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Accessible triple-phase boundary length: A performance metric to account for transport pathways in heterogeneous electrochemical materials

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HIGHLIGHTS

- The accessible TPB length is proposed as a new metric to characterize microstructures.
- The transport pathways to each TPB site in the structure are probed and characterized.
- Accessible TPB in SOFC and packed sphere structures exceeds one order of magnitude.
- Effects of local geometry and network topology on the accessible TPB are quantified.
- Presence of central segments indicates the non-uniform utilization of the structures.

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ABSTRACT

The performance of materials for electrochemical energy conversion and storage depends upon the number of electrocatalytic sites available for reaction and their accessibility by the transport of reactants and products. For solid oxide fuel/electrolysis cell materials, standard 3-D measurements such as connected triple-phase boundary (TPB) length and effective transport properties partially inform on how local geometry and network topology causes variability in TPB accessibility. A new measurement, the accessible TPB, is proposed to quantify these effects in detail and characterize material performance.

The approach probes the reticulated pathways to each TPB using an analytical electrochemical fin model applied to a 3-D discrete representation of the heterogeneous structure provided by skeleton-based partitioning. The method is tested on artificial and real structures imaged by 3-D x-ray and electron microscopy. The accessible TPB is not uniform and the pattern varies depending upon the structure. Connected TPBs can be even passivated. The sensitivity to manipulations of the local 3-D geometry and topology that standard measurements cannot capture is demonstrated. The clear presence of preferential pathways showcases a non-uniform utilization of the 3-D structure that potentially affects the performance and the resilience to alterations due to degradation phenomena. The concepts presented also apply to electrochemical energy storage and conversion devices such as other types of fuel cells, electrolyzers, batteries and capacitors.

1. Introduction

The advances of 3-D imaging methods during the last decade have significantly improved the understanding of the relationships between the microstructure and performance of heterogeneous materials for electrochemical energy conversion and storage [1–3]. Nowadays, metric and topological properties are measured directly on 3-D reconstructions of the materials imaged by e.g. x-ray nanotomography (XNT) or focused ion beam-scanning electron microscopy (FIB-SEM) serial sectioning [2–8]. This capability provides insight into how the assembly of the constituents, i.e. the

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morphology and topology of the phases and their interfaces, impact the material functionality, which is essential for the rational design of heterogeneous materials [9].

The relationship between the triple-phase boundary (TPB) length in solid oxide fuel or electrolysis cell (SOFC/SOEC) composite materials and the polarization resistance has been first ascertained using patterned electrode experiments [10–12]. The performance of SOFC/SOEC materials therefore largely depends upon the TPB length formed in the structure and the ability to transport ions, electrons and gas species to these TPB reaction sites. At present, the two functions are treated as partially coupled in several SOFC/SOEC performance and degradation studies. The approach is based upon the measurement of the effective transport properties of the phases and of the connected TPB length, which is the subset that has connected pathways for ions, electrons and gas species to flow to the electrolyte, current collection and gas channel, respectively. The development of methods for the accurate measurement of these properties, among others, using 3-D reconstruction has been the subject of significant effort [2,4,5,7,13–15]. The measurements are then applied to materials produced by different fabrication routes or subjected to aging or specific treatments and, in some cases, their effects on the electrode polarization resistance are assessed using continuum electrode models. This approach has contributed to significant improvements of our understanding of the detrimental effects of microstructural coarsening, contamination or redox cycling in SOFC/SOEC materials [6,8,16–23].

A main limitation of approaches based on averaged (e.g. effective) properties is that all the TPBs are treated as equally accessible. The visual inspection of 3-D imaging data suggests that this assumption is questionable and that significant local information is lost. In contrast, the TPB tortuosity and TPB critical pathway radius have been recently proposed for the characterization of the transport pathways to TPBs [24]. This approach, based on image processing, provides new insight into the factors that control the electrochemical performance of heterogeneous materials, but it is based on purely geometric concepts that highlight two specific and mostly local properties of the reticulate pathways, i.e. the shortest path length and the smallest constriction that must be passed through to access a TPB. Simulations based on lattice Boltzmann or finite element method that use as computational domain the imaged and meshed 3-D structures [4,25] are capable of quantifying accurately the access to TPB, including the combined effects of local 3-D geometrical features and topology of the microstructure. However, attempts to define dedicated TPB properties that inform on material performance and durability have been limited so far [4], partly because of the high computational requirements.

An analytical electrochemical fin model (ECF) has been recently developed as a screening tool for material design [26–29]. The method represents the heterogeneous structure as a network of segments. Each segment is characterized for simplification into 1-D axisymmetric shape profiles for which analytical solutions to the combined surface charge transport and charge transport problem exist. This simplification yields computation times that are at least three orders of magnitude faster than that of typical finite element simulations. The computation time for ECF does practically not exceed a few seconds for typical volume samples obtained by x-ray nanotomography (XNT) or focused ion beam – scanning electron microscopy (FIB-SEM). Comparisons with 3-D finite-element simulation results of artificial and real structures imaged by x-ray nanotomography and electrochemical impedance spectroscopy (EIS) measurements have shown that adequate sensitivity to local 3-D geometry and network topology is retained [28,29]. With such capabilities, the ECF method is not restricted to the calculations of standard transport properties or polarization resistance. The low computational requirement resulting from the implementation of analytical solutions extends its use as a method to probe heterogeneous structures, in a way similar to shortest-path algorithms to measure metrics relevant in graph theory, such as node betweenness, for instance [30]. However, the current approach is fully informed about all 3-D pathways in the complex structure.

In this study, the accessible TPB is proposed as a new measurement to characterize the access to TPBs in materials with multiple material phases and 3-D heterogeneity, and hence support the assessment and comparison of their performance. The approach extends measurements from existing purely geometric concepts to physical modelling to further the links between 3-D microstructural characterization and material performance.

This new measurement method applies the ECF method to a 3-D discrete representation of the heterogeneous structure provided by skeleton-based partitioning to sequentially probe the pathways to each TPB site, within each phase separately or together. The capability of the accessible TPB to characterize differences among materials and to extract additional information on the factors that control material performance and reliability compared to that of standard metric and topological properties is illustrated on composite SOFC/SOEC electrode materials and artificial packed sphere structures with controlled properties. The coherent sensitivity to local geometry and topology is tested using the differences in microstructures in the dataset and further, by local and targeted manipulation of the material.

2. Methodology

2.1. The concept of accessible TPB

The access to TPBs in a heterogeneous material depends upon the transport phenomena and the morphology and topology of the complex 3-D pathways within the phases. A simplified 2-D schematic of this problem in Fig. 1a illustrates the concept. The measure of the number or length of TPBs, based on 2-D micrograph or 3-D reconstruction is known as the total TPB. In Fig. 1a, the red square, blue circle and green diamonds indicate a selection of TPBs for illustration. Only part of this selection is available for electrochemical reaction, which depends upon several conditions. The two TPBs indicated by the red square and blue circle belong to the subset of connected TPBs, i.e., they have connected pathways to the exterior of the material within all the phases. However, the TPB connected through the red pathway has lower accessibility than the blue one, because of narrower constrictions and higher tortuosity. In real heterogeneous materials, the pathways to the TPBs are not single as in the 2-D simplification shown in Fig. 1a, but they are multiple, three dimensional, and reticulate.

Section 2.4 and 2.5 provides the detailed description of the accessible TPB measurements within the phases and how the combined and total accessible TPB are obtained. The accessible TPB within the phases is the measure of the effective conductivity σ of the ionic, electronic and pore transport path networks between each TPB and the electrolyte, current collection and gas channels, respectively. The upper bound is the material phase bulk conductivity σ_o and the subset of connected TPBs corresponds to $\sigma > 0$. The measurement of the access to each TPB yields a distribution with as independent variable the common logarithm of the conductivity ratio σ/σ_o. To prepare for the discussion of results, Fig. 1b is intended to provide an intuitive view of the information conveyed by accessible TPB measurements, using selected limiting cases. A value of $\log_{10}(\sigma/\sigma_o)$ of zero corresponds to the limiting case of an idealized material made of a superposition of materials, where each phase will conceptually occupy all the volume. Further, all TPBs are equally accessible, which yields a distribution with a single infinite peak at zero (i in Fig. 1b). In the case of a material made of an