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Topological Analysis of Metal and Metal Oxide Hybrid Nanostructures

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Solid oxide fuel cells are regarded as promising energy conversion devices due to their high efficiency [1]. The design of anode materials has also attracted substantial interest as it plays an important role in cell efficiency. In addition to percolation pathways for electron conduction, high density of electrochemical reaction sites, long-term stability, and high oxygen ionic conduction are also key requirements of anode materials [2]. Composites including a ceramic phase and a metal phase are the most commonly used anode materials due to the increased number of reaction sites and the interactions between both phases at the interface, where the existence of oxygen vacancies and defects promote oxygen ion transportation [3]. Moreover, the connectivity of ceramics is also a key factor in determining ionic conductivity.

The ability to controllably form immobilized heterostructures and identify ceramic connectivity is of special interest because they allow us to design nanostructures with desired properties. However, it is generally difficult to determine phase connectivity from complicated nanostructures. Betti numbers (β_0, β_1…), as topological invariants, can easily yield a measure of the degree of connectivity by calculating the number of connected components and holes [4]. Two structures are topologically equivalent, if they have the same Betti numbers. Here we prepared different interwoven nanostructures of Pt/CeO_2 by changing the syngas ratio. We also present a facile topological method for relating their structures with their ionic conductivities.

The preparation of Pt/CeO_2 composite bulk and powders was described in a previous work [5]. Different structures were attributed to different ratios of CO and O_2 syngas. TEM specimens were prepared by selecting a micro-particle on a Cu grid and milling it to about 80 nm thickness via a focused ion beam method. Then annular dark-field STEM observation was carried out using JEM-2100F (JEOL, Japan) operated at 200 keV. STEM images were processed to a uniform contrast by removing the background with fast Fourier transformation. The pipeline used to calculate the Betti numbers is displayed in Figure 1. The white and black regions correspond to Pt and CeO_2, respectively. The Binarized image in Figure 1(b) via Gaussian thresholding was obtained using Python coupled with the OpenCV library. As shown in Figures 1(c) and 1(d), close and open processing were applied to eliminate black (indicated by the red arrow) and white noise (indicated by the yellow arrow), respectively. The Betti numbers were calculated as a topological method from the binary image using the Chomp software [6]. A sandwich-like system with CGO ($Ce_{0.8}Gd_{0.2}O_{1.9}$) ‖ Pt/CeO_2 ‖ CGO was assembled to measure the ionic conductivity of Pt/CeO_2 hybrids, while both CGO electrodes were used to block charge conduction by electrons. The ionic conductivity of each nano-hybrid was examined using electrochemical impedance spectroscopy SP-150 (BioLogic, Japan) with temperatures ranging from 773K to 873K. The frequency range was 1-10^6 Hz with signal amplitude of 30 mV.

Figure 1 indicates that the contrast of the final binary image in Figure 1(d) is consistent with the original image in Figure 1(a). Similar lamellae structures with about 10 nm periodicity were observed from specimens heated under different syngas ratios. The factor β_0 represents the number of connected black CeO_2 domains and β_1 is the number of white Pt holes. As the ratio of CO and O_2 increased, β_0 subsequently increased. This result suggests that the connectivity of CeO_2 decrease with the decreased O_2 partial pressure. Figure 2 shows the typical impedance spectra obtained with the Pt/CeO_2 disk for a syngas ratio of 2:1 at different temperatures. The spectra consist of a high-frequency semicircle and a low-frequency semicircle, which correspond to the interface and bulk, respectively. From the resistance of the system, as estimated from the low-frequency intercept of the spectra with the real axis, the temperature dependency of the total conductivity was obtained. The activation energy for oxygen ionic conductivity was found to be about 0.83 eV according to the Arrhenius relation. The electrochemical impedance spectra of samples under different syngas ratios were also measured to investigate the effect of the syngas ratio on oxygen ionic conduction and the relationship between the CeO_2 connectivity and ionic conductivity.

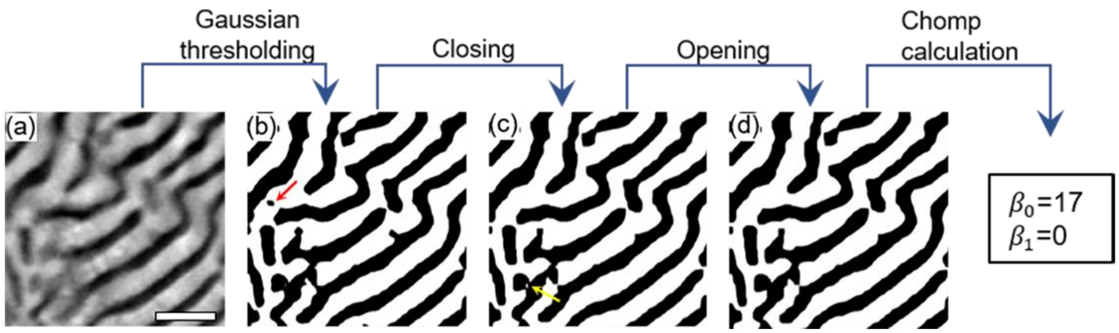

Figure 1. The pipeline for calculation of Betti numbers. The scale bar is 20 nm.

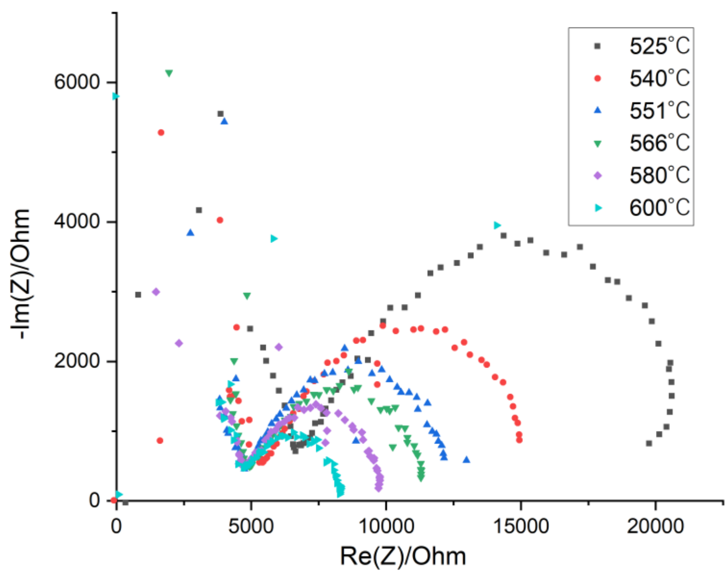

Figure 2. The typical impedance spectra obtained with the Pt/CeO2 disk in the syngas ratio of 2:1 at different temperature.

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