The effects of reduction temperature on the initial performances and short-time durability of nickel-yttria-stabilized zirconia composite solid oxide fuel cell anodes were investigated. The anode microstructures before and after 100 hours operation were quantitatively analyzed by three-dimensional reconstruction based on focused ion beam-scanning electron microscopy technique. The anode reduced at 500°C showed the worst initial performance and stability in operation which was attributed to the smallest specific nickel-yttria-stabilized-zirconia interface area and the porous nickel formed in low temperature reduction. The anode reduced at 800°C showed the smallest polarization resistance which was attributed to the largest active three phase boundary density. The anode reduced at 1000°C showed the most stable performance with polarization resistance enhanced in operation, which was attributed to the largest specific nickel-yttria-stabilized-zirconia interface area and the dense nickel phase formed in high temperature reduction. It is found that the performance of anode is determined not only by the active three phase boundary density but also the interface bonding between nickel and yttria-stabilized-zirconia in composite anode. Nickel-yttria-stabilized-zirconia interfacial bonding can be enhanced with the increase of reduction temperature, which is able to inhibit the nickel sintering and improve the anode performance stability in long-time operation.

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Solid oxide fuel cell (SOFC, hereafter), as a high efficiency and fuel flexibility energy conversion device, has been attracting more and more attentions in recent decades,1,2 while long time operation stability of SOFC electrodes remain as one of the main challenges. For the nickel-yttria-stabilized-zirconia (Ni-YSZ, hereafter) anodes, major anode degradation mechanism is attributed to the agglomeration of Ni phase, especially during the initial operation period (<200 hours). It has been reported that this initial agglomeration is associated with the initial fast sintering kinetics of Ni.3-12 Ni sintering results in the reduction of active three phase boundary (TPB, hereafter) density and Ni network connectivity.

The sintering mechanism depend on many process factors, such as, sintering temperature, fuel humidity and contaminants.13-16 A few investigations were conducted to investigate the influence of reduction temperature on the pure initial Ni particle microstructure. Plascencia and Utigard17 and Utigard et al.18 have studied the reduction process of NiO particles at different temperatures. It is shown that different initial reduction temperatures lead to totally different morphologies of Ni particles in millimeter-scale. Thus, for conventional composite anode, the corresponding initial performance and durability can be also influenced by the Ni morphological differences created during the reduction process. Several researchers have reported on the influence of reduction temperature on the initial Ni-YSZ microstructures.19-21 Jeangros et al.19,20 have observed NiO reduction process of NiO-YSZ composite anode in-situ in an environmental transmission-electron-microscopy at low temperature. It is reported that the reduction of NiO starts from 380°C at NiO-YSZ interface in a composite anode with very low hydrogen pressure. Zhu et. al.22 have reported that the initial microstructure of Ni-YSZ and the corresponding anode performances can be controlled by reduction and sintering processes of NiO to Ni. A model was proposed to qualitatively describe the reducing and sintering mechanisms and combined effects on anode microstructure changes at different initial reduction temperatures. However, no further quantitative investigation was conducted to support the model and the experimental results. Recently, three-dimensional (3D, hereafter) reconstructions of SOFC electrodes have been carried out by applying focused ion beam scanning electron microscopy (FIB-SEM) technique.13,23-28 This method provides quantitative information of composite cermet microstructure, such as active TPB density, phase percolation etc., which are strongly correlated to the electrode performance. Compared to the analysis based on 2D SEM images,13 FIB-SEM 3D reconstruction technique leads to more accurate microstructure analysis, and facilitates the possible 3D numerical simulation.

In this paper, the performance and microstructures of self-made SOFC anodes reduced at 500°C, 800°C and 1000°C were measured and compared. FIB-SEM 3D reconstruction technique was applied to quantitatively characterize the microstructures before and after 100 hours operations at 800°C. The corresponding microstructural parameters were investigated quantitatively to explain the influences of reduction temperature on the anode performance and durability in short-time operation.

**Experimental**

**Cell preparation.** — Electrolyte-supported cells were used in this study. The anode cermet powder was prepared by mechanically mixed NiO and YSZ powders (AGC Seimi Chem. Corp., Japan) for 48 hours, where the volume ratio of NiO to YSZ was 60% : 40%. The solid mixture was then mixed with terpineol solvent and the ethylcellulose binder in agate mortar to obtain anode slurry. The slurry was screen-printed onto commercial dense 8 mol% YSZ pellet (diameter 30 mm, thickness 0.5 mm, Tosco Nikkemi Corp., Japan) with a diameter of 10 mm. Anodes were sintered at 1450°C for 3 hours. The anode thickness was measured to be about 30 microns after sintering. The cathode material was prepared by mixing (La0.8Sr0.2)0.95MnO3 (LSM, hereafter) powder with YSZ powder in a mass ratio of 50% : 50%. Similar method as the anode was used to obtain cathode slurry. The cathode slurry was screen-printed onto the counter side of the pellet with a diameter of 10 mm. The cathode was then sintered at 1200°C for 2 hours.

**Electrochemical evaluation.** — For the anode side, Ni meshes was used as current collectors which were mechanically pressed against the electrodes by two inner alumina tubes. Gold rings were used as seals between two outer alumina tubes, which were also pressed against the cell by springs. The YSZ pellet was surrounded by a Pt wire as a reference electrode. Pt paste was used to enhance the conductive connection between Pt wire and YSZ pellet. Nitrogen was used as the protective gas in the initial heating up period. The furnace temperature was initially increased to 900°C with a ramp rate of 5°C min⁻¹.
...and then kept at 900°C for 1 hour to ensure the complete gas sealing of gold rings. The reduction of anode was conducted by introducing 5% hydrogen for the initial half of the reduction time and pure hydrogen for the other half subsequently to ensure full reduction of Ni phase. Three anodes were reduced at 500°C, 800°C and 1000°C for 120 minutes, 40 minutes and 15 minutes, respectively. The temperature range of 500°C–1000°C was determined by the requirements of complete gas-sealing of gold ring and the limitation of the setup. The environment temperatures of anodes reduced at 500°C and 1000°C were then changed to 800°C with the continuous supply of pure hydrogen with a rate of 10°C min⁻¹. The performances of anodes were then measured at 800°C with 3% H₂O humidified hydrogen as a fuel and pure oxygen as an oxidant (gas flows are 100 ml min⁻¹ for both anode and cathode). All experiments have been repeated 3 times to ensure the reproducibility. Electrochemical impedance spectroscopy (frequency range: 1–10⁵ Hz, AC signal strength: 10 mV) measurements were conducted using Solatron frequency analyzer (1255WB) at open circuit voltage (OCV, hereafter).

**FIB-SEM observation.**—The anodes after experiments were then analyzed by FIB-SEM (Carl Zeiss, NVision 40). All the samples were taken from the region close to the anode-electrolyte interface at the center of the anode. The samples were first infiltrated by low viscosity epoxy resin under low pressure atmosphere (ca. 15 Pa), so that the pores of the porous electrode could be easily distinguished during FIB-SEM observation. The cured samples were then polished by using Ar-ion beam cross-section polisher (JEOL Ltd., SM-0910). The details of dual-beam FIB-SEM observation technique are introduced in Refs. 23 and 27. The 3D microstructure of the Ni-YSZ anode was then virtually reconstructed based on a series of 2D images by Matlab and Avizo Fire 6.0 (Maxnet). The difference in brightness was used to distinguish the three phases of Ni, YSZ, and pore. After reconstruction, volume fraction, phase connectivity, specific interface area and TPB density were quantified based on the 3D microstructures.

**Results**

**Electrochemical evaluation experiment results.**—The anodes reduced at different temperatures were operated with a current density of 200 mA cm⁻² for 100 hours to investigate the initial performances and durabilities. Figure 1 shows the time variation of anode-to-reference (A-R, hereafter) terminal voltage for three anodes. It is seen that a relatively high degradation rate can be observed for the anode reduced at 500°C and its performance became very unstable after about 45 hours in operation. For the anode reduced at 800°C, degradation rate decreased with time and the performance tended to enter a stable stage with the proceeding of operation. For the anode reduced at 1000°C, the performance of anode was enhanced in the initial 10 hours and showed similar degradation process as the one reduced at 800°C in the rest of the operation. The A-R impedance spectra against time for three anodes are shown in Fig. 2 and the corresponding ohmic and polarization resistance evolutions were analyzed by equivalent circuit method as shown in Fig. 3. The anode reduced at 500°C showed the largest initial A-R ohmic resistance. It is seen that the ohmic resistances of three anodes increased with time with an average degradation rate of 0.30% h⁻¹, 0.24% h⁻¹ and 0.22% h⁻¹, respectively. At the same time, the anode reduced at 500°C also showed largest initial A-R polarization resistance. The polarization resistances of anodes reduced at 500°C and 800°C experienced continuous degradation while for the anode reduced at 1000°C, the polarization resistance decreased continuously in operation. The average polarization resistance degradation rates for three anodes were measured to be 0.44% h⁻¹, 2.09% h⁻¹ and −0.43% h⁻¹. It is seen that anode reduced at 1000°C showed the most stable performance during the operation process and based on the tendency of current experiments it can be predicted that in a longer operation, anode reduced at 1000°C will show a better durability than the other two anodes.

**Microstructure analysis.**—Figure 4 shows the 2D SEM images for the FIB-polished cross-sections of Ni-YSZ anodes before and after the 100 hours operation. White, gray and black regions correspond to Ni, YSZ and pore, respectively. When the reduction temperature was 500°C, open closed pores (fully filled by resin) can be observed uniformly distributed in Ni phase right before the operation, while most of the closed pores disappeared after 100 hours operation with Ni particle became round shape, which can be attributed to Ni sintering. For the anodes reduced at 800°C and 1000°C, relatively dense Ni particles can be observed both before and after operation without obvious shape change. The 2D particle size accumulations were quantified by intercept-length method as shown in Fig. 5. It is seen that Ni particle intercept-length increased obviously after the operation for the anode reduced at 500°C. On the other hand, for the anode reduced at 800°C, Ni particle intercept-length increased little and for the one reduced at 1000°C, Ni particle intercept-length did not increase after the operation. At the same time, it can be also seen that the initial Ni particle size increased with the increase of reduction temperature. YSZ particle size was not influenced by the reduction temperature.

The 3D microstructures of composite Ni-YSZ anodes reduced at 500°C, 800°C and 1000°C are shown in Fig. 6, which correspond to the SEM images shown in Fig. 4a–4f. Ni and YSZ phases are demonstrated as gray and green colors, respectively. In Fig. 7, the reconstructions of independent Ni networks corresponding to...
Figure 2. Comparison of A-R impedance spectra evolution in OCV against time within 3% H₂O hydrogen of anodes reduced at (a) 500°C, (b) 800°C and 1000°C.

Figure 3. A-R (a) ohmic resistance and (b) polarization resistance against time with anodes reduced at different temperatures.

Figure 4. SEM images of cross-sections of the anodes reduced at (a)(b) 500°C, (c)(d) 800°C and (e)(f) 1000°C after reduction and 100 hours operation with a current density of 200 A cm⁻², within 3% H₂O hydrogen. White: Ni, gray: YSZ, and black: Pore.
Figure 5. Particle size accumulation curves generated by intercept-length method for Ni and YSZ phases, before and after 100 hours operation, of anodes reduced at (a) 500 °C, (b) 800 °C and (c) 1000 °C.

Figure 6. 3D reconstruction images of composite anodes microstructures corresponding to Fig. 4a–4f. Gray: Ni and green: YSZ.
Fig. 6a–6f are shown. The gray color indicates the percolated Ni and the red color indicates isolated Ni phase without connection to the block facial boundaries. Yellow color indicates the unknown status phase which is defined as the phase isolated from the percolated phase with connection to the block facial boundaries. The unknown phase might either be isolated or percolated to the main network via neighboring phase which is out of the sample boundaries. The size of the FIB-SEM reconstruction thus may influences the quantification results of the sample, which is out of the range of this paper and requires further investigation. It can be seen that the anode reduced at 500°C experienced obvious Ni particle size increase and shape change which can be attributed to Ni sintering in operation. On the other hand, Ni phase in anodes reduced at 800°C and 1000°C experienced no obvious morphological change.

In order to quantitatively investigate the anode microstructural changes before and after operation, the phase volume fractions, percolation fractions, specific interface areas and TPB densities are summarized in Table I based on the 3D reconstructions shown in Figs. 6. In the operations, both of the intercept-length accumulation fraction and the percolation connectivity of YSZ phase did not change for three reduction temperatures, which means that YSZ phase experienced little morphological change and its network supported the anode structure as backbone skeleton. With very high percolation connectivities for all the reconstructions, YSZ was treated as a stable phase in this study. For Ni phase, it is seen that the initial percolation connectivity increased with the increase of reduction temperature. The anode reduced at 500°C shows the highest Ni percolation connectivity degradation rate in operation, about 0.166% h⁻¹ in average. For the anodes reduced at 800°C and 1000°C, the corresponding average degradation rates are 0.051% h⁻¹, 0.002% h⁻¹, respectively. At the same time, more isolated and unknown-status Ni phase were formed after operation with the anode reduced at 500°C. It is also seen that the specific Ni/YSZ interface area decreased after the operations for anodes reduced at 500°C and 800°C but increased for the one reduced at 1000°C. Anode reduced at 500°C showed the smallest specific Ni/YSZ interface area both before and after operation, which indicates its weakest Ni/YSZ interfacial bonding. Specific Ni-pore interface areas decreased in operation for anodes reduced in all three temperatures, which can be explained by the sintering of Ni driven by the reduction of surface free energy. For TPB densities, it is seen that the anode reduced at 800°C showed the largest total and active TPB densities before operation while the anode reduced at 1000°C showed the smallest ones. In operation, the anode reduced at 500°C showed the largest degradation rates for both total (45.8%) and active TPB (more than 50.0%) densities. For anode reduced at 1000°C an enhancement phenomena of both total and active TPB densities was observed in operation. After operation, anode reduced at 1000°C showed the largest total and active TPB densities.

In order to further investigate the microstructure of anode reduced at 500°C before operation, the cross-section and 3D reconstructions of anode right after the reduction at 500°C, before heating up to 800°C, are shown in Fig. 8. The volume fractions of Ni and YSZ were 29.8% and 34.9%, which indicate the full reduction of NiO. Large amount of sub-micron closed pores can be observed inside Ni particles. At the same time, clear gaps can be observed along most of the Ni/YSZ interface. The Ni particles right after reduction generally kept the original shapes of NiO particles, which means that the reduction of volume in NiO reduction process was achieved by the formation of closed pores. The specific Ni-YSZ and Ni-pore interface areas had been measured to be 0.42 μm² μm⁻³ and 5.62 μm² μm⁻³. The large specific Ni-pore interface area can be attributed to the highly porous Ni, which can promote the sintering of Ni in the later higher temperature operation. On the other hand, the very small specific Ni/YSZ interface area indicates a weak Ni-YSZ interfacial bonding formed in low temperature reduction. The Ni sintering promoted by sub-micron closed pores and the weak Ni-YSZ interfacial bonding after reduction can explain the very fast morphological change of Ni in a very short time (0.5 hour) when the anode reduced at 500°C was heated up to 800°C as shown in Fig. 4a.

**Discussion**

It is well known that active TPB density in Ni-YSZ anode strongly affect its electrochemical performance, i.e., both ohmic and polarization resistances. As shown in Table I, anode reduced at 800°C showed the largest initial active TPB densities in all
directions, which is corresponding to the smallest polarization resistance as shown in Fig. 3. The enhancement of active TPB densities in all directions for anode reduced at 1000°C thus explains the decrease of polarization resistance in operation. However, anode reduced at 500°C did not show the smallest initial active TPB densities in any direction, which can not explain the corresponding largest ohmic and polarization resistances as shown in Fig. 3. After 100 hours operation, the anode reduced at 500°C showed the lowest active TPB densities in all directions which explains the largest polarization resistance while the active TPB densities in all directions of anodes reduced at 800°C and 1000°C can not explain the corresponding polarization resistances. It seems that current active TPB density can not be used as the only parameter to predict anode performance.

For ohmic resistance, it is well known that the A-R ohmic resistance is determined by the ionic resistivity of YSZ, the electronic resistivity of Ni and any possible contact resistance at Ni/YSZ interface. Butz et al. have reported that Ni can diffuse quickly at commonly applied sintering temperatures into 8 mol% Y2O3-Zirconia phase. During the reduction of NiO to metallic Ni, which has a much lower solubility in YSZ, the excess Ni can be exsolved from YSZ and accelerates the appearance of fine tetragonal phase. The conductivity of YSZ can be affected by the cubic-tetragonal-crystal transformation which irreversibly reduces the YSZ ionic conductivity. However, without long-time operation, the degradation of YSZ ionic conductivity can not cause very large degradation on A-R ohmic conductance which irreversibly reduces the YSZ ionic conductivity. However, for anode reduced at 1000°C, the smallest initial ohmic resistance shown in Fig. 3 can not be explained by the corresponding smallest active TPB densities in all directions as shown in Table I, which also supports the assumption that anode performance can not be predicted by the only parameter of active TPB density.

### Table I. Volume fraction and percolation for Ni/YSZ anodes reduced at different temperatures before and after operation.

| Parameter                      | Reduction temperature | Phase       | Before operation | After 100 hours operation |
|--------------------------------|-----------------------|-------------|-----------------|--------------------------|
| **Volume fraction (%)**       | 500°C                 | Ni          | 24.35           | 26.56                    |
|                               |                       | YSZ         | 32.22           | 29.77                    |
|                               | 800°C                 | Ni          | 26.68           | 24.90                    |
|                               |                       | YSZ         | 34.52           | 31.46                    |
|                               | 1000°C                | Ni          | 29.91           | 29.86                    |
|                               |                       | YSZ         | 32.68           | 33.38                    |
| **Percolated phase percentage (%)** | 500°C                 | Ni          | 95.79           | 79.90 (↓16.6%)            |
|                               |                       | YSZ         | 97.79           | 97.46                    |
|                               |                       | Pore        | 99.81           | 99.82                    |
|                               | 800°C                 | Ni          | 96.41           | 91.49 (↓5.1%)             |
|                               |                       | YSZ         | 98.51           | 98.54                    |
|                               |                       | Pore        | 99.01           | 99.74                    |
|                               | 1000°C                | Ni          | 97.45           | 97.26 (↓0.2%)             |
|                               |                       | YSZ         | 98.94           | 99.22                    |
|                               |                       | Pore        | 99.66           | 99.65                    |
| **Unknown phase percentage (%)** | 500°C                 | Ni          | 3.91            | 11.40 (↑256.3%)           |
|                               |                       | YSZ         | 2.89            | 7.54 (↑153.0%)            |
|                               |                       | Pore        | 2.00            | 1.86 (↑7.0%)              |
|                               | 800°C                 | Ni          | 0.81            | 5.78 (↑631.5%)            |
|                               |                       | YSZ         | 0.61            | 0.98 (↑60.7%)             |
|                               |                       | Pore        | 0.55            | 0.88 (↑60.0%)             |
|                               | 1000°C                | Ni          | 0.52            | 0.47 (↓9.6%)              |
|                               |                       | Ni-YSZ      | 1.34            | 0.71 (↓47.0%)             |
|                               |                       | Ni-Pore     | 0.99            | 0.88 (↓11.1%)             |
|                               |                       | Ni-YSZ      | 0.84            | 0.65 (↓22.6%)             |
|                               |                       | Ni-Pore     | 0.62            | 0.66 (↑6.5%)              |
|                               |                       | Ni-Pore     | 0.89            | 0.76 (↓14.6%)             |
| **Isolated phase percentage (%)** | 500°C                 | Ni          | 0.81            | 5.78 (↑631.5%)            |
|                               |                       | YSZ         | 0.61            | 0.98 (↑60.7%)             |
|                               |                       | Pore        | 0.55            | 0.88 (↑60.0%)             |
|                               | 800°C                 | Ni          | 0.52            | 0.47 (↓9.6%)              |
|                               |                       | Ni-YSZ      | 1.34            | 0.71 (↓47.0%)             |
|                               |                       | Ni-Pore     | 0.99            | 0.88 (↓11.1%)             |
|                               |                       | Ni-YSZ      | 0.84            | 0.65 (↓22.6%)             |
|                               |                       | Ni-Pore     | 0.62            | 0.66 (↑6.5%)              |
|                               |                       | Ni-Pore     | 0.89            | 0.76 (↓14.6%)             |
| **Specific interface area (μm² μm⁻³)** | 500°C                 | Total       | 1.90            | 1.03 (↓45.8%)             |
|                               |                       | Active x(0→x) | 1.89           | 0.92                     |
|                               |                       | Active x(0←x) | 1.84           | 0.83                     |
|                               |                       | Active y(0→y) | 1.85           | 0.92                     |
|                               |                       | Active y(0←y) | 1.84           | 0.82                     |
|                               |                       | Active z(0→z) | 1.89           | 0.85                     |
|                               |                       | Active z(0←z) | 1.85           | 0.82                     |
|                               | 800°C                 | Total       | 2.22            | 1.42 (↓36.0%)             |
|                               |                       | Active x(0→x) | 2.19           | 1.37                     |
|                               |                       | Active x(0←x) | 2.18           | 1.36                     |
|                               |                       | Active y(0→y) | 2.18           | 1.36                     |
|                               |                       | Active y(0←y) | 2.18           | 1.36                     |
|                               |                       | Active z(0→z) | 2.18           | 1.36                     |
|                               |                       | Active z(0←z) | 2.18           | 1.36                     |
|                               | 1000°C                | Total       | 1.39            | 1.63 (↑17.3%)             |
|                               |                       | Active x(0→x) | 1.33           | 1.58                     |
|                               |                       | Active x(0←x) | 1.33           | 1.58                     |
|                               |                       | Active y(0→y) | 1.33           | 1.58                     |
|                               |                       | Active y(0←y) | 1.33           | 1.58                     |
|                               |                       | Active z(0→z) | 1.33           | 1.58                     |
|                               |                       | Active z(0←z) | 1.33           | 1.58                     |
the smallest. Consider about the contribution of specific Ni-YSZ area on active TPB density, it makes sense that anode reduced at 500°C showed the largest initial polarization resistances and anode reduced at 1000°C did not. The very small specific Ni/YSZ interface area of anode reduced at 500°C may also explain its instability of performance in operation. The quantification study on the influence of reconstruction scale and Ni/YSZ interface microstructure on TPB density is out of the range of this paper and requires further investigation in the future.

In the reduction process of anode, the residual stresses formed in NiO-YSZ sintering can be released by the reorganization of Ni.\textsuperscript{17-18} Reduction at low temperature, such as at 500°C, is dominated by volume reduction rather than limited Ni sintering. The solid volume reduction is achieved by the formation of large amount of sub-micron closed pores. It has been reported that the reduction process at low temperature starts from the grain surface or boundary of NiO with relatively low binding energy,\textsuperscript{19,20,22} which explains the gaps formed at Ni/YSZ interface and inside Ni particle. During the temperature rise from 500°C to 800°C before operation, the closed pores coalesced and vanished due to Ni sintering as shown in Fig. 4a. In this process, large specific Ni-pore interface area promotes the Ni sintering with its value changed from 5.62 μm\(^2\) μm\(^{-3}\) to 1.34 μm\(^2\) μm\(^{-3}\). At the same time, the Ni sintering-inhibition force based on Ni-YSZ interfacial bonding was weakened by the gaps formed at Ni/YSZ interface.\textsuperscript{23} In the reduction process at 800°C, the effect of Ni sintering tended to dominate the Ni morphological change. The closed pores coalesced and vanished fast with solid volume reduction. Certain larger closed pores formed in the coalescence of initial sub-micron pores remained inside Ni after reduction, as shown in Fig. 4c. Anode reduction at 1000°C is dominated by Ni sintering and only dense Ni particles can be observed as shown in Fig. 4e. It is seen that higher reaction temperature leads to further domination of Ni sintering mechanism in Ni morphological change and promotes the bonding between Ni and YSZ. As shown in Table I, reduction at 500°C and 800°C led to the decrease of specific Ni/YSZ interface area with an average degradation rate of about 0.01% h\(^{-1}\). In contrast, for anode reduced at 1000°C, the specific Ni/YSZ interface area was enhanced during the operation. The degradation rate of specific Ni/YSZ interface area supports the assumption that higher reduction temperature promotes the strengthening of Ni-YSZ interfacial bonding.

In order to further study the influence of anode reduction temperature on Ni-YSZ interfacial bonding, pure-Ni electrode cell\textsuperscript{24} was fabricated by following the same procedures as introduced in experimental section. The pure-Ni anodes were reduced at 500°C, 800°C and 1000°C in pure hydrogen and kept at 800°C with 3% H\(_2\)O humidified hydrogen for 100 hours. The cross-sectional SEM images are shown in Fig. 9. Similar Ni structures are observed as the composite Ni-YSZ anode as shown in Fig. 8a and Fig. 4. In the reduction at 500°C, Ni became full of sub-micron pores after reduction as shown in Fig. 9a and Ni-YSZ interfacial bonding was destructed by the gaps formed after temperature rise before operation as shown in Fig. 9b. The gaps at Ni/YSZ interface were enlarged after operation, with very limited Ni/YSZ interface remained in contact. When the pure-Ni anode was reduced at 800°C, part of Ni/YSZ interface lost contact after reduction because of the pores formed at interface. The coalescence of pores in operation at Ni/YSZ interface partially destructed the Ni-YSZ interfacial bonding and more than half of Ni/YSZ interface remained in contact. For the pure-Ni anode reduced at 1000°C, Ni was densified after reduction and contacted with YSZ surface tightly without obvious gaps. After the operation, almost no pore can be observed at Ni/YSZ interface, which proves the enhancement of Ni-YSZ interfacial bonding. It is seen that compared to the other two reduction temperatures, reduction at 1000°C leads to stronger Ni-YSZ interfacial bonding after reduction. The phenomena observed in all images were found uniformly distributed along Ni/YSZ interfaces. The assumption of enhanced Ni-YSZ interfacial bonding is thus supported by the pure-Ni experiment, which explains the enhanced specific Ni/YSZ interface area and TPB densities for anode reduced at 1000°C as shown in Table I.
Conclusions

Ni-YSZ composite anodes were reduced at temperatures of 500°C, 800°C and 1000°C and the electrochemical performances were measured in 3% H2O humidified hydrogen at 800°C. The microstructures before and after 100 hours operation have been quantitatively reconstructed by FIB-SEM technique. Active TPB density measured based on micro-scale 3D reconstruction is not enough to be used for predicting the anode performance without considering on specific Ni/YSZ interface area. The anode reduced at 800°C showed the highest initial performance which is attributed to the largest active TPB density. Anode reduced at 1000°C showed the most stable performance during the operation. The lowest degradation rates of both ohmic and polarization resistances are attributed to the enhanced Ni-YSZ interfacial bonding formed in high temperature reduction. The anode reduced at 500°C showed the highest degradation rates for both ohmic and polarization resistances which can be explained by the weakened Ni-YSZ interfacial bonding and the enhanced Ni sintering caused by large amount of sub-micron closed pores formed in low temperature reduction. It is seen that higher reduction temperature leads to the improvement of anode stability in a long-time operation. The quantification study on the influence of Ni-YSZ specific interface area and interfacial bonding on anode electrochemical performance should be further investigated in future.

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