

# Engineered Electrode Microstructure for Optimization of Solid Oxide Fuel Cells

Antonio Bertei\*, Benedetta Nucci, Cristiano Nicolella

Dipartimento di Ingegneria Civile e Industriale, Università di Pisa, Largo Lucio Lazzarino 2, 56126, Pisa, Italia  
[antonio.bertei@for.unipi.it](mailto:antonio.bertei@for.unipi.it)

This paper presents a mathematical model for the description of transport and reaction phenomena in porous composite electrodes for solid oxide fuel cell (SOFC) applications. The model is based on charge and mass balances, describing transport of charged and gas species along with the electrochemical reaction occurring at the solid/gas phase interface. Effective properties of the porous media are evaluated on numerically reconstructed microstructures. The correlation between electrode microstructure and electrochemical performance is investigated. In particular, the study focuses on how a distribution of particle size within the thickness may improve the air-electrode efficiency. The results show that distributing smaller particles at the electrolyte interface reduces the sensitivity of the cathode efficiency to the electrode thickness, with clear advantages from the manufactory point of view. However, the conditions for which this advantage is relevant, that is, particle size smaller than 0.10  $\mu\text{m}$  and porosity in the order of 15 %, are not technically achievable at the present.

## 1. Introduction

Solid oxide fuel cells (SOFCs) have attracted research interest due to their expected high efficiency of energy conversion, fuel flexibility and low emission of pollutants (Larminie and Dicks, 2003). An SOFC is an energy conversion device which operates at high temperature (usually higher than 600 °C) to electrochemically convert the chemical energy of a renewable or fossil fuel directly into electricity. The cell consists of two electrodes, namely the cathode (air-electrode) and the anode (fuel-electrode), wherein, respectively, oxygen is reduced and the fuel is oxidized. The electrodes are separated by the electrolyte, a dense ceramic layer which transports oxygen ions from the cathode, wherein they are formed, to the anode (Singhal and Kendall, 2003).

The cathode represents the main source of energy loss in hydrogen-fed SOFCs (Adler, 2004). Porous composite cathodes, consisting in sintered random packings of particles as illustrated in Figure 1a, are commonly used to improve the cell performance. Within the cathode, molecular oxygen reacts with electrons to form oxygen ions, therefore converting oxygen from the gas form into the ionic form. The reaction occurs at the three-phase boundary (TPB) between gas phase, electron-conducting particles and ion-conducting particles (Figure 1b). The global oxygen conversion rate depends on both the reaction rate at the TPB and the rate at which charge and mass are transported within the electrode (Bertei et al., 2011).

The transport and reaction phenomena occurring within the electrode can be described through conservation equations (Bertei et al., 2012a). Physically-based mathematical models (Bessler et al., 2007) have improved the understanding of the mechanisms governing the SOFC performance and allow the quantitative estimation of cell performance (Andersson et al., 2010).

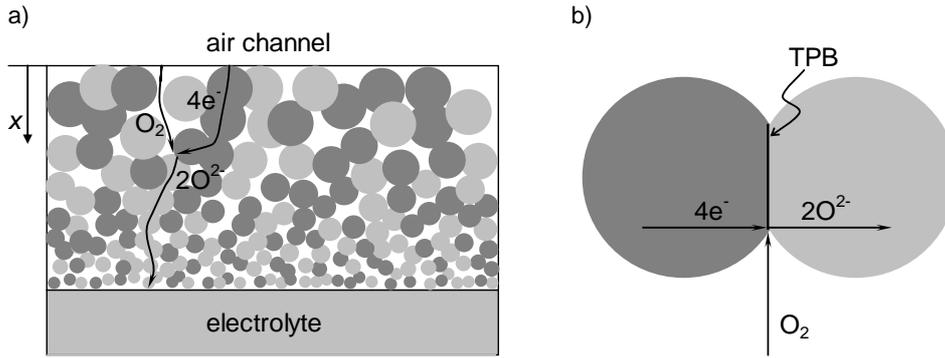


Figure 1: a) schematic representation of a composite SOFC cathode with a distribution of particle size along the thickness; b) reaction occurring at the three-phase boundary

In this paper, a mathematical model for the description of mass and charge transport phenomena coupled with electrochemical reaction at TPB is presented. Special attention is taken to the connection between electrode performance and microstructural properties, which significantly affect the electrode efficiency (Juhl et al., 1996). A numerical study on the effect of porosity and particle size is performed. In addition, the study addresses if a distribution of particle size along the electrode thickness (see Figure 1a) may improve the electrochemical performance, while in the past similar studies were performed considering a distribution of porosity (An et al., 2010).

The paper is organized as follows: in Section 2 the model is presented, Section 3 reports the numerical results obtained with the model, conclusions are summarized in Section 4.

## 2. Mathematical modelling

The model is based on the following main assumptions:

- Steady-state conditions;
- Uniform temperature;
- No mixed conduction in the electron-conducting and ion-conducting phases.

The model consists in the set of balance equations, reported in Table 1, for the three reacting species (molecular oxygen, electrons and oxygen ions) and for nitrogen, which does not react. The equations describe the consumption of molecular oxygen and electrons at the TPBs to form oxygen ions. The model was validated by Bertei et al. (2012b) over a wide range of temperatures and gas stream conditions for composite cathodes made of strontium-doped lanthanum manganite (LSM) as electronic conductor and yttria-stabilized zirconia (YSZ) as ionic conductor, which are the object of this study.

A linear distribution of particle size along the electrode thickness is considered for simulations as follows:

$$d(x) = d_{\min} + \kappa \cdot (L - x) \quad (1)$$

where  $d$  is the particle size along the axial coordinate  $x$ ,  $d_{\min}$  the particle size at the electrolyte interface,  $\kappa$  the gradient of particle size and  $L$  the electrode thickness.

As boundary conditions, at the air channel interface the oxygen ion flux is set to 0 while the inlet electron flux corresponds to the current density fed to the electrode. Both pressure and oxygen molar fraction are set equal to the gas stream conditions within the air channel. At the electrolyte interface, gas fluxes and electron flux are null since the electrolyte is a dense ion-conducting layer, while the outlet oxygen ion flux accounts for the total current density. The electric potential of the ion-conducting phase is set at 0 V as reference point (Zhu and Kee, 2008). The solution of the model allows the calculation of the electrode overpotential, which is the main performance index to be minimized (Costamagna et al., 1998).

As reported in Table 1, transport of charged species in solid phase is described according to the Ohm law. The gas transport within the pores is described as a function of pressure and oxygen molar fraction by using the Dusty-Gas Model (Mason and Malinauskas, 1983), which comprises convection and diffusion (both ordinary and Knudsen). The reaction rate at TPB follows a global electrochemical kinetics, reported in Table 2, which was experimentally obtained in patterned LSM/YSZ electrodes (Kenney and Karan, 2007).

Table 1: Model equations

Species	Balance equation	Flux
Electrons	$\frac{dN_e}{dx} = -\frac{i_{TPB}\lambda_{TPB}}{F}$	$N_e = \frac{\sigma_{el}^{eff}}{F} \frac{dV_{el}}{dx}$
Oxygen ions	$\frac{dN_o}{dx} = \frac{i_{TPB}\lambda_{TPB}}{2F}$	$N_o = \frac{\sigma_{io}^{eff}}{2F} \frac{dV_{io}}{dx}$
Molecular oxygen	$\frac{dN_O}{dx} = -\frac{i_{TPB}\lambda_{TPB}}{4F}$	$N_O = -\beta_o \frac{dy_o}{dx} - \gamma_o \frac{dP}{dx}$
Nitrogen	$\frac{dN_I}{dx} = 0$	$N_I = \beta_I \frac{dy_o}{dx} - \gamma_I \frac{dP}{dx}$

Table 2: Electrochemical kinetics (Kenney and Karan, 2007)

Quantity	Equation
Current density at TPB	$i_{TPB} = i_0 \left[ \exp\left(\alpha_a \frac{F}{RT} \eta\right) - \exp\left(-\alpha_c \frac{F}{RT} \eta\right) \right]$
Exchange current	$i_0 = i_0^{ref} \left(\frac{P_O}{P_O^{ref}}\right)^{0.375} \cdot \exp\left[-\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T^{ref}}\right)\right]$
Overpotential	$\eta = -\frac{RT}{4F} \ln\left(\frac{P_O^{ch}}{P_O}\right) - V_{el} + V_{io}$

Table 3: Model parameters and working conditions used in simulations

Quantity	Symbol	Value
Temperature	$T$	700 °C
Channel pressure	$P^{ch}$	$1.0 \cdot 10^5$ Pa
Oxygen molar fraction within the channel	$y_o^{ch}$	0.21
Applied current density	$I$	4000 A/m <sup>2</sup>
LSM volume fraction	$\psi_{el}$	50 %
LSM bulk conductivity	$\sigma_{el}$	$2.99 \cdot 10^4$ S/m
YSZ bulk conductivity	$\sigma_{io}$	0.84 S/m
Activation energy	$E_a$	$1.4 \cdot 10^5$ J/mol
Transfer coefficients	$\alpha_a - \alpha_c$	1.5 - 0.5
Reference current density (945 °C, $0.21 \cdot 10^5$ Pa)	$i_0^{ref}$	$2.5 \cdot 10^{-4}$ A/m

Effective properties used in the model, such as the effective gas diffusivity, the effective electric conductivity, the TPB length density, are evaluated through Monte-Carlo simulations on microstructures numerically generated by using a packing algorithm (Bertei et al., 2012c). This approach allows the elimination of empirical correlations and fitted parameters from the modelling framework. In Table 3, the main model parameters and working conditions are summarized, corresponding approximately to the best conditions currently used in SOFC applications (Nam and Jeon, 2006).

### 3. Results and discussion

#### 3.1 Porosity and particle size

Assuming no particle size distribution (i.e.,  $\kappa = 0$ ), the dependence of microstructural properties on porosity and particle size is reported in Figure 2. Microstructural properties are evaluated on numerically reconstructed electrodes through Monte-Carlo simulations. As the porosity decreases, both the effective electric conductivity and the TPB length per unit volume increase. In addition, the TPB length per unit volume increases as the particle size decreases while the effective conductivity is independent of the particle size.

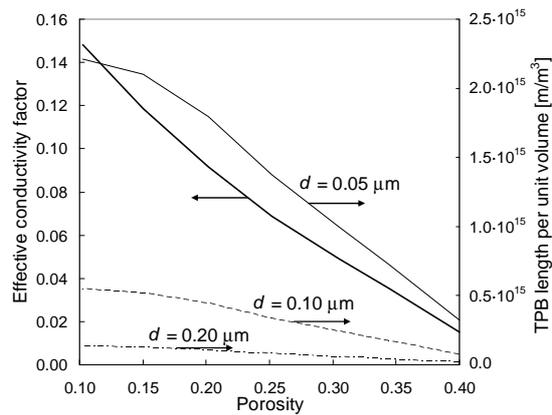


Figure 2: effective conductivity factor and TPB length per unit volume as a function of porosity and particle size from microstructural simulations

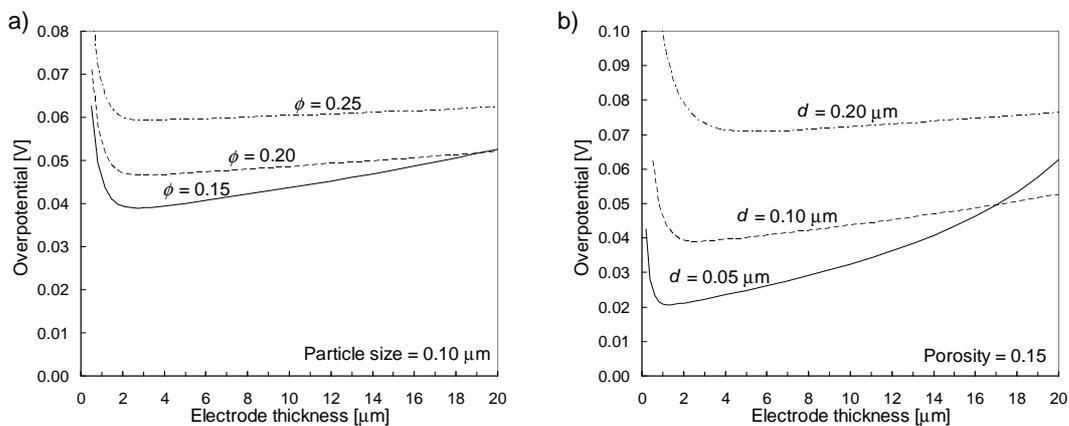


Figure 3: cathode overpotential as a function of thickness without distribution of particle size: a) constant particle size; b) constant porosity

The effect of microstructural modifications on the electrochemical behaviour of SOFC composite electrodes is reported in Figure 3. Given the porosity and the particle size, the cathode overpotential exhibits a minimum as a function of thickness. In fact, small electrodes are kinetically limited by the small number of reaction sites (that is, the small extension of TPB). On the other hand, concentration gradients in gas phase lead to an increase in cathode overpotential in thick electrodes.

Figure 3a shows that, given the particle size, as the porosity decreases, the minimum of cathode overpotential decreases, that is, the electrode becomes more efficient. The increase in electrode performance is due to the larger effective conductivity and TPB density per unit volume provided by the reduction in porosity, as discussed for Figure 2.

Given the porosity, Figure 3b shows that the minimum of cathode overpotential decreases as the particle size decreases. This is a consequence of the larger TPB length per unit volume as reported in Figure 2. On the other hand, both Figure 3a and 3b show that, after the minimum condition, the cathode overpotential increases with thickness, more sharply when small particle size and low porosity are used. This behaviour is due to the reduction in pore size, which leads to reduce the transport properties of the gas phase and, as a consequence, the supply of molecular oxygen to the reaction sites.

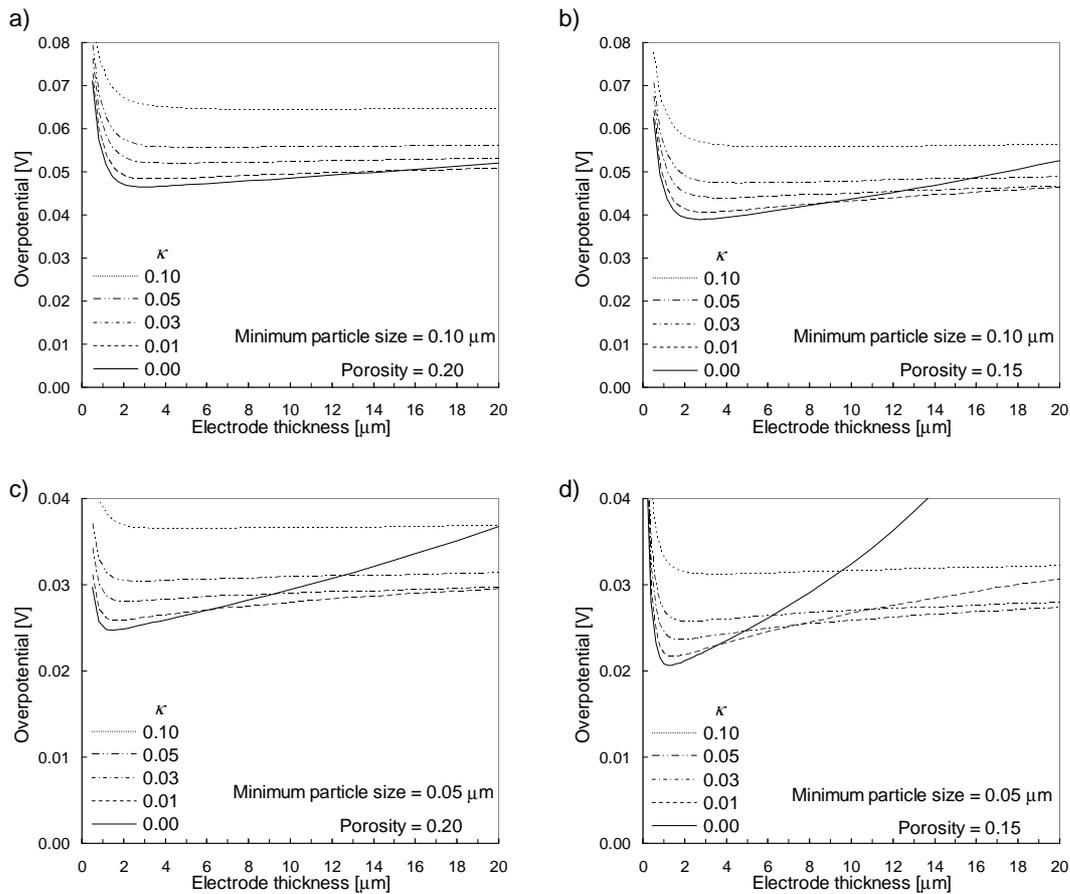


Figure 4: cathode overpotential as a function of thickness with particle size distribution

### 3.2 Distribution of particle size

The results reported in Section 3.1 suggest to use a distribution of particle size along the thickness as illustrated in Figure 1a. In fact, small particles at the electrolyte interface lead to increase the TPB length where the reaction occurs, while coarser particles in the remainder of the cathode promote gas transport, that is, the supply of molecular oxygen to the reaction sites.

Figure 4 shows the cathode overpotential as a function of thickness for cathodes with a linear particle size distribution along the thickness. Different porosities and minimum particle sizes  $d_{min}$  are analyzed.

The results show that as the gradient  $\kappa$  increases, the performance worsens since the cathode overpotential becomes larger. On the other hand, especially for small particles sizes (Figures 4c and 4d), a weak distribution of particle size (i.e.,  $\kappa = 0.01-0.03$ ) allows the stabilization of the overpotential with thickness since the minimum condition becomes less sharp. In fact, the performance becomes less sensitive to the electrode thickness if compared with the case with no particle size distribution ( $\kappa = 0$ ). This stabilization may help the manufactory of composite cathodes because a high precision in the electrode thickness is not required.

## 4. Conclusions

A model of transport and reaction in SOFC porous electrodes was developed and applied to composite cathodes to assess the dependence of electrode performance on the microstructural parameters, which were evaluated on numerically reconstructed microstructures.

The results showed that reducing both porosity and particle size has a positive effect on the cathode efficiency since the effective charge transport properties and the density of reaction sites increase. However, a significant sensitivity on the electrode thickness was revealed for the cathodes showing the

highest performances, which was due to the arising of gas transport limitations resulting from the decrease in pore size.

In order to overcome this limitation, a linear distribution of particle size along the thickness, with smaller particles at the electrolyte interface, was considered in the study. Numerical simulations showed that the cathode performance decreases as the gradient of particle size increases. However, for small gradients, the cathode overpotential becomes less sensitive to the thickness, which may be an advantage for the manufactory. Obviously, while the electrode overpotential becomes less sensitivity to the thickness, it is more sensitive to the particle size distribution.

It is noteworthy that the advantages of a distribution of particle size are significant only when small porosities and small particle sizes are used. However, for the current state-of-the-art, technological issues, such as the grain growth during the cell operation (Cronin et al., 2011), are expected in such conditions. Such technological issues may force to use bigger particles for which a distribution of size has no real advantage. Thus, nowadays the distribution of particle size along the thickness is not useful. This engineered microstructure may be a feasible solution to limit the sensitivity on the cathode thickness when it will be possible to use sub-micrometric particles without any secondary technological issue.

## References

- Adler S.B., 2004, Factors governing oxygen reduction in solid oxide fuel cell cathodes, *Chem. Rev.* 104, 4791-4843.
- An C.M., Song J.-H., Kang I., Sammes N., 2010, The effect of porosity gradient in a Nickel/Yttria Stabilized Zirconia anode for an anode-supported planar solid oxide fuel cell, *J. Power Sour.* 195, 821-824.
- Andersson M., Yuan J., Sundén B., 2010, Review on modeling development for multiscale chemical reactions coupled transport phenomena in solid oxide fuel cells, *Appl. Energy* 87, 1461-1476.
- Bertei A., Nicoletta C., Thorel A.S., 2011, Mathematical modelling of transports and reactions in an innovative solid oxide fuel cell, *Chemical Engineering Transactions*, 24, 127-132, DOI: 10.3303/CET1124022.
- Bertei A., Thorel A.S., Bessler W.G., Nicoletta C., 2012a, Mathematical modeling of mass and charge transport and reaction in a solid oxide fuel cell with mixed ionic conduction, *Chem. Eng. Sci.* 68, 606-616.
- Bertei A., Barbucci A., Carpanese M.P., Viviani M., Nicoletta C., 2012b, Morphological and electrochemical modeling of SOFC composite cathodes with distributed porosity, *Chem. Eng. J.* 207-208, 167-174.
- Bertei A., Choi H.-W., Pharoah J.G., Nicoletta C., 2012c, Percolating behavior of sintered random packings of spheres, *Powder Technol.* 231, 44-53.
- Bessler W.G., Gewies S., Vogler M., 2007, A new framework for physically based modeling of solid oxide fuel cells, *Electrochim. Acta* 53, 1782-1800.
- Costamagna P., Costa P., Antonucci V., 1998, Micro-modelling of solid oxide fuel cell electrodes, *Electrochim. Acta* 43, 375-394.
- Cronin J.C., Wilson J.R., Barnett S.A., 2011, Impact of pore microstructure evolution on polarization resistance of Ni-Yttria-stabilized zirconia fuel cell anodes, *J. Power Sour.* 196, 2640-2643.
- Juhl M., Primdahl S., Manon C., Mogensen M., 1996, Performance/structure correlation for composite SOFC cathodes, *J. Power Sour.* 61, 173-181.
- Kenney B., Karan K., 2007, Engineering of microstructure and design of a planar porous composite SOFC cathode: A numerical analysis. *Solid State Ionics* 178, 297-306.
- Larminie J., Dicks A., 2003, *Fuel cell systems explained*, Wiley, Chichester, UK.
- Mason E.A., Malinauskas A.P., 1983, *Gas Transport in Porous Media: The Dusty-Gas Model*, Elsevier, Amsterdam, the Netherlands.
- Nam J.H., Jeon D.H., 2006, A comprehensive micro-scale model for transport and reaction in intermediate temperature solid oxide fuel cells, *Electrochim. Acta* 51, 3446-3460.
- Singhal S.C., Kendall K., 2003, *High temperature solid oxide fuel cells: Fundamentals, design and applications*, Elsevier, Oxford, UK.
- Zhu H., Kee R.J., 2008, Modeling distributed charge-transfer processes in SOFC membrane electrode assemblies. *J. Electrochem. Soc.* 155, B715-B729.