



Geometrical modeling of microstructure of solid oxide fuel cell composite electrodes

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ABSTRACT

A model based on random packing of electron and ion conductor particles is developed to study the microstructure performance relationship of solid oxide fuel cell electrodes. This three-dimensional model takes into account special variations of triple phase boundary (TPB) by keeping track of all particles in the packing. Porosity of the media can be controlled and is set to 30%. Effect of particle size, electrode thickness, electrode composition and particle size ratio on the length of TPB line has been studied. The study shows that unlike what models based on percolation theory suggest, the electrode media is not homogeneous for electrochemical reaction. While increasing the thickness increases the length of the TPB to some extent, beyond that little or no improvement was observed. The study also revealed that adding a current collector layer made of electron conductors can increase the TPB line by at least 4%. While for particles of the same size maximum length of TPB was observed at equal volume percent of electron and ion conductor particles, for size ratio of particles other than one the maximum TPB tends to occur above or below 50% depending on the size ratio.

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1. Introduction

In addition to the increasing concerns about energy supplies for future, environmental issues such as air pollution and global warming has created an increasing motive towards the development of clean energy sources and equipments [1]. Fuel cells, in this regard have received much attention as efficient energy conversion systems and hydrogen is recognized as the most reliable source to fuel the future economy [2–4].

Apart from having zero emissions for clean fuels like hydrogen, silent operation and higher efficiencies compared to the other types of energy conversion devices, solid oxide fuel cells (SOFC's) have other remarkable characteristics that makes them the best choice among other types of fuel cells. Compact design of SOFC's and the absence of moving parts provide more reliable operation with minimal service personal [5]. The solid electrolyte and the absence of any liquid eliminate the problem of electrolyte movement and flooding in the electrodes which are observed in molten carbonate fuel cells (MCFC's) [6].

Despite a great progress in the development of other types of fuel cells and despite the fact that SOFC's also have improved since

their early recognition in 1937 [7], most of the experts in the field believe that solid oxide fuel technology is still in its infancy period. One of the big challenges for researchers is to decrease the operating temperature to at least intermediate values of around 600–800 °C. The reason for high operating temperature conventional SOFC's is that the ionic conductivity of YSZ (yttria-stabilized zirconia) and electrocatalytic activity of electrodes is very low at low temperatures. At lower temperatures thermal conductivity mismatch among materials, sealing problems and stability issues are easier to manage and it allows wider selection of less expensive materials [8].

Manufacturing problems are also to be solved. Electrolytes must be made thinner to reduce Ohmic resistance and cell sealing must be improved. The focus now, is on composite electrodes which are the mixture of electron and ion conductor and on the better understanding of microstructure of composite electrodes to achieve and obtain better overall cell performance. It has been demonstrated both experimentally and through simulation that the microstructure of composite SOFC electrodes has great impact on cell performance [9–13].

Current work deals with three-dimensional microstructure simulation of SOFC composite electrodes and it is the continuation of the previous work [12] which was on two-dimensional microstructure simulation of SOFC electrodes. The extra degree of freedom afforded by the third-dimension can create pathways in space for

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Nomenclature

d	diameter of the particles
e_l	electronic conductor
i_o	ionic conductor
L	thickness of electrode
L_{TPB}	length of triple phase boundary, also TPBL
r	ratios of the particles
S_{TPB}	active triple phase area
ϕ	volume fraction of electron or ion conductor particles

the triple phase lines that are not possible in two-dimensions. Hence this is an important step in the evolution of microstructure models that captures the complexity of composite electrodes in a realistic manner.

2. Review of electrode modeling

Electrochemical reaction in SOFC composite electrodes occurs in triple phase boundary (TPB) where ion conductor particles meet electron conductor particles and pores exist to conduct gas phase species. To be capable of performing electrochemical reaction, electron and ion conductors must be in contact with their corresponding base (i.e., current collector in case of electron conductors and electrolyte in case of ion conductors) through other particles of the same type. Whether the whole contact area is electrochemically active or it is only the contact perimeter depends on particle size and operating condition [14–16]. In the modeling environment both cases are practiced depending on the operating condition and assumptions of particle size [11,17]. Kenjo and Wada studied the capacitance of Pt–YSZ cathodes and showed that for particle size of 0.1 μm , not only TBL but whole contact area is electrochemically active [15]. Almost the same results were observed by Wang and Nowick for particles smaller than 0.2 μm , while for particles larger than 2 μm , they attributed whole electrochemical reaction to TBP line [16]. By investigating oxygen reduction active sites on LSM–YSZ interface, Horita et al. showed that for high overpotentials only TPB line is electrochemically active while for lower overpotentials they observed some traces of oxygen on inner regions of contact area [14]. Whether having whole contact region active or only part of it, it is important to have good contact between particles of the same type as well as the particles of different type and to optimize the structure to achieve maximum possible active area resulting in the better cell performance.

Porous electrode models based on percolation theory are one of the approaches to simulate composite electrodes [11,17–19]. This model as developed by Costamagna et al. captures most of the experimental observations but has its shortcoming [11]. Since it is based on percolation theory, the model takes into account only the electrode and electrolyte conducting chains which go all the way through the electrode and short chains that might contribute to electrode performance are ignored. For large electrode thickness/particle diameter ratios and inside percolation thresholds this does not introduce much error while for small electrode thickness/particle diameter ratios short chains are dominant and the model assumptions are no longer valid. This model cannot be used for electrode compositions outside the percolation threshold [11,20].

Studies based on this model show that not only the composition of electrode and size of particles affect electrode output, but also the size ratio of the particles has strong impact on the electrode performance. Costamagna et al. showed that resistance of the electrode

is minimized for the compositions of electrode close to percolation thresholds of electron conducting particles and this minimum tends to decrease for thicker electrodes. Increasing the thickness of the electrode on the other hand, increases the amount of Ohmic resistance of the electrode. Based on this study they concluded that an optimum value for electrode thickness must be chosen [11]. Virkar et al. applied Butler–Volmer and diffusion equations to the model and showed how composite electrodes are effective in reducing activation polarization by spreading the reaction zone further inside the electrode [21]. Chan and Xia later concluded that although electrochemically active sites might be present all over the electrode thickness, only very thin zone of the anode in the vicinity of electrolyte contributes to most of the current generation [22]. They attributed this observation to high electronic conductivity of electron conductor compared to very low ionic conductivity of ion conductors.

Random nature of structure of composite electrodes suggests that a random packing of electron and ion conductor particles will be able to model the behavior of electrode. Some people used structured packing of particles where electron and ion conductor particles are randomly distributed [10,12,23,24], while others use totally random packing of particles [25–28]. Although previously discussed porous electrode models based on percolation theory are capable of being extended to three-dimensional models, most of the work done in that framework was carried on in one-dimension along the electrode depth [11]. This simplification which is imposed mostly to decrease computational load, in fact does not have major impact on the results and is reasonable simplification without sacrificing the accuracy. The reason for this can be found in the intrinsic assumptions for those models. The medium of the electrode is assumed to be homogeneous in the amount of active sites and the electrolyte surface as well as current collector is assumed to have the same potential. Random packing models on the other hand need at least two-dimensions to represent the particles. Furthermore, their capability in predicting real world behavior of electrodes is very limited for 2D simulation [12]. This is because the average coordination number of particles in 2D is less than 3D case, resulting in different percolation behavior. Therefore simulations based on random packing models need to be conducted in three dimensions to obtain more realistic results.

Although results of all simulations based on random packing of particles show that there is a sharp decrease in electrode conductivity near percolation threshold, the onset of the variations differs for different works depending on the structure that is been chosen for the packing. While Sunde observed a sudden increase in electrode conductivity and decrease in polarization resistance for a simple cubic lattice structure of composite electrode near volume fraction

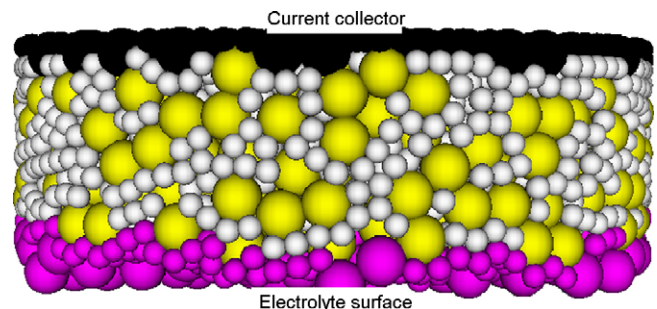


Fig. 1. Composite electrode created in the computer. White particles are electron conductors while yellow particles represent ion conductors. Bottom layer is the electrolyte surface made of ion conductors while top layer is totally electron conductor and acts as current collector. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

of 0.3 [23,25], Abel et al. applied the same resistor network model for a face-centered cubic (fcc) lattice showing that the onset of rapid rise in electrode admittance occurs at volume fractions very close to 0.2 [29]. The reason for this difference lies in different coordination number of the particles (6 and 12, respectively) which results in different percolation thresholds of about 0.312 and 0.199 for simple cubic and fcc lattices [30,31]. Studies showed that relative magnitude of electrode, electrolyte and reaction resistance are very important parameters in deciding the composition and thickness of the electrodes [25,26,29] and for the realistic experimental values of these parameters it is very important to optimize the geometry of electrode to obtain maximum TPB line for electrochemical reaction.

3. Development of the model

The current study is the continuation of our previous work [12] and part of ongoing efforts to understand the effect of microstructure on the performance of SOFC electrodes. Random structure of SOFC composite electrodes was built in 2D first by creating random packing of YSZ and LSM particles and then transforming the structure into a continuous geometry and then solving for relevant transport phenomena as well as electrochemical reaction. The current work deals with more realistic case of 3D simulation of the effect of geometry on the performance of composite electrodes.

The structure of composite electrode is simulated by completely random packing of spheres of different size using collision detection and location optimization. Starting with a layer of ion conductor at one end of electrode, the electrode is built by placing particles next to the previously formed layers and finding a stable close position of contact. The composition of the electrode, i.e., the volume fraction of each constituent is controlled during the formation process based on the relative amounts and ratio of particle sizes. A layer of electron conductor at the top acts as a net-like current collector for electrode assembly. Fig. 1 shows a composite electrode created in this manner. After creating the packing, to obtain a certain degree of overlap between particles the sintering behavior of particles is simply modeled by enlarging the size of the particles. Sunde argued that the length of TPB resulting from the contact between an ion conductor and an electron conductor particles of the same radius r is almost three times the radius, or: $L_{TPB}/r \approx 3$ [23]. For particles of the same size this ratio corresponds to almost 10% increase in particle size for two touching spheres and therefore 10% enlargement of particle size was used for all simulations. Packing density before sintering depends on the ratio of r_{io}/r_{el} and the maximum packing density of about 60% was observed for particles of the same size, which is less than the packing density that would be obtained if it was face-centered or body-centered cubic lattice (74.05 and 67.98%, respectively) and more than 52.33% for simple cubic lattice.

Porosity of the final composite electrode after resizing the particles was also calculated. This was done by subtracting overlapping volumes from the solid volume giving the possibility for two or three sphere to overlap [32,33]. The packing density thus obtained was between 74 and 77% corresponding to 23–26% porosity depending on the ratio r_{io}/r_{el} . Although many believe that this amount of electrode density is enough to guarantee negligible mass transfer resistance, the porosity was increased artificially to about 30% [34,35] to make sure that all contact points between particles of different types have easy access to gas species.

Electrochemical reaction on a single site inside a composite electrode requires the transfer of electrons, ions and gas phase species to or from the reaction site which gives rise to the concept of TPB discussed in review section. Considering the importance of TPB on the performance of SOFC electrode and direct effect of increas-

ing L_{TPB} on decreasing electrode losses [36], most of the current work is devoted to an investigation of this effect. After creating the packing of particles with two types of electron and ion conductor spheres, each particle starts to search for its neighbors (object oriented design) and therefore the role of each particle in the electrode will be specified. Some of the particles are electrochemically active and therefore there is TPB on one or few sites of those particles. Some of them only conduct electrons or ions while some others are completely isolated from the chain of same type particles and represent a loss for the electrode. L_{TPB} is calculated separately for each contact point considering the fact that for random packing of particles the degree of overlap and hence L_{TPB} might be different for different contact points.

4. Results and discussion

Electrode under study is a circular disk which might have different thicknesses to investigate the effect of thickness on the performance. Sunde used an electrode with square cross-section having 20 particles in each side and then used cyclic boundary condition [23,25,26]. Although the cyclic boundary condition implies an infinite electrode size, it does not reflect the random behavior of the packing. For small samples, especially when the electrode is thick, the results of simulation do not reflect the reality and usually L_{TPB} is underestimated. Beside that, more disperse and some times misleading results are obtained for different random structures of the same size when the diameter of the sample disk is small. Note that in reality, thickness of the electrode is very small compared to the diameter but such an electrode is impossible to create by simulation and therefore minimum reliable sizes must be selected. Fig. 2 shows the results of the dispersion study to determine the minimum acceptable diameter of the sample electrode disk so that the rest of the simulations could be performed based on this size. Simulation for each electrode sample has been performed 1000 times and the results of standard deviation are reported. As shown in this figure, point 1 corresponding to an electrode sample of 10 μm in diameter and having only about 100 electron or ion conductor particles in each layer represents more disperse L_{TPB} results. For bigger samples the standard deviation decreases, demonstrating more reliability for the data obtained from a single run. Calculations show that while the probability of getting values of L_{TPB} from a single run being 3% off the population mean is less than 40% for sample rep-

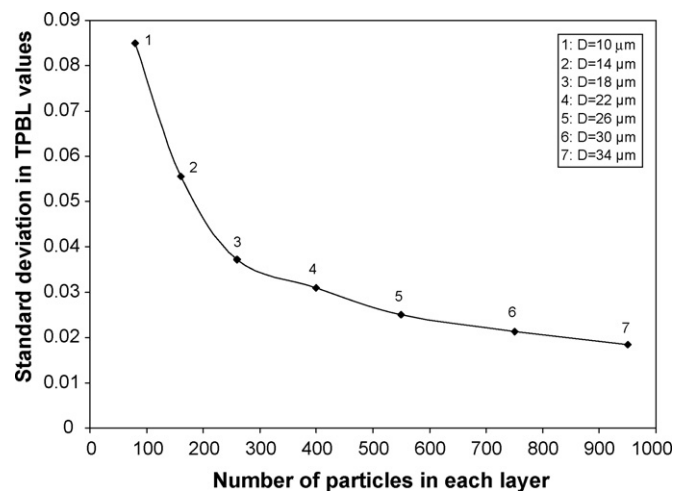


Fig. 2. Standard deviation in TPBL calculations for different electrode sizes. Each standard deviation point corresponds to population of 1000 computer simulations of random packing. $r_{ed} = r_{io} = r = 1 \mu\text{m}$ and $L_{TPB}/r \approx 3$.

resented by point 1, this probability is more than 98% for sample 6 and beyond. Therefore for the rest of this work the diameter of the container to create the packing of ion and electron conductors is chosen in a way that it contains more than 700 particles in each layer parallel to current collector.

Effect of particle size on the performance of composite electrodes has been investigated both theoretically [10,17,37] and experimentally [38,39]. Jiang et al. examined the effect of NiO particle size on the performance of the anode and observed much lower polarization resistance of less than $1 \Omega \text{ cm}^2$ for average particle size of $2.9 \mu\text{m}$ compared to much higher values of more than $4 \Omega \text{ cm}^2$ for average particle size of $10 \mu\text{m}$ [40]. Higher interfacial area between LSM and YSZ particles was observed by Song et al. for sample of electrode with finer LSM particles and for high enough sintering temperatures they observed lower polarization resistance for finer sample [38]. While lower polarization resistance can directly be attributed to higher L_{TBP} [36] all these observation can be cleared in the light of percolation theory and coordination number in random packing of particles. For random packing of particles of the same size, L_{TBP} is inversely proportional to the square of particles size while active interfacial area, S_{TBP} is inversely proportional to the particle size [11]:

$$\begin{aligned} L_{\text{TBP}} &\propto \frac{1}{r^2} \\ S_{\text{TBP}} &\propto \frac{1}{r} \end{aligned} \quad (1)$$

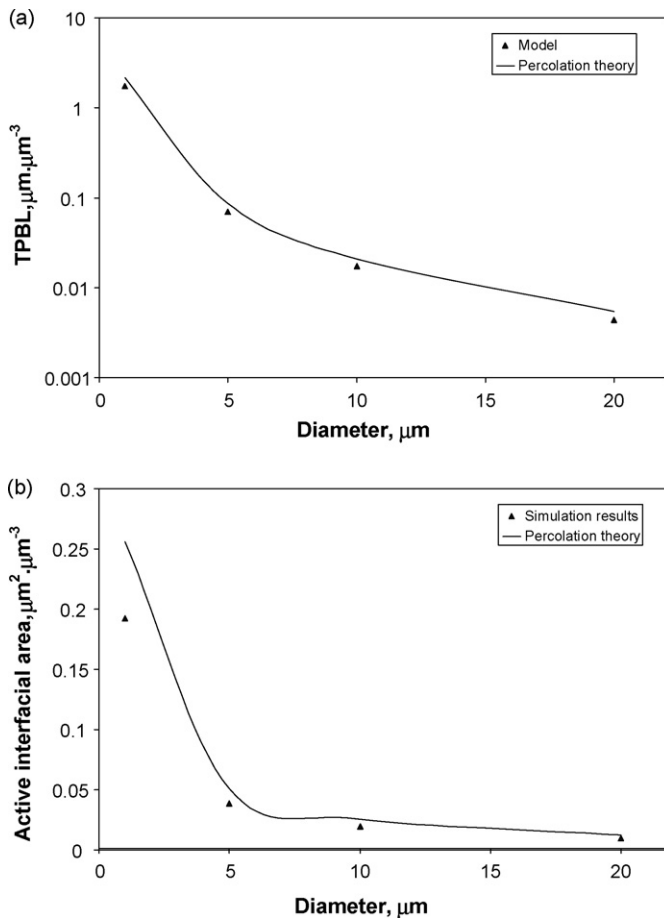


Fig. 3. (a) Dependence of TPBL and the diameter of particles. $r_{\text{io}} = r_{\text{el}}$, $L_{\text{TBP}}/r \approx 3$ and $\phi_{\text{io}} = \phi_{\text{el}} = 50\%$. (b) Dependence of active interfacial area the diameter of particles. $r_{\text{io}} = r_{\text{el}}$, $L_{\text{TBP}}/r \approx 3$ and $\phi_{\text{io}} = \phi_{\text{el}} = 50\%$.

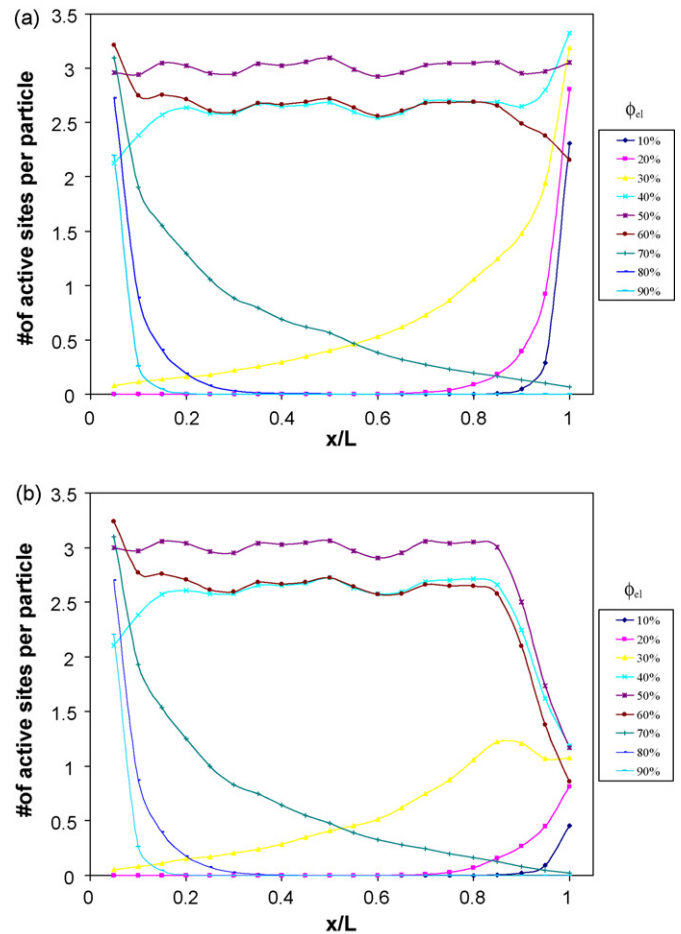


Fig. 4. (a) Concentration of active sites along the depth of electrode for different volume fractions of electron and ion conductors in the presence of CCL layer at the top. (b) Concentration of active sites along the depth of electrode for different volume fractions of electron and ion conductors in without CCL layer.

Fig. 3a and b shows the results of electrochemically active L_{TBP} and S_{TBP} obtained from the random packing of particles of the same size. Continuous curves indicate the predictions of percolation theory [11]. As it can be seen there is a very good agreement between the simulation and theory. Although small particles are favoured to create large L_{TBP} , very fine electrode particle size will create excessive mass transfer resistance and tends to increase concentration overpotential and therefore an optimum value of particle size must be taken. This optimum value depends on fuel cell operating parameters and especially electrode thickness [17,41].

One of the important results of the assumptions made on models based on porous electrode and percolation theory [11] is that electrochemically active sites are homogeneously dispersed within the electrode. It was shown however, in the previous work that this is not true especially when the volume fraction of electron and ion conductor particles is not at optimal value [12]. This conclusion is further proved by looking at Fig. 4a which shows the density of active sites along the electrode depth starting at electrolyte surface ($x/L = 0$) and ending at current collector ($x/L = 1$). For particles of the same size, only when: $\phi_{\text{io}} = \phi_{\text{el}}$, the distribution of active sites is completely homogeneous. This homogeneity also holds as long as ϕ_{io} and ϕ_{el} values fall between 40 and 60% excluding the end points. For particle concentrations which do not fall in the above-mentioned range, higher active sites densities tend to occur at either ends of the electrode. As it can be seen even for ϕ_{el} equal to 30% which roughly corresponds to percolation thresh-

old of the packing, most of the active site occurs at the surface of the electrode while for $\phi_{el} = 70\%$ higher active site densities will be observed at electrolyte surface. Although the total amount of active sites is the same in both compositions, in case of $\phi_{el} = 70\%$ there will be more active sites available in close vicinity of electrolyte which is favoured as the rate of the reaction tends to be higher close to electrolyte surface [12,22]. Therefore active sites will be better utilized when they are close to electrolyte surface. This finding leads to very important practical guideline in preparing SOFC composite electrodes. Applying optimum calculated composition to real electrodes is impossible giving the fact that particles have different size and always come with size distribution. Also sintering condition may change the effective size of particles and therefore alter optimum composition. Therefore with applying theoretically calculated optimum proportions to starting powders, one may end up with an electrode with ϕ_{el} higher or lower than desired. This finding suggests that selecting a starting powder concentration (ϕ_{el}) which tends to be few percent higher than calculated optimum value can guarantee maximum possible efficient active area and therefore it is always safer to overestimate the amount of electron conductor to be used in electrode mixture.

Results in Fig. 4a are obtained for the case of electrode covered at the top with a current collector layer (CCL) which is pure LSM (cathode) or Ni (anode). Effect of CCL in enhancing the performance of SOFC electrodes has been investigated experimentally [42,43] and theoretically [35,44]. This improvement in performance has been attributed to enhanced mass transfer and electric connectivity brought by CCL [43]. Although these are valid conclusions, simulation results of current work shown in Fig. 4b reveal other reason why CCL can improve the performance. Fig. 4b demonstrates the results of the same simulation as in Fig. 4a but for the case where there is no CCL layer made of LSM or Ni. Current collector in this case is a simple electron conductor incapable of conducting electrochemical reaction at TPB. There is appreciable amount of active sites lost in regions close to $x/L = 1$. More off is the composition from optimum value of 50%, more loss is observed as a result of eliminating CCL. Best case scenario ($\phi_{el} = 50\%$), 4% of active sites will be lost by eliminating CCL. Therefore covering the electrode with a layer of CCL will have noticeable effect on electrode performance in the form of decreasing polarization resistance.

Combined effect of electrode composition and thickness are shown in Figs. 5a, b and 6. Fig. 5a shows that for electron and ion conductor particles of the same size, maximum TPB length is obtained when $\phi_{el} = \phi_{io} = 0.5$. It also shows how the performance of electrode improves with increased L_{TBP} by increasing the thickness of the electrode. Ruud et al. showed that for a cathode made up of LSM and YSZ, the resistance of the electrode decreased by increasing the thickness up to some thickness and then remained constant [45]. This thickness at which the resistance levels off depends on particles size [19] as well as composition and conductivities of electronic and ionic phases. The results of Ruud et al. are justified from geometrical point of view by inspecting Fig. 5a and b. At low electrode thicknesses the rate at which L_{TBP} increases by increasing thickness is high and it levels off at higher thicknesses and we do not expect much improvements in amount of L_{TBP} for very thick electrodes. Juhl et al. reported the same phenomena in their experimental works [9] but the ‘critical thickness’ in case of their experiments was much lower of about 10 μm which could be the result of presence of relatively thick cathode CCL and lower porosity resulting in difficult mass transfer. Although the TPB length does not change beyond some thicknesses, polarization resistance of the electrode may further increase due to mass transfer and diffusion limitations for high current densities [17]. Fig. 6 shows how the volume percent of isolated particles change with electrode composition. At very low concentrations of electron conductor in the

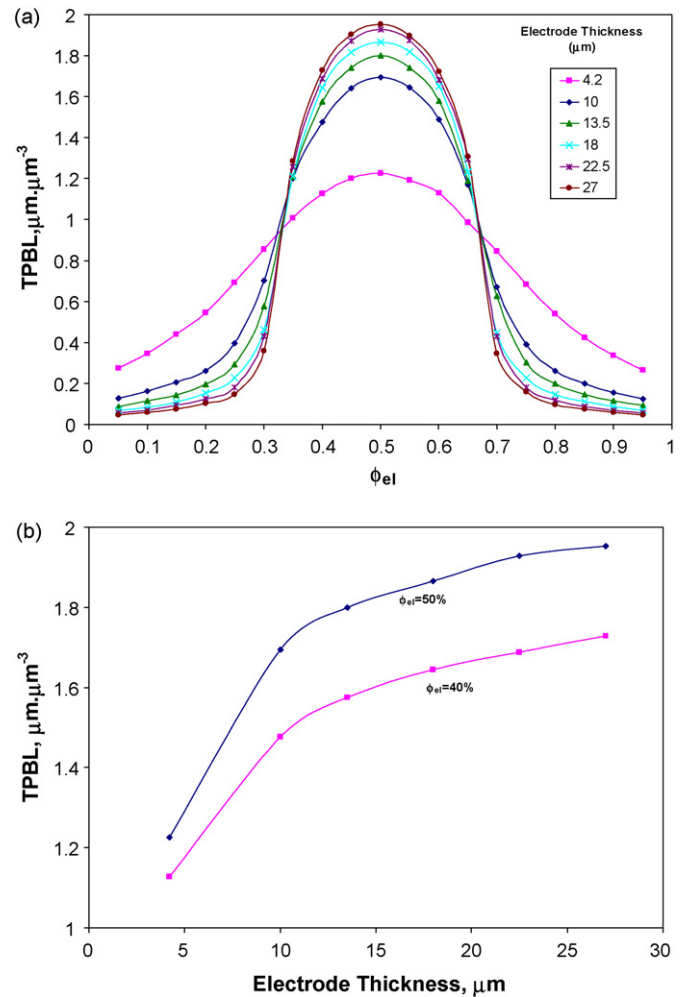


Fig. 5. (a) The effect of thickness is considerable at low thicknesses but levels off for higher thicknesses suggesting that there should be optimum value for the thickness taking reaction and mass transfer into account. $r_{io} = r_{el}$. (b) Effect of electrode thickness in the TPBL of the electrode. $r_{io} = r_{el}$.

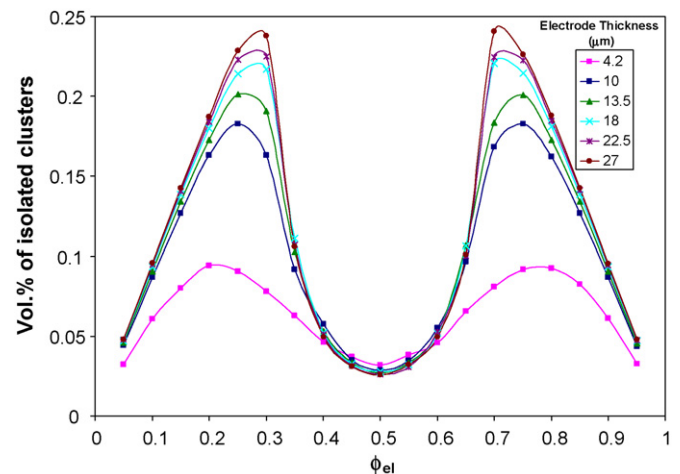


Fig. 6. Effect of the electrode thickness on the amount of isolated clusters inside the electrode. $r_{io} = r_{el}$ and $\phi_{io} = \phi_{el} = 50\%$.

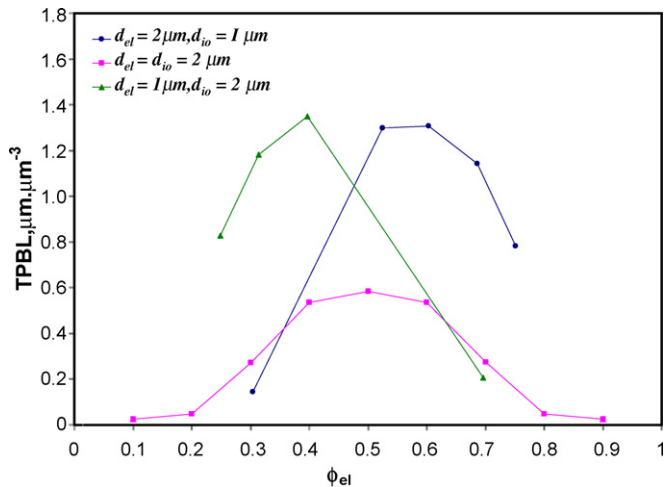


Fig. 7. Dependence of TPBL and volume fraction of ion conductor particles for different values of particle size ratio. Average electrode thickness is $30 \mu\text{m}$.

electrode, the reaction frontier is at the surface of the electrode and practically bulk of the electrode is made of ion conductors while most of the electron conductor particles at the surface are active which results in very low amount of isolated particles. As ϕ_{el} increases more and more electron conductor particle is introduced to a medium mostly occupied by ion conductors and hence loose connection to their base and therefore amount of isolated clusters increases. This increase continues until the concentration reaches percolation threshold and beyond that most of the isolated electron conductors connect together to form percolating chains and hence volume fraction of isolated clusters drops rapidly.

Effect of particle size ratio on TPB length is shown in Fig. 7. While for electron and ion conductor particles of the same size maximum TPB length occurs at $\phi_{el} = \phi_{io} = 0.5$, for d_{el}/d_{io} ratios above unity the maximum L_{TPB} tends to occur at higher ϕ_{el} values and for size ratios less than unity L_{TPB} maximizes at lower ϕ_{el} values. These results are comparable with the results obtained through models based on percolation theory [11,17,19]. It is important to mention that although size ratios $d_{el}/d_{io} = 2$ and $d_{el}/d_{io} = 0.5$ result in almost the same optimum TPB length; the second case is more favoured from overall polarization point of view. Ionic conductivities of typical ion conductors like YSZ is very small compared to electron conductivity of electron conductors and hence having more conduction path for ions by increasing volume fraction of ion conductor (lower ϕ_{el}) will decrease the polarization resistance, resulting in better cell performance.

5. Summary

In the current study we have developed a three-dimensional model to investigate the microstructure of SOFC electrodes and its characterization in terms of TPB length. While models based on percolation theory ignore the inhomogeneous nature of composite electrode structure and most of the models based on random packing fail to capture the real randomness of the electrode structure or only consider the case of electron and ion conductor particles of the same size, in this work we have built a realistic geometrical

model of the microstructure with as few assumptions as possible. Future work will be simulation of the electrochemical and Ohmic behavior and extending the work into continuous model capturing mass transfer and diffusion effects.

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