

# Geometrical modeling of the triple-phase-boundary in solid oxide fuel cells

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## Abstract

A geometrical model was developed to predict the influences of solid grain size, pore size and porosity on the triple-phase-boundary (TPB) length in electronic composite electrodes of solid oxide fuel cells. It shows that the TPB length is inversely proportional to grain size and can be optimized by the pore size and porosity.

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## 1. Introduction

Composite materials have been investigated in the past primarily because of their enhanced mechanical properties. For solid oxide fuel cells, composite electrode materials are of interest mainly because of an increased density of reaction sites, thereby resulting in improved cell performance. The triple-phase-boundary (TPB) in the composites is the active site for electrode reactions. Accordingly, the length of triple-phase-boundary plays an important role in overall performance of the cell. Electrochemical reactions in fuel cells involve ions, electrons and molecular species. In the solid oxide fuel cell (SOFC),  $O_2$  molecules react with electrons at the cathode to form  $O^{2-}$  ions which are transported from the reaction site by diffusion through the yttria stabilized zirconia (YSZ) electrolyte. Electrons are supplied via the Sr-doped  $LaMnO_3$  (LSM) electronic conductor. The reaction occurs at the triple-phase-boundary (TPB) site where YSZ and LSM are simultaneously in contact with  $O_2$ , i.e., an open pore. An analogous situation exists at the anode where Ni, YSZ and

the pore have a common line of contact. It is interesting to investigate the effect of the ratios of phases and microstructures of the composites on the length of TPB and consequently on cell performance.

The geometry of the anode has been modeled in different ways. Abel et al. [1] developed a resistor network model with Monte Carlo simulation. Results of the calculation showed that when an elementary reaction resistance  $R_r$  is not greater than transport resistance  $R_e$ , the maximum three-phase-boundary length does not lead to the largest admittance  $Y$  because most of the reaction occurs at the interface. However, when  $R_r$  is several orders of magnitude higher than  $R_e$ , more three-phase-boundary length is needed to maximize the admittance. Tanner et al.'s model [2] assumed that an electrolyte material in an electrode may be viewed as "tree-like" and protruding from the dense electrolyte surface with electrocatalyst particles spread over the surface in a connected network. His results suggested a significant benefit from making the microstructure (including porosity) as fine as possible. However, a contradictory result was derived from Maggio's model [3] which indicated an optimum range of pore radii necessary to reach the maximum limiting current density. Smaller pore sizes may result in poor limiting current density.

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In this paper, relationships between the length of the TPB versus grain size, pore size and porosity are modeled based on geometric analysis, providing some insight into the contradiction in the literature.

### 2. Modeling

This model assumes an electronic composite which contains two-solid-phases and a gas phase (pore), the solid grains being spherical and packed as shown in Fig. 1. The electronic and ionic conducting phases are present in equal volume amounts.

Two grains of two-solid-phases with an identical diameter  $D_s$  form a neck contact of diameter  $\alpha D_s$  ( $\alpha < 1$ ) between them. The exposed surface area of the solid grains is equal to the surface area of the pore phase. The number of two-solid-phase-boundaries ( $N_{2pb}$ ) can be obtained from the following equation when the solid phases have equal volumes and distribute uniformly:

$$N_s A_s^0 - N_{2pb} A^x = A_p \tag{1}$$

and

$$N_s = \frac{V_s}{V_s^0} = \frac{V_s}{(4/3)\pi(D_s/2)^3} = \frac{6V_s}{\pi D_s^3},$$

$$N_p = \frac{V_p}{V_p^0} = \frac{V_p}{(4/3)\pi(D_p/2)^3} = \frac{6V_p}{\pi D_p^3},$$

$$A_s^0 = \pi D_s^2, \quad A_p = A_p^0 N_p = \frac{6V_p}{D_p},$$

$$V_s + V_p = 1, \quad A^x = \left(\frac{\pi}{2}\right) D_s^2 (1 - \sqrt{1 - \alpha^2})$$

where  $N_{2pb}$  is the number of two-phase-boundary per unit volume;  $N_s$  the number of solid grains per unit volume;  $N_p$  the number of pores per unit volume;  $A_s^0$  the surface area of one solid grain;  $A^x$  the surface area disappeared due to the contact between two-solid-grains;  $A_p$  the total surface area of the pore phase per unit volume;  $D_s$  the diameter of a solid grain = grain size;  $D_p$  the diameter of a pore = pore size;  $V_s^0$  the volume of one grain;  $V_s$  the volume of solid per unit volume;  $V_p$  the volume of pores per unit volume = porosity.

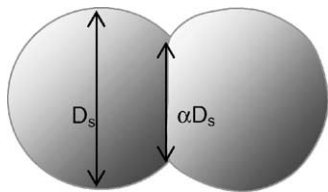
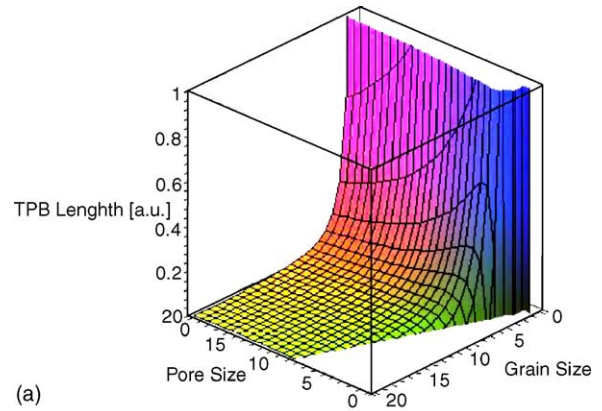
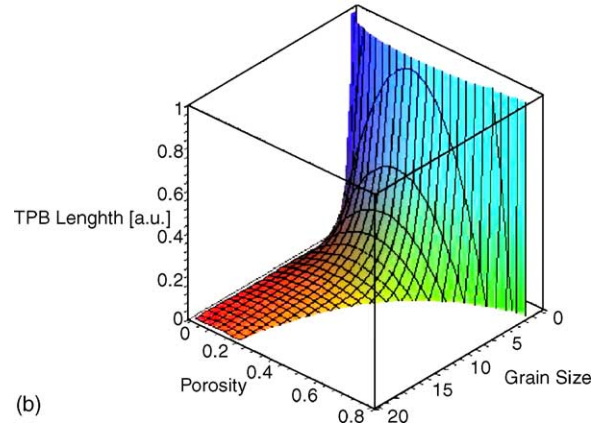


Fig. 1. Equal-sized grains of two-solid-phases in contact (one an ionic conductor and the other an electronic conductor) form a two-phase-boundary with diameter  $\alpha D_s$  ( $\alpha < 1$ ).



(a)



(b)

Fig. 2. 3D graph of the relationship between TPB length vs. grain size and porosity when the porosity is 30% (a) and the pore size is  $5 \mu\text{m}$  (b).

The length of the three-phase-boundary is given by the following equation:

$$L_{3pb} \propto N_{2pb}(\pi\alpha D_s)A_p = \frac{72\alpha[D_p - (D_p + D_s)V_p]V_p}{D_s^2 D_p^2 (1 - \sqrt{1 - \alpha^2})} \tag{2}$$

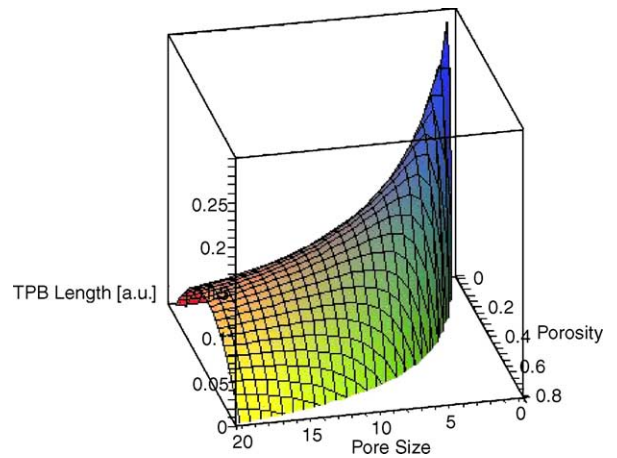


Fig. 3. 3D graph of the relationship between negative log of the TPB length vs. pore size and porosity when the solid grain size is  $5 \mu\text{m}$ .

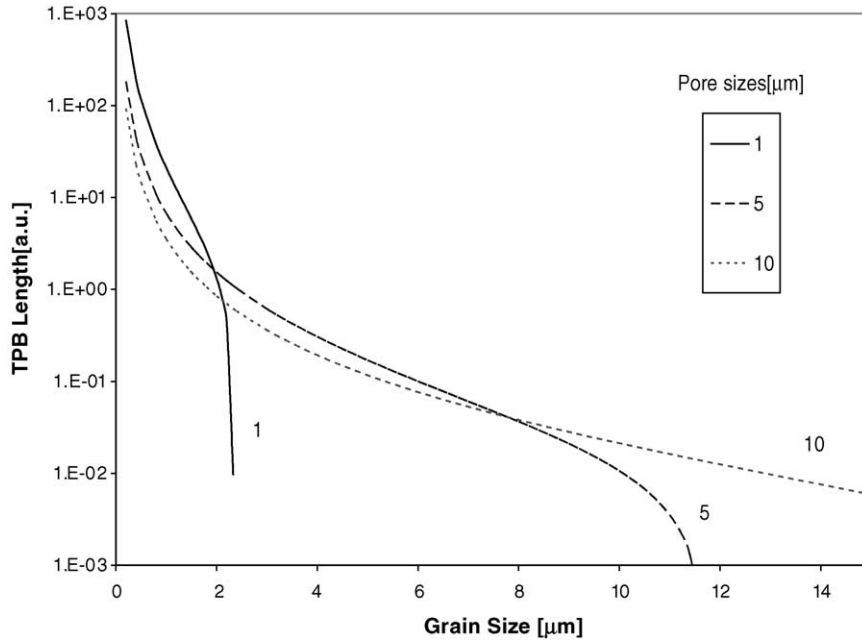


Fig. 4. Relationship between the TPB length and grain size of solid phase when porosity and  $\alpha$  are set to 30% and 0.7, respectively. The pore size varies as shown.

**3. Results and discussion**

Eq. (2) represents the triple-phase-boundary length as a function of  $D_s$ ,  $D_p$  and  $V_p$ . The TPB length is inversely proportional to the solid grain size  $D_s$ , and the relationship between the TPB length and  $D_p$  and  $V_p$  is schematically shown in Figs. 2 and 3 when  $\alpha$  is approximated to 0.7. There is little variation of TPB length over realistic value of  $\alpha$ , and therefore the effect of  $\alpha$  is not considered further.

The graphs in Fig. 2 clearly show that smaller grain size greatly increases the TPB length no matter how the pore size and porosity change. However, the TPB length decreases significantly and TPB domain shrinks when the grain size increases. For larger grain size, the TPB only covers the domain of larger pore size and lower porosity.

Fig. 3 indicates that a smaller pore size results in high TPB length only when porosity is low and further reducing the pore size would decrease the length. Overall TPB length decreases

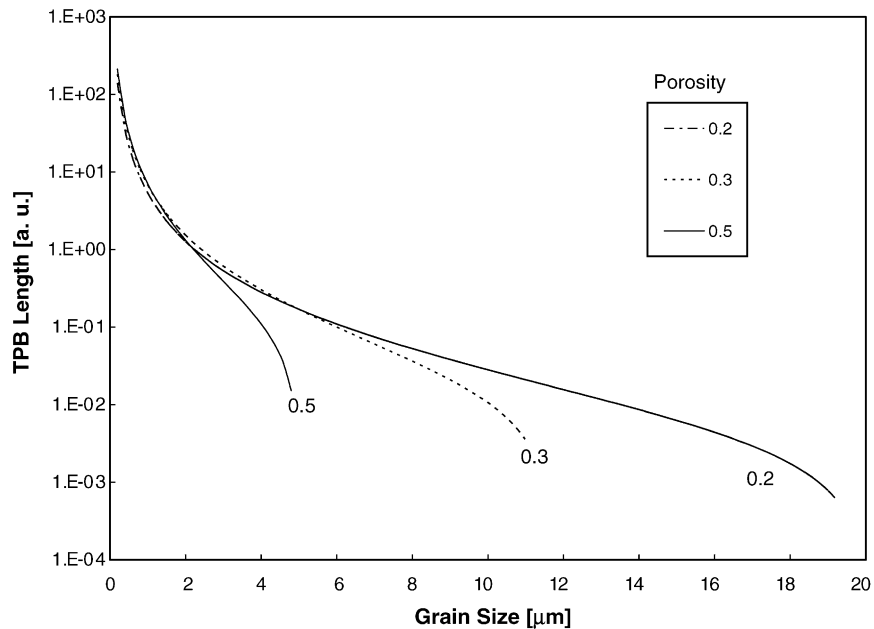


Fig. 5. Relationship between the TPB length and grain size as a function of pore volume (porosity). The pore size is 5 μm.

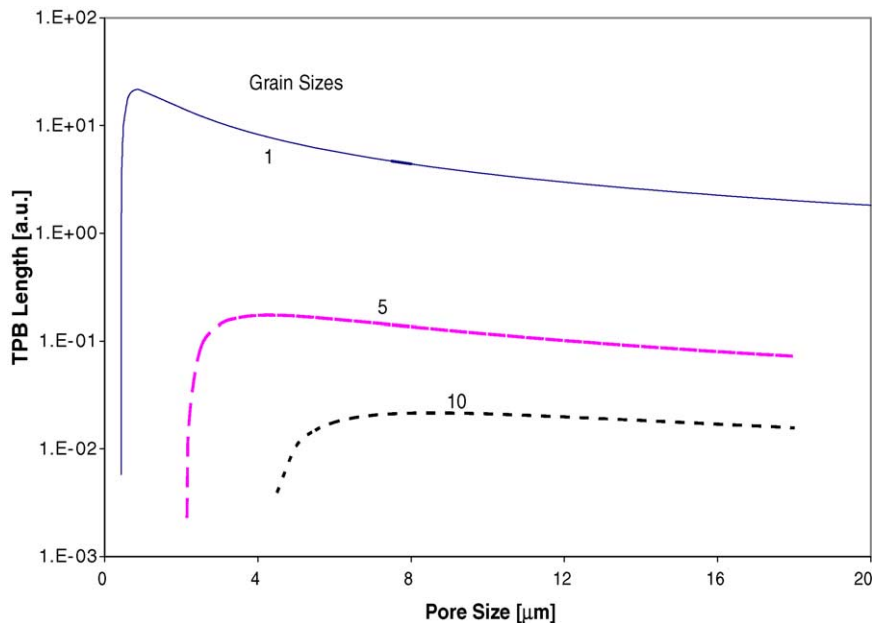


Fig. 6. Relationship between the TPB length and pore size. The porosity is 30%.

with increasing pore size but larger pores can tolerate much wider porosity range.

The 2D relationship between the TPB length and solid grain size, pore size or porosity will be discussed in more detail below.

First we examine the relationship between the TPB length and grain size which is plotted in Fig. 4 with porosity fixed at 30% and  $\alpha$  at 0.7.

Overall, the TPB length dependence exhibits three regions (Fig. 4). The triple-phase-boundary length decreases expo-

nentially with increasing grain size when the grain size is small, for example, the TPB length drops by two orders of magnitude when the grain size changes from 0.5 to 2  $\mu\text{m}$ . Hence, controlling the solid grain size is extremely important in maximizing the TPB length. With increasing grain size, the TPB length exhibits a relatively lower decrease. Larger pore sizes extend this stage of behavior. In the third stage, the TPB length decreases rapidly with increasing grain size. A worst case scenario occurs when pores are much smaller than the grains and the TPB length drops precipi-

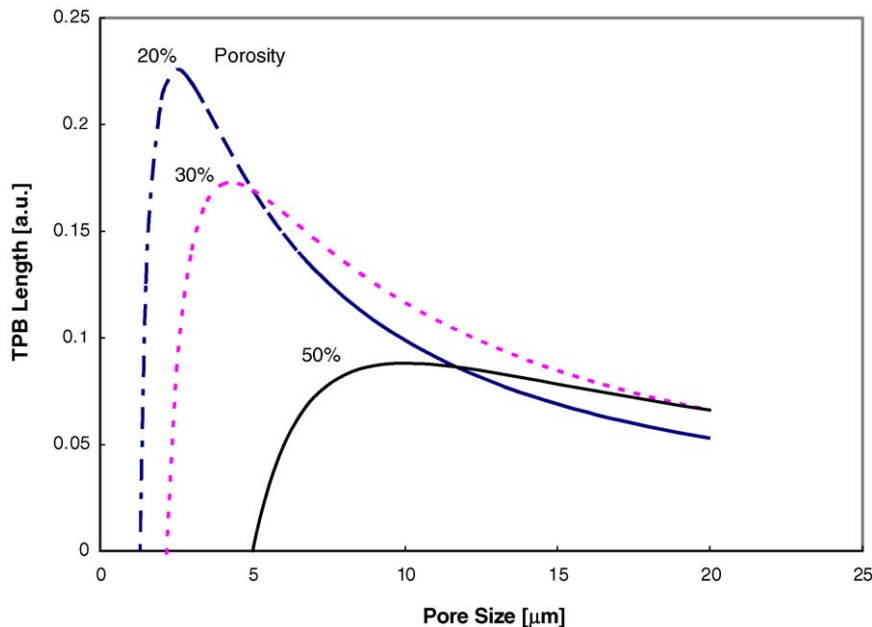


Fig. 7. Relationship between the TPB length and pore size at different porosities of 0.2, 0.3 and 0.5 and solid grain size of 5  $\mu\text{m}$ .

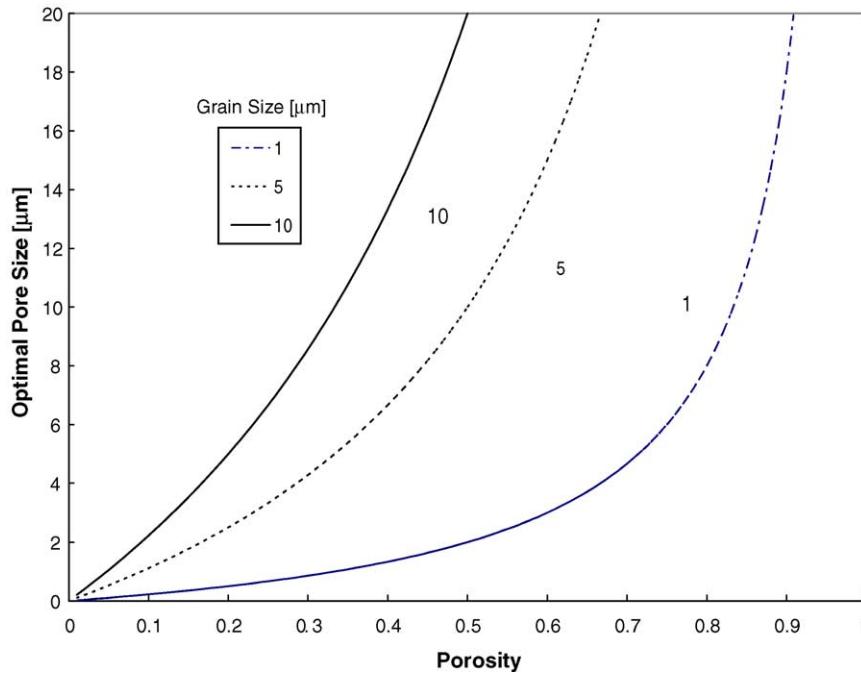


Fig. 8. Relationship between optimal pore size and porosity for different solid grain sizes of 1 and 10 μm.

tously. Large pores can tolerate a wider distribution of grain sizes before the TPB length suffers a severe drop. Generally speaking, a finer microstructure results in a longer TPB, which is in agreement with Tanner’s model [2]. A nanostructured composite would have good potential for SOFC application.

Fig. 5 shows the relationship between TPB length and grain size at different porosities when the pore size is 5 μm. The TPB length again decreases with increasing solid grain size. Note that at a high porosity, the TPB length would be less

tolerant of large solid grains. In other words, a higher porosity cannot support a large TPB length as grain size increases.

The pore size dependence of the TPB length is shown in Figs. 6 and 7. It indicates that TPB length increases sharply with increase of pore size and then reaches a maximum before decreasing. The decrease is at a much lower rate than the increase, e.g. when the grain size is 5 μm, the TPB length increases by orders of magnitude until the pore size reaches 3 μm but remains near the same value after 3 μm. Consequently there is an optimal pore size to maximize the TPB

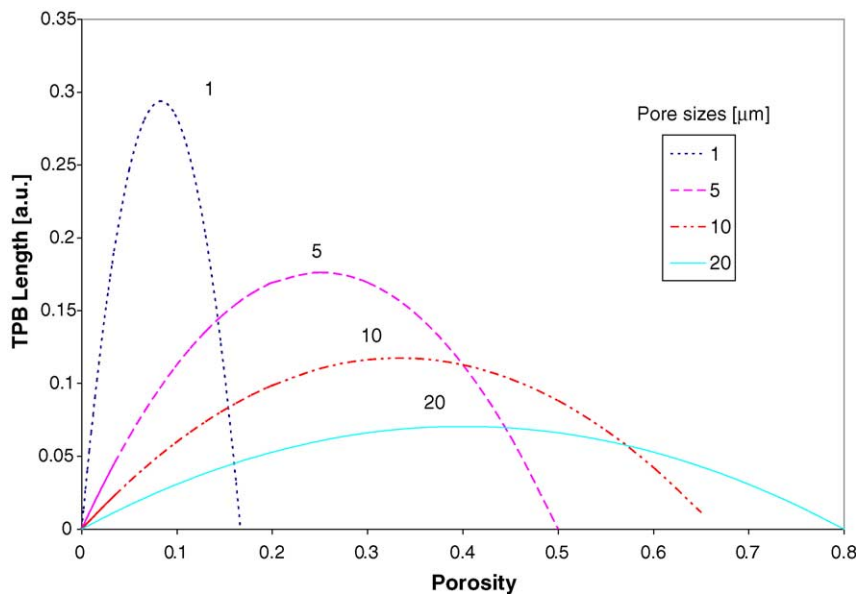


Fig. 9. Relationship between the LTPB and porosity at different pore sizes of 1, 5, 10, and 20 μm. The solid grain size is 5 μm.

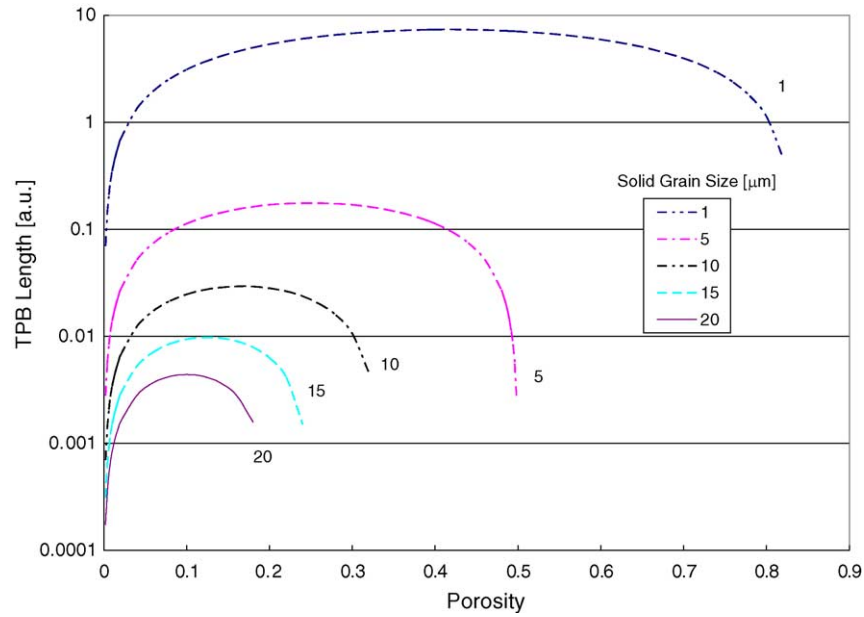


Fig. 10. Relationship between the TPB length and porosity at different solid grain sizes of 1, 5, 10, and 20 μm and a pore size of 5 μm.

length, which is in agreement with the results of Maggio’s model [3] and results [4]. The optimum pore size ( $D_p^{opt}$ ) at which the TPB length is maximized shifts to a higher value as grain size and porosity increase.  $D_p^{opt}$  can be obtained by differentiating Eq. (2):

$$\frac{\partial(L_{3pb})}{\partial D_p} = 0$$

from which we obtain:

$$D_p^{opt} = 2D_s \frac{V_p}{1 - V_p} \tag{3}$$

From Eq. (3), the  $D_p^{opt}$  is directly proportional to the solid grain size  $D_s$  and porosity  $V_p$  when  $V_p$  is very small, but approaches infinity as  $V_p$  goes to 1 (Fig. 8). In other words, a larger pore size would optimize the TPB length as the grain size and porosity increase.

In the SOFC case, a target of 30% porosity is usually maintained in the electrodes. If  $V_p = 30\%$  is substituted into Eq. (3), we obtain  $D_p^{opt} = (6/7)D_s$ . It is suggested from Figs. 6 and 7 that it is safe to maintain the pore size larger than 6/7 of grain size since the TPB length drops significantly if the pores are smaller than  $D_p^{opt}$ .

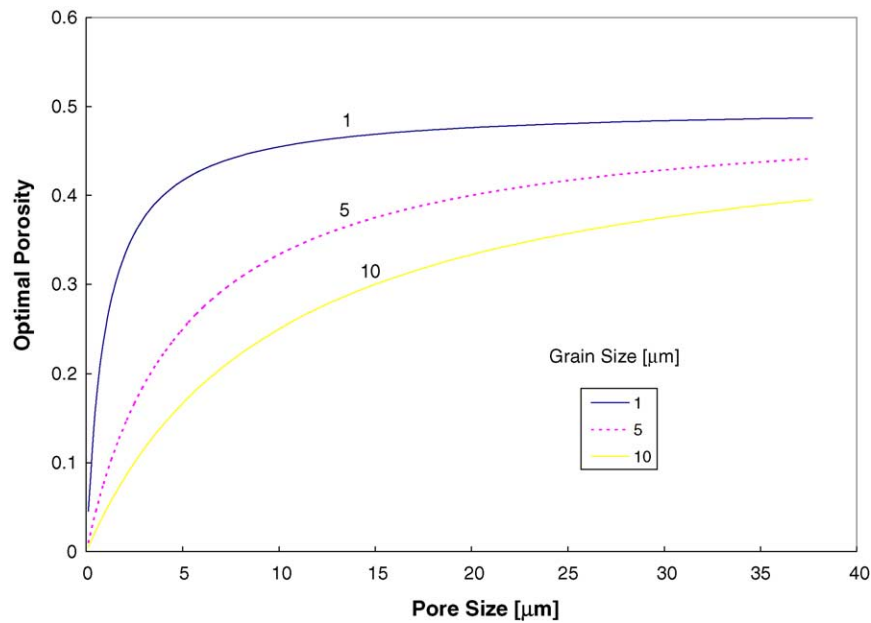


Fig. 11. Relationship between optimal porosity and pore size at different solid grain sizes of 1 and 10 μm.

Finally Figs. 9 and 10 show the dependence of the TPB length on porosity. The TPB length is also optimized by controlling the porosity at different pore or grain sizes. Previous work on SOFC performance measurement [4] supported the effect of porosity on the TPB length. The optimal porosity  $V_p^{\text{opt}}$  at which the TPB length is maximized can be derived from Eq. (1) in the same way as above:

$$V_p^{\text{opt}} = \frac{D_p}{2(D_p + D_s)} \quad (4)$$

It is indicated from Eq. (4) that when the pore size is much smaller than solid grain size,  $V_p^{\text{opt}}$  increases linearly with pore size but reaches a limit when the pore size becomes much larger than the solid grain size (Fig. 11).

The curves of TPB length versus porosity are symmetric about  $V_p^{\text{opt}}$ , which implies that deviation from  $V_p^{\text{opt}}$  in either direction would decrease the TPB length equally.

#### 4. Conclusion

As an important parameter of a three-phase (two-solid and one-pore-phases) electronic composite, the three-phase-boundary length is a function of size and volume fraction of the three phases. A finer solid grain size increase the TPB length exponentially, while the pore sizes and porosity have optimal values at which the TPB length can be maximized and the optimal values depend on grain and pore size and porosity. The curves of TPB length and pore size are asymmetric. The TPB length drops significantly faster on one side of the maximum than the other side. However, the dependence of the TPB length on porosity is symmetrical about the optimal porosity. Any deviation of porosity from the optimal decreases the TPB length equally.

We can combine the results of this analysis with the constraints on the fabrication of solid oxide fuel cell electrodes. The electrodes are sintered from micron-sized powder. The resulting grain size is approximately 5  $\mu\text{m}$  but could vary from 1 to 10  $\mu\text{m}$  or more. Pore size is non-uniform as some pores originate from inter-particles space and some from graphite which is added as a pore forming agent. We generally expect a pore size in the range of 1–10  $\mu\text{m}$  but larger pore size could be produced if desired. The target porosity is 30% with an allowable range of 20–40%. There is limited open porosity below 20% and poor crush strength above 40% porosity.

From our geometrical analysis aimed at maximizing the TPB length, we conclude that

1. A pore size of 5–10  $\mu\text{m}$  diameter is ideal when the grain size is 1–10  $\mu\text{m}$  (at 30% porosity). A 1  $\mu\text{m}$  grain size has a TPB length 2–3 orders of magnitude greater than a 10  $\mu\text{m}$  grain size.
2. A fine grain size of 1–2  $\mu\text{m}$  and high porosity (30% or greater) offer the best combination for maximizing TPB length. On the other hand, for a grain size distribution of 3–10  $\mu\text{m}$ , less than 30% porosity is optimum.
3. The TPB length has a low dependence on pore size beyond a critical limit. For 30% porosity, the critical ratio of pore to grain size is 6/7. Very poor performance is predicted below the critical ratio.
4. The TPB length is not highly sensitive to changing porosity near the optimal value. For example, for a 5 mm grain size, the TPB length changes by less than a factor of 2 between 10 and 40% porosities.
5. An ideal combination of parameters is predicted to be a pore size of 1–2  $\mu\text{m}$ , a grain size of 1–2  $\mu\text{m}$  and a porosity of 30–60% in order to maximize the number of TPB sites. From practical consideration, it would be difficult to limit grain growth to such small size during sintering and operation and provide adequate gas diffusion through such fine pores.

#### Acknowledgement

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