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Development and optimization of porosity measurement techniques

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Abstract

Different porosity measurement methods are investigated and compared to ascertain a relatively accurate and efficient method suitable for laboratory utilization. As model material $Sr_{0.895}Y_{0.07}TiO_{3-\delta}$ (SYT) ceramic material, which is designed as anode substrate for planar solid oxide fuel cells, is studied. Seven batches with different porosity are investigated using image analysis method and Archimedean porosimetry, operating under different conditions, and compare with the results from mercury porosimetry. The experimental results reveal for these methods different accuracies of the true porosity for different porosity ranges.

Keywords: B. Porosity; Measurement; Ceramics; Image analysis; Porosimetry

1. Introduction

As most materials both naturally and artificially are to some extent porous, their physical properties such as density, thermal conductivity and strength are all dependent on their porous structures [1–3]. The complexity and variety of porous material has led to the utilization of many experimental techniques for their characterization [4]. Thus, in former studies, large efforts have been invested in the development and refinement of different porosity measurement [1]. The principal techniques utilized for measuring porosity include image analysis method, Archimedeans porosimetry, mercury intrusion porosimetry, helium pycnometry and radiation scattering method [5,6]. Different methods rely on completely different physical principles, which lead to different advantages and limitations in application [5,6]. For example, image analysis measures both open and closed porosity but cannot distinguish between the two types; Archimedeans porosimetry is inexpensive and simple in operation to measure open porosity but cannot provide any information about pore shape, diameter and distribution condition; mercury porosimetry detects open porosity with high precision, but it is destructive to samples, however, it is frequently used for comparison and correlation because of its large range of applications.

The aim of this study is to investigate and compare different methods of porosity measurement to ascertain a relatively accurate and efficient method suitable for laboratory utilization. A specific ceramic material, $Sr_{0.895}Y_{0.07}TiO_{3-\delta}$ (SYT), which is designed as planar anode substrate in solid oxide fuel cells [7–9], is studied as model material. In this application the porous substrate should provide mechanical support for the electrochemical active layers [10–13] and at the same time permit a sufficient supply of the reaction gases, which raises questions on the optimum porosity level to satisfy both conditions. Therefore, the accurate measurement of porosity of the porous material is undoubtedly the first step to solid oxide fuel cell optimization.

Seven batches of SYT samples with different porosity are investigated through image analysis method and Archimedeans porosimetry. In image analysis method, light optical microscope (LOM) images and scanning electron microscope (SEM) images are utilized based on both manual and automatic thresholding routines, while in Archimedeans porosimetry, two different impregnation fluids, water and ethanol, are applied. Porosity measurement results are discussed and compared with results from mercury porosimetry.

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2. Experimental

2.1. Materials

Porous Y-substituted strontium titanate $Sr_{0.895}Y_{0.07}TiO_{3-\delta}$ (SYT) was produced from SYT powders by tape-casting in IEK-1, Forschungszentrum Jülich GmbH [7]. The density of the powder was measured by means of a helium gas pycnometer with the result of 4.8 g/cm^3. After casting, the sintering process was performed in a tube furnace on samples of 30×30 mm^2 in size. The decomposition of the organic additives occurred in air up to 500 °C including 1 h holding time. After the debinding process, the air atmosphere was changed to a reducing atmosphere of argon/hydrogen (Ar 96%/H_2 4%). During the sintering process, porous, zirconia-coated alumina substrates were used as sintering support.

The microstructure and physical properties of the material are validated in dependence on the sintering temperature. To obtain different porosities, different sintering temperatures were applied, varying from 1200 to 1340 °C in steps of 20 K. The density of the sintered substrates was determined geometrically (weight and volume). As theoretical density (TD) for fired SYT, 5.06 g/cm^3 was used [14]. The cumulative open pore volume, the average pore diameter and the pore size distribution of the fired samples were measured by means of Hg porosimetry (Pascal 140/Porosimeter 2000, Thermo Electron/Carlo Erba, Rodano/Milan, Italy) under low pressure and high pressure conditions.

2.2. Methodology

An overview of the current investigations can be seen in Fig. 1. Image analysis and Archimedean porosimetry were carried out in parallel with the same seven batches with different porosity. For image analysis, specimens were embedded in polymer resin and metallographically prepared for microscopy imaging (details see below). Both LOM images and SEM images were used for thresholding and porosity calculation. Thresholding was carried out both manually and automatically. For Archimedean porosimetry, the specimens were first dried in oven to eliminate possibly remaining moisture. Water and ethanol were used as impregnating fluids to investigate the influence of wettability on fluid impregnation. Weight of the samples was measured before and after impregnating and while the samples were immersed in fluid. Porosity was calculated afterwards. Immersing time and different conditions were studied and discussed.

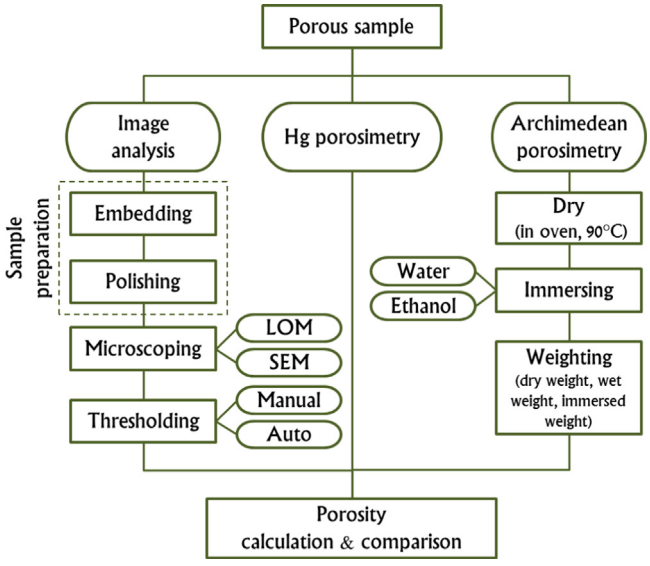

Fig. 1. Summary of the investigations performed in the present study.

2.2.1. Image analysis

The basic of image analysis is to set a proper threshold to gray-leveled image to extract objects (pores) from their background based on the degree of contrast between object and background. Thresholding creates binary from gray-leveled images by turning all pixels below the threshold to zero (black regions in binary image) and all pixels above the threshold to one (white).

Two methods were used: manual and automatic thresholding. Manuel threshold selection was carried out with the commercial software AnalySIS pro (version 5.0, Olympus Soft Imaging Solutions GmbH). Threshold sensibility test was also performed to check the porosity value sensibility to the threshold position. Automated thresholding was employed with MATLAB® based on the Otsu Method [15]. The Otsu method is implemented as "graythresh", details see MATLAB® manual documentation [16]. A global threshold (level) is computed and a binary image is converted from an intensity image according to this level, which is a normalized intensity value that lies in the range [0, 1].

For image analysis investigation, the samples from different batches were metallographically prepared. They were embedded (Buehler Epoxy 2000, solidified at room temperature under atmosphere pressure for 48 h), manually grinded (grinding papers from P500 to P2500) and semiautomatic polished. The polishing was carried out with a Buehler Minimet 1000, involving cloth polishing in 3 mm and 1 mm diamond suspension and a final step of 0.05 mm alumina suspension. The semi-automatic procedures helped to increase the reproducibility of polished cross-sections. LOM was used to obtain low magnification ($500 \times$) images. SEM (Zeiss SUPRA 50VP) was used to get images at $2500 \times$. Secondary electrons imaging was used, with an accelerating voltage of 10 kV, a working distance of 9.9 mm and an image size of 1024×720 pixels. The LOM images are of 555×416 pixels in size. 20 LOM images and 3 SEM images were taken for each sample. The parameters of LOM and SEM images are given in Table 1.

Table 1
Parameters of LOM and SEM images.

	Magnification	Amount of images	Resolution [pixels]	Real sample surface area of each image [μm^2]
LOM	500 ×	20	555 × 416	140 × 105
SEM	2500 ×	3	1024 × 720	45.7 × 32.3