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Morphology and electrochemical activity of SOFC composite cathodes: II. Mathematical modelling

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Abstract This paper presents a mathematical model of mass and charge transport and electrochemical reaction in porous composite cathodes for application in solid oxide fuel cells. The model describes a porous composite cathode as a continuum, and characterises charge and mass transfer and electrochemical kinetics using effective parameters (i.e. conductivity, diffusivity, exchange current) related to morphology and material properties by percolation theory. The model accounts for the distribution of morphological properties (i.e. porosity, tortuosity, density of contacts among particles) along cathode thickness, as experimentally observed on scanning electron microscope images of LSM/YSZ cathodes of varying thickness. This feature allows the model to reproduce the dependence of polarisation resistance on thickness, as determined by impedance spectroscopy on LSM/YSZ cathodes of varying thickness. Polarisation resistance in these cathodes is almost constant for thin cathodes (up to 10 μm thickness), it sharply decreases for intermediate thickness, to reach a minimum value for about 50 μm thickness, then it slightly increases in thicker cathodes.

Keywords Modelling · Composite electrodes · LSM-YSZ · Solid oxide fuel cells

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List of symbols

a	Contact surface area (m^2)
F	Faraday constant (C mol^{-1})
i	Current density (A cm^{-2})
j	Current density (A (contact point)$^{-1}$)
i_0	Exchange current (A cm^{-2})
j_0	Exchange current (A (contact point)$^{-1}$)
k	Compression factor
n_V	Density of contact points (contact point m^{-3})
R	Resistance (Ω cm^2)
R_g	Gas constant (J mol^{-1} K^{-1})
T	Temperature (K)
V	Potential (V)
X	Volume fraction
z	Axial coordinate (m)

Greek letters

α	Transfer coefficient
δ	Cathode thickness (m)
γ	Relative grey level
η	Overpotential (V)
ρ	Resistivity (Ω m)
τ	Tortuosity

Subscripts

el	Electronic
io	Ionic
p	Polarisation
tot	Total
tr	Transfer

Superscripts

0	Single-component material
cr	Percolation threshold
eq	Equilibrium
r	Relative

1 Introduction

Performance of electrodes for solid oxide fuel cell (SOFC) applications is determined, among other factors, by the extent of the surface area where the electrochemical reaction (i.e. electron transfer) occurs. To increase the active contact area between electrocatalyst and electrolyte (both in the solid state), SOFC electrodes are fabricated as random composite structures of electron-conducting and ion-conducting submicronic powders [1]. These composite structures must be porous to allow reactants and/or products in the gas phase to diffuse through the electrode to and/or from the active reaction sites.

Most of the energy losses in a hydrogen SOFC occur in the cathode, a random porous structure composed of electron-conducting particles (e.g. strontium-doped lanthanum manganite, LSM) and ion-conducting particles (e.g. yttria-stabilised zirconia, YSZ). Oxygen reduction by electron transfer from the electrocatalyst to form oxygen ions is the electrochemical process which takes place in a SOFC cathode. The active sites where this reaction occurs are located at the three-phase boundary between gas phase, electron-conducting phase and ion-conducting phase, to and from which reactants (molecular oxygen and electrons) and products (oxygen ions) are respectively carried. The overall cathode performance is determined by the relative rate at which the electrochemical reaction (i.e. electron transfer from the electrocatalyst to molecular oxygen) and the transport of reactants (i.e. electrons and molecular oxygen) and products (i.e. oxygen ions) take place.

The rate of electron transfer primarily depends on the mechanism by which oxygen in the gas phase is locally reduced at the active reaction sites. The exact details of the cathodic reaction process have not been completely elucidated, although it is generally accepted that reaction steps include adsorption and dissociation of molecular oxygen, migration of adsorbed species to the active reaction site, transfer of electrons to oxygen at the active reaction site [2]. The overall rate of electron transfer is the product of the specific rate at which the elementary event occurs at a single active site as well as of the total number of active reaction sites available in the cathode. The total number of active reaction sites in turn depends on the electrode microstructure, namely particle size, porosity, and volume fraction of the solid phases [3]. These structural properties also affect effective transport coefficients, such as chemical-species diffusivity, electronic conductivity, and ionic conductivity [4]. As a consequence, not only electrode catalytic activity (i.e. the rate at which the electron is transferred in the electrode), but also the rate at which electrical charges (i.e. electrons and ions) are carried by ohmic conduction, and gaseous species are carried by diffusion, will depend on electrode structure and morphology.

Porous composite cathodes have a complex morphology. Even if all relevant transport and kinetic parameters of elementary transport and electrochemical reaction events at the boundaries between two particles were known, predicting how the interplay of material properties and geometry (i.e. porosity, particle size, electrode thickness) affects cathode performance is often a demanding task. Recently, several aspects of property-performance relationships have been theoretically discussed at different levels of sophistication [5].

Despite crude simplifications, the continuum electrode approach—which models the porous composite structure of SOFC electrodes as a continuum phase characterised by effective transport and kinetic parameters (i.e. electronic conductivity, ionic conductivity, electrochemical reaction constants, gas diffusivity)—yields valuable results. This approach has been employed in several simulation studies of composite electrodes [6, 7]. The crucial task in modelling porous composite structures as continuum phases is to relate effective transport and kinetic parameters to geometrical and structural parameters. Effective conductivities of electron-conducting and ion-conducting phases are proportional to conductivities of the materials used in the composite and depend on the exact shape of the network formed by conducting particles. Percolation theory can be employed to determine the corresponding proportionality factor [8]. The electrochemical reaction rate constant can be related to the size (length or area, depending on the mechanism of charge transfer) of the three-phase boundary [9, 10], which can be rather uncertain to predict, because (i) the electrochemical reaction site is often unknown, and (ii) the size of the three-phase boundary at any single active reaction site depends on external factors, such as sintering degree. In addition to the microstructure, electrode thickness also affects the pathway taken by species participating in the electrochemical reaction. Polarisation resistance in porous composite cathodes is reported to decrease with increasing cathode thickness [1, 11], because of the increased number of available active reaction sites, until ohmic losses become dominant and limit the overall process rate, due to the increasing length of conduction pathways. As a consequence, for any operating conditions (i.e. temperature) and cathode morphology (i.e. porosity, particle size distribution) and composition, there will be an optimal thickness corresponding to the minimum polarisation resistance resulting from ohmic and activation losses. Optimal thickness can be theoretically estimated [5, 6, 12], and an asymptotic value will result [13], when (i) ion conduction and electrochemical kinetics are considered as rate limiting steps (i.e. much slower than oxygen diffusion and electron conduction), and (ii) uniform morphological properties are considered over the whole cathode thickness.

LSM/YSZ porous composite cathodes experimentally characterised in a companion paper [14] do not show such an asymptotic minimum of polarisation resistance at varying thicknesses. Polarisation resistance measured over a wide range of operating temperatures (800–900 °C) is almost constant in thin cathodes (with less than 10 μm thickness), it decreases in the intermediate range of thickness up to a minimum value observed at around 50 μm, then increases for thicker cathodes.

This behaviour cannot be predicted using assumptions commonly adopted for modelling porous composite cathodes. To give insight to the results reported by Barbucci et al. [14], this paper reports on theoretical investigations based on (i) experimental observations on the distribution of morphological properties along the thickness of porous composite cathodes, and (ii) a continuum approach to model SOFC porous composite cathodes accounting for variations of morphological properties along cathode thickness.

2 Mathematical modelling

A porous composite cathode is made of electron-conducting particles and ion-conducting particles, randomly distributed and sintered to give enough porosity for molecular oxygen diffusion (see Fig. 1). Electrochemical oxygen reduction occurs close to the contact surface between electron-conducting particles and ion-conducting particles, where electrons can be dispatched from the electronic collector through the electron-conducting phase, transferred to oxygen to produce ions, which are constantly carried away along the ion-conducting phase to the electrolyte (see Fig. 1). The electrochemical reaction (i.e. the electron transfer from the electron-conducting phase to oxygen) can be hosted at any point of contact between an electron-conducting particle and an ion-conducting-particle, provided that the gas phase

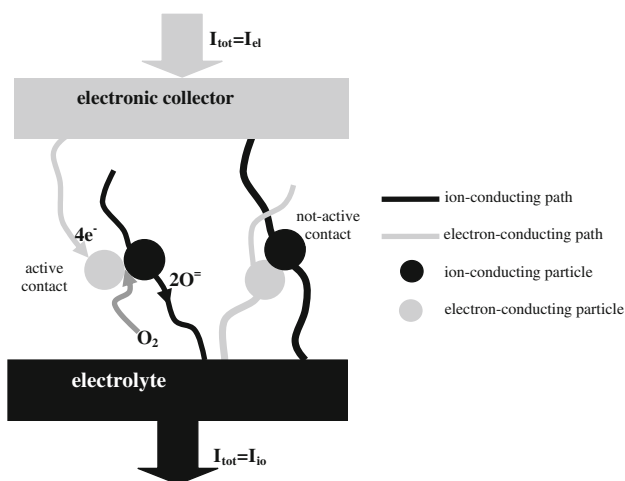**Fig. 1** Schematic view of a porous composite cathode

surrounds the contact point, and that the three phases (electron-conducting, ion-conducting and gas phase) are connected either with external sources of reactants (i.e. molecular oxygen from air and electrons from the electronic collector) or with sinks of products (i.e. oxygen ions to the electrolyte). During migration and transfer along the mixed percolative paths of connected electron-conducting particles and ion-conducting particles, electrical charges are subject to three types of resistance:

- Ohmic resistance along the electronic paths, determined by both structural properties (i.e. density and tortuosity of electron-conducting paths) and material properties (i.e. resistivity of the electron-conducting phase);
- Activation resistance to electron transfer, determined by both structural properties (i.e. density of active contacts between electron-conducting particles and ion-conducting particles), and electrochemical reaction mechanisms and kinetics;
- Ohmic resistance along the ionic paths, determined by both structural properties (density and tortuosity of the ion-conducting paths) and material properties (resistivity of the ion-conducting phase).

In addition, the overall process of charge migration and transfer may be retarded by molecular oxygen diffusion in the pores. Each of these four resistances contributes to determining the overall polarisation resistance of a SOFC cathode.

2.1 Performance/thickness relationship for porous composite cathodes

Polarisation resistance is affected by both morphology (i.e. density of active reaction sites, porosity, tortuosity) and cathode thickness. In particular, a thick cathode hosts a large number of active reaction sites, with reduced current flux per single contact point. As a consequence, thick cathodes show low activation resistance, but they may be affected by high ohmic losses. On the other hand, thin electrodes have low ohmic losses, but, due to the reduced number of active reaction sites, they are characterised by high activation losses. As a result, for any given selection of materials, morphology and operating conditions (i.e. temperature), an optimum thickness can be identified, with balanced ohmic and activation resistances to provide minimum energy losses associated with the charge flux through the electrode. Thicker cathodes with the same morphology will not show better performance (because any additional layer beyond the optimal thickness will not be active for electrochemical reaction), nor will they show higher polarisation resistance (unless electronic conduction or oxygen diffusion prevail over ionic conduction and

electrochemical reaction, which generally happens for thicknesses of no practical interest).

An asymptotic minimum of polarisation resistance at increasing cathode thickness can be theoretically estimated for any given set of effective material properties and operating conditions, using a continuum approach to model the cathode [12, 13]. Basic assumptions to be taken for optimal thickness estimation corresponding to minimum polarisation resistance are that: (i) materials are characterised by uniform distribution of physical and morphological properties in the whole cathode volume, and (ii) oxygen diffusion and electron conduction are fast processes compared to ion conduction and electrochemical reaction.

In contrast with these theoretical results on the effect of thickness on the performance of porous composite cathodes, experimental results presented in a companion paper [14] show a remarkably different behaviour. Polarisation resistance measured at different cathode thicknesses does not shows an asymptotic minimum, rather it is reported to be almost constant for thin cathodes (up to 10 μm thickness), sharply decrease for intermediate thicknesses, reach a minimum for 20 to 40 μm thickness ranges, and slightly increase in thicker cathodes.

2.2 Model assumptions

Variations of Polarisation resistance experimentally observed for different cathode thicknesses cannot be predicted when assuming uniform morphological properties of cathode materials [14]. The mathematical model presented in this work to give insight into these experimental results is based on the following assumptions:

– Steady state conditions.
– Uniform distribution of temperature in the whole cathode volume.
– Uniform distribution of other model variables (i.e. currents and potentials) and parameters (morphological, kinetic, and effective material properties) in any cross section of the cathode. This assumption results in a mono-dimensional model describing how variables and parameters change along the axial coordinate (i.e. thickness) of the cathode.
– Materials consisting of rigid spherical particles of a single size. This assumption allows the application of a simplified percolation theory. As a consequence of this assumption, the active reaction sites are the points of contacts between electron-conducting particles and ion-conducting particles.
– Negligible mass transfer resistance to oxygen diffusion through the cathode pores. As current density (i_{tot}) in SOFC cathodes is typically in the range of 1,000–5,000 A/m², oxygen flux ($N_{O_2} = i_{tot}/4F$) in the cathode

pores is so low that oxygen diffusion could become the rate limiting step, only for effective diffusivities lower by several orders of magnitude than diffusivity in the air, i.e. for very low porosity.
– Negligible ohmic resistance to electron conduction through the electron-conducting phase, compared to ohmic resistance to ion conduction through the ion-conducting phase.
– No mixed electronic-ionic conduction in either the electron-conducting phase or the ion-conducting phase.
– No electronic current at the cathode-electrolyte interface. This assumption is supported by the low number of active reaction sites at the interface compared to those in the bulk volume of the cathode.
– Electrochemical reaction kinetically limited by a single step, e.g. the transfer of a single electron, with no other limitation (e.g. adsorption, dissociation, migration).

2.3 Model equations

Cathode performance under different operating conditions (e.g. temperature) can be assessed by estimating overall polarisation resistance, defined as:

$$R_p = \frac{\eta_c}{i_{tot}} \tag{1}$$

with η_c defined as:

$$\eta_c = [V_{el}(0) - V_{io}(\delta)] - [V_{el}^{eq} - V_{io}^{eq}] \tag{2}$$

To determine polarisation resistance using Eq. 1, variations of current densities and potentials along the cathode axial coordinate are calculated by integration of electron and ion balance equations across an infinitesimal layer together with constitutive equations for conduction (Ohm law) and kinetics.

Charge balances:

$$\frac{di_{el}}{dz} = -n_v j_{tr} \qquad \frac{di_{io}}{dz} = n_v j_{tr} \tag{3}$$

Ohm law:

$$\frac{dV_{el}}{dz} = -\rho_{el}\tau_{el}^r i_{el} = 0 \qquad \frac{dV_{io}}{dz} = -\rho_{io}\tau_{io}^r i_{io} \tag{4}$$

The Butler–Volmer equation [15] is used to calculate the rate of charge transfer:

$$j_{tr} = j_0 \left(\exp\left(\alpha \frac{F}{R_g T} \eta \right) - \exp\left(-(1-\alpha)\frac{F}{R_g T}\eta \right) \right) \tag{5}$$

with overpotential defined as:

$$\eta = (V_{el} - V_{io}) - (V_{el}^{eq} - V_{io}^{eq}) \tag{6}$$

Equations 3, 4, 5, 6 are integrated with the following boundary conditions:

$$z = 0 \rightarrow i_{el} = i_{tot}; \quad i_{io} = 0 \tag{7}$$

$$z = \delta \rightarrow i_{el} = 0; \quad i_{io} = i_{tot} \tag{8}$$

2.4 Numerical solution

Since (i) the Butler–Volmer kinetic expression is not linear in the model variables (see Eq. 5), and (ii) effective material properties are not uniform along the axial coordinate, the model presented in this paper has to be numerically integrated. The steady-state set of differential and algebraic model Eqs. 3, 4, 5, 6, 7, 8 is solved using the numerical method of family lines implemented by the gPROMS Model Builder (Process System Enterprise, UK). This method involves discretisation of distributed equations as to the axial domain, whereby the problem boils down to the solution of a set of algebraic equations. The spatial domain of cathode thickness was discretised using the centred finite differences of fourth order over a uniform grid of 50 intervals.

3 Results and discussion

Key parameters (i.e. morphological parameters, kinetic parameters, and ohmic resistivities) must be estimated in order to solve model Eqs. 3, 4, 5, 6, 7, 8 and simulate cathode performance under different operating conditions. Model results validation using experimental data is then required to assess model reliability.

3.1 Model parameters

3.1.1 Cathode morphology

The experimental results on cathode morphology presented in the companion paper [14] confirm that cathode morphological properties vary along its axial coordinate. To take account of this feature in cathode modelling, the solid volume fraction in any cathode layer is assumed to be proportional to the grey level, i.e. the solid volume fraction linearly decreases along the axial coordinate with the same slope as the best linear fitting of data on the grey level, as determined by image analysis presented in the companion paper [14].

Porosity variation along cathode thickness will affect other morphological properties, namely density of active contact sites n_V and tortuosity. These morphological properties are calculated according to the percolation theory, as proposed by Bouvard and Lange [3], to describe the connectivity of random packings of rigid spherical particles. With this approach, morphological properties such as density of active contacts (i.e. those contacts among electron-conducting particles and ion-conducting particles connected
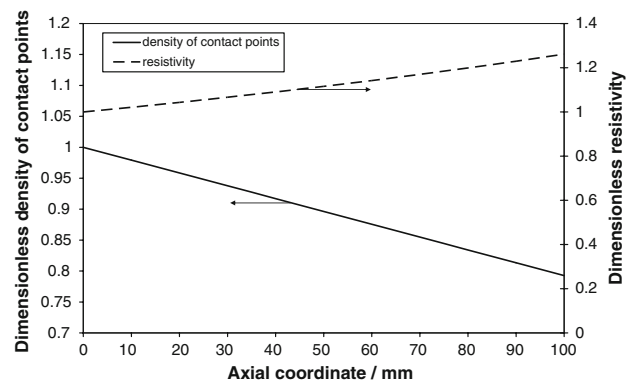
Fig. 2 Density of active contacts and resistivity of electron-conducting and ion-conducting paths as a function of position in the cathode

Table 1 Material properties, cathode design characteristics and operating conditions in the experiments performed by [14]

Material properties	
Electron conducting phase	
Material	LSM
Mean diameter	0.3 μm
Ion conducting phase	
Material	YSZ
Mean diameter	0.3 μm
Cathode design characteristics	
Diameter	5 mm
Nominal thickness	5–100 μm
Nominal porosity	40%
Volume fraction of ion-conducting particles	50%
Operating conditions	
Pressure	1 atm
Temperature	600–850 °C

to the electron collector and the electrolyte, respectively) and tortuosity of electron-conducting paths and ion-conducting paths can be estimated as a function of material properties, such as porosity, size, and volume fraction of electron-conducting and ion-conducting particles. Figure 2 reports changes—depending on the position along cathode thickness—of resistivity and density of active contacts between the solid phases, as calculated according to the approach proposed by Bouvard and Lange [3] for material properties of cathodes tested by Barbucci et al. [12] (see Table 1). In this case, the volume fraction of solid phases in the cathode is assumed to increase linearly with increasing grey level determined by image analysis on SEM pictures [14].

3.1.2 Effective resistivity of materials

YSZ (ion-conducting material) resistivity values, as determined by Carpanese [16] at different temperatures are listed

Table 2 YSZ Resistivity (sintered at 1,100 °C) at different temperature values

Temperature (°C)	YSZ resistivity (Ωm)
500	64.8
600	10.9
700	3
800	1.19
900	0.58

in Table 2. These values are regarded as those characterising a sintered—not completely dense—material. Therefore, they are higher than those expected for a dense sample, because of the reduced contact area among particles and longer conduction paths (due to the intrinsic tortuosity of a random packing of particles). The presence of electron-conducting particles in the cathode results into increased effective resistivity, because of the increased tortuosity of the ion-conducting path. The effective resistivity of the ion-conducting phase in the cathode can be calculated as:

$$\rho_{io} = \tau_{io}^r \rho_{io}^0 \tag{9}$$

where the relative tortuosity (τ^r) is the ratio between tortuosity in a composite material (made of two types of conducting particles) and that in a single-component material (made of a single type of conducting particles). Tortuosity in the composite material is expected to be very large (infinite), when the volume fraction of the conducting particles reaches the percolation threshold, and it will be equal to tortuosity of the single-component—not completely dense—material, when its volume fraction is equal to one. Relative tortuosity is calculated as:

$$\tau_j^r = \frac{k\left(X_j - X_j^{cr}\right) + 1 - X_j + X_j^{cr}}{k\left(X_j - X_j^{cr}\right)\left(1 + \frac{X_j^{cr}}{k\left(1 - X_j^{cr}\right)}\right)} \tag{10}$$

Eq. 10 is represented in Fig. 3, where it can be observed that the limits for percolation threshold ($X = X^{cr}$) and single-component material ($X = 1$) are complied with. The shape of the line in Fig. 3 depends on the value of compression factor k, chosen according to considerations discussed below (see paragraph on sensitivity analysis). Equation 10 correlates relative tortuosity of ion- (and electron-) conducting paths to morphological properties (i.e. percolation threshold X^{cr} and composition (X_{io}) of porous composite cathodes. Depending on compression factor k values, any type of dependency of relative tortuosity on composition, including both positive and negative curvatures, can be represented using Eq. 10. It is worth noting that no other correlating relationships between relative tortuosity and composition [3, 6] provide this feature.

The Arrhenius plot of intrinsic and effective YSZ conductivities presented in Fig. 4 shows that the conduction of
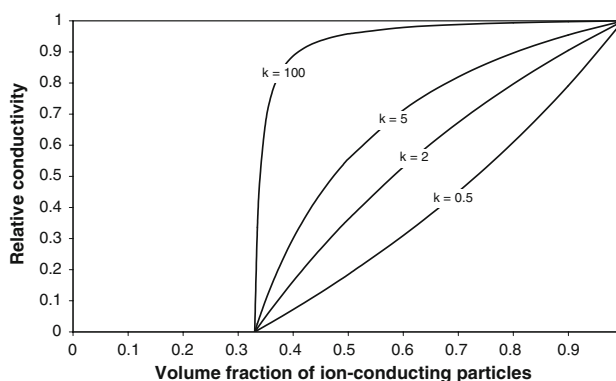
Fig. 3 Relative tortuosity as a function of cathode composition for different values of compression factor (κ)
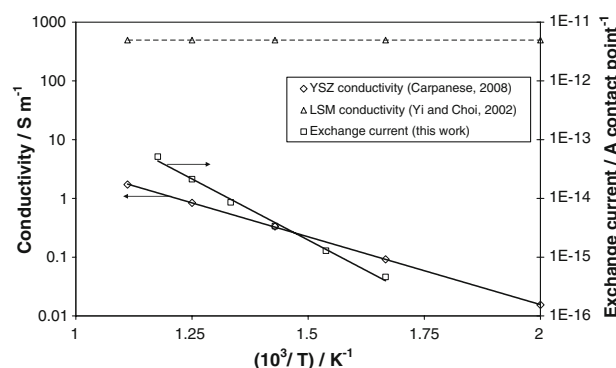
Fig. 4 Arrhenius plot for YSZ conductivity and exchange current

ions in the cathode can be regarded as a process activated by temperature.

LSM (electron-conducting material) conductivity, also plotted in Fig. 4, is reported to be almost constant with temperature within the range of operating conditions considered in this work, and 3–5 orders of magnitude higher than that of YSZ [17]. Hence, the validity of the assumption made in this work is confirmed, namely that ohmic resistance to electron conduction through the electron-conducting phase is negligible compared to ohmic resistance to ion conduction through the ion-conducting phase.

3.1.3 Electrochemical kinetics

Electron transfer kinetics is characterised by the Butler–Volmer equation, which, under the assumptions of single reaction step and negligible mass transfer resistance, reads as Eq. 5. The Butler–Volmer equation allows to calculate current density exchanged at a single contact point (j_{tr}) during the process of charge transfer, as a function of the overpotential between the electron-conducting phase and the ion-conducting phase. The corresponding kinetic parameter—the exchange current j_0—is related to the exchange current referred to the area of the contact surface as:

Table 3 Exchange currents of LSM/YSZ cathodes at different temperature values

Temperature (°C)	Exchange current $\times 10^{14}$ (A per contact point)
600	0.46
650	1.29
700	3.38
750	8.58
800	21.2
850	5.14

$$j_0 = i_0 a \qquad (11)$$

Since the area of the contact surface (a) is not readily obtainable from experimental observations, the two parameters i_0 and a cannot be estimated separately. In some cases, a is left and adjustable model parameters [6]. On the other hand, j_0 can be determined from dynamic measurements of cathode polarisation, provided that the density of contact points (i.e. the number of contact points per unit volume, n_V) is given.

In this work, a simplified discrete model of thin porous composite cathodes, as presented in a recent paper [12], is fitted on experimental polarisation curves obtained at different temperatures (in the range 600–850 °C) by Barbucci et al. [14] for a 10 μm nominal thickness cathode. Kinetic parameters obtained with this procedure are listed in Table 3.

As expected for a kinetic parameter, j_0 increases with increasing temperature. According to Eq. 11 the exchange current j_0 also depends on contact surface area, and it will change when particle size or the degree of sintering change.

Kinetic constants listed in Table 3, obtained from polarisation measurements at different temperatures, are correlated by the Arrhenius law, as shown by the high correlation factor of the best fit line of experimental data plotted in Fig. 4. This is a typical kinetic effect and it has to be attributed to dependence of j_0 on i_0 in Eq. 11, rather than to the contact area surface (a).

As can be observed in Fig. 4, activation energy (determined from the slope of the best fit lines) is similar for ion conduction and electron transfer, confirming that both ohmic resistance to ion conduction and electrochemical activation resistance to electron transfer may contribute to limiting the rate of the overall process of charge transfer and migration in a SOFC cathode within 600–850 °C temperature range.

3.2 Experimental validation

The mathematical model of a porous composite cathode developed in this work was tested using experimental data presented in a companion paper [14] on polarisation
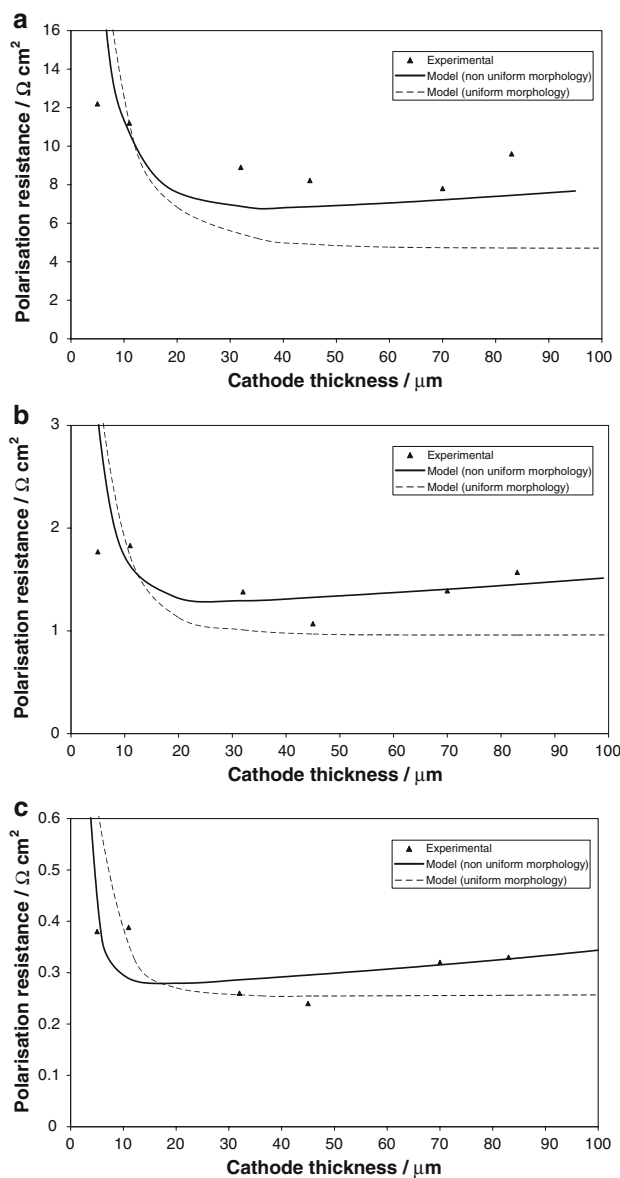
Fig. 5 Model validation with experimental data on polarisation resistance in cathodes of different thicknesses (Barbucci et al. [14])

resistance obtained by impedance spectroscopy on cathodes of different thicknesses operated at temperatures within 600–850 °C range. Experimental results are compared with model simulations in Fig. 5, where calculated and measured polarisation resistance is plotted as a function of cathode thickness for operating temperatures of 600 °C (Fig. 5a), 700 °C (Fig. 5b), and 800 °C (Fig. 5c). As can be observed in these figures, the model accurately reproduces the behaviour observed in the experiments over a wide range of operating conditions. In particular, the model predicts higher polarisation resistance for cathodes with thickness greater than the one corresponding to minimum resistance. This behaviour cannot be described when the whole cathode volume is assumed to have uniform
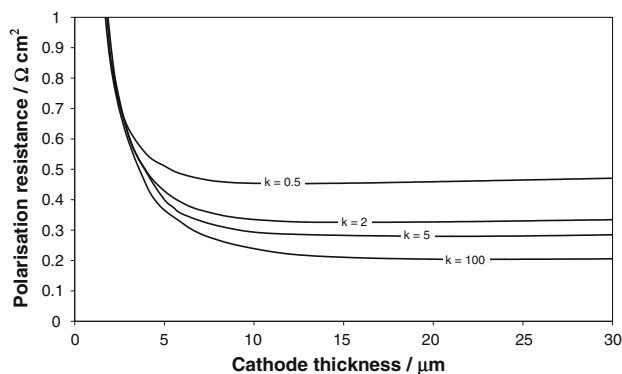
Fig. 6 Model sensitivity to compression factor variations: effects on polarisation resistance at 800 °C

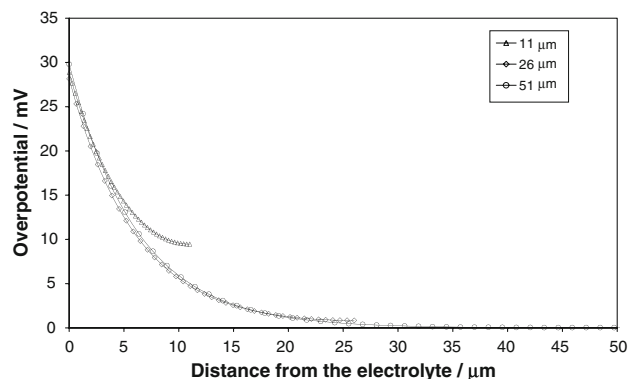**Fig. 7** Overpotential distribution in cathodes of different thicknesses

morphological properties. Under this assumption, the model predicts an asymptotic behaviour, as shown by the dashed lines in Fig. 5. The proposed model can reproduce the experimental results on the dependence of polarisation resistance on cathode thickness, because it takes non-uniform morphological properties into account.

The proposed model cannot satisfactorily predict the behaviour of thin cathodes ($\delta < 10$ μm), whose performance is strongly underestimated by the calculations. It should be taken into account that the physical properties of thin composite layers should not be described using three-dimensional percolation (as in this work), but the cross-over between two-dimensional (surfaces) and three-dimensional (volumes) systems should rather be considered [18]. In particular, composite materials made of conducting and non-conducting particles show remarkably higher conductivity near their boundaries than in their bulk. Interface thickness where this behaviour can be expected is just a few tenths of the typical size of the conducting phase. That would not have any practical relevance for the system discussed in this work, if the characteristic size were that of a single particle (see Table 1). The interface would extend more significantly when the characteristic size of the conducting phase were that of a cluster of conducting particles formed through non-homogeneous mixing, during powder preparation for cathode fabrication.

The reliability of model results presented in Fig. 5 for comparison with experimental data is affected by the estimation of uncertain parameters not obtained from experimental or literature data. In particular, compression factor k (i.e. relative tortuosity) plays a key role in model outcomes (see Fig. 6). k should therefore be regarded as an adjusted parameter.

3.3 Performance simulations

Cathodic processes in SOFCs discussed above (see Sect. 2) can be quantitatively described using model simulations.

Figure 7 shows the overpotential calculated as a function of axial position in three cathodes of 11, 26 and 51 μm, respectively. The overpotential is distributed over the whole thickness of the cathodes thinner than 26 μm, which are therefore active for electrochemical reaction throughout their volume, while part of the thickest cathode (51 μm) is not used for electrochemical reaction. The overpotential in this cathode is similar to that in the thinner cathode (26 μm), confirming that the active volume is the same in both cases. The unused part of the thicker cathode only serves as a bridge for the delivery of electrons to the active volume. The thinnest cathode (11 μm) has a higher overpotential than the other cathodes. This is because of the limited number of active reaction sites in the former, compared to the latter, which results in higher current per single contact for any imposed overall current. As a consequence, according to the Butler–Volmer kinetics (see Eq. 5), a higher overpotential between the electron-conducting phase and the ion-conducting phase is required for electron transfer.

According to the results presented in Fig. 7, the performance of a cathode not thicker than the critical thickness corresponding to minimum polarisation resistance (see Fig. 5) is related to the number of contacts and the specific rate of electron transfer. The product of the number of active contacts and exchange current can therefore be regarded as a design parameter for SOFC cathodes. Polarisation resistance is plotted in Fig. 8 as a function of the design parameter $n_V j_{0\delta}$ for three temperature values (600, 700, and 800 °C). At all temperatures, polarisation resistance decreases when the design parameter (i.e. the rate of electrochemical reaction in the whole cathode volume) increases. Minimum polarisation resistance is attained when electrochemical kinetics becomes much faster than ion conduction in the ion-conducting phase. As expected, different values of minimum polarisation resistance are calculated at different temperatures.
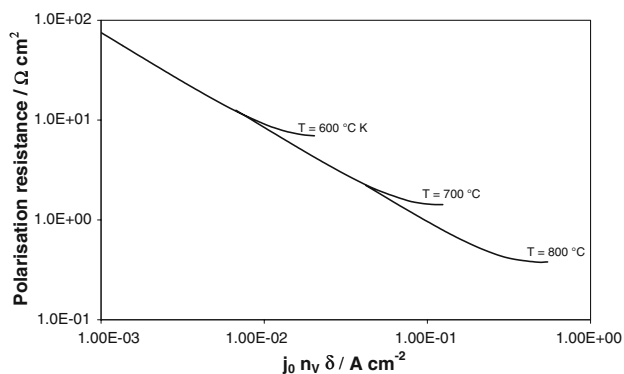
Fig. 8 Cathode performance as a function of design parameter $n_V j_0$

4 Conclusions

A mathematical model of electrochemical reaction and charge transport in porous composite cathodes for SOFCs was developed to give insight into experimental data on polarisation resistance in cathodes of different thicknesses. The model takes account of variations of cathode morphological properties, as observed on SEM pictures of cathodes with different thicknesses. The model is validated using experimental data, with a single adjustable parameter (compression factor) related to estimated tortuosity of ion-conducting paths in the cathode. Model simulations are used to define a design parameter, which allows a rough estimate of minimum polarisation resistance as a function of cathode design (thickness), material properties (density of active contacts, effective resistivity), kinetic parameters (exchange current) and operating conditions (temperature).

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