

# A novel approach to study the structure versus performance relationship of SOFC electrodes

Ali Abbaspour, K. Nandakumar\*, Jingli Luo, Karl T. Chuang

*Department of Chemical and Materials Engineering, University of Alberta, 504C Chem. Met. Bldg., Edmonton, Alta., Canada T6G 2G6*

Received 21 April 2006; accepted 9 May 2006

Available online 23 August 2006

## Abstract

The aim of this work is to develop a new rigorous model to study the structure performance relationship of solid oxide fuel cell (SOFC) electrodes. A new two-dimensional, geometrical model which captures the inhomogeneous nature of the location of electrochemical reactions based on random packing of electronic and ionic conducting particles has been developed. The results show that the concentration of oxygen inside the cathode in the 2D model is not only a function of the electrode depth but also changes along the width of the electrode. Furthermore the effect of composition of the electrode on the length of active three-phase boundary (TBP) and total polarization resistance has been demonstrated. A parametric study of the effect of the conductivity of ionic conductor and diffusion coefficient on the performance of the electrode has been given.

© 2006 Elsevier B.V. All rights reserved.

*Keywords:* Solid oxide fuel cells; Modelling; Electrode; Cathode

## 1. Introduction

The introduction of composite electrodes for solid oxide fuel cells (SOFC's) has opened a new promising perspective toward development and commercialization of SOFC's [1]. Despite simple single phase electrodes, cermet composite electrodes are mixture of electronic and ionic conductors and hence the electrochemically active region is not limited to the electrode–electrolyte interface and the reaction extends inside the electrode. As a result of increase in electrochemically active area, cermet composite electrodes improve the solid oxide fuel cell performance and allow larger power densities to be obtained [2,3].

In the present work we focus on modelling the electrochemical processes at the cathode in order to develop a better understanding of structure performance relationship of electrodes. Researches have been conducted in the past to study the effect of material and preparation methods on microstructure and performance of SOFC electrodes [4–7]. Although a wide variety of materials have been proposed and examined, lanthanum strontium magnite or LSM ( $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ) is considered to be the

most promising electron conductor along with Yttria-stabilized zirconia (YSZ) as an ion conductor. Apart from relatively high electronic conductivity and low ionic conductivity, LSM has good electrocatalytic properties for the reduction process that takes place in the cathode and its thermal expansion coefficient is very close to that of YSZ, which makes this pair a popular combination for use in composite electrodes [8–10].

Many parameters influence the performance of SOFC composite cathodes. Among those are size of electronic and ionic conductor particles, composition of the cathode, porosity and electrode thickness. Although some experimental work has been done to determine the effect of those parameters [3,7,11], broader study of SOFC cathodes through detailed simulation to obtain an optimized structure seems to be necessary.

Few models have been proposed by the previous researchers to describe the SOFC cathode operation. Despite minor differences in interpretation of reaction kinetics, most of these models rely on the homogeneity of composite electrode media for the electrochemical reaction and transport of ion, electron and material [12–14].

Costamagna et al. [12] considered whole contact area between electronic and ionic conductors to be active for the electrochemical reaction and calculated the active area using percolation theory and particle coordination number. They showed that simultaneous electronic and ionic conductivity inside the

\* Corresponding author. Tel.: +1 780 492 5810; fax: +1 780 492 2881.  
E-mail address: [kumar.nandakumar@ualberta.ca](mailto:kumar.nandakumar@ualberta.ca) (K. Nandakumar).

### Nomenclature

$C$	constant equal to $1.883 \times 10^{-2}$
$C_O$	concentration of oxygen
$D$	diffusion coefficient
eff	effective properties
el	electronic conductor
$f$	constant equal to $F/RT$ where $F$ is Faraday's constant and $R$ is gas constant
$i$	current density generated on the boundary ( $A\ m^{-2}$ )
$i_0$	exchange current density ( $A\ m^{-2}$ )
io	ionic conductor
$J$	current density inside ionic and electronic media ( $A\ m^{-2}$ )
$M$	molecular mass of gaseous species ( $gmol^{-1}$ )
$P$	pressure (Pa)
$T$	temperature (K)

### Greek letters

$\alpha$	charge transfer coefficient in Butler–Volmer equation ( $=0.5$ )
$\varepsilon$	porosity of the cathode
$\phi$	potential (V)
$\eta$	overpotential (V)
$\rho$	Resistivity ( $\Omega\ m$ )
$\sigma$	characteristic length of atoms in Eq. (9)
$\tau$	tortuosity of the cathode
$\Omega_D$	diffusion collision integral in Eq. (9)

electrode is not likely to happen for particles of the same size when concentration of one of the species is less than about 30 vol.% and depending on the relative size of ionic and electronic particles they obtained the minimum polarization resistances for the compositions of the electrode around 40 vol.%. Chen et al. [15] proposed a new kinetic model for electrochemical reaction and showed that polarization resistance assumes a relatively constant value over the wide composition range of about 37–63 vol.% of YSZ. They showed that the electronic current generation is much higher near the electrode–electrolyte interface and attributed this observation to the low ionic conductivity of YSZ [13].

Sunde [16] on the other hand used Monte Carlo method to show that while changing the conductivity of electron conductor particles does not have a pronounce effect on cell performance, increasing or decreasing the ionic conductivity and kinetic constants may have large impact on polarization resistance. Best performance has been found to fall within 40–60 vol.% of electron conducting particles.

## 2. Model development

Electrochemical reaction in a fuel cell composite electrode occurs at the contact area between electronic and ionic conducting particles. Furthermore, the electronic conductor (LSM

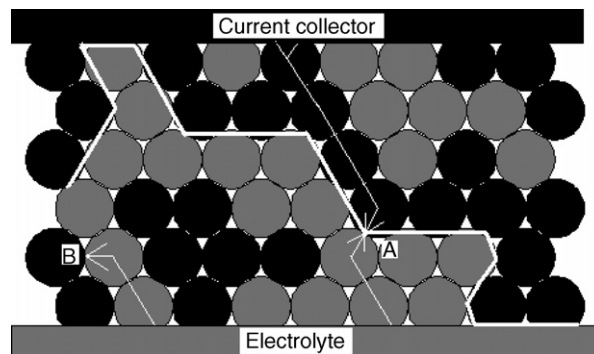


Fig. 1. Simplified schematic of a SOFC cathode showing the reaction line that starts from the left hand side of the electrode and extends to the right hand side.

for the cathode) must be connected contiguously between its contact with ionic conductor (typically YSZ) and the current collector through chains of other electronic conductors to be able to transfer the electron to the reaction point and similarly the ionic conductor must be connected to the electrolyte to conduct ions. To complete the process, open pores must be present to provide reactants for the reaction and to carry away the products of the electrochemical reaction. These conditions make the active site or active three-phase boundary (TPB) a very specific place in a sense that not all three-phase contact regions are active as assumed by the current models.

An ideal structure might be a co-continuous morphology that is commonly used in the polymer composite literature wherein every point within a phase is topologically connected to every other point within the same phase. Otherwise islands of one phase that are not connected to others are inactive and do not participate in the electrochemical processes. Realization of such morphologies depends in the fabrication processes and it is not commonly found in SOFC composite electrodes.

Fig. 1 illustrates the situation for a simplified 2D structure of a SOFC cathode. Black-coloured particles represent LSM particles while YSZ particles are represented by the grey-coloured regions. Supposing that pores are available all over the electrode to transfer reactant (oxygen in case of cathode) to the reaction sites, it is clear from this figure that not all contact points between LSM and YSZ particles are electrochemically active. For example contact point 'B' is not electrochemically active because the LSM particle is not connected to the current collector while the contact point 'A' is active as a result of capability of LSM and YSZ particles to conduct electrons and ions, respectively.

Connecting all electrochemically active TPB's a reactive line can be constructed for this 2D model of the cathode as shown in Fig. 1. The length of this line which is a measure of the available sites for the reaction is a function of composition of electrode. It is believed that the size ratio of the particles also has great impact on the length of this line [12,15].

Active line then divides the electrode into two parts, the upper part which is basically electron conductor and the lower part which is ion conductor. All YSZ particles falling in the upper part form isolated islands which are neutral to electrons and LSM particles below the active line are neutral to ion conduction by the same token. Although the isolated particles are electrically

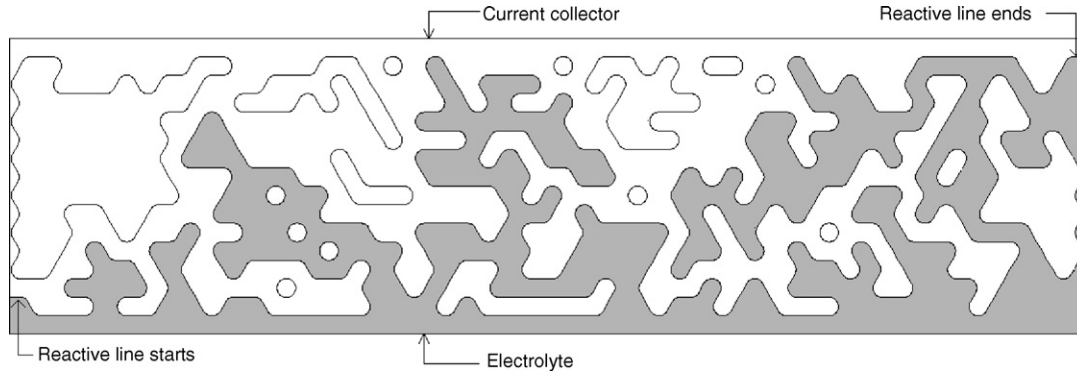


Fig. 2. Simplified schematic of a SOFC cathode showing the reaction line that starts from the left hand side of the electrode and extends to the right hand side.

neutral, they still are permeable to momentum, mass and heat. Fig. 2 is another more complex geometry obtained from randomly mixing of equal size YSZ and LSM particles and then transformation of the geometry into a continuous media of purely electronic or ionic conductors with pores all over the electrode. Grey-coloured continuous domain corresponds to YSZ while white-coloured continuous media indicates LSM. Note isolated white-coloured islands all over the electrode. As it can be seen the active TPB line is few orders of magnitude longer than electrode widths. The length of this line as discussed by the other people [12,15] is dependent on the ratio of electrode thickness to the particle size and also depends on the size ratio of electronic and ionic conductor particles.

The development of the model consists of the following steps:

1. Creating a random matrix of electronic and ionic conductor particles with prescribed composition similar to Fig. 1.
2. Transforming the data to a geometrical form similar to Fig. 2.
3. Model the transport and reaction processes in each domain using any multiphysics solver.

A computer code has been written to carry out the first and second steps and the third step is done using COMSOL® a commercial finite element software.

### 3. Governing equations

Ohm's law governs the electron and ion transfer inside electronic and ionic conductors along with the charge balance equation:

$$\nabla \phi_{el} = \rho_{el}^{eff} J_{el} \quad (1)$$

$$\nabla \phi_{io} = \rho_{io}^{eff} J_{io} \quad (2)$$

$$J_{el} = -J_{io} = i \text{ (in the active boundary)} \quad (3)$$

where  $\phi$  is voltage,  $\rho^{eff}$  the effective resistivity and  $J$  is the current density. Subscripts 'io' and 'el' represent ionic and electronic conductors, respectively. Symbol  $i$  denotes the transfer current density of the cathode which is an indication of the rate of electrochemical reaction taking place along the active line and is

expressed by the classical Butler–Volmer equation:

$$i = i_0 \left[ \frac{C_O}{C_O^*} e^{-\alpha f \eta} - e^{(1-\alpha) f \eta} \right] \quad (4)$$

where  $i_0$  is the exchange current density,  $C_O$  the oxygen concentration and  $C_O^*$  is the equilibrium oxygen concentration. Overpotential  $\eta$  in this equation is defined as:

$$\eta = E - E_0 = (\phi_{io} - \phi_{el}) - E_0 \quad (5)$$

where  $E_0$  is equilibrium potential of the electrode and is calculated from well known Nernst equation.

Effective porous media resistivity for electronic and ionic subdomain is calculated from pure material resistivity by the following equation [15]:

$$\rho_k^{eff} = \frac{\rho_k}{1 - \varepsilon} \quad (6)$$

where  $k$  refers to the electronic or ionic conductor and  $\varepsilon$  is the porosity which is set to average value of 34.66% [17].

The diffusion flux through the cathode can be determined using the well-known Stefan–Maxwell equation [18]:

$$-c \nabla x_i = \sum_{j=1, i \neq j}^n \frac{1}{D_{ij}^{eff}} (x_j N_i - x_i N_j) \quad (7)$$

where  $c$  is the total concentration of the gas mixture,  $x$  the mole fraction of species and  $N_i$  is the diffusive flux of specie  $i$ .  $D_{ij}^{eff}$  is the effective binary diffusion coefficient and carries the effect of both ordinary binary diffusion coefficient and Knudsen diffusion coefficient [19]:

$$\frac{1}{D_{O_2-N_2}^{eff}} = \frac{1}{D_{O_2-N_2}^{B,eff}} + \frac{1}{D_{O_2}^{K,eff}} \quad (8)$$

Binary diffusion coefficient can be calculated using kinetic theory by Chapman–Enskog relation [18]:

$$D_{ij}^B = CT^{3/2} \frac{\sqrt{(M_1 + M_2)/(M_1 M_2)}}{P \sigma_{12} \Omega_D} \quad (9)$$

Knudsen diffusion coefficient is a function of molecular velocity and radius of the pores. In this work experimental values reported by Zhao et al. [17] have been used.

Table 1  
Values of constants

Parameter	Value	References
$\rho_{el}$	$7.817 \times 10^{-5} \Omega \text{ m}$	[24]
$\rho_{io}$	$0.442 \Omega \text{ m}$	[24]
$i_0$	$2000 \text{ A m}^{-2}$	[19]
$T$	1073 K	
$\varepsilon$	34.66%	[17]
$\tau$	15.6	[17]
$D_{O_2}^{k,eff}$	$0.624 \text{ cm}^2 \text{ s}^{-1}$	[17]

Finally to calculate effective binary diffusion coefficients for the porous media from the values obtained using Eq. (8), the following equation based on Cussler [20] has been used:

$$D_{ij}^{B,eff} = \frac{\varepsilon}{\tau} D_{ij}^B \tag{10}$$

Tortuosity,  $\tau$ , of the porous media is set to 15.6 [17]. Table 1 summarizes the most important parameters and constants used in the model.

#### 4. Results and discussion

Fig. 3 shows the results obtained from the model for a cathode composed of about 2000 particles in a mixture of 50 vol.% of both LSM and YSZ. Applied overpotential to the electrode is 0.2 V. It can be seen in Fig. 3a that the concentration of reactant oxygen is not uniform along the cell width. Instead it changes depending on the density of electrochemically active points and the minimum concentration occurs near the electrode–electrolyte interface at regions of high active three-phase boundary. Fig. 3b shows the variation of current generation or the rate of electrochemical reaction along active boundary. This figure shows that although the concentration of oxygen is lower near the cathode–electrolyte interface, the reaction rate is higher in this region. This can be attributed to the lower ionic conductivity of YSZ. Since the ionic conductivity of YSZ is much smaller than the electronic conductivity of LSM the reaction tends to occur near the electrolyte to face smaller ionic resistance. This result is consistent with the results published by Chan and Xia [13] who reported the same phenomena for the anode. Although this trend holds for the practical range of the value of parameters, simulation showed that one cannot always expect higher reaction rates near the electrode–electrolyte interface. In fact apart from activation polarization or resistance, concentration and Ohmic resistances are both important in determining the rate of electrochemical reaction. If by any means oxygen supply to the reaction sites deep inside the electrode decreases it would result in electrode starvation at that points and the trend will be altered. This can happen when the porosity of electrode is not enough to transport the oxygen to reaction sites resulting in low effective diffusivity and thereby starvation of the cell near the electrode–electrolyte interface. Although it is not the case for LSM–YSZ, high electrocatalyst activity resulting in high exchange current density can also result in the alteration of the abovementioned trend.

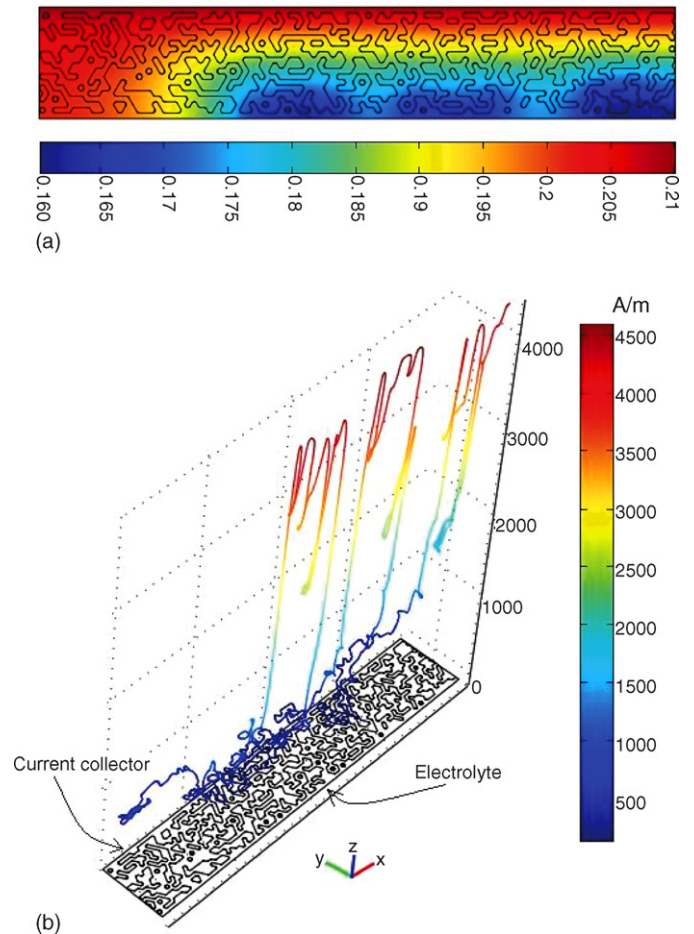


Fig. 3. (a) Mole fraction of oxygen inside the SOFC cathode obtained by the model. Upper boundary is current collector; lower boundary is cathode–electrolyte interface. Mole fraction of oxygen in the current collector side is set to 0.21. (b) Current generation along the active boundary.

Fig. 4 shows the dimensionless length of active line (length of active line per unit length of electrode width) as a function of LSM volume fraction. As pointed out by most of the authors [12,15] the length of active line or the active area assumes its

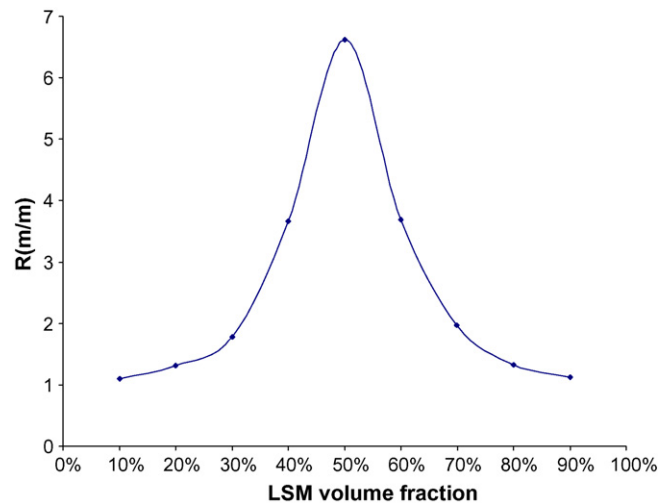


Fig. 4. Effect of composition on the electrode active area.

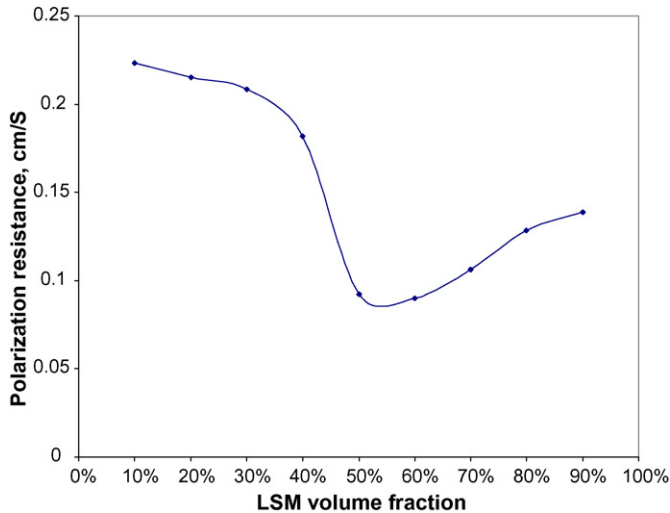


Fig. 5. Effect of composition on the overall polarization resistance of the electrode.

maximum value when the electrode is made up of equal amounts of electronic and ionic conductors of the same size.

The effect of electrode composition on the overall electrode resistance is shown in Fig. 5. Overall polarization resistance is defined as:

$$R = \frac{\eta}{I} \quad (11)$$

where  $I$  is the total current density of the electrode. As we can see the polarization resistance for the cell is minimum somewhere around 50–60 vol.% of the electron conductor. Although the length of active line is maximum at exactly 50% and the variations are symmetric according to Fig. 4, for polarization it is not symmetric and minimum resistance does not happen in the same composition. Even though activation polarization is minimum when the length of active line is maximum (50%), total polarization resistance depends on some other factors which tend to affect it. While the length of active area is only a function of the geometry of the electrode, the polarization resistance depends not only on the geometry but also on other parameters such as conductivities, diffusivity and electrode porosity. That is why different researchers obtained slightly different optimum composition of the electrode depending on the operating condition and parameters of their simulations or experiments while everybody agrees that the maximum active line or area occurs when equal amounts of LSM and YSZ particles of the same size are used.

Kenjo and Nishiya [3] and Haanappel et al. [21] reported the best performance for the electrode for the weight ratio of LSM and YSZ equal to 1. While the first group did not mention the size of the particles, second group used 1  $\mu\text{m}$  LSM particles. On the other hand, Ostergard et al. [7] and Kim et al. [11] obtained the minimum polarization resistance in their experiments when YSZ content was around 40%. Juhl et al. [22] reported the same results. On the simulation side also there are differences between reported data. While Costamagna et al. [12] report the minimum polarization resistance at about 37% of electronic conductor, Sunde [23] and Chan et al. [14] believe that for a wide range of

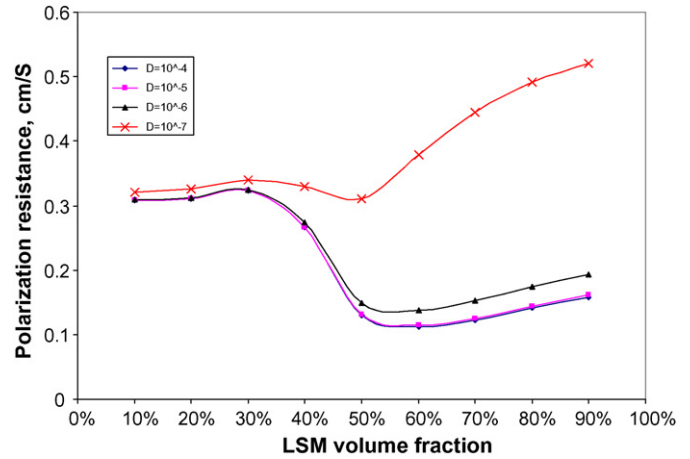


Fig. 6. Parametric study of the effect of diffusion coefficient on the overall polarization resistance of the electrode.

electrode composition of about 40–60% the polarization resistance remains constant at its minimum value.

Figs. 6 and 7 show a parametric study of the effect of diffusion coefficient and the conductivity of ion conductor on the performance of the electrode. Decreasing the diffusion coefficient which could be a result of decreasing porosity, can result in diffusion controlled process. According to the model increasing the volume fraction of electronic conductor pushes the electrochemical reaction sites towards the electrolyte, far from the air channel. This in turn increases the concentration polarization resistance and for small values of diffusion coefficient as it is shown in Fig. 6 concentration polarization resistance outweighs the increase in the length of active line or decrease in activation polarization resistance. Fig. 7 is a parametric study on the effect of conductivity of ion conductor in the cathode. Since the conductivity of ion conducting media is usually very low, change in the conductivity has pronounced effect on the performance of the electrode. This change in conductivity can be applied through changing the geometric features like particle size and porosity or variations in operating conditions like temperature. For high values of conductivity the minimum of

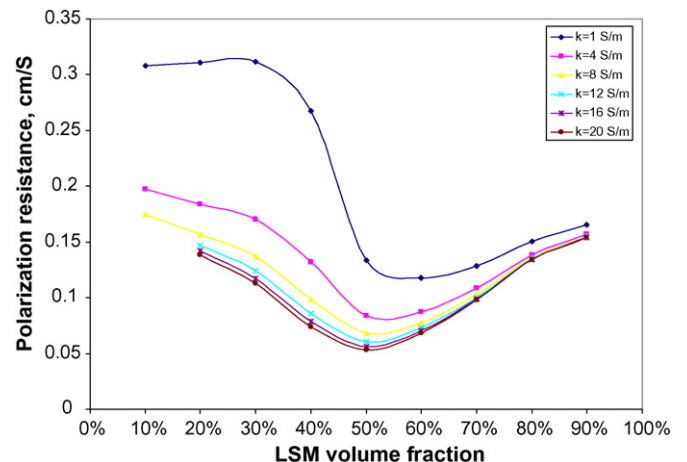


Fig. 7. Parametric study of the effect of the conductivity of ionic conductor on the overall polarization resistance of the electrode.

polarization resistance shifts exactly to 50% vol. of each component and the shape of the curve becomes more symmetric just like active area or active length curve of Fig. 4. The reason is that increasing the conductivity decreases the Ohmic resistance and thereby activation polarization determines the whole trend of the polarization resistance curve. Activation polarization is minimum when the active area is maximum or when the composition is 50%. A slight increase in polarization resistance with increasing the LSM volume fraction in the first stages is due to the fact that by increasing LSM composition in the first stages we are just introducing some small isolated patches of LSM into YSZ which decreases the conductivity of YSZ media hence increasing the polarization resistance. Same observation is reported for conductivity by Sunde [23].

## 5. Conclusions

A new 2D model based on random packing of electronic and ionic particles has been proposed. The model of transport processes based on this geometrical approach shows very good agreement with the other observed experimental and simulation data. This framework offers its own values and advantages, since in this model we can identify every reaction point, and hence it gives a better image of composite electrode performance. It can be used to study the reaction kinetics of electrode reaction.

We must extend this to 3D framework, which remains a purely geometrical problem to be solved, although the extra degree of freedom offered in a 3D geometry can alter the topological structure of the TPB significantly. Using this framework, we can also investigate the effectiveness of several alternate structured or patterned topologies to assess the most promising patterns.

## Acknowledgement

Financial support through an NSERC Strategic grant is gratefully acknowledged.

## References

- [1] R.J. Gorte, *AIChE J.* 51 (2005) 2377–2381.
- [2] T. Kenjo, S. Osawa, K. Fujikawa, *J. Electrochem. Soc.* 138 (1991) 349–355.
- [3] T. Kenjo, M. Nishiya, *Solid State Ionics* 57 (1992) 295–302.
- [4] A. Barbucci, R. Bozzo, G. Cerisola, P. Costamagna, *Electrochim. Acta* 47 (2002) 2183–2188.
- [5] J.H. Choi, J.H. Jang, S.M. Oh, *Electrochim. Acta* 46 (2001) 867–874.
- [6] E. Perry Murray, S.A. Barnett, *Solid State Ionics* 143 (2001) 265–273.
- [7] M.J.L. Ostergard, C. Clausen, C. Bagger, M. Mogensen, *Electrochim. Acta* 40 (2001) 1971–1981.
- [8] A. Hammouche, E.J.L. Schouler, M. Henault, *Solid State Ionics* 28–30 (1988) 1205–1207.
- [9] M.J.L. Ostergard, M. Mogensen, *Electrochim. Acta* 38 (1993) 2015–2020.
- [10] H. Kamata, A. Hosaka, J. Mizusaki, H. Tagawa, *Solid State Ionics* 106 (1998) 237–245.
- [11] J. Kim, G. Kim, J. Moon, Y. Park, W. Lee, K. Kobayashi, M. Nagai, C. Kim, *Solid State Ionics* 143 (2001) 379–389.
- [12] P. Costamagna, P. Costa, V. Antonucci, *Electrochim. Acta* 43 (1998) 375–394.
- [13] S.H. Chan, Z.T. Xia, *J. Electrochem. Soc.* 148 (2001) A388–A394.
- [14] S.H. Chan, X.J. Chen, K.A. Khor, *J. Electrochem. Soc.* 151 (2004) A164–A172.
- [15] X.J. Chen, S.H. Chan, K.A. Khor, *Electrochim. Acta* 49 (2004) 1851–1861.
- [16] S. Sunde, *J. Electrochem. Soc.* 143 (1996) 1930–1939.
- [17] F. Zhao, T.J. Armstrong, A.V. Virkar, *J. Electrochem. Soc.* 150 (2003) A249–A256.
- [18] R. Taylor, R. Krishna, *Multicomponent Mass Transfer*, Wiley Series in Chemical Engineering, New York, 1993, p.68.
- [19] S.H. Chan, K.A. Khor, Z.T. Xia, *J. Power Sources* 93 (2001) 130–140.
- [20] E.L. Cussler, *Diffusion: Mass Transfer in Fluid Systems*, Cambridge University Press, New York, 1997.
- [21] V.A.C. Haanappel, J. Mertens, D. Rutenbeck, C. Tropicz, W. Herzog, D. Sebold, F. Tietz, *J. Power Sources* 141 (2005) 216–226.
- [22] M. Juhl, S. Primdahl, C. Manon, M. Mogensen, *J. Power Sources* 61 (1996) 173–181.
- [23] S. Sunde, *J. Electroceram.* 5 (2000) 153–182.
- [24] J.R. Ferguson, J.M. Fiard, R. Herbin, *J. Power Sources* 58 (1996) 109–122.