

Modelling of a SOFC graded cathode

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Abstract

One approach to improve the cathodic performances in a SOFC is to use a composite electrode which typically consists in a two phase porous mixture of a solid electrolyte (YSZ) and an electrocatalytic material (M). In our model, the cathode is composed of a mono-disperse porous mixture of YSZ and M spherical particles. From simulations by means of a statistical approach, the percolation rate is optimized for a compact particle stacking, a sufficient thick electrode, a volume fraction of YSZ equal to 0.5 and by grading the electrode composition for large porosity values. A one dimensional homogeneous model also predicts better cathodic performances by grading electrode composition and increasing ionic conductivity within the composite electrode.

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1. Introduction

One way to enhance the cathodic performances of an intermediate temperature solid oxide fuel cell (IT-SOFC) is to elaborate a two phase composite electrode, composed of a mixture of a solid electrolyte (YSZ) and an electronic conducting electrocatalytic material M (typically LSM), which composition varies in some spatial direction. Such a design is intended to take advantage of certain desirable features of each of the constituent phases^{1,2} and to improve the functionality of individual layers. By using graded cathodes, polarisation resistances as low as $0.07 \Omega \text{ cm}^2$ at 850°C have been recorded,^{3,4} indicating that improvement of the microstructure is one of the key parameter to reach high electrochemical performances⁵ in case of oxygen reduction occurring at the triple phase boundary line. The theoretical analysis of the effect of electrode geometric parameters on charge transfer was mainly performed on anodes^{6–8} and in composite LSM–YSZ cathodes.⁹

The optimization of a composite cathode requires improvements of ionic and electronic conductivities to support ion and electron flows, as well as porosity for gas supply. In

this work, a theoretical model of a porous composite YSZ–M cathode is studied. The role of both electrode thickness and composition on the percolation rate is discussed by means of a statistical approach. Predictions from simulations are compared to experimental literature data.

2. Physical and mathematical descriptions

A schematic representation of the porous composite electrode is sketched in Fig. 1. It is assumed that spherical grains of both conductors are of same diameter $d_g = 1 \mu\text{m}$, and that the electrode is in perfect contact with a porous electronic current collector at the gas side and with dense YSZ. Adsorbed oxygens are formed from the oxygen gas according to a dissociative adsorption step which occurs on the pore walls. The adsorbed oxygen is reduced at the three phase boundary line with consumption of an oxygen vacancy $V_0^{\bullet\bullet}$ from YSZ, creating two electron holes h^\bullet in M and incorporation of an oxygen ion O_0^X into YSZ.¹⁰

The ionic conduction is the most relevant charge transport process occurring in a graded electrode.^{11,12} Ohmic losses in the well connected electronic conductor phase are neglected, and thus this phase can be regarded as equipotential. The mobility of oxygen vacancies in YSZ is a function of the electric

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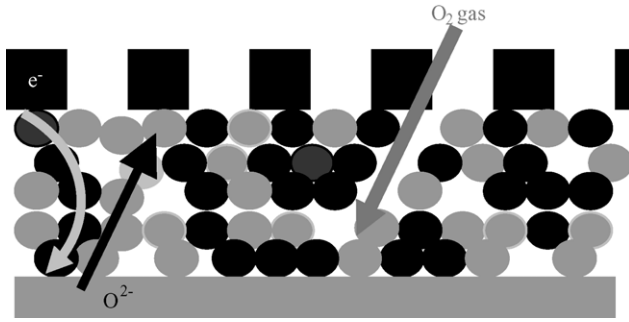


Fig. 1. Schematic representation of a mono-disperse porous YSZ–M cathode. Black circles: M grains; grey circles: YSZ grains; empty space: gas filled pores.

field. Based on a isothermal and one dimensional homogeneous model,¹³ the porous composite electrode is treated as an effective homogeneous medium characterised by an effective ionic conductivity κ^{eff} which depends on the microstructural features of the electrode:

$$\kappa^{\text{eff}} = T_{\text{per}} \varepsilon_a \frac{1 - \varepsilon}{\tau} \kappa \quad (1)$$

where T_{per} is the percolation rate (ionic + electronic); κ , the ionic conductivity of YSZ; ε_a , the volume fraction of YSZ; ε , the porosity and τ , the tortuosity.

The overpotential distribution in the porous electrode can be calculated by means of the oxygen vacancy balance and Ohm's law within the ionic phase yielding the following equation:

$$\kappa^{\text{eff}} \frac{d^2 \eta}{dx^2} - 2Fr_e = 0 \quad (2)$$

where r_e is the charge transfer rate.¹⁰ This differential equation has to be solved together with the following boundary conditions: the local current density is nil at the gas/electrode interface ($x=0$) and the electrode overpotential is constant at the electrode/YSZ interface ($x=L$). Solving mass and charge balance equations yields the distribution of electrode overpotential versus the position x within the porous electrode. The total current per unit surface area of composite electrode is then calculated as a sum of the faradaic current densities along the electrode thickness:

$$i = -2F \int_0^L r_e(x) dx \quad (3)$$

The distribution of ε_a through the electrode is assumed to vary linearly versus the position x according to:

$$\varepsilon_a = \frac{x}{L} \Delta \varepsilon_a + \frac{2\bar{\varepsilon}_a - \Delta \varepsilon_a}{2} \quad (4)$$

where $\bar{\varepsilon}_a$ is the average volume fraction of YSZ while $\Delta \varepsilon_a$ is the magnitude of the related gradient expressed by:

$$\Delta \varepsilon_a = \varepsilon_a(L) - \varepsilon_a(0) \quad (5)$$

For the percolation calculation, the mixture of spherical particles of both conductors was treated either as a face cen-

tered cubic lattice (high compactness fcc) or a simple cubic lattice (low compactness c). Each sphere (YSZ or M) has 12 nearest neighbours in the former (high compactness) and only 6 in the less compact one. The porosity was varied by substituting spheres by voids. Under this assumption, it is possible to simulate the mean pathways of ions and electrons through the electrode. Since both ionic and electronic percolations are similarly described for spherical grains, only the overall percolation is simulated by using a statistical model based on a Boolean approach. Such an approach requires to generate random matrices including some non-active zones due to porosity. Each grain crossed by ions or electrons is treated as a non-isolated grain. Accordingly, the percolation rate T_{per} represents the ratio of the number of non-isolated grains to the total number of grains.

3. Results and discussion

Calculations of the percolation rate were performed several times to determine a statistical evolution. In order to describe the geometry, we have considered the number of grains per cube edge N_e . As could be expected, the percolation rate is an increasing function of N_e for both stackings (Fig. 2). Regardless of the N_e value, T_{per} is always found higher for a compact stacking and an asymptotic value equal to 0.996 is reached for $N_e > 15$. These results suggest that the higher the electrode thickness, the better is the percolation, in agreement with improved electrochemical performances observed experimentally.¹⁴ In order to reduce computing times, N_e was chosen equal to 20 for further simulations.

Fig. 3 shows the percolation rate versus the volume fraction of YSZ for both lattices. In agreement with the above results, the percolation rate is typically higher for a fcc stacking. Despite T_{per} is equal to 1 for $\varepsilon_a = 0$ and $\varepsilon_a = 1$, these peculiar cases are not of interest because no delocalization of the oxygen reduction within the electrode can be reached (i.e. a porous metallic electrode on a dense YSZ substrate or a porous YSZ substrate in contact with a porous current collector, respectively). Regardless of the stacking, T_{per} is

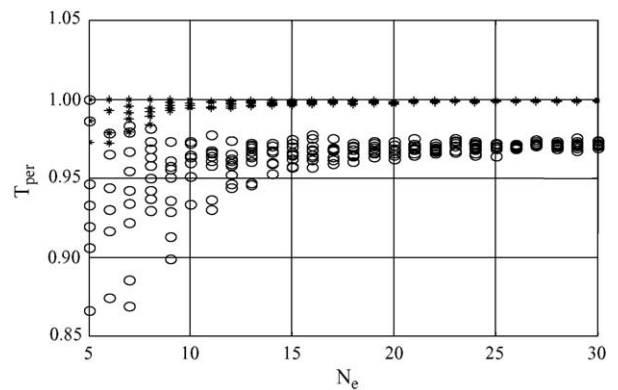


Fig. 2. Percolation rate vs. the electrode volume for c (○) and fcc (*) stackings (10 launches).

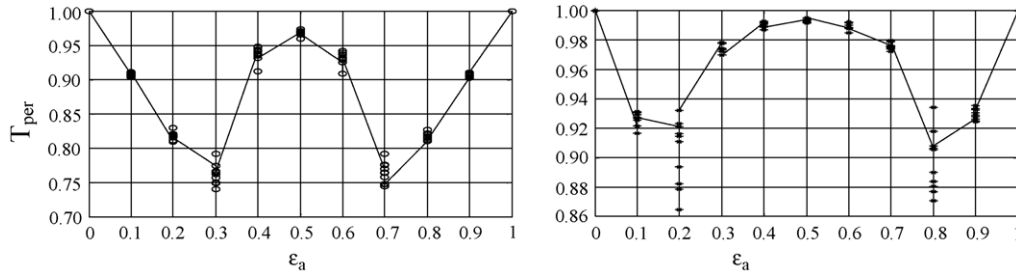


Fig. 3. Percolation rate vs. the volume fraction of YSZ for c (○) and fcc (*) stackings ($N_c = 20$, 10 launches).

optimal for $\epsilon_a = 0.5$, as already reported in the literature.^{5,15} A peculiar effect is that the composition range within T_{per} is optimal, is wider for a compact stacking. Both recorded minima correspond to the percolation threshold for a granular mixture.^{16,17} These results are confirmed by simulations of Iosevich et al.¹⁸ and impedance measurements performed by Hodgson et al.¹⁹

In porous composite electrodes, one way to better accommodate the different thermal expansion coefficients of YSZ and M is to grade the composition. The percolation was thus simulated for a cubic stacking by varying the gradient $\Delta\epsilon_a$ and the porosity ϵ (Fig. 4). For low porosity values, there is no real gain in the percolation rate by grading composition. T_{per} is higher for an homogeneous electrode composition ($\Delta\epsilon_a = 0$ in Eq. (4)). However, a composition gradient is required to reach sufficient percolation rates for higher porosities. The higher the porosity, the higher must be $\Delta\epsilon_a$. In agreement with experimental data,² the statistical approach predicts that better electrochemical performances might be recorded when there is no electronic conductor at the electrode/YSZ interface and only M in contact with the current collector at the gas side.

An increasing composition gradient results in a reduced ionic ohmic drop due to an optimized ionic migration process by enlarging cross sectional area (Fig. 1). The predictions of our model are in well agreement with the results of Wang et al.²⁰ which have confirmed that the effectiveness of

a LSM–YSZ composite cathode can be improved by increasing intimate contacts area between YSZ particles and the YSZ substrate. A decrease of the polarisation resistance of similar cathodes was also interpreted by an enhancement of contacts between spherical grains.² Since the electrode consists of pure electronic conductor at the external surface when $\Delta\epsilon_a = 1$, a better current collecting can also be anticipated.

In order to confirm the main influence of the effective ionic conductivity of a composite electrode (Eq. (1)) on the recorded electrochemical performances,²¹ simulations were performed as a function of the ionic conductivity of YSZ for two extreme composition gradients ($\Delta\epsilon_a = 1$ and $\Delta\epsilon_a = 0$).¹⁰ The reported results clearly indicate that grading composition is helpful to improve ionic transport through the electrode and, thus, electrochemical performances for operating temperatures lower than 800 °C.

4. Conclusion

Based on simple particle stackings, the statistical model predicts the variation of the percolation rate versus both electrode morphology and composition in well agreement with literature data. For instance, the higher the electrode thickness, the higher is the percolation rate. Reported results clearly indicate that improved cathodic performances require a control of both parameters, keeping in mind that increasing porosity should be damaging. Although the effective ionic conductivity is of peculiar importance, one can expect that grading the electrode composition is the best way to increase the oxygen reduction rate in IT-SOFCs.

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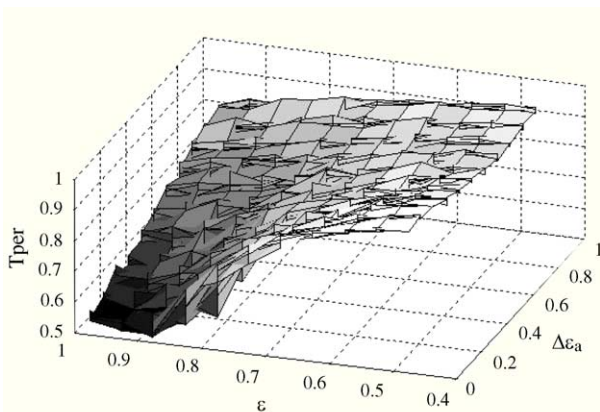


Fig. 4. Percolation rate as functions of porosity and composition gradient for a cubic stacking ($N_c = 20$, $\epsilon_a = 0.5$, 10 launches).

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