Journal of Power Sources 196 (2011) 3178–3185

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Percolation micro-model to predict the effective properties of the composite electrode with poly-dispersed particle sizes

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ARTICLE INFO

Article history:
Received 22 September 2010
Received in revised form
19 November 2010
Accepted 22 November 2010
Available online 27 November 2010

Keywords:
Solid oxide fuel cell
Composite electrode
Coordination number
Percolation theory
Inter-particle conductivity
Triple phase boundary

ABSTRACT

A percolation micro-model is developed to predict the effective properties of the composite electrode consisting of poly-dispersed electronic and ionic-conducting particles. The analytical expressions for the percolated triple-phase-boundary (TPB) lengths, hydraulic pore radius and intra/inter-particle conductivities have been formed. The model shows that the percolated TPB lengths of a composite electrode consisting of poly-dispersed particle sizes for both materials (i.e., having a normal distribution with a non-dimensional standard deviation of 0.4) are about 32% lower than that of the composite electrode with mono-sized particles. And the higher percolated TPB lengths can be achieved by reducing the mean particle size of each material and narrowing the particle size distribution. A composite cathode may benefit from it, because of its low electrochemical activity. The model also shows that the composite electrode with large mean particle size radii ratio between the electrode- and electrolyte-materials and broad particle size distributions can not only provide higher inter-particle ion conductivity, but also reduce the percolation volume fraction threshold of the electrode-material. And this may be helpful for a composite anode to obtain a higher overall ion conductivity.

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1. Introduction

The application of a composite electrode with both electronic and ionic conducting materials has been regarded as an attractive alterative compared to the electrode with single material by extending the electrochemical reaction zone from the dense electrolyte into the composite electrode [1–4]. This in turn may significantly increase the solid-oxide-fuel-cell (SOFC) performance [5–8]. A typical porous composite electrode is a mixture of the electronic conducting materials (i.e., lanthanum-doped strontium manganate (LSM) for cathode and Ni for anode) and ionic conducting materials (i.e., yttria-stabilized zirconia (YSZ)) [3,5]. And a proper SOFC composite electrode may have, but is not limited to, the following characteristics: (i) a proper thermal conductivity that matches the other components, (ii) a sufficient mechanical strength to support the cell, (iii) a percolated porous path for the reaction species to transport from the channel into the reaction sites. The 'percolated' in here is defined as the contiguous connection through the whole electrode structure, (iv) a percolated electronic conducting path (through Ni or LSM) for the electrons to conduct from the reaction spots to the current collector, (v) a percolated ionic conducting path (through YSZ) for the ions to propagate from the dense electrolyte to the reaction spots, (vi) the percolated triple-phase-boundaries (TPBs) to support the electrochemical reaction. As the electrochemical reaction refers to electrons, ions and reaction species, it can only occur at the TPBs, where the electronic conducting, ionic conducting and porous phases coexist (i.e., Ni-YSZ-pore) and each phase belong to a percolated network, respectively. These TPBs are defined as the percolated TPBs [9]. These percolated TPBs, however, are only potential electrochemical active. How much part of them can be active again rely on the composite electrode properties and the thickness of the composite electrode [4]. Conclusively, the SOFC performance is significantly affected by the composite electrode properties. This in turn relies on the particular microstructure of the composite electrode. As the fabrication technology of a composite electrode becomes sophisticated, the understanding of the detailed knowledge of microstructure and its effect on the electrode properties are receiving considerable attentions [5,10–13].

In the past decades, parametric studies for the composite electrodes have been widely made by many researchers through experiments [10,11,14–16], random packing reconstruction methods [17–20] and percolation micro-models [7,9,21–24]. (i) The experimental methods rely primarily on the stereological meth-

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doi:10.1016/j.jpowsour.2010.11.107

ods [10,25–27]. Recently, the focused ion-beam scanning electron microscopy has been attempted to obtain the high resolution 3D image of a composite electrode [10,11,14,28–29]. All of them greatly enhance the understanding of the composite electrode microstructure and are helpful for developing the theory model in relating the microstructure and the electrode properties. Certainly, the theory approaches are also necessary, because the experimental methods are still expensive and time consuming, and require the use of the hard-to-access facilities (i.e., focused ion-beam, synchrotron radiation facilities and laser scanning confocal microscopy) [10,11,14,30]. (ii) The random packing reconstruction methods are mainly based on the random packing of sphere particles, in which a composite electrode is considered as a porous structure formed of randomly distributed sphere particles. Ali et al. [19], Schneider et al. [18], and Golbert et al. [17] have reconstructed the binary composite structures with mono size particles for each material to evaluate the percolated TPB lengths. Recently, Kenney et al. [20] have further extended the model and reconstructed a binary composite structure with poly-disperse particles to predict the effective electrode properties. However, only limited properties have been calculated, the prediction of some other electrode properties such as the hydraulic pore radius, intra/inter-particle conductivities and so on have not yet been achieved by the random packing reconstruction methods as far as we know. And it is difficult to incorporate the reconstructed structures into the cell-level models for simultaneously exploring the effects of various microstructure parameters on the SOFC performance. (iii) The percolation micro-models use the percolation theory and coordination number theory to represent the microstructure of a composite electrode developed by the random packing reconstruction methods. And analytical expressions are derived to relate the electrode properties and the microstructure parameters [22,31]. Therefore, the percolation micro-model can be considered as an extension of the random packing reconstruction method, and is sufficiently accurate enough in predicting the electrode properties from the microstructure parameters [22,24]. It is also convenient in coupling with the cell-level models [4]. Bouvard et al. [32] and Suzuki et al. [31] have developed the micro-models to represent the microstructure of a binary random packing sphere structure. And the percolation micro-models have been further developed by Costamagna et al. [22], Chan et al. [21] and Janardhanan et al. [24] to relate the composite electrode microstructure and the effective properties. Recently, Chen et al. [9] have generalized the percolation micro-model of a binary random packed system to a model of 3-component random packed system for predicting the effective properties of a composite electrode with LSM particles, coarse and fine YSZ particles. More recently, the percolation micro-models have been further incorporated into the cell-level models to evaluate the effects of electrode microstructure parameters on the SOFC performance [7,8,23].

In the early work, each material phase of the composite electrode was limited to the mono-sized particles. But, the SOFC composite ceramic electrodes are typically poly-disperse powders that each material may have a broad particle size distribution, and this can have significant impacts on the effective electrode properties. In this paper, a percolation micro-model is developed to predict the effective properties of the composite electrodes with a distributed particle sizes that match the actual ceramic powders. Analytical expressions are derived to predict the percolated TPB lengths, intra/inter-particle conductivities, etc. based on the microstructure parameters. The percolation micro-model is validated through comparing with the random packing reconstruction method. Furthermore, all the effective properties are represented in non-dimensional form for providing generality in practical applications. And the percolation micro-model is particularly focused on the applications in optimizing the SOFC cathodes and anodes, respectively.

2. Theory and method

2.1. Percolation micro-model for the composite electrodes with multiple particle sizes

2.1.1. Coordination number and microstructure parameters

Consider a multi-component mixture of randomly packed spherical particles with M type particle sizes. The average number of contacts Z_k between k-type particles and all neighboring particles is [9],

$$Z_k = \sum_{\ell=1}^{M} Z_{k,\ell}, \tag{1}$$

where $Z_{k,\ell}$ is the number of contacts between a k-particle and all the neighboring ℓ-particles. It can be estimated as [9],

$$Z_{k,\ell} = 0.5\left(1 + \frac{r_k^2}{r_\ell^2}\right)\bar{Z}\frac{\psi_\ell/r_\ell}{\sum_{k=1}^{M}\psi_k/r_k}, \tag{2}$$

where r_k is the radius of k-particle. $\bar{Z}$ is the average coordination number of all particles, which is widely assumed to be 6 [21,22,33,34]. ψ_k is the volume fraction of all k-particles.

2.1.2. Effective electrode properties and coordination number

A porous composite electrode is usually assumed to have two type materials: the ionic-conducting electrolyte-phase material (labeled as 'el' such as YSZ) and electronic-conducting electrode-phase material (labeled as 'ed' such as Ni or LSM). Due to the ceramic powders are typically poly-disperse powders, a composite electrode consisting of m type particle sizes for the electronic-conducting material (designated as ed_1, $\mathrm{ed}_2, \ldots, \mathrm{ed}_m$) and n type particle sizes for the ionic-conducting material (designated as el_1, $\mathrm{el}_2, \ldots, \mathrm{el}_n$) is initially considered in here ($m+n=M$).

Denoting ψ_{ed_k} and ψ_{el_k} as the volume fraction of ed_k- and el_k-particles, respectively. The total volume fractions of the electronic-conducting and ionic-conducting materials can be estimated as,

$$\psi_{\mathrm{ed}} = \sum_{k=1}^{m}\psi_{\mathrm{ed}_k}, \qquad \psi_{\mathrm{el}} = \sum_{k=1}^{n}\psi_{\mathrm{el}_k}. \tag{3}$$

And the relative volume fraction of each type particle sizes within the electronic-conducting and ionic-conducting materials can be represented as

$$\psi^0_{\mathrm{ed}_k} = \frac{\psi_{\mathrm{ed}_k}}{\psi_{\mathrm{ed}}}, \qquad \psi^0_{\mathrm{el}_k} = \frac{\psi_{\mathrm{el}_k}}{\psi_{\mathrm{el}}}. \tag{4}$$

The percolated TPB lengths per unit volume ($\lambda^V_{\mathrm{TPB,per}}$) is proportional to the contact perimeter between ed_k-particle and el_ℓ-particle ($l_{\mathrm{ed}_k,\mathrm{el}_\ell}$), the number of contact points per unit volume, which is the product of the numbers of ed_k-particles per unit volume ($n^V_{\mathrm{ed}_k}$) and their coordination numbers with other el-particles ($Z_{\mathrm{ed}_k,\mathrm{el}_\ell}$), and the probabilities of ed_k- and el_ℓ-particles belonging to the percolated clusters (P_{ed_k} and P_{el_ℓ}),

$$\lambda^V_{\mathrm{TPB,per}} = \sum_{k=1}^{m}\sum_{\ell=1}^{n} l_{\mathrm{ed}_k,\mathrm{el}_\ell} n^V_{\mathrm{ed}_k} Z_{\mathrm{ed}_k,\mathrm{el}_\ell} P_{\mathrm{ed}_k} P_{\mathrm{el}_\ell}. \tag{5}$$

As indicated in Fig. 1, the contact perimeter ($l_{\mathrm{ed}_k,\mathrm{el}_\ell}$) can be estimated as $l_{\mathrm{ed}_k,\mathrm{el}_\ell} = 2\pi\,\min(r_{\mathrm{ed}_k}, r_{\mathrm{el}_\ell})\sin\theta$, where r_{ed_k} and r_{el_ℓ} are the radii of ed_k-particles and el_ℓ-particles, θ is the contact angle.

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