

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 approach, 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.

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 those 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 performances [5] 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 firstly discussed by means of a statistical approach. The peculiar influence of a composition gradient and the effective ionic conductivity on simulated polarisation curves is then investigated by using the homogeneous model. 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 Figure 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 (regardless of the nature of the particle):



where s stands for an adsorption site and O-s for an adsorbed oxygen. This step is assumed at equilibrium and obeys to the Langmuir isotherm (relative coverage of adsorbates $\theta \ll 1$).

The adsorbed oxygen is reduced at the three phase boundary line with consumption of an oxygen vacancy $V_0^{\bullet\bullet}$ from YSZ, creation of two electron holes h^{\bullet} in M and incorporation of an oxygen ion O_0^X into YSZ:



and the related charge transfer rate is given by:

$$r_e = av_{tpb}\Gamma \left(k_e \exp\left(-\frac{2\alpha F}{RT}\eta\right) \theta c_v^{YSZ} - k_{-e} \exp\left(\frac{2(1-\alpha)F}{RT}\eta\right) (1-\theta) \right) \quad (3)$$

where η is the electrode overpotential, k_e and k_{-e} are the forward and backward kinetic constants, α is the symmetry factor, c_v^{YSZ} is the oxygen vacancy concentration in YSZ and Γ is the maximal concentration of adsorbates. The specific electrochemical area av_{tpb} can be expressed from the extension zone around the three phase boundary line which depends on grain size (d_g) and number of grains (N_g) [10].

The local faradaic current density j_f through the electrochemical surface is expressed from the charge transfer step (Eq. (2)) by:

$$j_f = -2F r_e \quad (4)$$

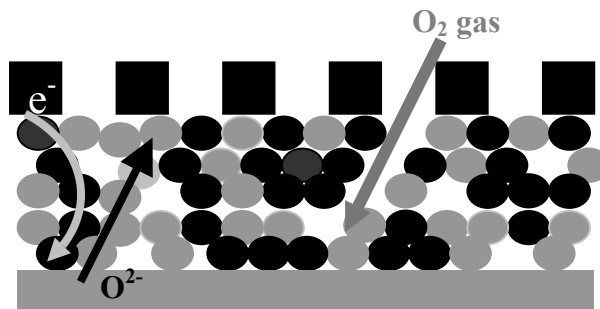


Figure 1. Schematic representation of a mono-disperse porous YSZ-M cathode. Black circles: M grains; grey circles: YSZ grains; empty space: gas filled pores.

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 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:

$$\kappa^{\text{eff}} = T_{\text{per}} \epsilon_a \frac{1-\epsilon}{\tau} \kappa \quad (5)$$

where T_{per} is the percolation ratio, κ is the ionic conductivity of YSZ, ϵ_a is the volume fraction of YSZ and τ is the tortuosity.

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

$$\kappa^{\text{eff}} \frac{d^2\eta}{dx^2} - 2Fr_e = 0 \quad (6)$$

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 of composite electrode is then calculated as a sum of the faradaic current densities (Eq. (4)) along the electrode thickness:

$$i = -2F \int_0^L r_e(x) dx \quad (7)$$

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

$$\epsilon_a = \frac{x}{L} \Delta\epsilon_a + \frac{2\bar{\epsilon}_a - \Delta\epsilon_a}{2} \quad (8)$$

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

$$\Delta\varepsilon_a = \varepsilon_a(L) - \varepsilon_a(0) \quad (9)$$

For the percolation calculation, the mixture of spherical particles of both conductors was treated either as a face centred 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 substitution of a sphere by void. 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 the porosity. Each grain crossed by ions or electrons is treated as a non-isolated grain. Accordingly, the percolation ratio T_{per} represents the ratio of the number of non-isolated grains to the total number of grains.

3. Results and discussion

The standard values for the parameters used for numerical simulations of the polarisation curves are listed in Table 1. The kinetic constants were chosen in order to obtain cathodic current densities similar to the ones recorded in experimental SOFC working conditions. Calculations of the percolation rate were performed several times to determine a statistical evolution.

Table 1. Standard parameters used for simulations.

Parameter	Refs	Parameter	Refs
$T = 1073.15 \text{ K}$	This work	$\varepsilon = 0.3$	This work
$L = 5 \cdot 10^{-5} \text{ m}$	This work	$\varepsilon_a = 0.5$	This work
$P_{O_2} = 0.2 \text{ atm}$	This work	$\kappa = 1 \text{ S m}^{-1}$	[15]
$c_v^{YSZ} = 6 \cdot 10^3 \text{ mol m}^{-3}$	[14,15]	$\tau = 1.3$	This work
$av_{tpb,0} = 1 \text{ m}^{-1}$	This work	$\theta_{eq} = 10^{-4}$	[14]
$\alpha = 0.5$	[14,16]	$\Gamma = 10^{-5} \text{ mole m}^{-2}$	[14]

3.1. Effect of the electrode thickness

In order to describe the geometry, it is simpler to consider 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 (Figure 2). Regardless of the N_e value, T_{per} is always 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 experimental [17]. In order to reduce computing times, N_e was chosen equal to 20 for further simulations.

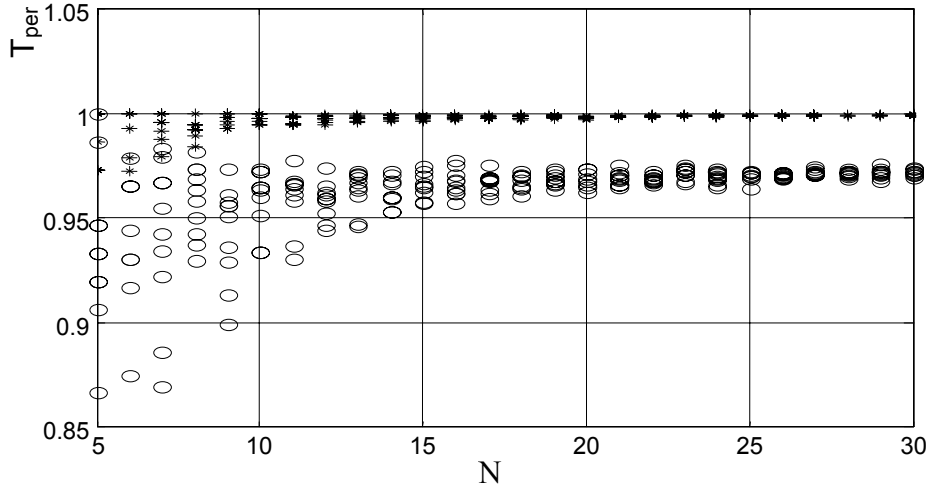


Figure 2. Percolation versus the electrode volume for c (O) and fcc (*) stackings (10 launches).

3.2. Effect of composition

Figure 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 $\epsilon_a = 0$ and $\epsilon_a = 1$, 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 optimal for $\epsilon_a = 0.5$, as already reported in the literature [5,18]. 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 [19,20]. These results are confirmed by simulations of Ioselevich et al. [21] and impedance measurements performed by Hodgson et al. [22].

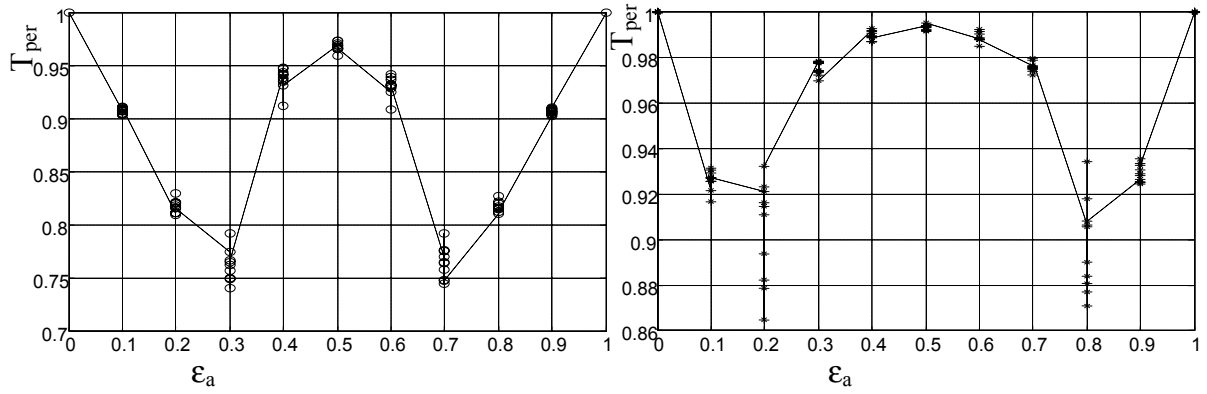


Figure 3. Percolation rate versus the volume fraction of YSZ for c (O) and fcc (*) stackings ($N_e = 20, 10$ launches).

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 (Figure 4). For low porosity values, there is no real gain in the percolation rate by grading composition. T_{per} is higher for an homogeneous composition of the electrode ($\Delta\epsilon_a = 0$ in Eq. (8)). 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. This is confirmed by the results of Figure 5 showing the polarisation curves simulated from our homogeneous model.

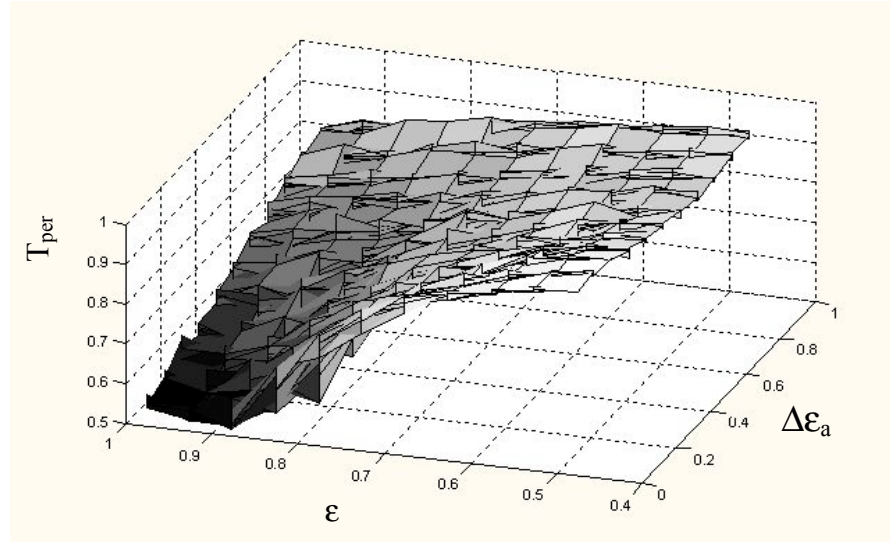


Figure 4. Percolation rate as functions of porosity and composition gradient for a cubic stacking ($N_e = 20$, $\varepsilon_a = 0.5$, 10 launches).

For a given activation polarisation, an increasing composition gradient results in a reduced ionic ohmic drop due to an optimized ionic migration process by enlarging cross sectional area. The predictions of our model are in well agreement with the results of Wang et al. [23] 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 $\Delta\varepsilon_a=1$, a better current collecting can also be anticipated. Let us mention that simulations were performed by fixing the specific electrochemical area av_{tpb} to a constant value.

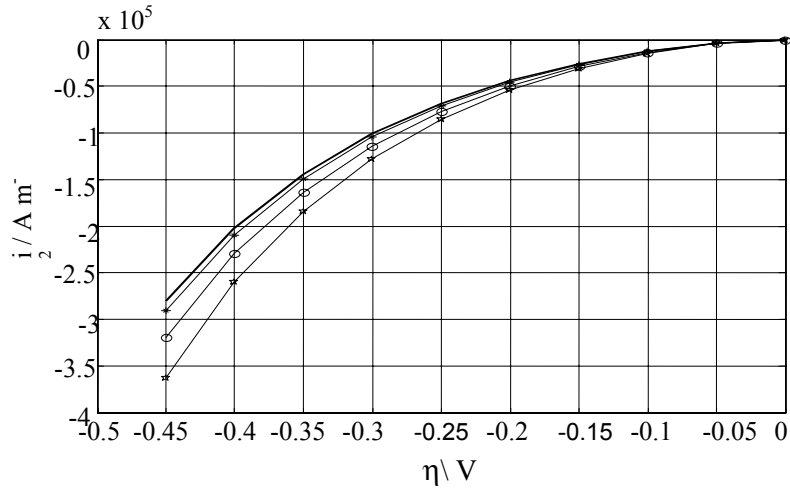


Figure 5. Influence of composition gradient on simulated cathodic polarisation curves

($\varepsilon=0.3$, $\bar{\varepsilon}_a=0.5$). ($/$) $\Delta\varepsilon_a = 1$; (O) $\Delta\varepsilon_a = 0.5$; ($*$) $\Delta\varepsilon_a = 0.1$; ($—$) $\Delta\varepsilon_a = 0$.

3.3. Effect of ionic conductivity

In order to confirm the main influence of the effective ionic conductivity of a composite electrode (Eq. (5)) on the recorded electrochemical performances [24], simulations were performed as a function of the ionic conductivity of YSZ for two extreme composition gradients ($\Delta\varepsilon_a = 1$ and $\Delta\varepsilon_a = 0$). As shown in Figure 6, grading improves the oxygen reduction kinetics for ionic conductivity values up to 1 S m^{-1} . When κ is equal to 10 S m^{-1} , value corresponding to an operating temperature around typically $1100 \text{ }^\circ\text{C}$ for YSZ, the electrochemical performances of both kinds of electrode are similar. The current density is even higher for a homogeneous composite cathode ($\Delta\varepsilon_a = 0$) when $\kappa = 100 \text{ S m}^{-1}$. Without any variation of porosity and grain size, the recorded variation does not originate from a decreasing specific electrochemical area. It only corresponds to a significant increasing current constriction effect near the gas/electrode interface with the κ value [9]. 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 $800 \text{ }^\circ\text{C}$.

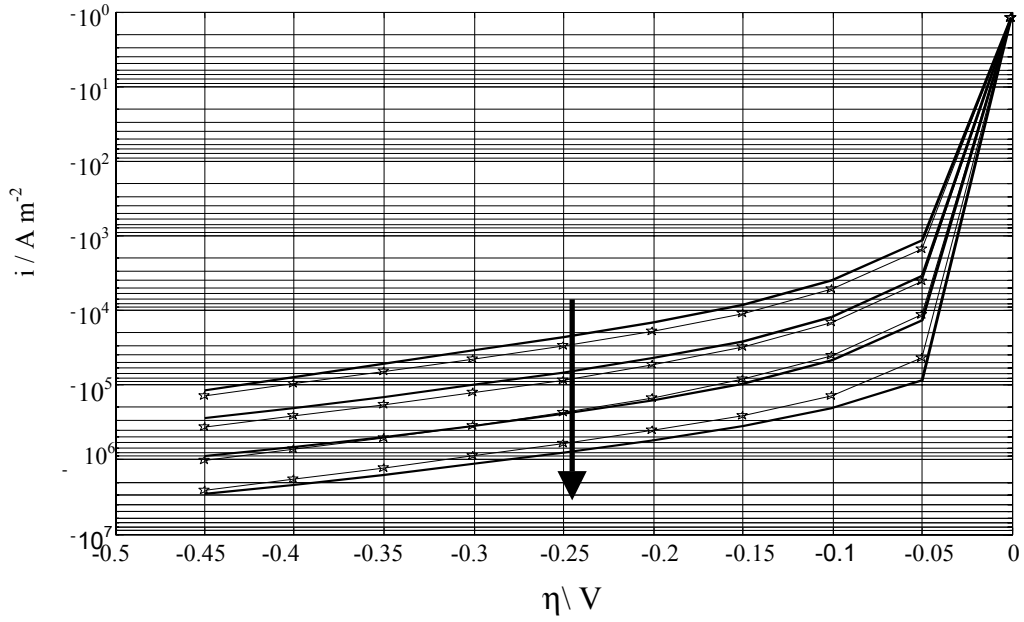


Figure 6. Influence of ionic conductivity on simulated cathodic current density ($\epsilon=0.3$, $\bar{\epsilon}_a=0.5$). (---) $\Delta\epsilon_a = 1$; (—) $\Delta\epsilon_a = 0$. The arrow indicates increasing ionic conductivity value ($\kappa=0.1, 1, 10$ and 100 S m^{-1}).

5. 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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