



Multi scale and physics models for intermediate and low temperatures H^+ -solid oxide fuel cells with $H^+/e^-/O^{2-}$ mixed conducting properties: Part A, generalized percolation theory for LSCF-SDC-BZCY 3-component cathodes

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H I G H L I G H T S

- Generalized percolation theory for typical H^+ -SOFC composite cathodes.
- Effects of the microstructure parameters on H^+ -SOFC electrode characteristics.
- Coexisting sites of O_2 , e^- , and O^{2-} transport paths for oxygen reduction reaction.
- Coexisting sites of O^{2-} , H^+ and H_2O transport paths for vapor formation reaction.
- Effective e^- , O^{2-} , H^+ conducting and gas diffusing capabilities.

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H^+ based solid oxide fuel cell (SOFC) composite cathodes are generally agreed to be of quite different relationships among the microstructure parameters, electrode properties and detailed working processes from the conventional O^{2-} -SOFC composite cathodes. In this paper, the percolation theory is significantly generalized and developed to suit most of the typical H^+ -SOFC composite cathodes with e^-/H^+ , e^-/O^{2-} or $e^-/H^+/O^{2-}$ mixed conducting characteristics; not just limited to the BCZY, SDC and LSCF materials. It provides an easy way to investigate the effect of microstructure parameters on the H^+ -SOFC electrode characteristics in quantity. The studied electrode properties include: i) the potential coexisting sites of O_2 , e^- , and O^{2-} transport paths for the oxygen reduction; ii) the potential coexisting sites of O^{2-} , H^+ and H_2O transport paths for the vapor formation; iii) the effective e^- , O^{2-} , and H^+ conducting and gas diffusing capabilities of the composite cathodes, and so on. It will be helpful for the H^+ -SOFC composite cathode manufacture to achieve the expected properties. Furthermore, it is also an important step for the developing of the multiphysics-model in manuscript part B to study the effect of the microstructure parameters on the H^+ -SOFC working details.

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1. Introduction

Solid oxide fuel cell (SOFC) is considered as a promising energy

converting technology due to the efficiency, cleanliness and capability of working with various fuels [1–6]. In the past decade, extensive efforts were devoted to lowering the working temperature of SOFCs to the low and intermediate temperature range, because high temperature enforces strict material cost limitation, compatibility constraint and challenging operational complexity [1,7,8]. As one of the potential alternatives, the proton conducting based SOFCs (H^+ -SOFC) have been receiving more and more

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attentions [9], because of lower activation energy of proton transport compared with that of O^{2-} transport and the vapor formation at the cathode other than the anode side [10,11]. Low activation energy implies the proton conductivities of these materials have less temperature dependence. Producing the vapor at the cathode side would significantly benefit the anode-support type H^+ -SOFCs due to the following reasons: faster fuel transport greatly decreases the concentration overpotential within the support anode; the fuel will not be diluted during the working process and higher fuel utilization and Nernst potential can be expected [10]; easy to control the fuel-vapor ratio for the reforming of the hydrocarbon fuel.

Cathode is considered to be one of the most important components to support the H^+ -SOFC performance. Up to now it can be divided into three types: the pure electronic conducting medium (i.e., Pt); the e^- and O^{2-} mixed conducting mediums (i.e., LSM-SDC, LSCF and LSCF-SDC) [12]; and the e^- , O^{2-} and H^+ mixed conducting mediums (i.e., LSCF-BZCY and NBSCF) [10,13]. Taking the e^- , O^{2-} and H^+ mixed conducting cathode as an example, more and more functions are required to achieve the high H^+ -SOFC performance. These functions consist of, but not limited to the following characteristics: a) sufficient coexistence sites of the O_2 , e^- and O^{2-} transport paths to support the electrochemical reaction of oxygen reduction; b) enough coexistence sites of the O^{2-} , H^+ and vapor transport paths to support the electrochemical reaction of vapor formation; c) high species transport capabilities for both the oxidant and produced vapor; d) high e^- , O^{2-} and H^+ conducting capabilities; e) proper thermal conductivity to match with other components; and f) sufficient mechanical strength to resist the vapor producing pressure around the cathode/dense electrolyte interface. Obviously, the H^+ -SOFC performance is a tradeoff of the H^+ , O^{2-} , e^- conducting, species diffusing and the electrochemical reaction processes for both the oxygen reduction and vapor formation. In other words, the O^{2-} , H^+ , e^- and species will choose the most convenient path to be transported and converted among each other to achieve the minimal potential drop; and this relies on how to obtain a good compromise among the detail effective properties by adjusting the cathode composition and microstructure parameters. Therefore, as the art of the H^+ -SOFC composite cathode manufacture developing, there is an increasing need to find a convenient approach to present the effect of the detail cathode compositions and microstructure parameters on the effective electrode characteristics.

The stereological techniques are considered to be effective methods to figure out the high resolution 3D image of the cathode microstructure [14,15]. Although they can enhance the understanding on the microstructure morphology, only a very small configuration region of the whole electrode structure can be figured out; and the experimental processes are expensive and time consuming. Percolation theory is generally considered as an effective engineering approach to predict the particle connecting conditions within a composite medium from the microstructure parameters; and these connecting conditions will further affect effective mechanical, electrochemical, electric and thermal conducting properties of the composite medium. The empirical expression of coordination numbers were used by Bouvard [16] and Suzuki [17] to represent the microstructure connecting conditions within a binary random packing sphere medium. Then, the theory was further developed by Costamagna et al. [18] to relate these coordination numbers with the electrode properties. After that, the percolation theory was widely used to predict the effects of microstructure parameters on the effective properties of composite mediums [19–22]. Recently, the empirical expressions that were used to calculate the coordination number was revised to satisfy the conservation principle of overall contact numbers [23]; and the

percolation theory was generalized to suit a 3-component convenient composite electrodes (i.e., Coarse and fine YSZ- and LSM-particles). Then the effect of the typical poly-disperse particle size distribution of each material [24,25] and the pore former was further considered into the percolation model [26]. More, recently, the percolation theory was further generalized to suit the O^{2-} -SOFCs composite electrode using the mixed conducting materials (i.e., LSCF-SDC and LSCF-LSM) [6].

It is well known that the typical H^+ -SOFC composite cathodes with e^- , H^+ , O^{2-} mixed conducting characteristics show very different functional requirements from the conventional O^{2-} -SOFC composite cathodes. Thus, developing of a proper method to present the effect of the microstructure parameters on their specific characteristics in quantity is essential to guide the H^+ -SOFC composite cathode manufacture to achieve the expected properties. Furthermore, it is also an important step for the developing of the multiphysics-model in manuscript part B to predict the effect of the microstructure parameters on the H^+ -SOFC working details; and find the proper parameters to achieve the best balance among the H^+ , e^- , O^{2-} conducting, gas diffusing and the electrochemical reaction processes for both the oxygen reduction and vapor formation. In this paper, the percolation theory is significantly generalized and developed to suit most of the typical H^+ -SOFC composite cathodes with e^-/H^+ , e^-/O^{2-} or $e^-/H^+/O^{2-}$ mixed conducting characteristics; not just limited to the LSCF-SDC-BZCY materials. Then, all the calculated results are presented in nondimensional form to provide considerable generality in practical application. It is an important step to relate the microstructure parameters with the H^+ -SOFC electrode properties in quantity; and can enhance our understanding on how to adjust the microstructure parameters to achieve the expected effective cathode properties for a specific H^+ -SOFC.

2. Theory and model

Taking the typical 3-component LSCF-BZCY-SDC composite cathode as an example, the developing of the generalized percolation theory for various H^+ -SOFC composite cathodes are illustrated. It is necessary to mention that the application of the developed percolation theory will not be limited to the composite cathode using LSCF, SDC and BZCY; it can also be applied to many types of H^+ -SOFC composite electrodes using different compositions that possess the e^-/O^{2-} , e^-/H^+ or $e^-/O^{2-}/H^+$ mixed conducting properties. Although the proton conducting material $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ may also present the O^{2-} and e^- conducting capabilities, their values are negligible compared with the H^+ conductivity of BZCY, e^- conductivity of LSCF and the O^{2-} conductivities of both LSCF and SDC materials around the inter and low temperature regimes [11,27,28]. Thus, it is reasonable to consider BZCY as a pure proton-conduction material in this study.

2.1. The microstructure image and physical-chemical processes within the typical H^+ -SOFC LSCF-BZCY-SDC composite cathode

As the electrochemical reactions and the O^{2-} , e^- , H^+ , O_2 and vapor transporting processes within the H^+ -SOFC composite cathodes are complicated and very different from that within the convenient O^{2-} -SOFC cathodes, the microstructure diagram of a typical LSCF-SDC-BZCY 3-component H^+ -SOFC composite cathode is depicted in Fig. 1 to provide a way to easily understand its working process and particular property requirements. Different color particles indicate LSCF-, SDC- and BZCY-particles. Arrows with different colors represent the e^- , O^{2-} , H^+ and reactant species transporting paths. Different from the conventional O^{2-} -SOFCs, the electrochemical reactions within an H^+ -SOFC consists of both the

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