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Stochastic geometrical modeling of solid oxide cells electrodes validated on 3D reconstructions

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ABSTRACT

An original 3D stochastic model, based on the truncated plurigaussian random fields, has been adapted to simulate the complex microstructure of SOC electrodes. The representativeness of the virtual microstructures has been checked on several synchrotron X-ray and FIB-SEM tomographic reconstructions obtained on typical LSCF, LSC and Ni-YSZ electrodes. The validation step has been carried out by comparing numbers of electrode morphological properties as well as the phase effective diffusivities. This analysis has shown that the synthetic media mimic accurately the complex microstructure of typical SOC electrodes. The model capability to simulate different types of promising electrode architectures has also been investigated. It has been shown that the model is able to generate virtual electrode prepared by infiltration resulting in a uniform and continuous thin layer covering a scaffold. With a local thresholding depending on the position, continuous graded electrodes can be also produced. Finally, the model offers the possibility to introduce different correlation lengths for each phase in order to control the local topology of the interfaces. All these cases illustrate the model flexibility to generate various SOC microstructures. This validated and flexible model can be used for further numerical microstructural optimizations to improve the SOC performances.

1. Introduction

The climate change, the rarefaction of fossil fuels in conjunction with the growing worldwide demand for energy have drastically increased the need of clean and sustainable energy sources. However, the use of intermittent renewable technologies such as solar panels or wind turbines requires new solutions to match the fluctuations between the demand and the production. A new flexible energetic vector for storing energy is thus required to absorb the peaks of electricity production or consumption. The dihydrogen gas, which presents a high ratio of energy to mass, is considered as one of the most relevant choices for this vector. In this view, the high-temperature electrochemical systems appear as a promising technology for the efficient and reversible gas to electricity conversion [1,2]. Indeed, thanks to their high flexibility, the same electrochemical device can be alternatively used in fuel cell mode for electrical power generation and steam electrolysis mode for dihydrogen production [3] (i.e. in Solid Oxide Fuel Cell – SOFC – mode or in Solid Oxide Electrolysis Cell – SOEC – mode). This type of high-temperature electrolyser-fuel-cell is constituted by a stack of elementary Solid Oxide Cells (SOCs), each one being composed of a dense electrolyte sandwiched between two porous electrodes. State-of-the-art for SOC components are Yttria Stabilized Zirconia (YSZ) for the electrolyte and Ni-YSZ cermet for the H_2 electrode [1,2]. The O_2 electrode is currently made of Mixed Ionic Electronic Conductors (MIECs) such as Lanthanum Strontium Cobalt (LSC) or Lanthanum Strontium Cobalt Ferrite (LSCF).

The manufacturing routes for Solid Oxide Cells (SOCs) are based on typical ceramic processing such as screen printing, tape casting or dip-coating [4]. Other original methods, based on catalyst infiltration [5] or Electrostatic Spray Deposition (ESD) [6], have been recently proposed to improve the SOCs efficiency. Thanks to the large variety of these methods, a wide range of electrode microstructures is liable to be produced and adapted to each SOC applications (*i.e.* fuel cell, steam electrolysis, reversible system, etc.). Indeed, the microstructure of the electrodes plays a major

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Nomenclature

$i = X, Y, Z$	phase name (–)	ρ_i	the correlation function of i (–)
$\bar{i}$	complementary phase of i (–)	p	probability density function (–)
C_i	the covariance function of i (–)	FFT	Fast Fourier Transform (–)
ε_i	the volume fraction of i (–)	l	correlation length (μm)
S_p^i	the specific surface area of i (μm^{-1})	G_{ij}	bi-Gaussian random field (–)
S_p^{ij}	the interfacial specific surface area between i and j (μm^{-1})	D_i	domain or cell related to the phase i (–)
		π	mathematical constant Pi ≈ 3.1416 (–)
Ω	3D domain (–)	ξ_{TPB}	density of Triple Phase Boundary lengths (μm^{-2})
V_Ω	domain volume (μm^3)	τ_i^{geo}	geometrical tortuosity (–)
G_i	random gaussian field of phase i (–)	β_i	constrictivity parameter (–)
λ_X	threshold (–)	M_i	Microstructure-factor (–)
$N(0,1)$	standard normal distribution (–)	d_p	mean phase diameter (μm)
U	uncorrelated gaussian random noise (–)	δ	proportion of connected phase (–)
ω	the weight function (–)		

role in the global cell performances by controlling the rates of the electrochemical reactions which depend on each SOC application [7–10]. As a consequence, the electrode microstructure can be tuned to design more efficient SOC for each particular utilization. Nevertheless, the electrodes present a complex three dimensional microstructure for which the basic relationships between the three-dimensional characteristics of the microstructure and the electrode properties are not still precisely understood. Thus, several studies [11–14] have been recently proposed in an attempt to improve the knowledge of such relations, which are essential before optimizing the microstructure.

During the last decades, advances in 3D characterization have been achieved to image the SOC electrode microstructure. Different techniques based on Focused Ion Beam sectioning coupled with a Scanning Electron Microscope (FIB-SEM) [15–17], X-ray absorption tomography [18–20] or holotomography [10,21,22] have been successfully employed to reconstruct the SOCs electrodes microstructures with a high spatial resolution (at the scale of few tens of nanometers). Some authors [14,17,23–26] have taken advantage of these techniques to study the links between the electrode microstructural parameters. However, this approach is time consuming as it needs the manufacturing and the characterization of several cells. For this reason, the number of reconstructed electrodes was limited. In general, the evolution of microstructural parameters such as the specific surface area, the tortuosity factor or the Triple Phase Boundaries lengths TPBls (defined as the lines where the electronic, ionic and gas phase meet) are plotted as function of the phase volume fractions with few points [23,24]. These data are thus insufficient to fully understand and validate the proposed complex relationships linking the electrode microstructure parameters [11,13]. In order to increase the amount of data required to fit accurately these relationships, an alternative method consists of generating representative synthetic microstructures by numerical means.

For this purpose, a lot of attempts have been devoted to the development of relevant 3D geometrical models able to mimic the actual microstructure of both two-phase electrodes (i.e. porous LSCF for example) and three-phase composite electrodes (i.e. Ni-YSZ cermet for example). Most of the published methods are related to stochastic models based on random sphere packing algorithms [27,28]. In this frame, many authors have assumed a uniform particle size whereas only few studies have taken into account a more realistic distribution on the sphere radii [29,30]. As a general matter, the sphere packing algorithms are decomposed into 2 steps. The first one is related to the creation of "seeds" corresponding to the positioning of the spheres. The second step is dedicated to the simulation of the "sintering" process in order to densify the microstructure up to the desired porosity. The first step can be done by the so-called "drop & roll" algorithm [9,29,31,32] or by the random positioning of "seeds" on a lattice structure [27,33,34]. However, these methods are too much constrained, and hence, they are not able to account for the full stochastic nature of the actual SOCs electrodes. For example, the positioning of spheres on a lattice results in a structuration of the final microstructure that is not realistic regarding the SOC microstructure. Furthermore, the Drop and Roll method yields an irrelevant anisotropy in the synthetic microstructures [37]. To overcome this issue, some authors have developed algorithms with a pure random positioning of spheres [35,36]. The second step of the sphere packing methods is based on basic geometrical operations to increase the surface contact between particles (i.e. sphere radius expansion [32,33,35,37] or overlapping [9,29,31] and creation of necks [34]). Aside from these pure geometrical approaches, the Discrete Element Method (DEM) has also been employed to simulate the initial sphere packing by computing the mechanical contact between the particles [12,38]; while the densification can be simulated by modelling the physical sintering process [12]. All these iterative methods need rather intensive CPU resources especially for the DEM computations.

In addition to the sphere packing, other stochastic models based on geostatistical simulations can be used to generate synthetic microstructures [39]. Different iterative methods based on the minimization of correlation functions between the synthetic microstructure and a real segmented image have been used to generate three-phase Ni-YSZ electrodes [40,41]. It is worth mentioning that non-iterative methods can be useful to simulate a microstructure in a short time. For this purpose, Neumann et al. [42] have proposed a generalization of a multi-steps model decomposed in a homogeneous Poisson point process, a beta skeleton algorithm followed by the voxel phase labelling. With the same objective, Lanzini et al. [43] have applied the truncated Gaussian random field model to the SOC electrodes by considering a medium constituted of two phases (i.e. the pores with one solid phase). Abdallah et al. [44] have applied the Boolean random sets and the truncated plurigaussian random field model to generate a porous Ni-YSZ composite electrode. In the last case, the three sets related to the three electrode phases were obtained with set operations on the two underlying segmented independent Gaussian random fields.

It is worth noting that few studies have been devoted to validate the morphological representativeness of the numerical SOC microstructures compared to the real ones. As a general matter, the sphere packing methods yield a final microstructure that keeps the geometry of the initial spheres. Therefore, as pointed out in [28], the relevance of this morphology can be questionable if com-