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Three-dimensional microstructural changes in the Ni–YSZ solid oxide fuel cell anode during operation

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Abstract

Microstructural evolution in solid oxide fuel cell (SOFC) cermet anodes has been investigated using X-ray nanotomography along with differential absorption imaging. SOFC anode supports composed of Ni and yttria-stabilized zirconia (YSZ) were subjected to extended operation and selected regions were imaged using a transmission X-ray microscope. X-ray nanotomography provides unique insight into microstructure changes of all three phases (Ni, YSZ, pore) in three spatial dimensions, and its relation to performance degradation. Statistically significant 3D microstructural changes were observed in the anode Ni phase over a range of operational times, including phase size growth and changes in connectivity, interfacial contact area and contiguous triple-phase boundary length. These observations support microstructural evolution correlated to SOFC performance. We find that Ni coarsening is driven by particle curvature as indicated by the dihedral angles between the Ni, YSZ and pore phases, and hypothesize that growth occurs primarily by means of diffusion and particle agglomeration constrained by a pinning mechanism related to the YSZ phase. The decrease in Ni phase size after extended periods of time may be the result of a second process connected to a mobility-induced decrease in the YSZ phase size or non-uniform curvature resulting in a net decrease in Ni phase size.

Keywords: Solid oxide fuel cell; Ni–YSZ anode; Ni coarsening; Degradation; Dihedral angle

1. Introduction

Power and electrical efficiency losses in a solid oxide fuel cell (SOFC) can result from changing composition and microstructure of cell components during operation [1–5]. These changes have been found to reduce the SOFC operating voltage achieved at constant current depending on the cell design and operating conditions [1]. Performance degradation of the SOFC can result from several phenomena, including microstructural changes in the electrode, reactions between materials to form new phases and contamination of active interfaces [2–5]. The coarsening of Ni particles in SOFC anodes is one widely observed example of such deleterious microstructural evolution [1,6–10].

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Focused ion beam scanning electron microscopy (FIB-SEM) and X-ray nanotomography permit three-dimensional imaging of composite electrodes at unprecedented scales [1,11–14], distinguishing them from other imaging techniques applied to explore microstructure and composition in SOFC electrodes. SEM serial sectioning approaches, including FIB-SEM, have fostered a greater understanding of the microstructure and composition in SOFC anodes and cathodes [11,15] and have advanced the understanding of Ni–YSZ anode degradation mechanisms, particularly Ni coarsening behavior [1,6]. However, serial sectioning approaches result in the loss of the imaged sample and are often restricted to *ex situ* experimental investigations. Full-field X-ray nanotomography permits the non-destructive imaging of anode samples [12,13], with elemental sensitivity achieved for anode microstructures by applying a tunable X-ray source in conjunction with differential absorption imaging across the Ni *K*-absorption edge [13]. Applying X-ray absorption near-edge structure (XANES) spectroscopy in combination with full-field X-ray nanotomography can expand these capabilities by allowing chemical speciation based on chemical bonding states discerned the XANES spectra [16]. These advances may allow for *in situ* measurement opportunities with an appropriate environmental chamber [17,18].

The present work extends transmission X-ray microscopy (TXM) techniques to the exploration of degradation in SOFC anodes. X-ray nanotomography measurements of anodes subjected to extended operation have been performed using differential absorption imaging to further elucidate degradation associated with microstructural evolution in the anode phases. Digitized reconstructions of the volumetric data have enabled elemental mapping and microstructural characterization of the Ni, YSZ and pore phases of aged SOFC anodes at a spatial resolution of 32 nm (based on TXM zoneplate characteristics [13]). Ni coarsening is observed as indicated by the statistically significant growth of Ni particle diameters over extended cell operation. Dihedral angle calculations for anode microstructures suggest the Ni–YSZ system performance may decay under long-term cell operating conditions. The particle sizes and dihedral angles are used in a thermodynamic model to provide a hypothesis on the primary modes and mechanisms of microstructural reconfiguration. Specifically, Ni coarsening is found to be driven by particle curvature, which supports primary growth through particle agglomeration. We hypothesize that this growth is constrained by the YSZ phase through a pinning mechanism [19,20]. Furthermore, results suggest that, at long operational times, the decrease in YSZ phase size, possibly linked to Zr or Zr^{4+} mobility [21,22], may result in a decrease in Ni phase size.

2. Methodology

2.1. Sample preparation and statistical analysis

Initial microstructural characterization has been completed on regions taken from SOFC anodes subjected to extended operation. Microstructural evolution and the associated degradation of these anodes has been previously investigated using SEM [1,6]. Details of the test cell configurations and operational conditions are provided by Faes et al. [1]. The regions measured in the present study were taken from 250 μm thick tape-cast Ni–YSZ anode supports (HTceramix SA, Switzerland). These supports were tested in a short stack configuration with YSZ electrolytes and lanthanum strontium ferrite (LSF) cathodes [1]. The anode regions measured were acquired from anode support pieces extracted from these test cells at set operational time intervals (0 h (reference), 158, 240 and 1130 h). A total of nine regions were measured using X-ray nanotomography combined with differential absorption imaging. The allocation of these regions among the operational times studied is outlined in Table 1. Sectioning was performed with both traditional techniques and FIB milling. An example of a mounted cylindrical sample produced by FIB milling is shown in Fig. 1a. These FIB-milled samples exhibit improved transmission characteristics compared to traditionally sectioned regions, due in part to the more uniform cross-sections achieved. Anode regions extracted using traditional sectioning are designated T##, while regions sectioned with FIB milling are designated F##, where ## is a two-digit region identifier.

The anode regions imaged using X-ray nanotomography were segmented into sample volumes 125^3 voxels in size, corresponding to a cube approximately 6.6 μm on a side. Details of the segmentation and characterization approach are provided in a later section of this work. To support the microstructural evolution observed in the characterization results, the statistical significance of the operational time as a predictor of microstructural evolution was investigated using a one-way layout analysis of variance (ANOVA) [30]. The statistical test applied in this ANOVA was an *F*-test with $\alpha = 0.05$. Samples segmented from each anode region were treated as replicates representing the operational times investigated. The number of samples taken from each operational time considered in the one-way layout ANOVA is given in Table 1. A total of 21 distinct samples were characterized to provide data for this statistical analysis.

2.2. X-ray nanotomography measurements

X-ray nanotomography measurements were completed using the TXM at beamline 32-ID-C of the Advanced Photon Source (APS). Details of this TXM configuration and the nanotomography measurements are available in the literature [13,23]. The energy level tuning capability of the TXM at beamline 32-ID-C permits the nondestructive 3-D mapping of elemental composition within the SOFC anode by providing access to the Ni *K*-absorption edge (*K*-edge) at 8.333 keV. Slightly below this energy level the solid phases in the anode exhibit comparable X-ray transmission behavior, while Ni absorption increases abruptly by a factor of 5 across the edge. Acquiring images above