Characterization and Modelling of Structure and Transport Properties of Porous Ceramics

D. Penner, L. Holzer

A general scheme of material design and virtual testing of porous ceramics is presented, which provides new strategies for efficient development and optimisation of such materials. The development cycle contains three stages, which can be repeated, until the final targeted properties are reached. The first stage is the preparation of porous ceramics with properties in the region of interest and thorough 3D-investigation and characterization of the porous microstructure. In the second step, microstructure data either directly from real materials or indirectly from a virtual, stochastic model are fed into a numerical model to calculate the physical property of interest, e.g. permeability, diffusivity, thermal conductivity or electrical conductivity of pore fluids. Finally, an evaluation of data representing microstructure characteristics as well as macroscopic properties for a wide range of fabrication scenarios yields as a third step a validated model, which leads to the definition of optimised design guidelines. This optimisation cycle is then closed with the production of a porous ceramic material with improved physical properties. The successful implementation of such scheme is demonstrated here with the development of porous zirconia membranes as electric liquid junction for pH-sensors.

Introduction

It is well known, that ceramics having a wide scale of porous morphologies are used in many different applications such as bio-ceramics, chemical engineering, exhaust gas treatment, filtration etc. [1, 2]. Porous systems ranging from an entirely open pore network e.g. for catalyst supports to entirely closed pore structures e.g. for insulation materials exist. The application of such porous ceramic systems is quite often connected to specific transport properties, e.g. flow of media in filtration, ion conductivity in electrochemical membranes or thermal conductivity in insulation materials. All these transport properties are known for bulk and dense materials but in case of biphasic materials (bulk and pores) such properties could be calculated only if the geometry of the biphasic material is known in detail.

On the other hand, ceramic engineering methods provide different routes to tailor porosity and microstructure to a certain degree. Typical methods to produce and to adjust porosity are partial sintering, use of pore formers or templates, foaming, freezing or size exclusion of particles. Typical development schemes involve preparation of sets of samples and measurement of the resulting properties. By optimisation strategies, sometimes supported by "design of experiment" methodologies, the target properties can be reached.

By employing a strategy of model generation and virtual material testing this process might be significantly optimised. Fig. 1 shows a general scheme of development cycles, which involve different stages of

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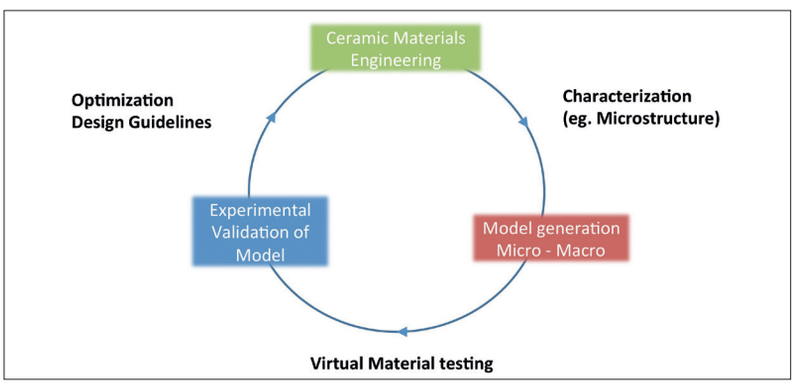

Fig. 1 General scheme of material development cycles, which involve different stages of preparation, characterization and analysis of properties

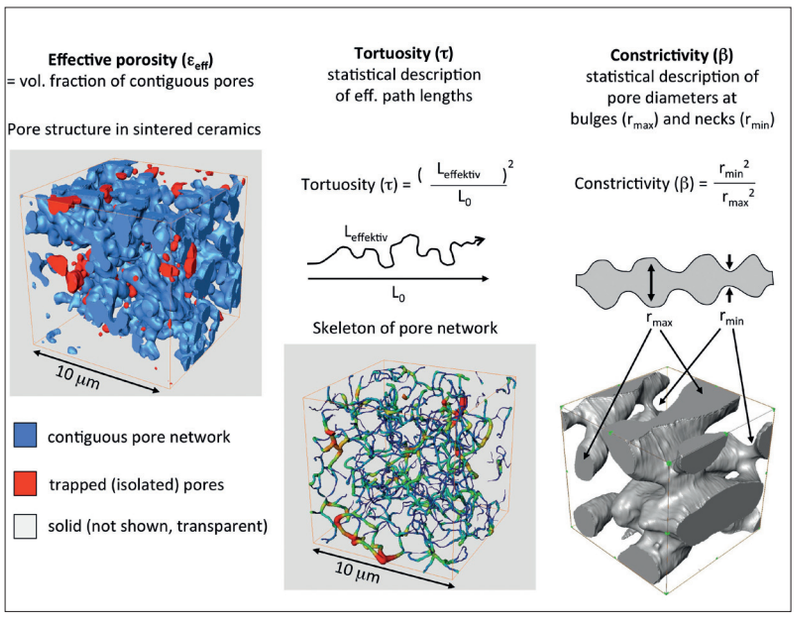

Fig. 2 Illustration of the three dimensionless microstructure characteristics (i.e. effective porosity, tortuosity and constrictivity), which control transport in porous media such as effective electrolyte conductivity; Details and references are given in text.
Note: for viscous flow and permeability hydraulic radius as a 4th parameter has to be taken into account

preparation, characterization and analysis of properties. As a starting point a small set of samples or an already existing state of the art material is thoroughly investigated and relevant geometrical parameters are characterized.

By creating virtual structures with similar or varying structural features a bigger set of virtual samples is generated. These structures are than fed into a numerical program to calculate effective macroscopic properties. Programs like GeoDict [3] have implemented the physical laws of interest and compute spatially resolved solutions of e.g. transport properties with respect of the fed virtual microstructures.

As a result, any changes of structural parameters of a porous material yield new specific macroscopic properties like electrical conductivity, permeability or diffusivity. Finally, simple potential relationships can be derived from this approach and the validity of the model can be tested with the existing samples or new ones.

If the overall validity is proven, design guidelines for ceramic engineering could be provided to produce materials with optimised properties.

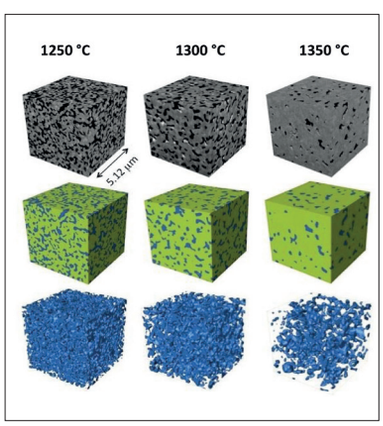

Fig. 3 3D-reconstructions and visualization of porous ZrO_2 based on FIB-tomography (10 nm resolution) for three different sintering temperatures [5] (with permission of Elsevier)

3D-imaging for microstructure characterization

As pointed out above, detailed characterization routines are the basis for generation of a suitable virtual material testing model. Fig. 2 illustrates the three main microstructure characteristics, which control the effective transport properties in porous materials (e.g. electrical conductivity of a liquid electrolyte in the pores). These can be described as follows:

- effective porosity (ε) is the volume fraction occupied by the contiguous pore network.
- tortuosity (τ) is a statistical correction factor, which accounts for the effective path lengths through the pore network.
- constrictivity (β) is a correction factor, which accounts for the variation of pore diameters.

In addition:

- hydraulic radius (r_h) is a characteristic, which accounts for viscous effects at the pore walls.

These four microstructure characteristics represent the so-called higher order topological properties. Reliable determination of these properties requires in depth 3D-analysis based on tomography. Depending on the materials microstructure (pore and particle sizes) a suitable tomography technique has to be chosen: the resolution of X-ray tomography/micro-CT is typically in the µm-range. Resolution of FIB-SEM tomography ranges approximately from 5–50 nm.

Even higher resolutions of approximately 1 nm can be reached with TEM-tomography. 3D-reconstruction and visualization is then performed with standard software tools (fiji, avizo, geodict) and for extraction of the above mentioned microstructure characteristics (e.g. geodesic tortuosity τ_{geod}, constrictivity β, hydraulic radius r_h) we also use in-house algorithms. For detailed descriptions of the 3D-characterisation methods we refer to previous publications [4].

Fig. 3 shows examples of 3D-reconstructions from a porous ZrO_2 material based on FIB-tomography (10 nm res.). In this case, detailed 3D-investigations were performed in order to optimise the pore structure for its application as a liquid junction in pH sensor. The liquid junction limits the outflow of viscous electrolyte from the electrode compartment and at the same time provides high ionic conductivity through the pores of the junction [5]. Such challenging requirements can only be fulfilled with detailed know-how of the relationships between microstructure characteristics and effective transport properties, as will be explained below.

Quantitative microstructure characterisation

Microstructure characteristics are extracted from tomography data based on 3D-image analysis. Fig. 4 represents the pore characteristics of ZrO_2 membranes introduced in Fig. 3. When increasing the maximum sin-

tering temperature from 1250–1350 °C (at 1 h dwell time for all samples) the porosity decreases from 30–10 %. At high temperatures the connectivity in the pore network is partially lost.

Therefore, at 1350 °C 50 % of the total porosity is present as closed pores which do not contribute to the transport of material through the membrane. As a consequence the transport pathways in the remaining interconnected pores become longer, which means that tortuosity increases significantly.

Another important effect of increasing sintering temperature is microstructure coarsening and its effect on constrictivity. This is shown in Fig. 4 bottom.

When increasing the sintering temperature from 1250 °C to 1350 °C the average size of pore bulges (r_{max}) increases moderately from 75 nm to 100 nm. However, at higher sintering temperatures (>1300 °C) the average size of the bottlenecks (r_{min}) is significantly reduced from >50 nm to ca. 20 nm.

Hence the above mentioned loss of connectivity at high temperatures goes hand in hand with a decrease of the average bottleneck size. r_{max} and r_{min} are measured from tomography data with two different 3D-methods, which are the continuous pore size distribution (cPSD) and simulation of mercury intrusion (MIP-PSD), as described in Münch and Holzer [6].

The influence of bottleneck size and pore size on effective transport properties are captured with the parameter β (constrictivity), which is defined as the ratio of average cross-section area of bottlenecks ($\pi\ r_{min}^2$) over average cross-section area of pore bulges ($\pi\ r_{max}^2$) [7]. As shown in Fig. 4, constrictivity drops at high sintering temperatures (>1300 °C) mainly due to the shrinking of bottlenecks ($\pi\ r_{min}$).

Virtual testing and quantitative micro-macro relationships

Controlled design of materials with specific properties requires quantitative knowledge of the relationships between microstructure and effective (macroscopic) properties. In order to establish such quantitative relationships for transport properties in porous media, the authors used a virtual testing approach in collaboration with Ulm University/DE (details are given in previous publications [5, 8–10]).

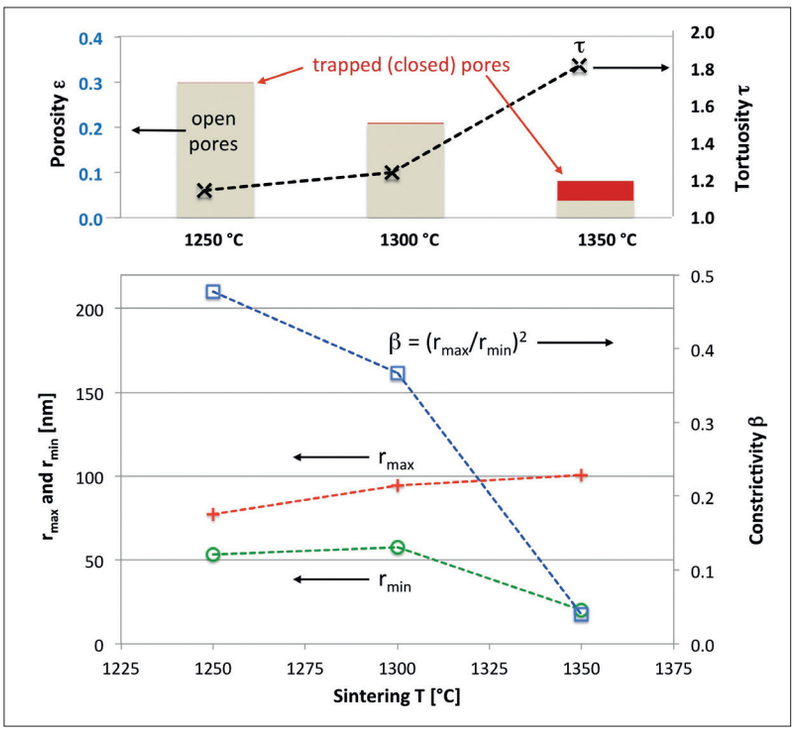

Fig. 4 Quantitative characteristics of the pore structure derived from 3D-data of porous ZrO_2 (see Fig. 3). The example illustrates the influence of sintering temperature on microstructure characteristics, which control transport properties in porous media; for a detailed description see Holzer et al. [5]

The methodical approach is illustrated in Fig. 5.

A stochastic model is set up, which is capable to provide a large number of virtual 3D-structures with very different characteristics (ε, β, τ, r_h). These structures are used as input for numerical simulation of transport (e.g. with GeoDict), which provide effective

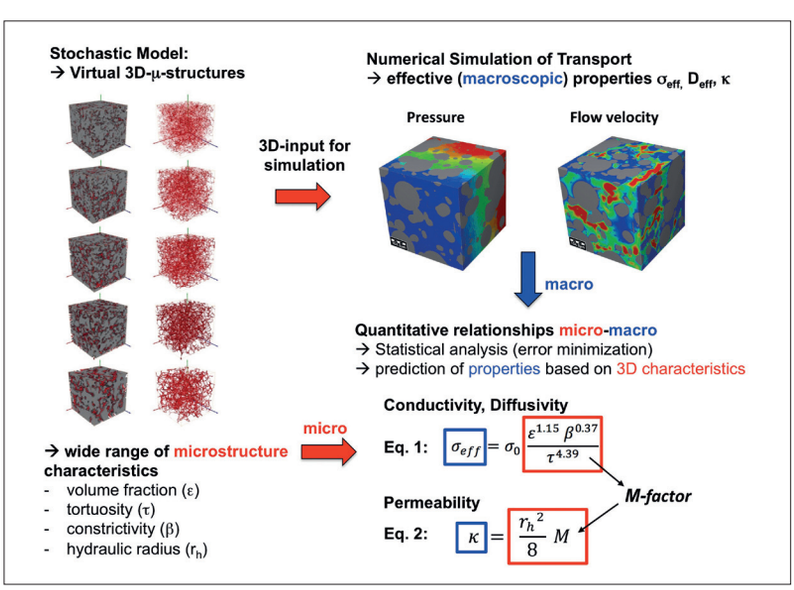

Fig. 5 Quantitative micro-macro relationships are established based on a virtual testing approach [10], which allows reliable prediction of effective transport properties based on 3D-microstructure characteristics. The knowledge of quantitative micro-macro relationships is the basis for controlled design of materials with optimised pore structure and performance

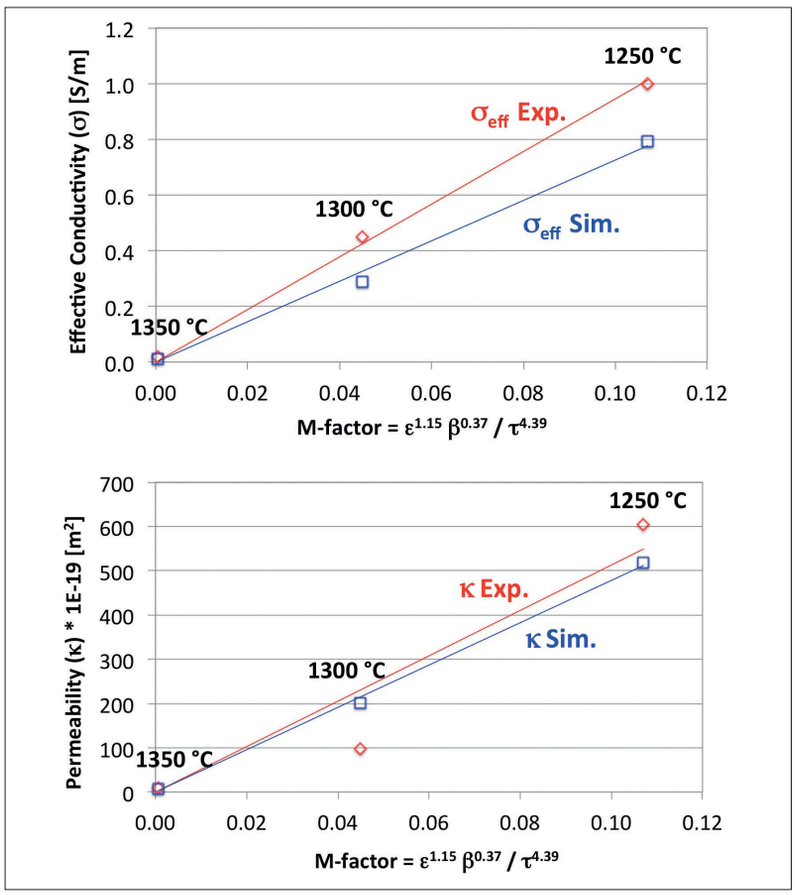

Fig. 6 M-factor of three sintered ZrO_2 plotted versus conductivity (top) and permeability (bottom). These effective properties are either derived from experiments (red) or from numerical simulations (blue). The linear trends and consistency of data show the high prediction power of the M-factor and associated micro-macro relationships (Eq. 1–2)

macroscopic properties such as conductivity (σeff), diffusivity (D_{eff}) and permeability (κ). More than 8000 different microstructures were analysed in this way.

The data were then used to determine quantitative relationships between microstructure characteristics and effective properties by means of statistical error minimization.

The two equations given in Fig. 5 have a high prediction capability because they are based on a large variation of different (virtual) microstructures. This means that effective transport properties (conductivity, permeability, diffusivity) can be reliably predicted based on knowledge of the microstructure characteristics.

The equations replace older, semi-empirical expressions (e.g. Carman-Kozeny, Katz-Thomson, Archie's Law, Van Brakel and Hertjes), which were established at a time where detailed 3D-characterisation techniques were not yet available. In this context it is also important to note that conductivity and diffusivity are dependent entirely on dimensionless characteristics (ε, β, τ /Eq. 1) and the joint effects of these characteristics can be summarized into a so-called microstructure factor (M). For prediction of viscous flow and permeability (κ) the hydraulic radius has to be considered additionally (Eq. 2).

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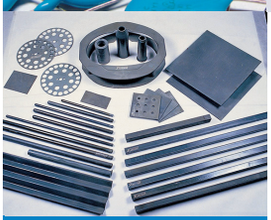


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Validation of micro-macro relationships

Fig. 6 documents the prediction power of micro-macro relationships (Eq. 1–2) and of the associated M-factor derived from microstructure analysis. The M-factor (x-axis) of those ZrO_2 samples with varying microstructures due to sintering temperatures is plotted versus effective transport properties (y-axis), i.e. electrical conductivity (Fig. 6 top) and permeability (bottom), respectively. The effective transport properties are either determined experimentally (red) or from numerical simulation (blue) with 3D-input from tomography.

The plots in Fig. 6 indicate that simulations and experiment give very similar results. Furthermore linear trends are obtained when plotted versus the M-factor, which supports the high prediction capability of the M-factor and of the associated micro-macro expressions. In context with Eq. 1– 2, the slopes of trend lines in Fig. 6 can be interpreted as the intrinsic electrolyte conductivity (top) and as hydraulic radius associated with permeability (bottom), respectively.

Meanwhile, the quantitative expressions were successfully applied in numerous investigations for prediction of effective properties and as a basis for purposeful optimisation of microstructure and associated properties. Examples of such investigations include electronic conductivity and electrochemical performance of composite electrodes in solid oxide fuel cells (SOFC) [11, 12] as well as liquid and gas permeability in partially saturated gas diffusion layers (GDL) of PEM fuel cells [13, 14].

Virtual testing as a basis for controlled materials design

The combination of advanced 3D-characterisation methods and virtual materials testing with the today available repertoire of methods for production of tailored porous architectures and structures enables optimised and accelerated materials development. As a consequence of a thorough material microstructure characterization enabling the prediction of the transport properties the number of experiments can be significantly reduced once fundamental correlations of structure and physical properties are understood, design guidelines can be derived, which have to be transformed subsequently into the appropriate material engineering strategy.

If e.g. the virtual testing implies a positive effect of reduced tortuosity, available methods for production of elongated and oriented pores should be considered. If e.g. an enhanced hydraulic radius might be favourable, pore former particles could be used and so on. With the production of real samples according to design guidelines the optimisation loop is finally closed.

Depending on the results the virtual testing cycle must be repeated under adjusted boundary conditions and with appropriate model refinements, which can be done in relatively short time. In this way, the efforts and costs for otherwise extensive experimental testing can be reduced significantly.

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