dividing the volume of a given phase by the total volume. The connectivity, dead-end rate and isolated rate are calculated via dividing the number of voxels with corresponding labels (as mentioned above) by the total given phase volume. Analysing the dead-end and isolated rate of anodes fabricated under different preparation conditions will disclose the variation of microstructures and provide a guide for experiments.

In Figure 3, the active TPBs are marked green to distinguish from the other TPBs (red) in the entire volume. The total TPB density is 6.807×10^5 m $cm^{-3}$and the active TPB density is 5.598×10^5 m cm^{-3}. These values show slightly less than other reported results [3-5], it may due to that the microstructure of Ni-YSZ anode has been degraded after long-term used. On the basis of the above computation, 82.239 % of the total TPB density is active.

5. Conclusion

In this study, quantitative analysis methods were demonstrated to calculate SOFC microstructural parameters such as volume fraction, connectivity and active TPB density. The results show that the proposed methods help to detect the microstructures of anodes and optimize structure.

Acknowledgments

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