

Short communication

Three-phase boundary length in solid-oxide fuel cells: A mathematical model

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Abstract

A mathematical model to calculate the volume specific three-phase boundary length in the porous composite electrodes of solid-oxide fuel cell is presented. The model is exclusively based on geometrical considerations accounting for porosity, particle diameter, particle size distribution, and solids phase distribution. Results are presented for uniform particle size distribution as well as for non-uniform particle size distribution.

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1. Introduction

Three-phase boundary (TPB) is a geometrical parameter that is of crucial importance for the performance of solid-oxide fuel cells (SOFC) [1]. In general a high TPB is required for high electrochemical performance. Even though there are number of publications concerning the modeling of SOFCs, most of these models lump the TPB length in the exchange current density parameter, which makes the modeling task much easier [2–5]. Nevertheless, it is important to understand the influence of electrode micro-structure on the TPB length. Deng et al. [6] reported a mathematical model to calculate the TPB length for mono-sized particles. Their expression leads to a TPB length with units of m/m^4 . It is quite difficult to conceptualize a physical quantity with the above mentioned units. Furthermore, their model do not account for the coordination number between the ionic and electronic conductors. In most cases of a composite electrode, one is interested in the volume-specific TPB length.

In an interesting article Wilson et al. [7] reported the three-dimensional reconstruction of a SOFC anode using ion-beam scanning electron microscopy to determine the micro-structural properties. They estimated the volume-specific TPB length for

their sample to be $4.28 \times 10^{12} \text{ m}/\text{m}^3$. Brown et al. [8] reported that Ni constituted the fraction of larger particles with the particle sizes raging $0.5\text{--}3.0 \mu\text{m}$, while YSZ phase particle size distribution were $0.5\text{--}1.0 \mu\text{m}$. So it is also important to consider the volume specific TPB length for cases with two different mono-sized particle distributions. Schnieder et al. [9] reported the discrete modeling of composite electrode and developed an analytical model for calculating the TPB length. They reported that the maximum TPB length is obtained when the volume fraction of ionic conducting particles is 50%. They also developed an analytical model for calculating the TPB length, which, however, predicts non-zero coordination number, even when the ionic phase volume fraction is zero. Similar to the anode, the three-phase boundary length in cathode is important for the electrochemical reduction of oxygen. Chan et al. [10] reported an analytical expression for the calculation of TPB length. In this work we present the development of a mathematical model to describe the volume-specific TPB length per unit electrode volume from a geometrical perspective.

2. Model development

The model presented here is developed by considering a geometric volume of a composite electrode characterized by its porosity ϕ and particle radii r_1 and r_2 . It is assumed that the ionic and electronic solid phases are made up of spherical particles.

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Nomenclature

a	radius of lens (m)
d	distance between the sphere centers (m)
L_{tpb}	average TPB length (m)
M	ratio of the number of ionic and electronic particles
N_p	total number of particles
N_{p1}	number of particles with radii r_1
N_{p2}	number of particles with radii r_2
r	radius (m)
vL_{tpb}	volume specific TPB length (m/m ³)
V_l	volume loss (m ³)
V_t	total volume (m ³)
V_{tl}	total volume loss (m ³)
Z	average coordination number
Z_e	coordination number of electronic conductor
Z_i	coordination number of ionic conductor
Z_{i-e}	coordination number between ionic and electronic conductor

Greek letters

α	mean radius ratio
ϕ	gas-phase porosity
ϕ_e	volume fraction of electronic phase
ϕ_i	volume fraction of ionic phase
ψ	fractional overlap

Subscripts

e	electronic
i	ionic

Here r_1 is the radius of the larger sphere, r_2 that of the smaller one, and d is the distance between the centers of two spheres. (In the analysis presented here we assume the electronic conductors are larger than the ionic conductors [8].) Further, the intersection of the spheres is a curve lying in the plane parallel to the x - y plane, whose radius a is given by

$$a = \frac{1}{2d} \sqrt{4d^2r_1^2 - (d^2 - r_2^2 + r_1^2)^2} \tag{2}$$

The intersection of two spherical particles is only possible under the following constraint which is derived from Eq. (2)

$$d < r_1 + r_2 \tag{3}$$

In a porous electrode several combinations of the spherical particles are possible. For the sake of clarity few examples are considered here. In Fig. 2(a) there are 10 spherical particles and 11 intersection volumes, and each intersection leads to different volume losses depending on d . If the value of d entering in Eq. (1) is the average value for the porous media, then for the case shown in Fig. 2(a), the total volume loss is $11 \times V_l$; where V_l is the average volume loss. For the case in Fig. 2(b), there are eight particles and eight intersection volumes. However, some intersection volumes are overlapped by the adjacent intersection, in this case the total volume loss V_{tl} is expressed as

$$V_{tl} = N_p(1 - \psi)V_l \tag{4}$$

where ψ is the fractional overlap and N_p is the number of particles. When $\psi = 0$, there is no overlap, and the case becomes similar to that discussed in Fig. 2(a). There may also be cases where

$$V_{tl} = (N_p - 1)(1 - \psi)V_l \tag{5}$$

We start the model development by considering the intersection of two spherical particles as shown in Fig. 1. The volume of the three-dimensional lens common to both the spheres as a result of intersection is given by

$$V_l = \frac{\pi(r_1 + r_2 - d)^2(d^2 + 2dr_2 - 3r_2^2 + 2dr_1 + 6r_2r_1 - 3r_1^2)}{12d} \tag{1}$$

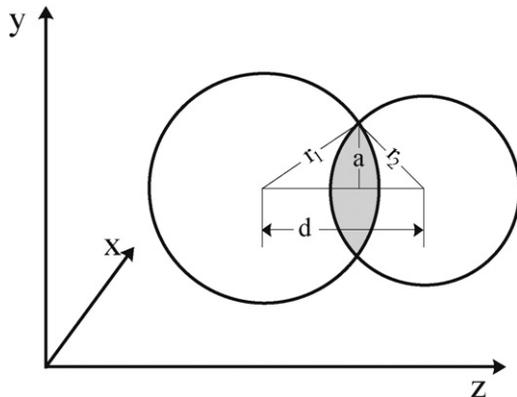


Fig. 1. Intersection of two spherical particles.

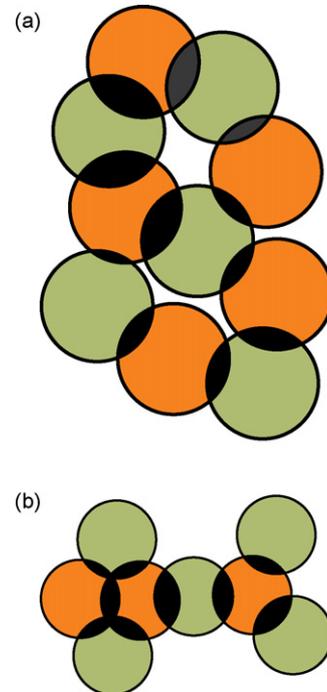


Fig. 2. Two possible combinations of spherical particles in a composite electrode.

as in the case of a three sphere intersection with two intersection volumes. However, for a homogenized porous media we consider the case given by Eq. (4). Let V_t be the total volume of the electrode under consideration, then

$$(1 - \phi)V_t = N_{p1} \frac{4}{3}\pi r_1^3 + N_{p2} \frac{4}{3}\pi r_2^3 - (N_{p1} + N_{p2})(1 - \psi)V_1, \quad (6)$$

where ϕ is the gas-phase porosity, N_{p1} the number of particles with radius r_1 , and N_{p2} is the number of particles with radius r_2 . If M is defined as the ratio between the number of particles

$$M = \frac{N_{p2}}{N_{p1}} = \frac{\phi_2 r_1^3}{\phi_1 r_2^3}, \quad (7)$$

where ϕ_1 and ϕ_2 are the volume fraction of particles with radii r_1 and r_2 , respectively. Then N_{p1} can be calculated from Eq. (6) as

$$N_{p1} = \frac{(1 - \phi)V_t}{(4/3)\pi(r_1^3 + Mr_2^3) - (1 - \psi)(1 + M)V_1}. \quad (8)$$

The total number of particles N_p is then given by

$$N_p = N_{p1} + N_{p2} = \frac{(1 - \phi)V_t(1 + M)}{(4/3)\pi(r_1^3 + Mr_2^3) - (1 - \psi)(1 + M)V_1} \quad (9)$$

The length of boundary due to the intersection of two spheres is given by the circumference of a circle. This becomes a “three-phase” boundary length only if the intersecting particles are of different phases and the intersection is associated with a pore space. Therefore, the average TPB length of a composite electrode is given by

$$L_{tpb} = N_p Z_{i-e} \phi 2\pi a, \quad (10)$$

where Z_{i-e} is the co-ordination number between the ionic and electronic conductors. That is the number of ionic particles surrounding a given electronic particle. According to Bouvard and Lange [11] the coordination number of electronic conductor Z_e in a mixture of ionic and electronic conductors is given by

$$Z_e = 3 + \frac{Z - 3}{\phi_e + \phi_i \alpha^2}, \quad (11)$$

and that of the ionic conductor is given by

$$Z_i = 3 + \frac{(Z - 3)\alpha^2}{\phi_e + \phi_i \alpha^2}. \quad (12)$$

Here Z is the average coordination number, ϕ_i the volume fraction of the ionic particles, ϕ_e the volume fraction of the electronic particles, and α is the mean radius ratio of ionic to electronic conducting particles, i.e.

$$\alpha = \frac{r_i}{r_e}. \quad (13)$$

From simple statistics the average coordination number between these two kinds of particle; i.e. the number of ionic

particles surrounding an electronic particles and vice versa can be written as

$$Z_{i-e} = Z_{e-i} = \phi_i \phi_e Z_i Z_e. \quad (14)$$

The total TPB length per unit volume or the volume-specific TPB vL_{tpb} length is then given by

$$vL_{tpb} = \frac{\phi(1 - \phi)(1 + M)Z_{i-e}2\pi a}{(4/3)\pi(r_1^3 + Mr_2^3) - (1 - \psi)(1 + M)V_1} \quad (15)$$

In the case of mono-sized particles with equal volume distribution of ionic and electronic phases the total number of particles is given by

$$N_p = N_{p1} + N_{p2} = \frac{(1 - \phi)V_t}{(4/3)\pi r^3 - (1 - \psi)V_1} \quad (16)$$

The volume-specific TPB length (vL_{tpb}) is then given by

$$vL_{tpb} = \frac{\phi(1 - \phi)Z_{i-e}2\pi a}{(4/3)\pi r^3 - (1 - \psi)V_1} \quad (17)$$

3. Results and discussion

3.1. Uniform particle size distribution

The following results are presented for mono sized particles for both ionic as well as for electronic phases. Quite obviously Eq. (17) predicts maximum volume specific TPB length (vL_{tpb}) at 50% porosity while other parameters are fixed. Fig. 3 displays the influence of grain size on vL_{tpb} as a function of gas-phase porosity ϕ for equal volume distribution of ionic and electronic particles. As predicted by Eq. (17), maximum vL_{tpb} is observed at 50% porosity for all the grain sizes considered and the vL_{tpb} increases with decreasing grain size. For the results presented in Fig. 3, the average distance between the particles is assumed to be 90% of the particle radius and a coordination number (Z_{i-e}) of 7.2 is used. From the order of magnitude the results are in good agreement with the experimental evaluation of vL_{tpb} by Wilson et al. [7].

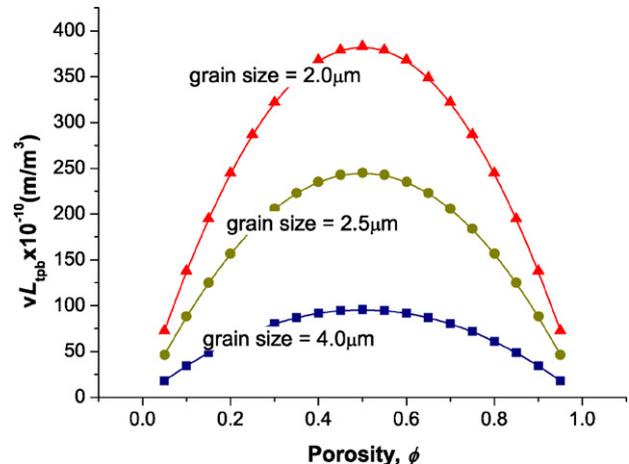


Fig. 3. Volumetric TPB length as a function of gas-phase porosity for various grain sizes for mono-sized particles with equal volume distribution (cf. Eq. (17)).

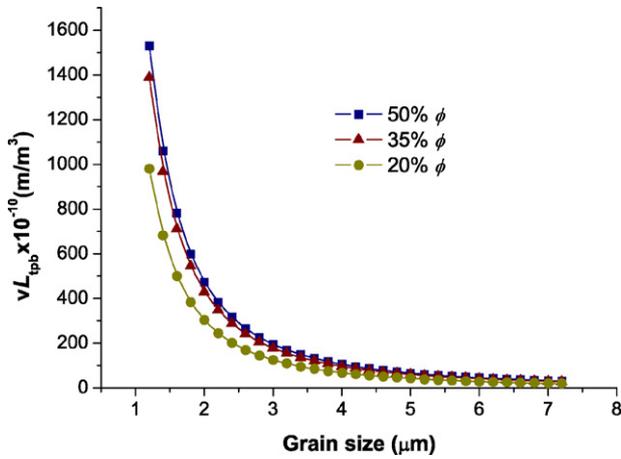


Fig. 4. Volumetric TPB length as a function of grain size for various porosities.

Fig. 4 displays the vL_{tpb} for various porosities as a function of grain size. For these calculations the distance between the particles is kept at 90% of the particle radius. Like in the previous case maximum vL_{tpb} is for smaller grains and increase with increasing porosity. However, it should be noticed that, increasing the porosity above 50% will bring down the vL_{tpb} , as it is obvious from Eq. (17).

The influence of the average distance between the particles on vL_{tpb} is shown in Fig. 5. For the calculations, the grain size is kept constant at 2.5 μm . As the distance between the particle increases the vL_{tpb} decreases. Quite obviously when the distance between the particle increases the radius of the plane formed by the intersection of the two spheres decreases, which leads to shorter length for the curve and hence shorter vL_{tpb} . As evident from Eq. (17), the vL_{tpb} increases linearly with coordination number, which is shown in Fig. 6. Fig. 7 displays the influence of over fraction ψ on vL_{tpb} . As expected the vL_{tpb} is high for low over fractions.

3.2. Non-uniform particle size distribution

Fig. 8 depicts the vL_{tpb} against the volume fraction of the ionic phase (ϕ_i) for various particle diameters for the ionic

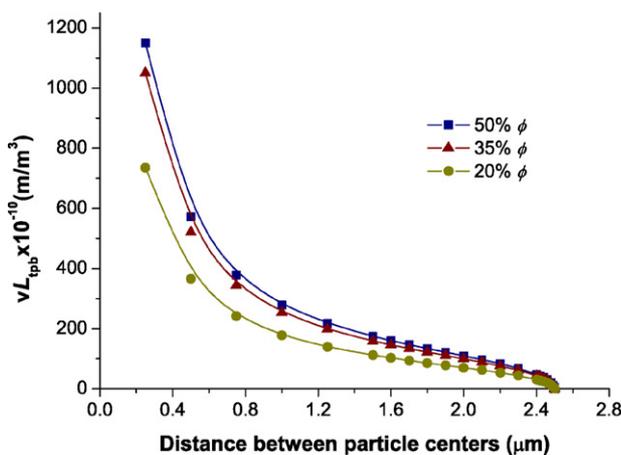


Fig. 5. Volumetric TPB length as a function of the distance between the particle centers for various porosities.

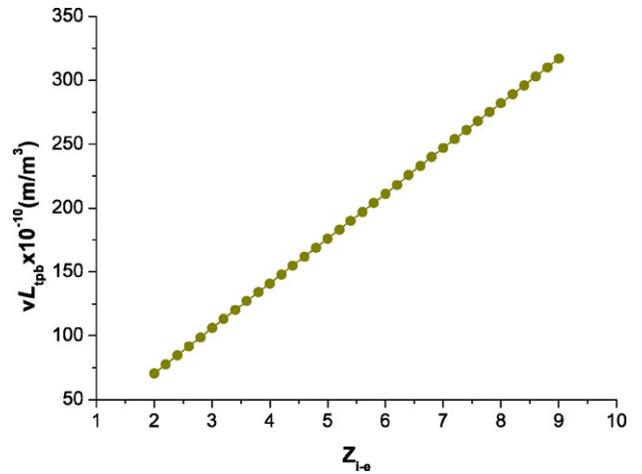


Fig. 6. Volumetric TPB length as a function of coordination number for a grain size of 2.5 μm .

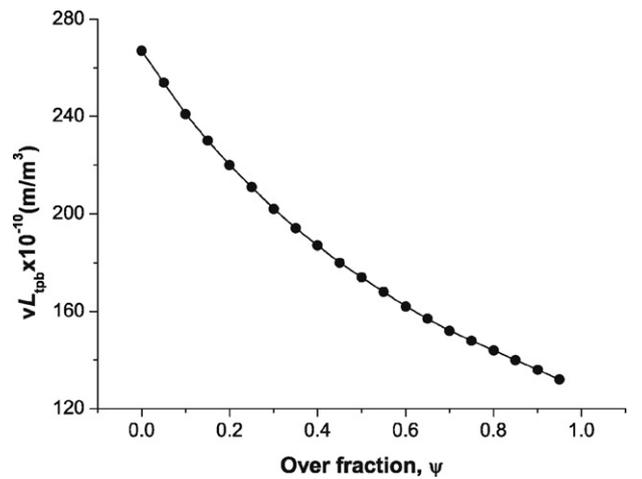


Fig. 7. Volumetric TPB length as a function of over fraction.

phase. The particle size of the electronic phase is kept constant at 3.0 μm , and an average coordination number (Z) of 6 is assumed. Generally, the vL_{tpb} increases with decreasing particle diameter. However, the porosity for the maximum vL_{tpb}

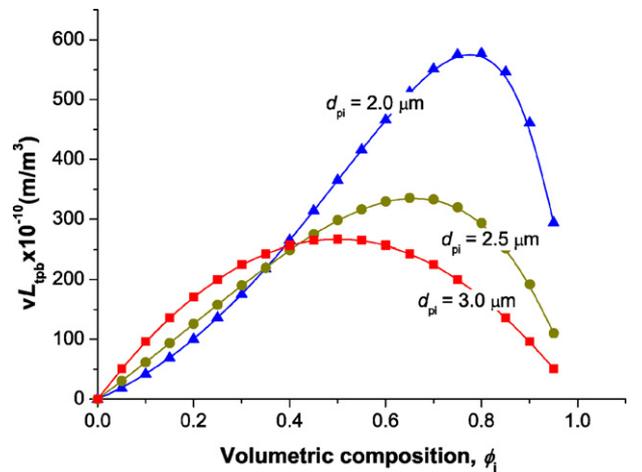


Fig. 8. Volumetric TPB length as a function of the volume fraction of ionic conductor for various grain sizes of the ionic conductor.

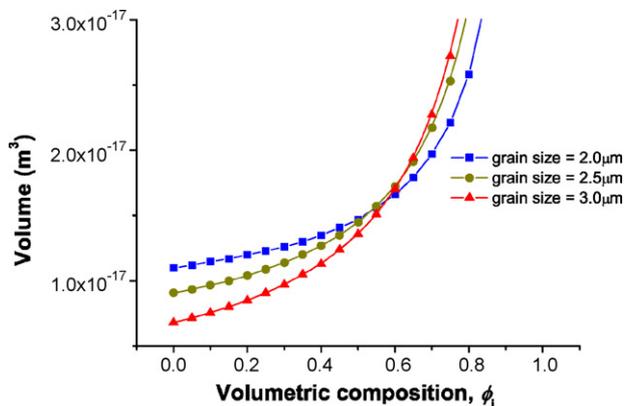


Fig. 9. Total solid phase volume as a function of the volume fraction of ionic conductor for various grain sizes of the ionic conductor.

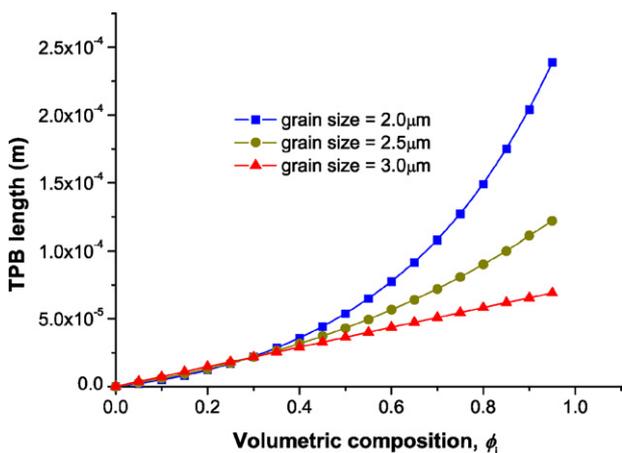


Fig. 10. TPB length as a function of the volume fraction of ionic conductor for various grain sizes of the ionic conductor.

is different for different volume fractions. It may be interesting to note that the vL_{tpb} is higher for higher grain size at lower volumetric composition of ionic phase. This is mainly because at lower ion conductor volume fractions, the total volume of the solid phase is lower with higher grain size, while the three phase area is nearly the same. The total solid phase volume of higher grain size is lower because of the higher volume loss (V_l). The total solid phase volume as a function of volumetric composition is displayed in Fig. 9, and the three-phase area is shown in Fig. 10.

Fig. 11 displays the vL_{tpb} for two different cases, a case where the particle size of the ionic phase is larger than that of the electronic phase, and a case where the particle size of the electronic phase is larger than that of the ionic phase. When the electronic phase particle diameter is smaller compared to the ionic phase, the maximum in vL_{tpb} occurs at lower volume fraction of the ionic phase. And, when the electronic phase particle diameter

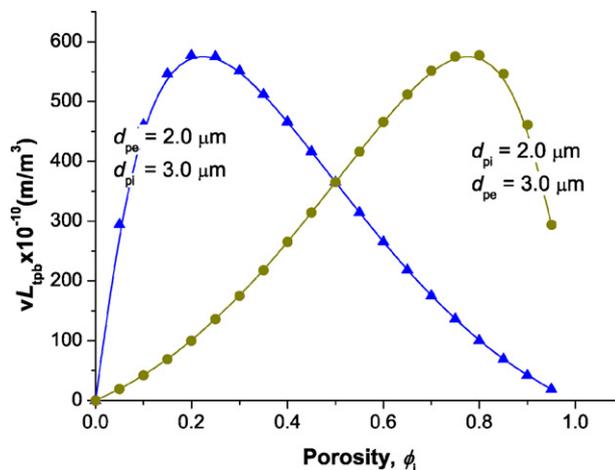


Fig. 11. Influence of size of ionic and electronic conductor on volumetric TPB length.

is larger compared to the ionic phase, the maximum in vL_{tpb} occurs at higher volume fraction of the ionic phase.

4. Conclusions

We have developed a mathematical model for volume-specific TPB length vL_{tpb} based simple geometrical concepts. The model takes into account of the micro-structural properties porosity, particle diameters, and volume fractions of ionic and electronic phase. The geometrical model gives result which are in reasonable agreement with experimental evaluation of vL_{tpb} [7]. The model presented can be used for the calculation of volume specific TPB length for uniform particle size distribution as well as for non-uniform particle size distribution.

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