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Three-dimensional random resistor-network model for solid oxide fuel cell composite electrodes

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ABSTRACT

A three-dimensional reconstruction of solid oxide fuel cell (SOFC) composite electrodes was developed to evaluate the performance and further investigate the effect of microstructure on the performance of SOFC electrodes. Porosity of the electrode is controlled by adding pore former particles (spheres) to the electrode and ignoring them in analysis step. To enhance connectivity between particles and increase the length of triple-phase boundary (TPB), sintering process is mimicked by enlarging particles to certain degree after settling them inside the packing. Geometrical characteristics such as length of TBP and active contact area as well as porosity can easily be calculated using the current model. Electrochemical process is simulated using resistor-network model and complete Butler–Volmer equation is used to deal with charge transfer process on TBP. The model shows that TPBs are not uniformly distributed across the electrode and location of TPBs as well as amount of electrochemical reaction is not uniform. Effects of electrode thickness, particle size ratio, electron and ion conductor conductivities and rate of electrochemical reaction on overall electrochemical performance of electrode are investigated.

1. Introduction

Electrochemical process which leads to power generation in a solid oxide fuel cell (SOFC) takes place in so called triple-phase boundary (TPB) inside the composite electrode. TPB is the contact point between two percolating ion conductor and electron conductor particles which has access to open pores to transport gaseous reactants or products. Due to the composite nature of the electrode, formation of TPB inside the bulk of electrode and the overall performance of SOFC is influenced by various geometrical factors as well as electrochemical properties of materials forming the electrode and transport characteristics of the media [1–9]. That is why the optimization of electrode structure and material is very important and many studies are being conducted to develop an electrode structure which maximizes electrode performance and minimizes losses [10–15]. Due to the structural complexity of the electrode and the role of different phenomena on the overall performance, detailed simulation of electrode performance is computationally very expensive.

Early attempts to model SOFC electrodes were mostly based on percolation theory and Monte-Carlo simulations [1,7,16–18]. Despite the ability of these models in predicting the composite electrode performance, they must be used inside percolation threshold and they underestimate the amount of TPB. This is because these models ignore TPBs made between short chains of electron and ion conductors that do not go all the way from one end of the electrode (current collector) to the other end (electrolyte) [16].

With the development of fast computers, more detailed and computationally demanding models have recently been considered. These models are based on two- or three-dimensional packing of particles as electron or ion conductors [9,11,13,19–21]. Our first work [11] was a 2D model of circles to simulate the distribution of TPBs inside the electrode and revealed that the reaction distribution inside the electrode is not uniform. The effect of LSM (lanthanum strontium manganate) and YSZ (yttria-stabilized zirconia) conductivities and mass transfer coefficient on overall polarization resistance was studied and it was shown that while for low ionic resistance, all TPBs inside the electrode have almost the equal amount of contribution to current generation, for high ionic resistance TPB locations near electrolyte are more favoured and current generation near current collector is small. The second work [9] was a more realistic case of 3D electrode simulation. The effect of LSM and YSZ volume percentages, particle size and particle size ratio and electrode thickness was studied on the amount and distribution inside the electrode.

Schneider et al. [19,20] used a 3D packing of mono-sized particles and the resistor-network model to model the performance of SOFC electrodes. In their analysis however; linear form of Butler–Volmer equation was considered to account for charge

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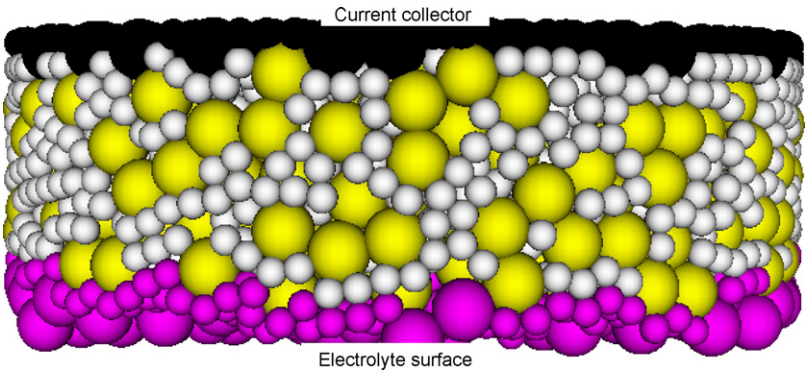

Fig. 1. Composite electrode created in the computer. White particles are electron conductors while yellow particles represent ion conductors. Bottom layer is electrolyte surface made of ion conductors while top layer is totally electron conductor and acts as current collector.

transfer process at TPB. This simplification limits the validity of the results to low current densities. Unlike this group, Koyama et al. [13] used distribution of particle size in their packing but they averaged properties over transverse sections parallel to the electrolyte. Sintering is usually accounted by enlarging particles to create a certain degree of overlap between adjacent particles [9,13,19]. Kenney et al. [21] performed a geometrical assessment of TPB length, contact area and pore size for random packing of particles. Their results showed that for porosities larger than 25%, over 99% of pores belong to percolating network which is believed to guarantee negligible mass transfer resistance [7,12].

Due to the importance of TPB length in the performance of the electrode, most of the modeling work mentioned above aimed at relating the effect of geometrical parameters on TPB length. TPB length however, is not the only important parameter [22]. Maximizing TPB guarantees that there is maximum amount of reaction sites available for charge transfer process while overall performance depends on electrical, electrochemical and transport characteristics of electrode material [6,10,18] as well as spatial distribution of TPB [9,11].

In the current work, we have used random packing of particles to model SOFC composite electrodes. Geometrical analysis of the model has been addressed elsewhere [9] and this work focuses on electrochemical performance of the model electrode. Random resistor-network model has been used to obtain current–overpotential characteristics but unlike other models [19,20,23] the analysis is not restricted to ohmic and linear expression for charge transfer equation and a complete analysis has been conducted.

2. Description of the model

The detailed description of the model has been given in our previous work [9] which deals with structural and geometrical aspects. SOFC electrode is modeled by random packing of LSM and YSZ spherical particles of different or same size. The electrode components or spheres are added to the electrode by collision detection and location optimization and then the particles are enlarged to certain extent [16] to create enough contact area. Fig. 1 shows a typical model composite electrode. Top and bottom layers are designated current collector and electrolyte layer respectively.

Void volume is calculated by subtracting the total volume of spheres after expansion from the apparent volume of the electrode considering the overlapped volume of two or three particles [24,25] as shown in Fig. 2a and b. It is very unlikely that four particle have common volume of intersection. Depending on size ratio r_{io}/r_{el}, porosities of 23–26% were obtained and although these are believed to be enough to guarantee negligible mass transfer effects [7,12], porosity was increased to 30% by introducing some void particles.

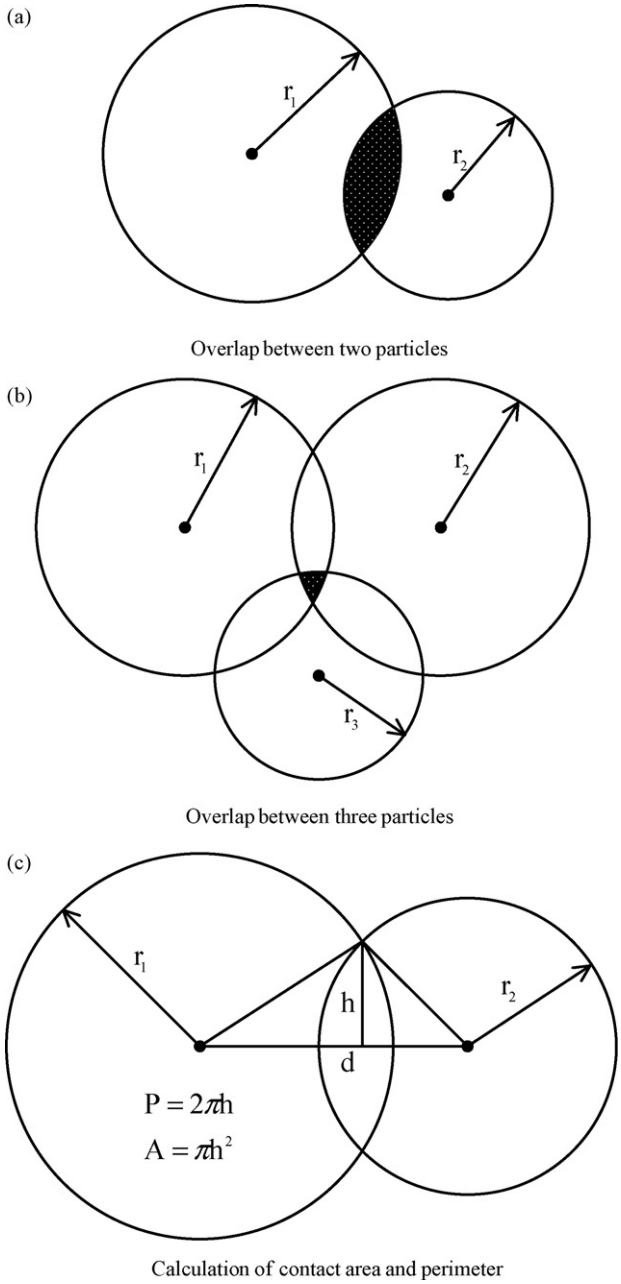

Fig. 2. Volume of intersection between (a) two particles and (b) three particles. (c) Calculation of L_{TPB} and interfacial area between contacting particles.