Observing the Microstructural Evolution of Ni- Yttria-Stabilized Zirconia Solid Oxide Fuel Cell Anodes

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Abstract

This report describes a transmission X-ray microscopy observation of the high-temperature microstructural evolution of a solid oxide fuel cell Ni-Yttria-stabilized zirconia (Ni-YSZ) anode. Unlike prior studies that compared microstructural differences between different anodes, this three-dimensional measurement directly shows the changes occurring in the same region of an anode, enabling a new understanding of evolutionary processes. High-temperature ageing for 48 h at 1050°C yielded substantial structural changes in the Ni, YSZ and pore networks, including coalescence of Ni particles, leading to a three-fold decrease in three phase boundary length. Implications for fuel cell long-term degradation are discussed.

1. Introduction

Solid oxide cells (SOCs) have been investigated for clean efficiency electricity generation [1, 2], renewable fuel production, and electricity storage [3, 4]. The microstructural stability of the Ni-YSZ fuel electrode has been widely discussed as one of the critical causes of performance degradation. A number of studies have revealed substantial changes in Ni particle size with time at temperature [5-8]. The evolution of Ni-YSZ microstructure has also recently been explored via three-dimensional (3D) tomography [6, 9], and in one case directly related to electrochemical performance degradation [5]. In these prior studies, electrode evolution was characterized by observing anode structure and properties after ageing, and comparing with a similar electrode that had not been aged. The same is true in previous studies of the evolution of other SOC electrodes, *e.g.*, observing the effect of elevated temperature on LSM-YSZ cathodes [10]. There are a few drawbacks to this approach: (1) uncertainties and errors arise from comparing different electrode samples, due to sample-to-sample variations; (2) only averaged microstructural quantities, *e.g.* surface area or three-phase boundary density, can be observed, not the actual evolution of the structure; and (3) when a measured 3D Ni-YSZ image was used as the starting point of a phase-field simulation of the microstructure evolution [11], there was no measured evolved microstructure for comparison with the simulated structure.

X-ray tomographic measurement techniques such as transmission X-ray microscopy (TXM) [5, 12-14] are non-destructive, a feature that has been used to advantage to follow the time evolution of a material, as discussed by Rowenhorst. [15] Typically, the structural evolution is sufficiently fast that the measurements can be

performed in real time, *e.g.*, on an X-ray beamline. In one case, $(\text{La,Sr})(\text{Co,Fe})\text{O}_3$ cathodes were observed during heating up to 700°C in the TXM, but the times and temperatures were too low to yield significant structural changes [16]. In fact, the changes of interest in SOC degradation typically occur over long times, such that it is necessary to evolve the structure outside of the beam [17]. However, when a sample is re-introduced into the TXM, the resulting images are no longer aligned with the original images. For example, in a previous TXM study of the Ni-YSZ anode air oxidation process done outside of the TXM [18], the before and after images were not registered. In addition, the ageing or oxidation temperature in the above experiments was limited to 700°C to avoid mechanical failure of the TXM specimen, which was mounted to a metal sample holder pin with a Pt weld. These prior reports reveal that there are significant challenges in doing beam-line studies of SOC electrode evolution. First, an electrode sample geometry must be found that can be repeatedly aged at elevated temperature for long times and then re-introduced into the microscope for measurements. Second, the different 3D reconstructed images must be registered with nm-scale accuracy.

As described below, we have met these challenges and demonstrated the repeated observation of the microstructure of a Ni-YSZ anode with intervening high-temperature ageing steps. This methodology eliminates uncertainties and errors from comparing different electrodes and enables direct comparison with 3D microstructure simulations; thus, it should help enable a new understanding of electrode evolutionary processes.

2. Experimental

2.1. Sample Preparation

Anode supported half cells were prepared as described elsewhere[9]. An anode support with 50:50 wt.% NiO-YSZ was prepared by dry pressing, followed by colloidal drop coating of an anode functional layer, also with 50:50 wt.% NiO-YSZ, and a thin YSZ electrolyte layer. These structures were then co-fired in air at 1400°C, and then heated to 800°C for 3h in a 5% H_2 / 3% H_2O / 92% Ar gas mixture to fully reduce the nickel oxide. No cathode was used.

The challenge in preparing the samples for TXM was to create a separated volume of the sample small enough to image with TXM – which has a 40 μm field of view – and yet large enough to be handled and aged. During initial attempts to employ a conventional sample preparation method – Focused Ion Beam (FIB)-milling an appropriate-shaped sample and then mounting it on a metal pin using a Pt weld [13] – the sample was lost after high-temperature ageing, probably because the Pt weld failed. Thus, a new method was developed. The sample was fractured and a piece with a sharp tip was selected (Figure 1a). It was then thinned by mechanical polishing on a slight bias, removing the bulk of the anode support and producing a sharp tip. (Figure 1b and Figure 1d) Then, an FEI Helios Nanolab 600 dual-beam FIB/SEM was used to mill the tip of the sample into a ~40 μm diameter and ~80 μm height cylinder (Figure 1c, Figure 1e and Figure 1f). The milling was done in two steps. First, a rough milling was done to clean the area around the tip and remove excess material. A top-down view of the tip after that first step is shown in Figure 1e. Then, a precise cylindrical milling was

carried out, which yielded the final tip. Figure 1f, Figure 1g and Figure 1h show the final sample at different magnifications and under different angles.

Full field X-ray nano-tomography was carried out at the TXM beamline X8C, National Synchrotron Light Source, Brookhaven National Laboratory [19]. Full rotation tomography sets were collected for each data set at two different X-ray energies, below (8300 eV) and above (> 8332 eV) the Ni absorption K-edge, to facilitate the segmentation process. A standard Filtered Back Projection Reconstruction was then performed [20]. For each data set, a cylinder ~ 40 μm in diameter and height was obtained, with a voxel size of 38.9 nm. A first 3D image data set was collected on the as-reduced sample.

Given that SOFCs are expected to operate at $\sim 800^\circ\text{C}$ and degrade over $> 40,000$ h, most aging experiments are done at higher temperatures to accelerate electrode changes, allowing observations over a reasonable time frame [5, 21]. The ultimate aim is to develop microstructural evolution models that can accurately predict changes occurring over long times at lower temperature [22]. For the present experiments, a temperature of 1050°C was selected, based on prior work [5], in order to yield moderate anode structural changes over relatively short times. The sample was aged at 1050°C for 24 hours, in a 5% H_2 / 3% H_2O / 92% Ar gas mixture similar to a typical anode fuel gas. After cooling and re-mounting in the TXM, an image data set was collected. The same ageing process (24 h at 1050°C) was then repeated, for a total of 48 h of ageing, and another data set collected.

2.2. Image registration, analysis and microstructural quantification

Prior to segmentation, aged electrode image data sets were registered with respect to the non-aged sample. Registration was done using a mutual information method as described by Gulsoy *et. al.* [23]. Mutual information is a measure of the similarity between corresponding pixels between two arbitrary dimensionality datasets. It is defined here using the difference between Shannon entropies of the individual image datasets and the joint entropy. The core of the cylinder, corresponding to the areas with the best contrast that were also furthest removed from the sample edges, were selected and cropped from each of the TXM datasets. Images were processed to improve the brightness and contrast and a simple thresholding algorithm was used to segment the data. The nickel phase was segmented from the above-edge data. For the pore phase, the above-edge data was subtracted from the inverted below-edge data, to allow for more accurate segmentation [5].

Macrohomogeneous morphological information including phase volume fraction, surface areas, particle size distributions, phase connectivity and triple phase boundaries (TPBs), were calculated using methods described elsewhere [9, 13, 24]. Algorithms were written in-house for the image processing programming language, Interactive Data Language (IDL). Tortuosity was computed as described elsewhere [25].

3. Results and discussion

Figure 2a shows an example cross sectional image taken from the TXM 3D data set for the as-prepared SOC with Ni-YSZ electrode. The image shows the entire thickness of the anode functional layer (AFL), along with portions of the YSZ electrolyte at the bottom and the Ni-YSZ support at the top. The support can be distinguished from the

AFL by the coarser structure and higher porosity. Figure 2b shows the representative image of the same sample obtained after a total of 48 h of ageing. The images in Figure 2 were not aligned, but were clearly from the same region, as indicated by the elongated pore seen in the anode support of both images. The most obvious ageing effect is the appearance of large nickel particles on the outer surfaces of the sample cylinder. This illustrates the strong tendency of Ni to coarsen under these conditions, when not constrained within a YSZ matrix. Less pronounced coarsening is also apparent within the Ni-YSZ support and in the AFL.

The large Ni particles at the sample edges in Figure 2b constitute an experimental artifact, since such edges are not present in the AFL of an operating SOC. This could potentially compromise the accuracy of the present measurements, if the Ni content inside of the cylinder was reduced by Ni accumulation outside of the initial sample volume. However, the Ni, YSZ, and pore volume fractions were found to not vary measurably over most of the inner volume of the cylinder, and the Ni-YSZ ratio agreed well with the values expected based on the initial AFL composition, indicating that only the near-edge regions were affected. This also shows that Ni loss by volatilization was not significant. Thus, cropping the data sets, taking a limited region furthest from the edges of the TXM sample, appears to be sufficient to eliminate edge effects.

Figure 3 shows representative two-dimensional sections from the registered 3D data sets, for the as-reduced and aged anodes. This illustrates the quality of the image contrast, the segmentation process, and the evolution of anode structure. The top row shows images taken with X-ray energy of ~8332 eV (at/above the Ni absorption K-edge), showing the full width of the AFLs. The second row shows magnified images of a

portion of the AFL near the center of the imaged volume. In both these rows, the Ni networks are clear from their bright contrast, and the Ni coarsening due to ageing is obvious, especially in the anode support. The third row shows the same regions as composite images where the above-edge images were subtracted from the inverted below-edge data. As discussed previously [5, 13], this composite image shows pores with bright contrast. The bottom row shows the segmented images from the same region, where the Ni phase was obtained from the above-edge image, the pore phase from the composite image, and the YSZ was taken as all other areas. General trends observed include the elimination of a number of small Ni particles and pores, as well as cases where initially separated Ni particles join together, circled in red on the segmented images. The overall high quality of the image registration between the different samples is evident.

Microstructural characteristics obtained from the reconstruction data sets are shown in Table 1. The reconstructed volume was $\sim 5000 \mu\text{m}^3$ in each case, large enough to expect statistical error $< 4\%$ [26]. The measured phase volume fractions did not vary appreciably with ageing, and agreed with the expected volume fractions within $\sim 1 \text{ vol}\%$. Unlike prior reports comparing 3D microstructures [5, 6], where sample-to-sample and statistical variations were convoluted with measurement errors, in the present result the experimental errors should be a measure of the imaging and segmentation errors. Specific surface areas generally decrease with increasing ageing time – the one exception is a few percent increase in YSZ specific surface area. Again, this gives an indication of the 3D measurement/segmentation errors. Average tortuosity values for the different phases and cells were computed. Ni phase had a constant

tortuosity of ~ 1.6 , YSZ of ~ 1.1 . As previously observed [5], the pore tortuosity increased slightly with ageing from 1.45 to 1.88. All values are within the same range as for similar cells which tortuosity has been computed with the same method previously tests [5, 13, 27]. Errors due to the image registration process are also possible; particularly if the optimization scheme finds a local minimum. However, visual inspection of the registration results confirmed that the registration process reached the correct minimum in mutual information. Therefore, the accuracy of the registration is limited by the change in the image data between CT scans, which is approximately one voxel.

Figure 4 presents 3D visualizations of a selected portion of the as reduced, 24 h aged, and 48 h aged AFL. In the structural images, increases in the average Ni and pore feature sizes with increasing ageing time are evident. This is consistent with the decreases in surface area shown in Table 1. There is a corresponding decrease in the density of TPB lines. The figure indicates which TPB lines are active and inactive, [28] the latter being $\sim 12\%$ of the total, due mainly due to a small fraction ($< 2\%$) of isolated pores. The active TPB densities decreased strongly during the first 24 h of ageing, from $5.83 \mu\text{m}^{-2}$ to $2.29 \mu\text{m}^{-2}$, with relatively little further decrease after the second 24 h anneal to $2.07 \mu\text{m}^{-2}$.

Figure 5 shows magnified views of the AFL Ni (top row) and pore (middle row) structure from a portion of the image volumes shown in Figure 4, chosen to illustrate some of the changes that occur during ageing. In the upper middle portion of the images, a narrow neck between Ni particles is seen to grow in size with increasing ageing time. In the middle left portion, two initially separated Ni particles join to form an elongated Ni region, during the second 24 h anneal. Note that the Ni particles were

separated by a thin section of YSZ in the as-reduced structure. Thus, the Ni coalescence process could only occur because of the evolution of the YSZ structure. This is not always the case, however, as the neck between Ni particles shown in Figure 3 that forms between 24 and 48 h of ageing forms in a region that was originally pore. Figure 5 (b) shows consolidation of a number of smaller pores, mostly in the lower to middle regions of the image, into larger pores after ageing. These changes are all consistent with the general trend of coalescence and feature-size growth that decreases surface area and hence interfacial energy. Figure 5 (bottom row), which presents the mean curvature of the nickel phase, illustrates the reduction in curvature associated with this reduction in interfacial area. There is, however, one non-intuitive change near the middle of the imaged region, where a neck forms between Ni regions after 24 h ageing, but disappears after 48 h ageing. It may be that the disappearance of the neck is part of a larger change that reduces overall interfacial energy, but it will be necessary to carry out detailed simulations of the structural evolution to fully understand this observation.

One of the Ni coalescence events noted above occurred between Ni particles originally separated by an ~ 200 nm thick YSZ region. Since this corresponds to only 5 voxels in these images, this could possibly be an error in the imaging and segmentation process. However, the preponderance of the evidence suggests that this region was initially YSZ. First, it was not possible to “convert” this region to pore by re-segmenting the data with reasonable parameters. Second, similar coalescence events between initially YSZ-separated Ni particles are seen in other regions of the data set. Third, in the present data an average of 28% of the YSZ voxels change during each ageing step;

thus, there is enough YSZ mobility under these ageing conditions to explain the elimination of the thin YSZ region. This not surprising given that the present ageing temperature of 1050°C (1323 K) corresponds to ~45% of the YSZ melting point, 2700°C (2973 K), high enough to expect significant evolution. Overall, these results suggest that the Ni phase, which is strongly constrained within a YSZ matrix with relatively little free pore volume, has its coarsening limited by the evolution of the YSZ phase. This is consistent with the normal view that the more stable YSZ phase constrains Ni coarsening; but at high enough ageing temperatures and times, the YSZ itself can evolve, thereby allowing Ni evolution.

4. Conclusions

The microstructural evolution of a solid oxide cell Ni-YSZ electrode has been observed using transmission X-ray microscopy. Methods were developed for sample preparation and for acquiring microstructural data with intervening *ex situ* ageing steps, and an effective image registration process was demonstrated. The comparison of as-reduced and aged Ni-YSZ showed volume fractions that agreed within ~ 1 vol%, indicating that image and reconstruction errors were relatively small. One new result is that some Ni particle coalescence events involved elimination of an intervening YSZ region; this demonstrates how the YSZ network serves to limit Ni coarsening. This suggests that prior structural evolution models, where the YSZ phase was assumed immobile [29] or with very limited mobility [11, 30], will need to be modified.

Prior phase-field modeling of SOC Ni-YSZ electrode evolution used 3D image data as a starting point for the simulation[11, 31, 32], but there was no experimental

aged structure for comparison with the simulated one. The 3D TXM measurements demonstrated here provide the structural evolution data needed for comparison with phase-field model simulations, and will thereby allow development of more realistic structural evolution models.

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6. References

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Figure 1: Illustration of the sample preparation method and geometry. Schematic views of the cell after fracture (a), after polishing (b), and after ion milling to form a tip (c). SEM images of the tip after mechanical polishing (d); after rough FIB milling in top-down view (e); and after completed FIB milling of the cylindrical tip in top-down view (f), low-magnification side view (g), and high-magnification side view (h).

Figure 2: Two-dimensional cross-sections from the 3D image data sets showing the entire imaged cylinder for the not aged (a) and 48 h aged (b) electrodes. The slight streaking, observable near the edges of the images, is due to the back projection algorithm used in image processing; this artifact is eliminated during image processing prior to segmentation.

Figure 3: Representative two-dimensional sections from the data sets for the as-reduced (left column), 24 h aged (middle column), and 48 h aged (right column) anodes. The top row shows the above-edge (>8332 eV) images at lower magnification covering the entire width of the AFL, while the second row shows magnified views of a smaller region. The third row shows the inverted below-edge (8300 eV) images after inversion and subtraction of the above-edge images, a procedure that highlights the pore phase. The bottom row shows the magnified segmented images.

Figure 4: 3D image renderings of a selected portion of the as reduced (left), 24h aged (middle), and 48h aged (right) AFL. The top row shows the Ni (green) and pore (blue)

phases, with the YSZ phase transparent. The bottom row shows the TPB lines in the same volume, with the active TPBs shown in green and the inactive TPBs shown in red. The areas indicated by the red box are shown at higher magnification in Figure 5.

Figure 5: Magnified 3D Image renderings of a selected portion of the as reduced (left), 24h aged (middle), and 48h aged (right) AFL. The top row shows the Ni network (green), the middle row shows the pore network (blue), and the bottom row shows Ni surface curvature.

Table 1: Summary of the measured 3D structural data

a)

b)

c)

d)

e)

f)

g)

h)

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Graphical Abstract