

Correlated Resistor Network Study of Porous Solid Oxide Fuel Cell Anodes

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A resistor network model is developed for solid oxide fuel cell (SOFC) composite anodes, in which solid electrolyte grains, metal particles, and pores are considered on the same footing. The model is studied by a Monte Carlo simulation on a face-centered cubic lattice, with a random distribution of the three components over the lattice sites. The concept of active bonds is used; the bond between a metal and an electrolyte site is conductive (reaction-active) if the sites belong to clusters connected to the solid-electrolyte membrane or metal current collector, respectively, and if the bond has at least one neighbor site which is a part of a pore cluster connected with the fuel supplying gas channels. Active bonds are characterized by an elementary reaction resistance, inactive bonds are blocking. The total inner resistance of the anode is calculated as a function of composition and the elementary reaction resistance, R_r , vs. ion transport resistance, R_e (of a "bond" between two solid-electrolyte grains). Compositions which provide the lowest inner resistance for a given R_r/R_e ratio are revealed. Across-the-sample distribution of the current through the three-phase boundary is investigated. The higher the R_r/R_e ratio, the larger areas of the three-phase boundary are used; however, if the ratio is low, the reaction occurs only very close to the anode/membrane interface to avoid ion transport limitations. A scaling law for the reaction penetration depth inside the anode, $N_r \propto (R_r/R_e)^\beta$ (where $\beta \leq 0.5$) is suggested in accordance with the Monte Carlo results. In line with the existing experimental data, the simulation and scaling estimates reveal the interplay between the reaction penetration depth and the anode thickness, which determines the thickness effect on the inner resistance.

INTRODUCTION

Progress in solid electrolyte fuel cells (SOFC) essentially depends on the improvement of its four elements: the cermet composite anode, the solid electrolyte membrane, the mixed ion-electron conducting cathode, and interconnect materials.¹ The robust and efficient interconnectors are a task of material chemistry and electrical engineering. Better membranes (ion conducting at lower temperatures, more stable thermodynamically and mechanically) are foreseen together with proper modifications of zirconia-based electrolytes or synthesis of new oxygen ion conducting compounds. The progress in ceramic technology influences the improvement of Ni-yttria stabilized zirconia (YSZ) composite anodes, which could be facilitated by a better understanding of the electrochemical processes at the metal-electrolyte-gas three-phase boundary, statistical geometry of the composite, and its electrical properties. This refers to porous composite cathodes, as well, though their development is rather dominated by material chemistry: synthesis of nonstoichiometric mixed conductors with an optimum combination of electronic and ionic transport properties, and better understanding of the role of defects and grain boundaries.

The electrodes, and first of all, the "fuel electrode," the anode, are the subject of interdisciplinary research where interfacial electrochemistry meets statistical physics of random heterogeneous media, and where relatively simple physical models may be applied. Percolation network models^{2, 3} offer here a convenient framework for analysis of structural and electrical properties. We focus below on the anodes, though many of the ideas discussed can be applied, as well, for the modeling of cathodes.

The structure of the cermet anode, composed of metal particles (nickel), electrolyte particles of the same material as the membrane (yttrium stabilized zirconia), and pores, is determined by its five main functions.

It must provide

1. A voluminous metal/solid electrolyte/pore space three-phase boundary for reaction events (recombination of an oxygen ion from the electrolyte with two hydrogen atoms or a carbon monoxide molecule adsorbed on the metal, which generates two electrons), spanning through the composite.
2. A continuous path for electrons from the reaction spots to the current collector.
3. A continuous way for oxygen ions from the membrane to the reaction spots.
4. A continuous, diffusion-unlimited transport of the fuel (hydrogen gas or/and carbon monoxide) from the massive gas channels of the current collector to the reaction spots and transport of the reaction products (water vapor or carbon dioxide) back to the gas channels.
5. Mechanical stability of the junction between the current-collector and the membrane.

The optimal structure is determined by a competitive interplay of all five requirements.

From the point of view of the three-phase boundary and the mechanical stability, the best would be the composites with grains and pores of the finest size allowed by the fabrication technology. However, this would lead to strong transport limitations for the fuel supply and the products release. Therefore, the size of the grains is usually not much smaller than 1 μm . Grains of the pore-forming material occupy typically some one-third of the total volume of the initial mixture. This gives, after their removal, the same scale of porosity in the composite.^{1,4}

The fulfillment of the first four functions automatically leads to a large active three-phase boundary. If all the requirements are fulfilled, the anode will work, but this is not enough: one should minimize its internal electrical resistance. The thicker anodes have a larger volume-spanning three-phase boundary, but how does their resistance depend on the size? The ion diffusion limitations hamper the access of oxygen ions to the peripheral regions, far from the membrane. How deep into the anode will the ions diffuse before they react? This depends on the reaction rates relative to the ion transport rates. When the reaction is slow and rate determining, there is enough time for ions to reach all parts of the three-phase boundary. If the reaction is fast, it occurs mainly in a thin layer near the membrane. The anode, in this case, can be made thinner because the increase of its thickness does not add a useful three-phase boundary; the optimum thickness will then be determined by the mechanical stability of the composite. As both the reaction and diffusion rates are temperature dependent, the temperature variation may affect the balance between the two stages.

Understanding the interplay between the structure and function may help to construct better anodes. For this we need an adequate model of the anode which would cover its electrochemical, electrical, and mechanical properties. In this paper, we concentrate on the first two aspects, leaving aside the mechanical properties (which can impose their own constraints on the design of the anode).

RANDOM NETWORK MODELING AND THE CONCEPT OF ACTIVE BONDS

A random network model of the anode was suggested by Sunde.⁵ In his model, solid electrolyte and metal particles are randomly distributed along the sites of the cubic lattice (a later extension⁶ considers also randomly packed structures, including those formed by particles of different size). The bonds between the electrolyte sites are characterized by an elementary conductance of the electrolyte, and the bonds between the metal sites by elementary metal conductance. To all the bonds between the metal and solid electrolyte sites, Sunde attributes the reaction conductance, i.e., there are no blocking bonds in the model. This implies that there is an access of

the fuel to all the contacts between the metal and electrolyte particles, provided by intrinsic voids between the grains and defect vacancies in randomly packed structures.

The latter, however, does not seem to be close to the most common real situation. Indeed, SOFC anodes do not operate without specially fabricated porosity, unless the size of the grains and thereby voids between them is large (but then the performance is poor). As we have mentioned, typically one-third of the volume of commercial anodes is occupied by pores,^{1,4} the network of which guides the fuel to the metal-electrolyte grain pairs. Thus, pores must be considered in the model on the same footing as the metal and electrolyte particles.

Ioselevich, Kornyshev, and Lehnert (IKL)⁷ have introduced the notion of active bonds between the metal and electrolyte sites. The bonds are active, i.e., not blocking, only if they have a neighboring pore which belongs to a continuous cluster of pores connected to the current-collector/gas channel side of the anode. This condition is necessary, but not sufficient; only those metal/solid electrolyte pairs are active in which the metal particle is a part of a metal cluster connected to the current collector and the electrolyte particle belongs to an electrolyte cluster connected to the membrane. These constraints would give, generally, a much smaller number of active bonds than in the Sunde model, where all metal-electrolyte bonds are active. Figure 1 illustrates the notions of the IKL model⁷ by means of a two-dimensional cartoon, exaggerating the real, three-dimensional situation.

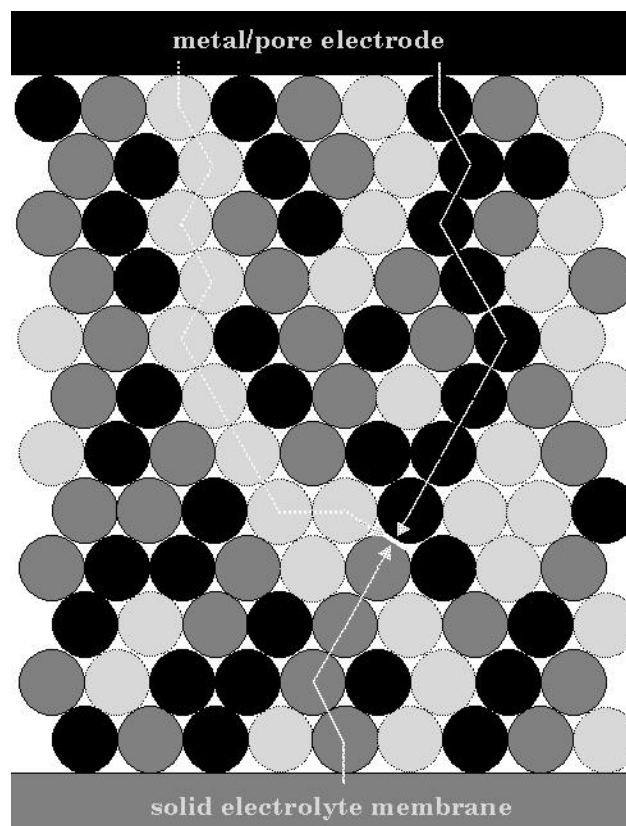


Fig. 1. A model of the SOFC anode (a two-dimensional sketch).⁷ The black, white, and gray circles represent metal grains, solid electrolyte grains, and pores, respectively. The two solid lines show the way of the current through the system. At the three-phase boundary (where the "arrows" meet) the ionic current in the solid electrolyte phase transforms into the electronic current in the metal. The dashed line marks the way for the fuel through the pore space.

Indeed, far from the percolation threshold in all three components, the number of active bonds is not much smaller than the total number of bonds, but this is not true close to the percolation threshold in each of the components.

Though the site occupation is random both in the Sunde and IKL models, the latter deals with the correlated properties of the system of the sites of three sorts, where the properties of a bond depend on the bond neighbors. The IKL model thus refers to a class of correlated percolation models, the properties of which are, at present, insufficiently studied.⁸

In Ref. 7, only statistical geometry aspects of the problem were studied, the number of active bonds and its variation in time, subject to an algorithm of spontaneous sintering of metal particles (degradation). In the present paper we extend the IKL model on the calculation of electrical properties of the corresponding correlated resistor network, investigating still a time-invariant system. We use the Monte Carlo simulation of the sites occupation and an extension of the method for the treatment of resistor networks, applied earlier to dense metal/solid electrolyte composites.⁹ We calculate, thereby, the stationary state admittance as a function of composition for different values of the "key" parameter, the ratio between the "elementary reaction resistance" and "ionic resistance" of the corresponding bonds (also the main parameter in the Sunde model⁵). We study the distribution of the current through active bonds along the sample. This allows us to find out how deep the reaction penetrates into the composite, depending on this ratio. Aspects of the variation with time of the anode admittance and of the current distribution, subject to the IKL patterns of degradation,⁷ will be considered in a publication to follow.

MODEL AND THE METHOD OF CALCULATION

In order to obtain the overall admittance of the anode and current distribution through the three-phase boundary, we use a resistor-network model, which allows us to calculate the potential at each node and current through each resistor branch.

The lattice

The model is based on the face-centered cubic (fcc) lattice, which represents a dense packing of particles of the same size (metal, electrolyte, pores). In this respect it is closer to reality than a normal cubic lattice. As we consider pores on the same footing, there is no strong need in the use of random packing models,⁶ the fcc lattice being a reasonable starting approximation.

Sites of the lattice are randomly occupied either by metal particles, solid electrolyte particles, or pores, with probabilities p_m , p_e , p_p , respectively; $p_m + p_e + p_p = 1$. The sites represent the nodes of the resistor network. The conducting properties of each contact pair of grains are modeled by a resistor between the corresponding two nodes. The resistors represent bonds between the sites.

The size of the lattice studied is 24 layers in x , y , and z directions, unless otherwise stated. The boundary conditions are cyclic in the x , y plane. In z direction, the system represents a slab. It has two boundaries, which are placed before the first z layer and after the last z layer. The plane before the first z layer represents the equipotential surface of the current collector, which means that all bonds connected with it are "linked" to the

leads and gas transport channels. The last z layer contacts the solid electrolyte membrane. The surface of the latter stands in the resistormodel as another equipotential surface.

Bonds and circuits

Since we have three different sites, we have six different bonds. The resistance of the bond joining any pore site with any other site is infinite, which leaves only three kinds of bonds to be considered. The resistance between two solid electrolyte sites (R_e) is normalized to 1 (Fig. 2a). The resistance between two metal sites (R_m) is set to $4.5 \times 10^{-6} R_e$ (Fig. 2b), corresponding to the actual ratio of the bulk specific resistances of nickel and YSZ at 950°C , the typical SOFC working temperature. According to the definition of active bonds, the resistance between a metal and an electrolyte site depends on the three conditions. If the metal site belongs to a metal cluster connected with the current collector, the electrolyte site belongs to a cluster of electrolyte particles connected with the membrane, and at least one of the four neighbors in the plane perpendicular to the bond belongs to a pore cluster connected with the (porous) current-collector, the bond will be called active, and its resistance set to $R_m/2 + R_e/2 + R_r$ (Fig. 2c). Otherwise, the bond is called inactive, and its resistance is infinite.

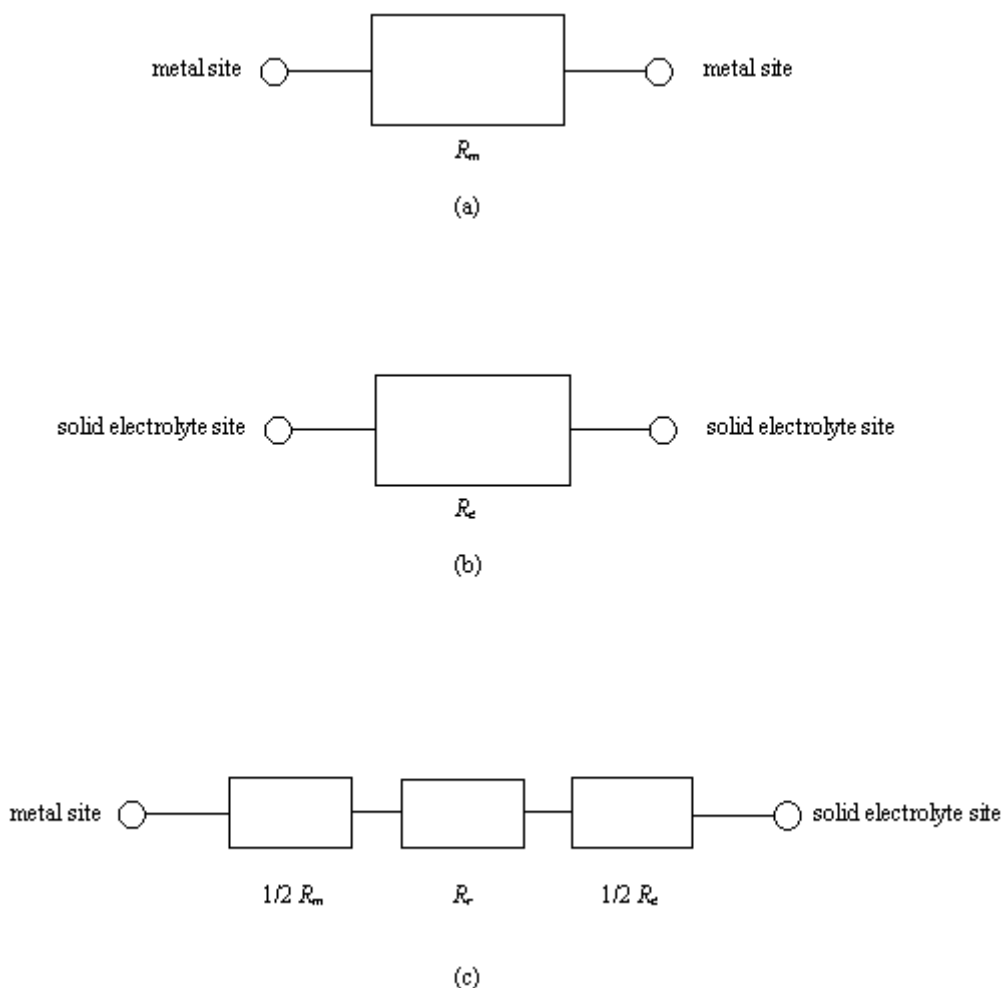


Fig. 2. Equivalent electrical circuits for the bonds between two metal sites (a), between two solid-electrolyte sites (b) and, for an active bond between a metal and a solid-electrolyte site (c).

R_r is the elementary, twograin resistance of the electrochemical reaction, responsible for the "conversion" of the ionic current in the solid electrolyte phase into the electronic current in the metal phase. Its values studied in this paper are set between R_e and $10^4 R_e$, with $10^3 R_e$ taken as a typical estimate (see Ref. 5 and the discussion therein).

Admittance and current calculation

The overall inner resistance of the anode, R is calculated by setting the potential of 1 V to the solid electrolyte membrane and zero potential to the current collector. (In the working anode, one does not apply an external voltage, but the voltage (current) is generated by the reaction at the threephase boundary. A linear resistor network allows the current to flow in both directions, while in the SOFC anode the negative charge flows from the electrolyte to the metal. The "diode" character of the bonds, is, however, unimportant close to equilibrium, i.e., in the limit of small currents, controlled by the external load. One may then speak about an ohmic inner resistance of the anode, R , which could be evaluated by a linear resistor network simulation with bonds equally conductive in both directions. This corresponds to the method of calculation of the internal resistance of a power source, standard in electrical engineering: all internal, reaction-caused voltage sources are removed, but an external voltage is applied. The same approach is used in Ref. 5.)

Then a system of coupled linear equations is constructed by the node potential method¹⁰ and solved by adapted preconditioned biconjugate gradient method.¹¹ The solution gives the potential of each node. We therefore can calculate the current through each z layer and the overall admittance of the system (Fig. 3).

We can also calculate the distribution of the current which flows through all active bonds from the solid electrolyte phase to the metal phase across the anode (Fig. 4). The sum of all these currents through active bonds is equal to the total current through the system.

RESULTS AND DISCUSSION

Admittance of the system

The anode admittance, i.e., the inverse internal resistance, $Y = 1/R$, calculated per one site of the slab lateral cross section (i.e., per unit surface area) and given in the units of $(R_e)^{-1}$ is shown in Fig. 3. We present the results at the pore portion, $p_p = 0.3$. The content of the metal is varied from $p_m = 0$ to $p_m = 0.7$, as played on the abscissa of each graph (correspondingly, the amount of electrolyte varies as $p_e = 0.7 - p_m$). The parameter, which varies in the (a)-(f) series, is the elementary reaction resistance R_r : it increases from (a) to (f).

The graph (a) shows the admittance of the system for $R_r = R_e$. Note the increase of conductivity for p_m near the percolation threshold, p_c , equal to 0.2 for the infinite fee lattice.⁸ After p_m reaches 0.4, the conductivity stays at the plateau. Obviously, for this case the reaction is not the limiting stage, and the maximum three-phase boundary does not lead to the largest admittance. The latter is larger for the larger metal content for a trivial reason; with an increase of the metal content its boundary moves to the membrane, and the path through the solid electrolyte diminishes. Shortly after the percolation threshold, most of the metal sites are parts of an infinite cluster. Making it more dense does not change the resulting conductance, since the conductivity does not limit the current; on the other hand the corresponding decrease of the electrolyte component does not decrease much the reaction area, since all the events takes place at the boundary with the membrane. All this results in a

"plateau" with a slight tendency of decrease at the largest values of p_m . This tendency strengthens, however, with an increase of the elementary reaction resistance because more three-phase boundary is needed here, which leads to the maximum of the admittance (graphs (b)-(e)). The maximum gradually moves toward equal portions of the metal and electrolyte (e), which provide the largest three-phase boundary. Simultaneously, the increase of R_r diminishes the absolute value of the admittance. The initial decrease of admittance at small p_m , seen on graphs (a) and (b), is obvious: below the percolation threshold the only effect of increase of a portion of the metal component is the dilution of electrolyte clusters, which hampers the conductance through them. These are the impressions from a coarse look at this series. A more detailed analysis reveals a number of more subtle features. Since p_p was fixed at 0.3, the system is percolating in all three phases for $0.2 < p_m < 0.5$. At $R_r = R_e$ the conductivity of an active bond is close to the conductivity between two solid electrolyte sites, while the bond between two metal sites has a conductivity 2.2×10^5 times higher than the conductivity between two solid electrolyte sites. For this case one should, actually, expect the maximum of admittance at $p_m = 1 - p_c - p_p = 0.5$, which one can envisage looking at graph (a). The admittance does not drop more strongly for $p_m > 0.5$ because the conductance of an active bond is not much smaller than the conductance of a bond between two electrolyte sites. Graph (b) shows the case where the active bond conductance is an order of magnitude smaller than the electrolyte conductance; now we get a decrease after $p_m > 0.4$. Since the conductance of an active bond is the lowest among the other conductive bonds, it determines the system behavior. The maximum number of metal electrolyte bonds corresponds to $p_m = (1 - p_p)/2 = 0.35$, and the maximum number of active bonds should lie close to this point. Since the second dominating bond is the bond between two solid electrolyte sites, the maximum of admittance is reached slightly to the left of 0.35 (between 0.25 and 0.35), where there are more parallel bonds between solid electrolyte sites than between metal sites. With an increase of R_r to $R_r = 10^2 R_e$ (c) and to $R_r = 10^3 R_e$ (d), the decrease of admittance at large p_m becomes stronger, making the curve more symmetric. At $R_r = 10^4 R_e$ (e) active bonds fully control the admittance, and their maximum number sets at $p_m = (1 - p_p)/2 = 0.35$.

The admittance is nonzero at $p_m = 0$ since then the reaction simply takes place at the current collector side. As it costs the ions to pass across the whole anode, the admittance is low in this case. On some of the graphs (where reaction limitations do not dominate), we see a small increase of admittance with $p_m \rightarrow 0$. This is, presumably, an artifact of the model in which any site on the current collector side provides both the electronic conductance and the fuel supply. Thus any electrolyte site in the plane neighboring the current collector appears to be (artificially) a part of an active bond. This exaggerates the number of active bonds in this limit. Small additions of the metal may only reduce this "option," which leads to a slight initial decrease of the admittance with an increase of p_m .

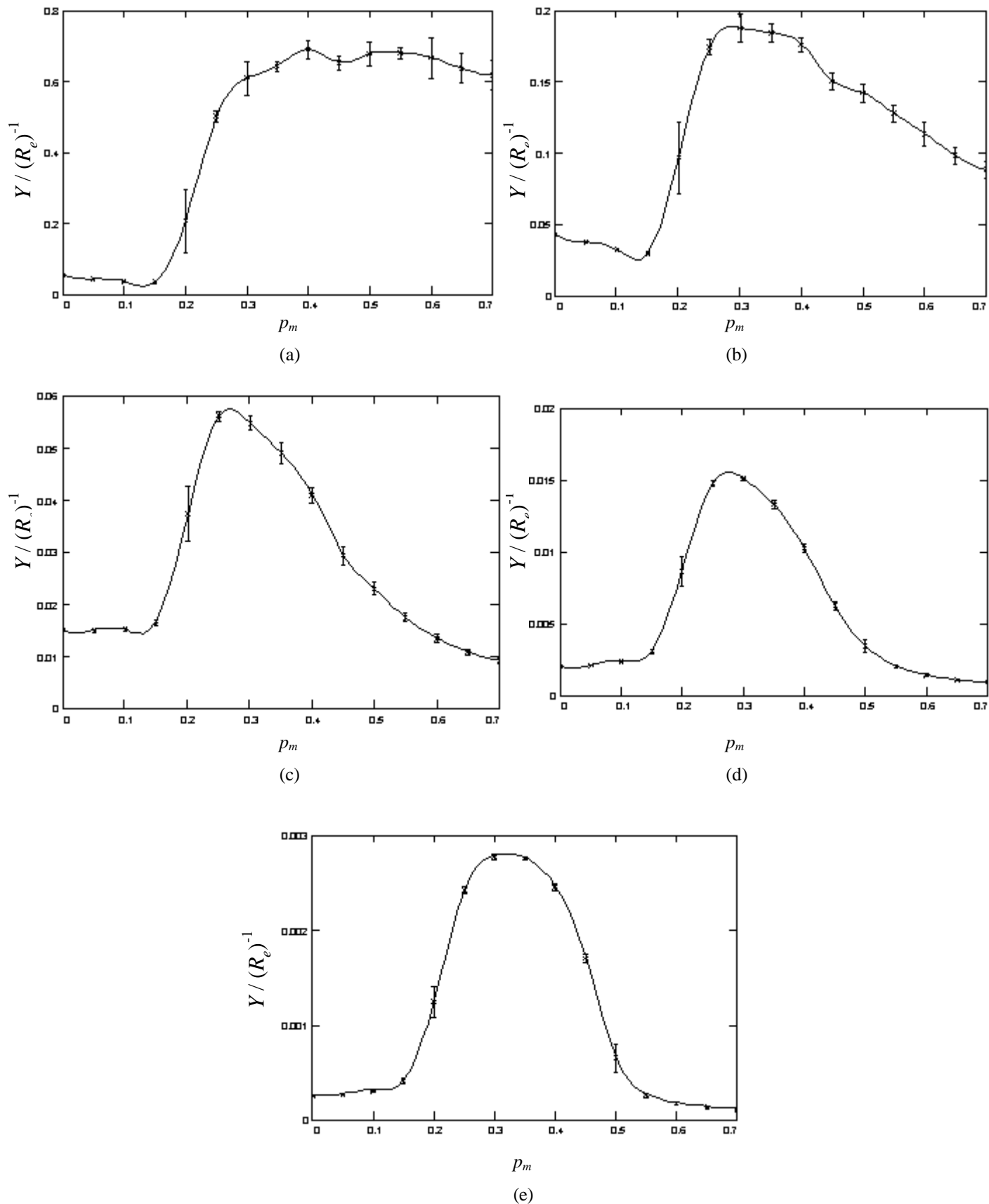


Fig. 3. Anode admittance (in the units of $1/R_e$), calculated per one cross-sectional site. Dependence on the fraction of metal particles p_m (for $p_p = 0.3$), of different values of the elementary reaction resistance: $R_r/R_e = 1$ (a), 10 (b), 10^2 (c), 10^3 , (d) 10^4 (e); $R_m/R_e = 4.5 \times 10^{-6}$.

Current through the three-phase boundary: scaling law for the reaction penetration depth

Let us introduce the distribution of the current through active bonds across the sample, $J_{act}(z)$, i.e., across every z layer, calculating lengths in the units of the spacing between the layers. Since the current in the sample cannot bypass active bonds, the total current, J , is equal to the sum of the active-bond currents through all the layers

$$[1] \quad J = \int_0^N dz J_{act}(z)$$

where N is the thickness of the anode (total number of the layers). One may then introduce a mean reaction penetration depth

$$[2] \quad \bar{N} = \frac{1}{J} \int_0^N dz (N - z) J_{act}(z)$$

In the case of an exponential decay

$$[3] \quad J_{act}(z) = \frac{J}{\frac{N}{1 - e^{-\frac{N-z}{N_f}}}} e^{-\frac{N-z}{N_f}}$$

with the decay length N_f , measured in the number of the layers counted from the edge of the membrane

$$[4] \quad \bar{N} = N_f - \frac{N}{e^{\frac{N}{N_f}} - 1}$$

Thus, for $N \gg N_f$, $\bar{N} \approx N_f$, but when $N \ll N_f$, $\bar{N} \approx N/2$.

The distribution of the current through active bonds, normalized to the total current through the anode is shown in Fig. 4. (The current through an active bond is counted as positive if it flows from the electrolyte to the metal site of the bond.) The results are plotted for: $p_m = p_e = p_p = 1/3$. Graph (a) shows the current distribution for $R_r = R_e$. Only the bonds which are very close to the membrane are used here for the current passage; there is no current through bonds more than four layers away. Further increase of R_r [from (b) to (d)], involves more and more active bonds. Already at $R_r = 10^3 R_e$ the majority of active bonds participate in the conduction of the current. At $R_r = 10^4 R_e$ (e), the curve is almost flat, i.e., all active bonds of the system are employed, no matter how far they are from the membrane. All the graphs fit the exponential decay law well (Eq.3) (solid lines) with decay lengths N_f increasing from (a) to (e): 1.38, 2.93, 9.89, and 38.34.

At compositions which are considerably above the percolation threshold in each component, it is possible to give a rough scaling estimate of N_f . We do it by ignoring the finite size scaling and assuming that the sample is much thicker than the penetration depths, i.e., $N \gg N_f$ and $\bar{N} \approx N_f$. Consider two counterparts of the anode internal resistance, $R = R_{ion} + R_{react}$ where R_{ion} is due to the oxygen ion transport to the reaction front and R_{react} is due to the reaction at the front, both calculated per one grain cross-sectional area. The former is, roughly, proportional to the characteristic path of an ion, i.e., to the penetration depth, $R_{ion} \propto R_e N_f$, while the latter is inversely proportional to the surface of the reaction front, which scales as a volume: $R_{react} \propto R_e N_f$. Equalizing $R_{ion} = R_{react}$ [or minimizing $R(N_f)$, which gives the same result], we obtain $N_f \propto (R_r/R_e)^{1/2}$. This is close to our numerical findings. Fig. 5 shows the log-log plot of the N_f dependence on R_r/R_e .

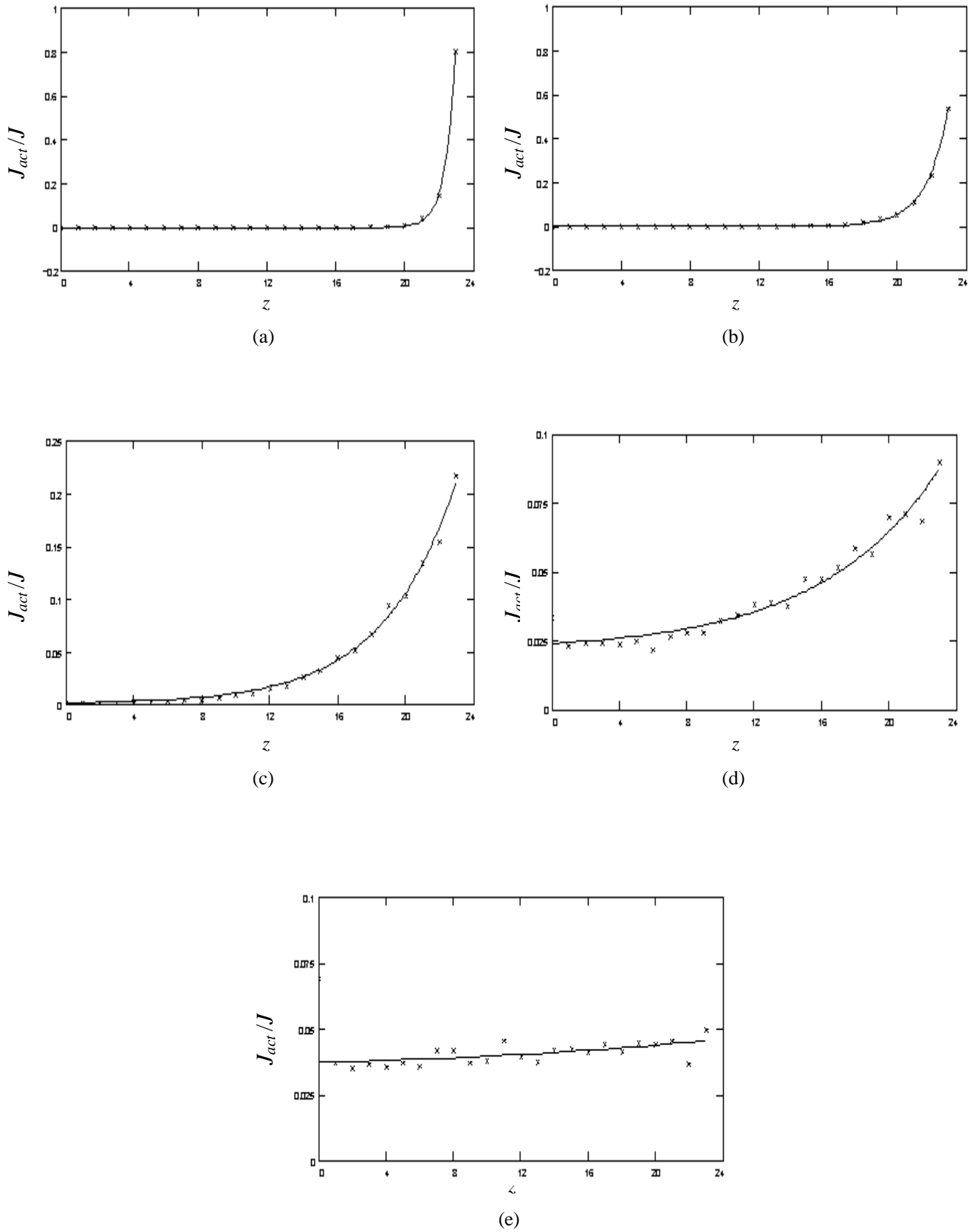


Fig. 4. Current through active bonds normalized to the total current showing the distribution along the z axis for different values of the elementary reaction resistance (the parameter set is the same as in Fig.3).

It reproduces well the scaling law

$$[5] \quad N_f \propto (R_r / R_e)^\beta$$

with $\beta = 0.37$, which is, however, somewhat smaller than the predicted 0.5. Note that the largest N_f point on this graph cannot be treated without the finite size scaling corrections, strictly speaking.

One may speculate about possible reasons for this difference. Indeed, for the system of 24 X 24 x 24 sites at $p_m = p_e = 1/3$ we are neither too close nor too far from the percolation threshold, as the percolation correlation length⁸ is smaller but not much smaller than the size of the system. Thus some elements of the fractional scaling may be present, which are typical close to the percolation threshold: $R_{ion} \propto R_e(N_f)^\nu$. $R_{react} \propto R_r(N_f)^{1-m}$; ν is the exponent of the ion path to the front, and m is the chemical dimension of the employed three-phase boundary, giving thereby $\beta = (\nu + m - 1)^{-1}$. The value of ν should be close to the so-called d_{min} which in three-dimensions ≈ 1.3 ,¹² and m may be smaller or larger than 2. Thus, $(\nu + m - 1) > 2$, i.e., $\beta < 0.5$ is possible. With the increase of the system size, the contribution of the "Euclidean" scaling will be more pronounced, and $\beta = 0.5$ should be recovered, unless we miss some deeper reasons for the smaller values of β .

The optimal size of the anode

Consider the anode with the composition $p_m = p_e = p_p = 1/3$. Let R_r be the largest resistance in the problem, having put, following Sunde,⁵ $R_r = 10^3 R_e$. How much sense does it make to increase the anode thickness at a given particle size, i.e., the total number of layers N , in order to extend the three-phase boundary? Is there an upper limit? The answers follow from Fig. 6, which is easy to understand. As we have shown in the previous section, for every ratio R_r/R_e there is a reaction decay length, N_f , limited by the ion transport. The larger R_r/R_e , the larger this depth (see, e.g., the scaling Eq. 5). Increase of N above N_f would not affect the anode admittance, because all the currentlines at distances larger than N_f will go through the metal clusters. Since the metal resistance is negligible relative to the ion transport resistance, the decrease of admittance due to longer ways through the metal will not be seen. This explains why the admittance in Fig. 6, where the anode thickness varies from 4 to 100 layers, levels off. These results are in qualitative agreement with experiments of Kenjo et al.¹³ Similar type of plots have recently been obtained by Sunde in his "all bonds" calculations.¹⁴

Thus, with strong reaction limitations, the acting SOFC anode does not behave as a usual resistor. Indeed, its internal resistance does not grow with the anode thickness: it stays constant for large anodes, but it increases with a decrease of the thickness in the small thickness range. Such a behavior would be typical for any composite, where conductors of two kinds are mixed and the charge transfer between them goes across the phase boundary, which increases with the size of the composite.¹⁴ This behavior was experimentally observed for specially designed composites.¹³ Here, we have rationalized it by simple scaling arguments and illustrated by the simulation.

In summary, in order not to lose in the active threephase boundary, the anode must not be too thin. However, an increase of its thickness above N_f would not affect its electrical characteristics, although it may provide a better mechanical stability. The value of N_f can be evaluated according to Eq. 5, where the elementary reaction resistance R_r is to be extracted from special electrochemical measurements (see, e.g., Ref. 15 and 16).

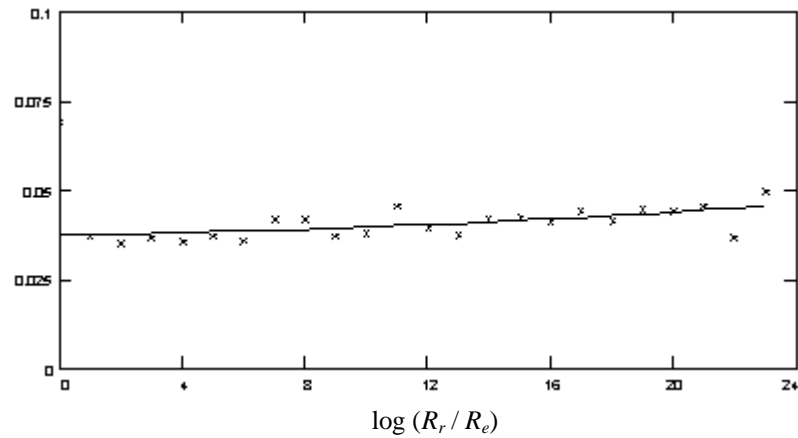


Fig. 5. The dependence of the reaction decay length $h N_f$ on R_r / R_e (verification of the scaling law Eq. 5). Values of N_f are obtained by fitting the curves of Fig. 4 to Eq. 3.

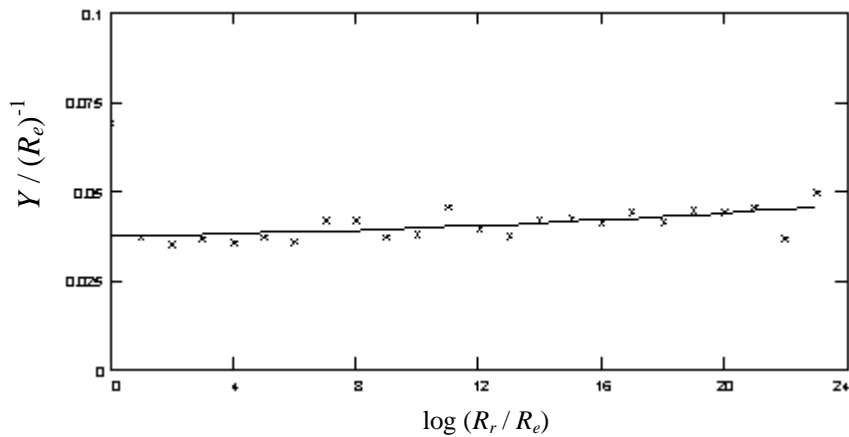


Fig. 6. The anode admittance per one cross-sectional site (in the units of $1 / R_e$) as a function of the thickness (measured in the number of the layers, N). $R_r / R_e = 10^3$; $R_m / R_e = 4.5 \times 10^{-6}$.

Effects of the size of the particles

The results for admittance were plotted in dimensionless units, being scaled to the conductance of the bond between two electrolyte sites, $S_e = 1/R_e$. Conductances of the two other bonds were scaled to the same value. A table of plausible estimates for bond conductances is given in Ref. 14, which may be used to restore the results in dimensional units. The admittance of the slab per unit surface area, S , is related to our calculated dimensionless admittance per site of the cross-section, Y , as: $S = Y S_e / S$, where S is the cross-sectional area per one site. In terms of the specific conductance of the solid electrolyte, k_e one gets $S_e = k_e A S / a$. Here $A (<1)$ is the proportionality coefficient between the two-grains resistor effective cross-sectional area and the slab area per one site, a is the characteristic size of the grain. Hence, $S = Y k_e A / a$.

Would that mean that $S \propto k_e/a$? Generally not, because Y itself depends on the "key ratio" of the bond resistances in a special way. Indeed, when $(R_r/R_e) \gg 1$, and $N_f \gg N$, i.e., all the active three-phase boundary is used but the process is still reaction determined, S must not depend on the ionic transport resistance at all. Here Y must be equal to the number of active bonds multiplied by the reaction conductance, $S_r = 1/R_r$. The latter, given in the units of $1/R_e$ cancels the scaling factor, and $S \approx n_a S_r / S$, where n_a is the number of active bonds per site of the cross section. If the three-phase perimeter between the two grains is not a fractal, $S_r \propto a$ and $S \propto 1/a$. However, when $N_f < N$, S depends on S_e and S_r , and the grain-size dependence of S will be more complex.

Increase of the grain size at a fixed number of the layers would basically decrease the admittance per unit surface area. On the other hand, if the grain size is fixed, variation of S with an increase of the number of the layers is determined by the variation of Y . We remind that Y increases when the number of the layers is small but is constant for thick enough samples.

The dependence of the "key ratio" on the size of the particles with surface fractal geometry¹⁷ could be more subtle. $R_e \propto 1/a$ and $R_r \propto 1/a^d$, where d is the dimension of the three-phase perimeter at the junction of the metal and electrolyte grains. The key ratio, therefore, scales as $R_r/R_e \propto a^{1-d}$. If the grain surfaces are fractal and the contact is tight, $d > 1$. A poor contact may generate $d < 1$. Finally, the "Euclidean" three-phase lines with $d = 1$ are also possible. Consequently, this ratio may increase, decrease, or stay constant with an increase of the particle size.

How does the particle size affect the dependence of the admittance on the number of the layers? Since the plateau is reached earlier the smaller the decay length, which scales as $N_f \propto a^{(1-d)\beta}$ three scenarios are possible.

With the increase of a

$d > 1$: the plateau will be reached at smaller number of the layers

$d < 1$: the plateau will be reached at larger numbers of the layers

$d = 1$: no effect of the particles size on the "leveling-off" rate.

It would be interesting to check these predictions experimentally. If verified, the grain-size effect on the dependence of admittance on the anode thickness may bring information about fractal or nonfractal patterns of the grain contacts, and thereby on the degree of wetting of electrolyte grains by metal grains. How large is this effect? The largest difference in the perimeter dimensions can hardly exceed 0.5. Thus, for a fourfold increase of the particle size one may expect a maximum 100% variance of N_f but this would be only 15% if the variation of d is confined, say, between 0.9 and 1.1.

CONCLUSION

We have shown that the key parameter determining the electrical properties of the anode is the ratio of the elementary reaction resistance of a metal-electrolyte grain junction to the ion transport resistance of the electrolyte grains. The larger the ratio, the deeper the reaction penetrates into the anode, i.e., the larger the amount of the three-phase boundary in the anode used to conduct the current. Knowing the ratio, one may decide what should be the minimum thickness of the anode not affecting the performance; it scales, roughly, as a square root of this ratio or slower. Measurements determining the exchange currents at the nickel/YSZ interface, using microelectrodes in a configuration which would mimic the three-phase boundary, could be essential for experimental evaluation of the "key parameter" and corresponding estimates.

Understanding the nonlinear current-voltage plots for the anodes requires much more sophisticated analysis. Still, the lessons from the linear network modeling help to understand the main trends in the system behavior, as a function of size and composition, which are likely to be manifested in the full voltage range, though unexpected nonlinear effects cannot be excluded.

Variation of the grain size in a monodisperse composite can give, according to our scaling estimates, additional information about the geometry of the grain junctions. Treatment of polydisperse anodes will require an extension of the model. One could introduce here fluctuations of the bond conductances, but this would not cover differences in the statistical geometry. The latter could be accounted for using the methods developed, e.g., in Ref. 14.

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