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Quantitative analysis of 3D structures in metal-oxide composites

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Homology analysis is an efficient topological method of interpreting the shape of data [1]. Several researches have applied it to describe and classify material structures, including metallic glasses [2] and polycrystals [3]. A quantitative interpretation of structures is necessary to find correlation in the structure-property relationship, which can be accomplished using the Betti numbers, β_i [4]. In the case of a two-dimensional (2D) structure image, the essential structure information, such as connectivity components and 1D holes, can be extracted and represented by β_0 and β_1, respectively. Via STEM images, we previously showed that the connectivity of the CeO_2 phase, β_0, plays an important role in the oxygen ionic transportation of Pt#CeO_2 composites [5]. However, this dependence does not work for the network structure, because isolated CeO_2 phases might be connected three-dimensionally. Therefore, 3D structural analysis is necessary for network structures to verify the relationship between the CeO_2 connectivity and ionic conductivity.

In the present study, Pt#CeO_2 composites with different structures were prepared by increasing the annealing temperature from 500 ℃ to 800 ℃ under CO and O_2 syngas. The ionic conductivities of the composites were measured using impedance spectroscopy, in the same manner as described in our previous work [5]. Focused ion beam (FIB) was used to thin the powders for observation. The STEM tomography technique was performed with a JEM-2100F (JEOL) microscope operated at 200 kV using a high tilt specimen holder. A tilt-series was acquired over an angular range of ±60° with a 2° tilt increment. Regarding the algorithm for 3D reconstruction, the weighted backprojection and simultaneous iterative reconstruction techniques were employed in DigitalMicrograph (Gatan). The generated stack slices were then binarized using the OpenCV library in Pycharm. Postprocessing including median filter, segmentation, and visualization was performed using the Avizo software (Thermo Fisher Scientific). The connectivity of the CeO_2 phases, i.e., the number of CeO_2 components (β_0), was obtained both through the Avizo analysis and chomp calculation [6].

For temperature increments in the range of 500–700 ℃, the Pt#CeO_2 composites were exhibited a lamellar structure with increasing periodicity, whereas the composites annealed at 800 ℃ exhibited a network-like appearance. Ionic conductivity measurements indicated that the parameters, activation energy E, and pre-exponential factor $\sigma_0$increased as the annealing temperature increased. This suggests that the CeO_2 connectivity was improved, and thus, β_0 decreased, from conclusions referred before. Figure 1 shows cross-sectional HAADF-STEM images and corresponding binary images of the Pt#CeO_2 composites annealed at 600 ℃ and 800 ℃. The black and white phases correspond to the CeO_2 and Pt phases, respectively. Upon calculating the β_0 value from these 2D sectional binary images, the composites at 800 ℃ were found to exhibit the highest β_0 value, which is in contrast with the trends predicted via the ionic conductivity measurements. This is because, at 800 ℃, some separated CeO_2 phases are connected at a deeper thickness, as can be confirmed by the 3D structure of the 800 ℃ sample shown in Figure 2. The adjacent phases with the same color belong to the same component. From the 3D structure analysis, the β_0 value of the 800 ℃ sample was found to be lower than that of the 600 ℃ sample, which is inversely proportional to the ionic conductivity parameters (E and σ_0). Further 3D reconstructions of the 500 ℃ and 700 ℃ samples will be performed in the future. These results provide strong evidence for the relationship between the CeO_2 phase connectivity and ionic conductivity of Pt#CeO_2 composites.

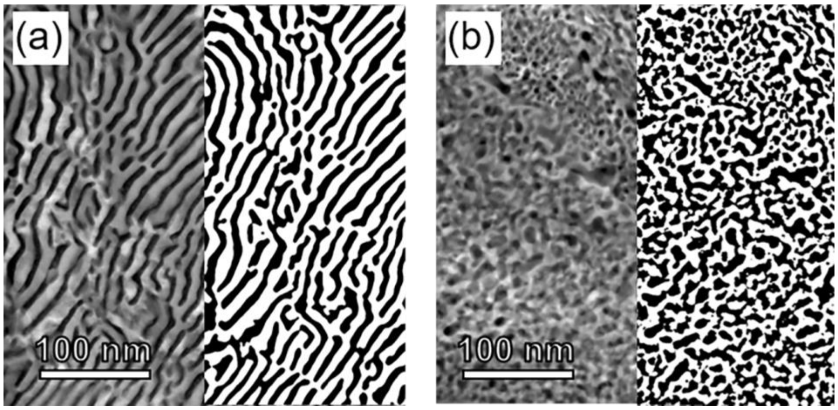

Figure 1. STEM images and corresponding binary images of Pt#CeO2 prepared at 600 ℃(a) and 800 ℃ (b).

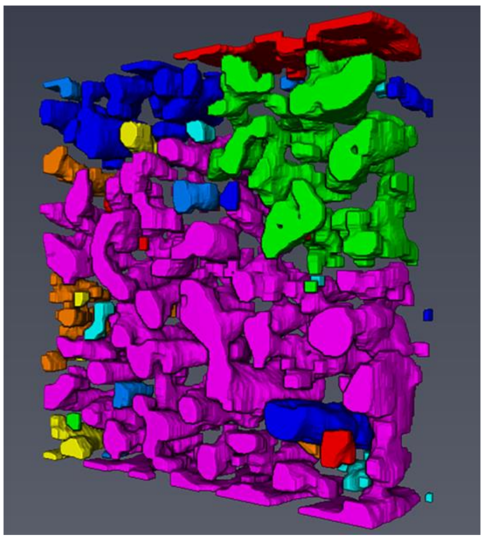

Figure 2. Reconstructed 3D image of the Pt#CeO2 composites annealed at 800 ℃.

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