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A novel approach for the quantification of inhomogeneous 3D current distribution in fuel cell electrodes

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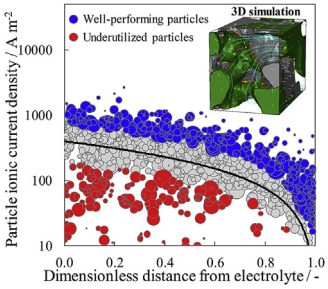
HIGHLIGHTS

- Proposed particle-based method to quantify the 3D current distribution in electrodes.
- Current distribution at particle level is scattered within porous microstructures.
- 30% of electrode volume is underutilized as particles do not transfer enough current.
- Safe operation and advanced microstructural design can be based on this 3D method.
- This novel 3D methodology overcomes the limitations of macrohomogeneous modeling.

GRAPHICAL ABSTRACT



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ABSTRACT

The electrode microstructural properties significantly influence the efficiency and durability of many electrochemical devices including solid oxide fuel cells. Despite the possibility of simulating the electrochemical phenomena within real three-dimensional microstructures, the potential of such 3D microstructural information has not yet been fully exploited. We introduce here a completely new methodology for the advanced characterization of inhomogeneous current distribution based on a statistical analysis of the current of each particle within the microstructure. We quantify the large variation in local current distribution and link it to the particle size dispersion, indicating how particle coarsening can trigger further degradation. We identify two classes of particles: those transferring more current than average, which show 10–40% more particle-particle contacts, and those producing more current than average, characterized by ~2.5 times larger three-phase boundary length per unit volume. These two classes of particles are mutually exclusive, which implies that up to the 30% of the electrode volume within the functional layer is underutilized. This fundamental insight goes well beyond the predictions of continuum modeling, allowing us to revisit the current standards regarding safe operating conditions and to suggest alternative strategies based on nanoparticle infiltration, template-assisted synthesis and additive manufacturing for designing more durable electrodes.

1. Introduction

The twenty-first century is expected to witness the transition from the abundant use of fossil fuels to a clean and sustainable energy economy based on renewable resources [1]. In this scenario, electrochemical energy conversion and storage, as provided by fuel cells and

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batteries, will play a prominent role [2,3]. Both these key technologies generally employ porous electrodes, typically consisting of a dispersion of granular particles or agglomerates, to extend the electrochemical reaction into a larger volume and thus decrease the internal losses of the energy conversion processes [4].

It has been widely recognized that the electrode microstructural characteristics significantly affect the electrochemical efficiency and durability of both fuel cells and batteries [5–9]. This has been widely investigated in the literature especially for solid oxide fuel cells (SOFCs) [10,11], which are chosen as the main focus of this study. Traditionally, the electrochemical behavior of the electrodes has been interpreted using macro-homogeneous models [12–16], which describe the conservation and transport of charged and chemical species in 1D or 2D by assimilating the porous microstructure to a homogeneous continuum, with averaged microstructural properties represented by effective transport and geometrical parameters [17,18]. Such effective microstructural properties were estimated only by using percolation models [19,20] until 3D tomography enabled the reconstruction of the real electrode microstructure [21–25].

However, despite the availability of the full structural details across different length scales, microstructural analysis has to date been still largely limited to obtaining averaged parameters, which characterize the electrode structure as a whole. Some examples include the tortuosity factor [21,26,27], which is a measure of how convoluted the conduction and diffusion pathways are, or the three-phase boundary (TPB) density [28,29], which is the length per unit volume of the contact perimeter among different conducting phases where charge-transfer occurs. In this way, complex 3D information is reduced to a single averaged value to simplify modeling. While simulating the transport and reaction processes within the reconstructed 3D microstructure has become computationally affordable [30–42], the full potential of such a three-dimensional electrochemical simulation has not yet been totally exploited. For example, 3D electrochemical simulation has been used to predict voltage profiles along the electrode thickness or polarization curves, which can be done with high fidelity by continuum models too [43–47]. However, 3D electrochemical simulation can be used to go beyond the predictions of macro-homogeneous models and to quantify the heterogeneous distribution of electrochemical processes [48,49], assessing the occurrence of hot spots or unbalanced current distribution which may trigger degradation phenomena [38,39], so that to identify their primary causes in order to guide the rational design of the electrode microstructure. Notably, at the present no experimental technique is capable to probe such three-dimensional inhomogeneous current distribution, thus modeling represents the only strategy currently available to provide this type of advanced guidelines. To the best of our knowledge, to date there are no published studies regarding the three-dimensional quantification of inhomogeneous current distribution and its implications on performance optimization and degradation. Such an improved understanding can be achieved by resolving the conducting phases into individual particles and characterizing the current distribution at the micro/nanoscopic particle level.

In this paper we propose a completely new methodology for the advanced microstructural characterization at the particle level, moving away from viewing the microstructure as a monolithic block, and explore its potential in both real and synthetic 3D electrodes, enabling identification of regions with specific properties relevant to performance as well as prediction and design of improved micro and nanostructures. As a case study to apply this methodology, we consider the functional layer of a porous SOFC anode made of Ni as the electron-conducting phase and scandia-stabilized zirconia (ScSZ) as the ion-conducting phase (see Fig. 1a). First, we mesh the digitally reconstructed phases (Fig. 1b) and solve for the transport and electrochemical reactions of charges and gas species within the 3D electrode microstructure, thus obtaining the electric potential, current density and gas concentration in every point of the corresponding phase (Fig. 1c). Then, the microstructure is resolved into individual particles (Fig. 1d and e), allowing for the quantification of the statistical distribution of current and other truly three-dimensional properties at the particle level. This approach enables exploitation of the full information contained in 3D microstructural datasets, enabling fundamental understanding of the reasoning behind inhomogeneous current and/or potential distributions, with their consequent impact on electrode lifetime, and suggesting strategies for the advanced design of porous electrodes.

2. Materials and methods

2.1. 3D tomography and generation of synthetic microstructures

The electrode under consideration is a porous SOFC anode made of Ni and ScSZ (solid volume fraction Ni/ScSZ equal to 40/60), operating at 973 K in 97% H_2–3% H_2O gas mixture [50,51], wherein the following electrochemical reaction:

$$H_{2(g)} + O^{2-}_{(ScSZ)} \rightarrow H_2O_{(g)} + 2e^{-}_{(Ni)} \quad (1)$$

is assumed to occur at the three-phase boundaries (TPBs) between the Ni, ScSZ and pore phase. The microstructure of this real electrode was reconstructed by using 3D tomography as described by Tariq et al. [52]. The electrode was impregnated with epoxy resin under vacuum to enhance the phase contrast during focused ion beam-SEM (FIB-SEM) tomography. A Ga-ion beam was used to mill a region of $\sim 2{\cdot}10^3\ \mu m^3$ for a total electrode thickness of 17 μm and thus acquire consecutive images with a voxel resolution of 30 nm. SEM images were aligned and segmented by using ImageJ [53] and Avizo 7.0.1 (Visualization Science Group, Mérignac, France). Fig. 1a shows a 3D rendering of the microstructure analyzed. The reconstructed domain can be viewed as the functional layer of a typical anode-supported SOFC. Notably, the functional layer is more relevant than the supporting layer in terms of 3D inhomogeneous current distribution because, in the functional layer, transport phenomena and electrochemical reactions interact each other. On the contrary, the supporting layer may be effectively described with a continuum approach [54].

Three synthetic microstructures were generated by using the packing algorithm described by Bertei et al. [55] and converted in voxel-basis by using isotropic voxels of 30 nm. The three synthetic structures consisted of a three-dimensional random arrangement of overlapping spherical particles within a box with square base of $12^2\ \mu m^2$ and thickness of 16.8 μm, nominally having the same porosity (~30%), Ni solid volume fraction (~40%) and mean particle diameter (~1.2 μm) of the tomographic dataset. The first synthetic structure, named “Synth 00”, was produced by using mono-dispersed particles while the other two structures, “Synth 20” and “Synth 40” respectively, were generated according to a Gaussian distribution of the particle diameter, centered at 1.2 μm, with a nominal standard deviation of 20% and 40%, respectively. A 3D rendering of the synthetic microstructures is shown in Fig. S1.

Both the real and synthetic microstructures were meshed in Simpleware ScanIP 7.0 (Synopsys, Mountain View, USA) to obtain conformal meshes of $\sim 40{\cdot}10^6$ elements.

2.2. Electrochemical modeling

The 3D numerical model, implemented in Comsol 5.2 [56] and reported in Table S1, is based on the conservation of electrons, oxygen ions and hydrogen within the corresponding phases, that is, Ni, ScSZ and pore phase, respectively. The physics and electrochemistry are kept as simple as possible to highlight only the effect of the 3D microstructure on the inhomogeneous current distribution. Within the bulk of each phase there is neither production nor consumption of charged or chemical species. The electronic and ionic current densities, I_e and I_O,