Calculation of Contact Angles at Triple Phase Boundary in Solid Oxide Fuel Cell Anode Using the Level Set Method

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Abstract:

A level set method is applied to characterize the three dimensional structures of nickel, yttria stabilized zirconia and pore phases in solid oxide fuel cell anode reconstructed by focused ion beam-scanning electron microscope. A numerical algorithm is developed to evaluate the contact angles at the triple phase boundary based on interfacial normal vectors which can be calculated from the signed distance functions defined for each of the three phases. Furthermore, surface tension force is estimated from the contact angles by assuming the interfacial force balance at the triple phase boundary. The average contact angle values of nickel, yttria stabilized zirconia and pore are found to be $143^{\circ}\sim 156^{\circ}$, $83^{\circ}\sim 138^{\circ}$ and $82^{\circ}\sim 123^{\circ}$, respectively. The mean contact angles remained nearly unchanged after 100 hours operation. However, the contact angles just after reduction are different for the cells with different sintering temperatures. In addition, standard deviations of the contact angles are very large especially for yttria stabilized zirconia and pore phases. The calculated surface tension forces from mean contact angles were close to the experimental values found in the literature. Slight increase of surface tensions of nickel/pore and nickel/yttria stabilized zirconia were observed after operation. Present data are expected to be used not only for the understanding of the degradation mechanism, but also for the quantitative prediction of the microstructural temporal evolution of solid oxide fuel cell anode.

Key words: Solid oxide fuel cell anode, Microstructure, Contact angle, Surface tension, Level set method, Focused ion beam scanning electron microscopy

1. Introduction

Solid oxide fuel cell (SOFC) is one of the most efficient devices for converting hydrocarbon fuels into electrical power and possesses high fuel flexibility [1]. Thus, it is expected as a promising power generation device in the near future. SOFC is usually operated in the temperature range of 973 to 1273 K, which results in the challenges of long time stability and durability. Performance degradation of electrodes has been considered to be one of the major obstacles for commercialization. It is widely accepted that the electrochemical reactions in the nickel(Ni)- yttria stabilized zirconia(YSZ)anode take places at confined spatial sites called triple phase boundary (TPB) where YSZ, nickel and pore are in contact. Therefore, the three dimensional microstructures of the anode have a significant impact on the resultant performance of SOFC [2]. Thus, quantifying the morphology of triple phase boundary is very important for understanding the anode degradation. A number of studies on anode microstructure have been carried out in order to characterize and quantify the cell performance and degradation process. Microstructural parameters such as surface area, volume fraction, triple phase boundary length and tortuosity factor are calculated to evaluate the anode performance [3,4]. Comparison with the impedance spectroscopy data is useful to determine the relationship between polarization resistance and microstructural change [5]. Chen et al. [6] simulated the coarsening process of Ni-YSZ composite anode by the phase field method in order to predict temporal evolution of cell performance. The coarsening kinetics of Ni-YSZ anodes has

been found to be strongly related to the Ni-YSZ contact angles [6]. In their simulation results, two contact angles are assumed to be fixed, that is, 93° and 120° . However, these values are taken from experimental or empirical values. Tsoga et al. [7] experimentally measured the non-reactive contact angle between Ni and 8YSZ at 1500°C and reported that the contact angle is 117° . The contact angle and surface tension force are indispensable parameters for the simulations of Ni-YSZ anode coarsening process such as a phase field method [6] and a Monte Carlo method [8]. However, studies on contact angles and surface tension forces of Ni-YSZ anode are still very limited. In the present study, we develop a numerical method to calculate the contact angles and surface tension forces of the Ni-YSZ anode using the Ni-YSZ anode microstructure reconstructed by focused ion beam-scanning electron microscope (FIB-SEM) [4].

2. Experiment

Electrolyte-supported button cell is used in this study. The anode cermet was prepared by ball-milling NiO and YSZ powders (AGC Seimi Chem. Corp.) for 48 hours where the volume ratio of Ni to YSZ is 43:57. The powder was then mixed with terpineol solvent and the ethylcellulose binder in an agate mortar to obtain anode slurry. The slurry was screen-printed onto commercial dense 8 mol% YSZ pellet (diameter 20 mm, thickness 0.5 mm, Fine Ceramics Corp., Japan) with a diameter of 10 mm, and then sintered in an electric furnace [3]. The anodes were discharged in 3% H_2O humidified hydrogen with a current density of 0.2 A cm^{-2} at 800°C . In order to investigate the

effects of sintering temperature on contact angles and surface tension, the anodes were sintered at three different temperatures, 1400 °C, 1450°C, and 1500°C. The anode sample after experiments were observed by FIM-SEM (Carl Zeiss, NVision 40) [3]. The samples were first infiltrated by epoxy resin under low pressure atmosphere (ca. 15Pa), so that the pores of the porous electrode could be easily distinguished during FIB-SEM observation. The cured samples were then polished by Ar-ion beam cross-section polisher (JEOL Ltd., SM-09010). The details of dual-beam FIB-SEM observation procedure has been introduced in [4]. The 3D microstructure of the Ni-YSZ anode as shown in Fig.1 was then virtually reconstructed based on a series of 2D images by Matlab and Avizo Fire 6.0 (Maxnet). It was reported that the anode sintered at 1450°C provided best initial performance and the lowest degradation rate compared to the anode sintered at other temperatures [9]. Table 1 shows the sizes of anode samples sintered at 1400 °C, 1450°C, and 1500°C.

3. Numerical Method

3.1 Level set method

The level set method developed by Osher&Sethian [10,11,12] is a numerical technique for tracking deformed interfaces. One of the advantages of the level set method is that one can handle moving interfaces or surfaces on a fixed Cartesian grid without explicitly tracking the interface. In the level

set method, the interface Γ is represented implicitly as the zero level set surface of a continuous function ϕ . Therefore, it can be expressed as

$$\Gamma = \{x | \phi(x, t) = 0\}. \quad (1)$$

The interfacial normal vector $\vec{n}$ is defined at the interface by the following equation:

$$\vec{n} = \frac{\nabla \phi}{|\nabla \phi|}. \quad (2)$$

Fig. 2 shows the process of obtaining level set function from FIB-SEM reconstructed data. A series of two dimensional (2D) cross-section images of each sample are obtained by FIB-SEM measurement. Since cubic voxel is desirable in the calculation, the 2D images are resized to a cubic structure. The resized images are reconstructed into three dimension by Avizo software (FEI Visualization Sciences Group) as shown in Fig. 3. Then, SDF-lib C++ library code [13] is used to obtain signed distance functions of Ni, YSZ and pore from the output files of Avizo.

The level set function and the original FIB-SEM structures are compared in Fig. 4. A 2D image from FIB-SEM is shown in Fig. 4(a), whose pixel size is $33.9 \times 33.9 \times 33.9 \text{ nm}^3$. Calculated level set functions of Ni, YSZ and pore phases are visualized in Fig. 4 (b), (c), and (d), respectively. As a whole, good agreement is obtained between the original SEM image and the calculated level set functions, although some trivial differences can be seen. It was found that level set structure largely depends on the resolution of the microstructure, which means that highest resolution in FIB-SEM is favorable for accurate shape prediction using the level set function.

3.2 Calculation of normal vectors and contact angles at the TPB

A schematic of TPB is shown in Fig.5. Ni, YSZ and pore are represented by the three different level set functions, ϕ_{Ni} , ϕ_{YSZ} and ϕ_{pore} , respectively. Using Eq. (2), the normal vector of the interface between Ni and pore is given as follows:

$$\vec{n}_{\text{Ni/Pore}} = \frac{\nabla \phi_{\text{Ni}}}{|\nabla \phi_{\text{Ni}}|} \text{ at Ni-pore interface.} \quad (3)$$

Similarly, the normal vectors of the other interfaces are expressed as

$$\vec{n}_{\text{Ni/YSZ}} = \frac{\nabla \phi_{\text{Ni}}}{|\nabla \phi_{\text{Ni}}|} \text{ at Ni-YSZ interface,} \quad (4)$$

$$\vec{n}_{\text{YSZ/Ni}} = \frac{\nabla \phi_{\text{YSZ}}}{|\nabla \phi_{\text{YSZ}}|} \text{ at YSZ-Ni interface,} \quad (5)$$

$$\vec{n}_{\text{YSZ/Pore}} = \frac{\nabla \phi_{\text{YSZ}}}{|\nabla \phi_{\text{YSZ}}|} \text{ at YSZ-pore interface,} \quad (6)$$

$$\vec{n}_{\text{Pore/Ni}} = \frac{\nabla \phi_{\text{Pore}}}{|\nabla \phi_{\text{Pore}}|} \text{ at pore- Ni interface,} \quad (7)$$

$$\vec{n}_{\text{Pore/YSZ}} = \frac{\nabla \phi_{\text{Pore}}}{|\nabla \phi_{\text{Pore}}|} \text{ at pore-YSZ interface,} \quad (8)$$

where subscript A/B indicates the interface between A and B phases.

According to the geometrical relationship shown in Fig.1, the contact angles of Ni, YSZ and pore are calculated as follows:

$$\theta_{\text{Ni}} = 180^\circ - \arccos(\vec{n}_{\text{Ni/Pore}} \cdot \vec{n}_{\text{Ni/YSZ}}), \quad (9)$$

$$\theta_{\text{YSZ}} = 180^\circ - \arccos(\vec{n}_{\text{YSZ/Ni}} \cdot \vec{n}_{\text{YSZ/Pore}}), \quad (10)$$

$$\theta_{\text{Pore}} = 180^\circ - \arccos(\vec{n}_{\text{Pore/Ni}} \cdot \vec{n}_{\text{Pore/YSZ}}). \quad (11)$$

At the TPB, ideally, the six normal vectors given by Eqs. (3) to (8) should lie on the same

two-dimensional plane, which is orthogonal to the direction of the TPB. However, due to the limited resolution of the digitized FIB-SEM data, numerical errors are unavoidable during the successive procedures. In addition it is not always ensured that all the six vectors exist on the same plane. Consequently, the sum of θ_{Ni} , θ_{YSZ} and θ_{Pore} cannot amount to be exactly 2π . In order to overcome the difficulty mentioned above, the six normal vectors in Eqs. (3) to (8) are projected on the single plane which is orthogonal to the most likely direction of the TPB.

As shown in Fig. 5, the normal vectors of Ni, YSZ and Pore at TPB are given respectively according to Eq. (2) as follows:

$$\vec{n}_{\text{Ni}} = \frac{\nabla \phi_{\text{Ni}}}{|\nabla \phi_{\text{Ni}}|}, \quad \vec{n}_{\text{YSZ}} = \frac{\nabla \phi_{\text{YSZ}}}{|\nabla \phi_{\text{YSZ}}|}, \quad \vec{n}_{\text{Pore}} = \frac{\nabla \phi_{\text{Pore}}}{|\nabla \phi_{\text{Pore}}|}. \quad (12)$$

Then we try to calculate the most-likely TPB direction unit vector $\vec{a}$ which is normal to all the three normal vectors in Eq. (12) by applying a least square method. For simplicity, the three normal vectors in Eq. (12) are denoted as $\vec{b}_j^1$, $\vec{b}_j^2$ and $\vec{b}_j^3$, respectively. The subscript j represents the vector component in x , y , z directions and superscripts 1, 2, 3 represent Ni, YSZ and Pore. The most-likely TPB direction is defined so as to minimize J , which is the sum of the square of the inner products between the TPB direction and the normal vectors.

$$J = \sum_{k=1}^3 \left(a_1 b_1^k + a_2 b_2^k + a_3 b_3^k \right)^2. \quad (13)$$

Since $\vec{a}$ is a unit vector from its definition, $\vec{a}$ needs to satisfy the following condition:

$$a_1^2 + a_2^2 + a_3^2 = 1. \quad (14)$$

The above problem can be considered as a minimization problem of J under the restriction given by

Eq. (14). This is equivalent to solve the minimizing problem of Lagrangian L defined as follows:

$$L = \sum_{k=1}^3 (a_1 b_1^k + a_2 b_2^k + a_3 b_3^k)^2 - \lambda (a_1^2 + a_2^2 + a_3^2 - 1), \quad (15)$$

where λ is a Lagrangian multiplier.

The differentials of L with respect to the vector component of $\vec{a}$ are given as follows:

$$\frac{\partial L}{\partial a_1} = 2\{(B_{11} - \lambda)a_1 + B_{12}a_2 + B_{13}a_3\}, \quad (16)$$

$$\frac{\partial L}{\partial a_2} = 2\{B_{12}a_1 + (B_{22} - \lambda)a_2 + B_{23}a_3\}, \quad (17)$$

$$\frac{\partial L}{\partial a_3} = 2\{B_{13}a_1 + B_{23}a_2 + (B_{33} - \lambda)a_3\}, \quad (18)$$

where

$$B_{ij} = \sum_{k=1}^3 b_i^k b_j^k. \quad (19)$$

The most likely TPB direction vector $\vec{a}$ is obtained by simultaneously satisfying the stationary conditions, i.e., $\frac{\partial L}{\partial a_1} = \frac{\partial L}{\partial a_2} = \frac{\partial L}{\partial a_3} = 0$, and Eq. (14). Since it turns out to be impossible to obtain

$\vec{a}$ analytically, we employ the following iterative procedure. Suppose a candidate of $\vec{a}$ is given

by the cross product of normal vector of Ni and YSZ in Eq. (12) as follows:

$$\vec{a} = \vec{n}_{Ni} \times \vec{n}_{YSZ}. \quad (20)$$

We attempt to correct $\vec{a}$ so as to converge it to the solution minimizing J . In accordance with Eqs.

(16) to (18), the correction Δa_j of each vector component should be given as follows:

$$\Delta a_1 = -\frac{\partial L}{\partial a_1} = -2\{(B_{11} - \lambda)a_1 + B_{12}a_2 + B_{13}a_3\}, \quad (21)$$

$$\Delta a_2 = -\frac{\partial L}{\partial a_2} = -2\{B_{12}a_1 + (B_{22} - \lambda)a_2 + B_{23}a_3\}, \quad (22)$$

$$\Delta a_3 = -\frac{\partial L}{\partial a_3} = -2\{B_{13}a_1 + B_{23}a_2 + (B_{33} - \lambda)a_3\}. \quad (23)$$

Considering that the vector norm is kept unity after the correction,

$$a_1^2 + a_2^2 + a_3^2 = (a_1 + \Delta a_1)^2 + (a_2 + \Delta a_2)^2 + (a_3 + \Delta a_3)^2 = 1. \quad (24)$$

Therefore, we obtain

$$a_1\Delta a_1 + a_2\Delta a_2 + a_3\Delta a_3 = 0. \quad (25)$$

Here, the products of the correction such as $\Delta a_i \Delta a_j$ are neglected, since they are sufficiently smaller than the first order of Δa_j .

The Lagrangian multiplier λ in Eqs. (21) to (23) can be determined so as to satisfy Eq. (25), which results in:

$$\lambda = B_{11}a_1^2 + B_{22}a_2^2 + B_{33}a_3^2 + 2(B_{12}a_1a_2 + B_{23}a_2a_3 + B_{13}a_1a_3). \quad (26)$$

Finally, the present iterative procedure is summarized as follows.

- 1) Determine a candidate of $\vec{a}$ by Eq. (20).
- 2) Calculate λ by solving Eq. (26).
- 3) Calculate the corrections of each vector component by Eqs. (21) to (23).
- 4) Update $\vec{a}$ by adding Δa_j , i.e. $a_j + \Delta a_j$.
- 5) Iterate the above procedures until the resultant $\vec{a}$ converges.

3.3 Calculation of contact angles

In this sub-section, six normal vectors given by Eqs. (3) to (8) are projected onto the plane which is

normal to most likely TPB vector $\vec{a}$. Fig. 6 shows the case where $\vec{n}_{\text{YSZ/Pore}}$ does not lie on the plane orthogonal to $\vec{a}$. The cross product of normal vectors $\vec{a}$ and $\vec{n}_{\text{YSZ/Pore}}$ are used to obtain the following projected normal vector:

$$\tilde{\vec{n}}_{\text{YSZ/Pore}} = \frac{\vec{a} \times \vec{n}_{\text{YSZ/Pore}} \times \vec{a}}{|\vec{a} \times \vec{n}_{\text{YSZ/Pore}} \times \vec{a}|}. \quad (27)$$

The other five normal vectors in Eqs. (3) to (8) are also projected onto this plane in the same way.

They are respectively denoted by $\tilde{\vec{n}}_{\text{Ni/Pore}}$, $\tilde{\vec{n}}_{\text{Ni/YSZ}}$, $\tilde{\vec{n}}_{\text{YSZ/Ni}}$, $\tilde{\vec{n}}_{\text{Pore/Ni}}$ and $\tilde{\vec{n}}_{\text{Pore/YSZ}}$ as shown in Fig. 7.

Ideally, two normal unit vectors of different level set functions at the interface should lie on a single straight line. However, the normal vectors projected onto the most likely TPB direction no longer satisfy this condition exactly as schematically shown in Fig. 7. For example, the projected $\tilde{\vec{n}}_{\text{Ni/Pore}}$ and $\tilde{\vec{n}}_{\text{Pore/Ni}}$ vectors are not pointing the opposite direction. Hence, we make the final modification so as to align them in the same direction as shown by the yellow vectors in Fig. 7. The resultant orthogonal vectors of the interfaces are obtained by the difference of two normal vectors on the same numerical grid as follows:

$$\vec{\bar{n}}_{\text{YSZ/Ni}} = \frac{\tilde{\vec{n}}_{\text{YSZ/Ni}} - \tilde{\vec{n}}_{\text{Ni/YSZ}}}{|\tilde{\vec{n}}_{\text{YSZ/Ni}} - \tilde{\vec{n}}_{\text{Ni/YSZ}}|}, \quad (28)$$

$$\vec{\bar{n}}_{\text{Pore/YSZ}} = \frac{\tilde{\vec{n}}_{\text{Pore/YSZ}} - \tilde{\vec{n}}_{\text{YSZ/Pore}}}{|\tilde{\vec{n}}_{\text{Pore/YSZ}} - \tilde{\vec{n}}_{\text{YSZ/Pore}}|}, \quad (29)$$

$$\bar{n}_{\text{Ni/Pore}} = \frac{\tilde{n}_{\text{Ni/Pore}} - \tilde{n}_{\text{Pore/Ni}}}{\left| \tilde{n}_{\text{Ni/Pore}} - \tilde{n}_{\text{Pore/Ni}} \right|}. \quad (30)$$

Accordingly, the other three opposite normal vectors are obtained as

$$\bar{n}_{\text{Ni/YSZ}} = - \frac{\tilde{n}_{\text{YSZ/Ni}} - \tilde{n}_{\text{Ni/YSZ}}}{\left| \tilde{n}_{\text{YSZ/Ni}} - \tilde{n}_{\text{Ni/YSZ}} \right|}, \quad (31)$$

$$\bar{n}_{\text{YSZ/Pore}} = - \frac{\tilde{n}_{\text{Pore/YSZ}} - \tilde{n}_{\text{YSZ/Pore}}}{\left| \tilde{n}_{\text{Pore/YSZ}} - \tilde{n}_{\text{YSZ/Pore}} \right|}, \quad (32)$$

$$\bar{n}_{\text{Pore/Ni}} = - \frac{\tilde{n}_{\text{Ni/Pore}} - \tilde{n}_{\text{Pore/Ni}}}{\left| \tilde{n}_{\text{Ni/Pore}} - \tilde{n}_{\text{Pore/Ni}} \right|}. \quad (33)$$

Finally, the six normal vectors Eqs. (28) to (33) are applied to calculate the contact angles on the triple phase boundary. Namely, Eqs. (9)to (11) are modified as follows:

$$\bar{\theta}_{\text{Ni}} = 180 - \arccos(\bar{n}_{\text{Ni/YSZ}} \cdot \bar{n}_{\text{Ni/Pore}}), \quad (34)$$

$$\bar{\theta}_{\text{YSZ}} = 180 - \arccos(\bar{n}_{\text{YSZ/Ni}} \cdot \bar{n}_{\text{YSZ/Pore}}), \quad (35)$$

$$\bar{\theta}_{\text{Pore}} = 180 - \arccos(\bar{n}_{\text{Pore/YSZ}} \cdot \bar{n}_{\text{Pore/Ni}}). \quad (36)$$

This way, it is guaranteed that the sum of the three angles becomes exactly 2π , i.e.,

$$\bar{\theta}_{\text{Ni}} + \bar{\theta}_{\text{YSZ}} + \bar{\theta}_{\text{Pore}} = 2\pi.$$

3.4 Calculation of surface tension forces

Assuming a static force balance at TPB, the surface tension of interfaces can be calculated from the obtained contact angles. The surface tensions acting at TPB are illustrated in Fig.8. The balance of

the surface tensions at TPB in equilibrium leads to the following relationships in the two orthogonal directions:

$$\gamma_{\text{Ni/YSZ}} + \gamma_{\text{Ni/Pore}} \cos \bar{\theta}_{\text{Ni}} + \gamma_{\text{YSZ/Pore}} \cos \bar{\theta}_{\text{YSZ}} = 0. \quad (37)$$

$$\gamma_{\text{Ni/Pore}} \sin \bar{\theta}_{\text{Ni}} = \gamma_{\text{YSZ/Pore}} \sin \bar{\theta}_{\text{YSZ}}. \quad (38)$$

4 Results and Discussions

The calculated average contact angles of three samples sintered at 1400 °C are listed in Table 2. The total sums of three angles are always 360°, which means that six normal vectors are successfully projected onto the plane orthogonal to TPB. This validates the present calculation process. The average contact angles of Ni, YSZ and pore are 143°~147°, 93°~98° and 119°~123°, respectively. Chen et al. [14] used 141°, 121° and 98° for the equilibrium contact angles of Ni, YSZ and pore in their model, assuming that YSZ phase has a very small mobility. However, FIB-SEM images show that the contact angle of YSZ is around 95°, which is much smaller than the value used in Chen et al. [14]. Probability density functions of contact angles are plotted in Figs. 9 to 11. Although average contact angle of Ni keeps almost unchanged after 100h and 250h discharge, distribution profiles are quite different from each other. In addition, standard deviations of the contact angles are very large especially for YSZ and pore phases. Table 3 shows standard deviations of average contact angles after 650h discharge for the samples sintered at 1450 °C. Average contact angles and standard deviations during 100h discharge for the samples sintered at 1500 °C are shown in Table 4. From the

tables, we can see that the contact angles of different sintering temperature samples are quite different, which indicates the complex nature of the sintering process.

If surface tension of any one phase is known, surface tensions of other two interfaces can be calculated assuming a static balance. In the present study, the surface tension value of 1.4 Jm^{-2} for YSZ/Pore which is reported in Ref. [6] is used to calculate the surface tension forces of Ni/Pore and Ni-YSZ. Surface tensions of each interface for the sample sintered at 1400°C are given in Table 5. The surface tension values of approximately 1.9 Jm^{-2} for Ni/Pore and 1.95 Jm^{-2} for Ni-YSZ are reported in Refs. [15] and [6]. These values are close to our calculation results. Tables 6 and 7 show the surface tension on the interface for the sample sintered at 1450°C and 1500°C , respectively. From Tables 5 to 7, it can be noted that surface tensions of Ni/Pore and Ni-YSZ seem to show some increase after operation.

5. Conclusions

In the present study, a level set method is applied to calculate the contact angles at the triple phase boundary of Ni-YSZ anode reconstructed by FIB-SEM. An accurate estimation method of the contact angles at the triple phase boundary is proposed to overcome the limited resolution of images obtained by FIB-SEM and the resultant numerical errors in the level set function. A proposed numerical technique to estimate the most probable TPB direction from the interfacial normal vectors

gave exactly 2π for the total sum of the three angles. This validates that the present interpolation approach works well. The average contact angle values of Ni, YSZ and pore are found to be $143^{\circ}\sim 156^{\circ}$, $83^{\circ}\sim 138^{\circ}$ and $82^{\circ}\sim 123^{\circ}$, respectively. The mean contact angles remained nearly unchanged after operation. However, the contact angles just after reduction showed large difference for the cells with different sintering temperatures. In addition, standard deviations of the contact angles are very large especially for YSZ and pore phases. The calculated surface tension forces from mean contact angles were close to the experimental values found in the literature. Slight increase of surface tensions of Ni/Pore and Ni/YSZ were observed after operation. The obtained average contact angles surface tension data are expected to be used as basic parameters for simulating Ni-YSZ anode coarsening, which is regarded as one of main causes for degradation.

Acknowledgments

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Tables

Table 1

Sintering temperature	After initial reduction [μm^3]	After 100h discharge [μm^3]	After 250h discharge [μm^3]	After 650h discharge [μm^3]
1400°C	12.7×7.8×9.8	11.6×8.1×9.4	11.4×7.6×9.9	—
1450°C	18.3×10.6×8.4	18.5×12.1×7.0	—	14.0×8.3×11.1
1500°C	11.9×7.2×11.1	11.5×6.5×11.2	—	—

Table 2

Sample	Ni		YSZ		Pore	
	Mean [deg]	Standard Deviation [deg]	Mean [deg]	Standard Deviation [deg]	Mean [deg]	Standard Deviation [deg]
After initial reduction	143.2	24.7	98.3	44.7	118.5	38.9
100h discharge	147.4	24.0	92.7	46.2	119.9	40.5
250h discharge	142.7	27.3	94.5	44.5	122.8	40.9

Table 3

Sample	Ni		YSZ		Pore	
	Mean [deg]	Standard Deviation [deg]	Mean [deg]	Standard Deviation [deg]	Mean [deg]	Standard Deviation [deg]
After initial Reduction	142.6	25.9	135.2	37.2	82.2	39.8

100h discharge	155.7	24.0	82.7	48.3	121.6	42.5
650h discharge	153.1	24.3	88.8	52.5	118.1	46.7

Table 4

Sample	Ni		YSZ		Pore	
	Mean [deg]	Standard Deviation [deg]	Mean [deg]	Standard Deviation [deg]	Mean [deg]	Standard Deviation [deg]
After initial reduction	134.7	28.5	138.3	32.3	87.0	36.6
100h discharge	144.9	25.1	112.8	44.6	102.3	41.3

Table 5

Samples	YSZ/Pore [Jm ⁻²]	Ni/Pore [Jm ⁻²]	Ni/YSZ [Jm ⁻²]
After initial reduction	1.40	2.31	2.05
100h discharge	1.40	2.60	2.25
250h discharge	1.40	2.30	1.94

Table 6

Samples	YSZ/Pore [Jm ⁻²]	Ni/Pore [Jm ⁻²]	Ni/YSZ [Jm ⁻²]
After initial reduction	1.40	1.62	2.28
100h discharge	1.40	3.37	2.90
650h discharge	1.40	3.09	2.93

Table 7

Samples	YSZ/Pore [Jm ⁻²]	Ni/Pore [Jm ⁻²]	Ni/YSZ [Jm ⁻²]
After initial reduction	1.40	1.31	1.97
100h discharge	1.40	2.24	2.38

Figure and Table Captions

Fig. 1 SEM images of anodes sintered at 1400°C (left), 1450 °C (middle) and 1500°C (right).

Fig. 2 The process of obtaining level set function from FIB-SEM reconstructed data.

Fig. 3 Three dimensional reconstructed microstructures of the sample sintered at 1450 °C. After reduction (left), after 100h discharge (middle) , after 250h discharge (right) , Green: Ni, Blue: YSZ.

Fig. 4 Comparison between SEM and level set function images. (a) FIB-SEM, level set functions of (b) Ni,(c) YSZ and (d) Pore. Ni: white, YSZ: grey, Pore: black.

Fig. 5 Normal vectors of the interfaces at the vicinity of triple phase boundary.

Fig. 6 Triple phase boundary direction vector.

Fig. 7 Normal vector projected into the plane orthogonal to the TPB direction

Fig. 8 Surface tensions and contact angles at triple phase boundary

Fig. 9 Probability distribution function of local contact angles for the sample sintered at 1400 °C

Fig. 10 Probability distribution function of local contact angles for the sample sintered at 1450 °C.

Fig. 11 Probability distribution function of local contact angles for the sample sintered at 1500 °C.

Table 1 The sizes of anode samples sintered at three different temperatures, 1400 °C, 1450 °C, and 1500 °C.

Table 2 Average contact angles and standard deviations of Ni, YSZ and pore at triple phase boundary for the samples sintered at 1400 °C.

Table 3 Average contact angles and standard deviations of Ni, YSZ and pore at triple phase boundary for the samples sintered at 1450 °C.

Table 4 Average contact angles and standard deviations of Ni, YSZ and pore at triple phase boundary for the samples sintered at 1500 °C.

Table 5 Surface tensions at triple phase boundary for the sample sintered at 1400 °C.

Table 6 Surface tensions at triple phase boundary for the sample sintered at 1450 °C.

Table 7 Surface tensions at triple phase boundary for the sample sintered at 1500 °C.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11