Supporting Information

Effect of nano-scale $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ infiltrant and steam content on Ni–$(Y_2O_3)_{0.08}(ZrO_2)_{0.92}$ fuel electrode degradation during high-temperature electrolysis

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This section of the supplemental materials provides additional microstructural data obtained in this work.

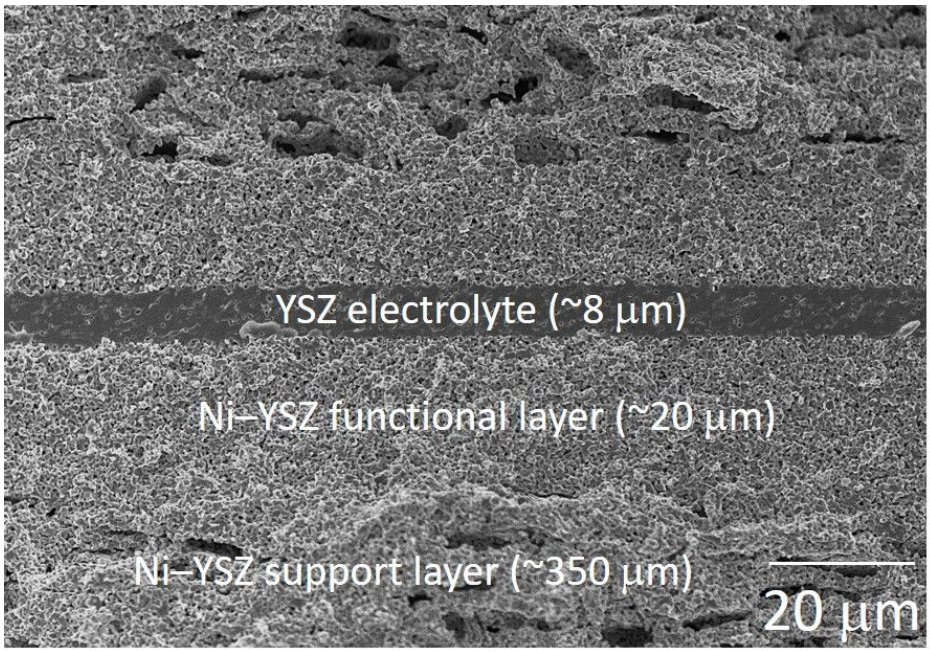

Figure S1. Cross-sectional SEM image of a Ni–YSZ supported symmetric cell.

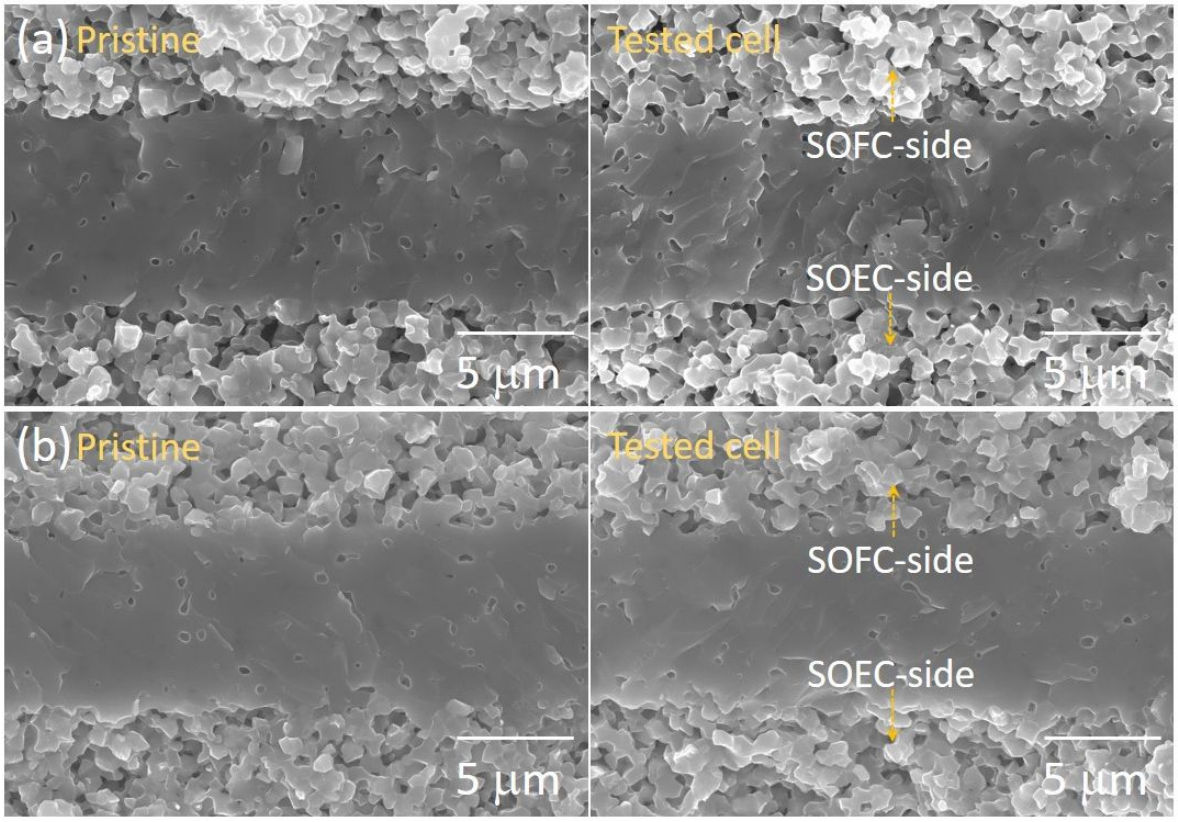

Figure S2. Cross-sectional SEM images for the electrolyte and a portion of the electrodes taken from the (a) Ni–YSZ and (b) Ni–YSZ:GDC cells before and after the life tests.

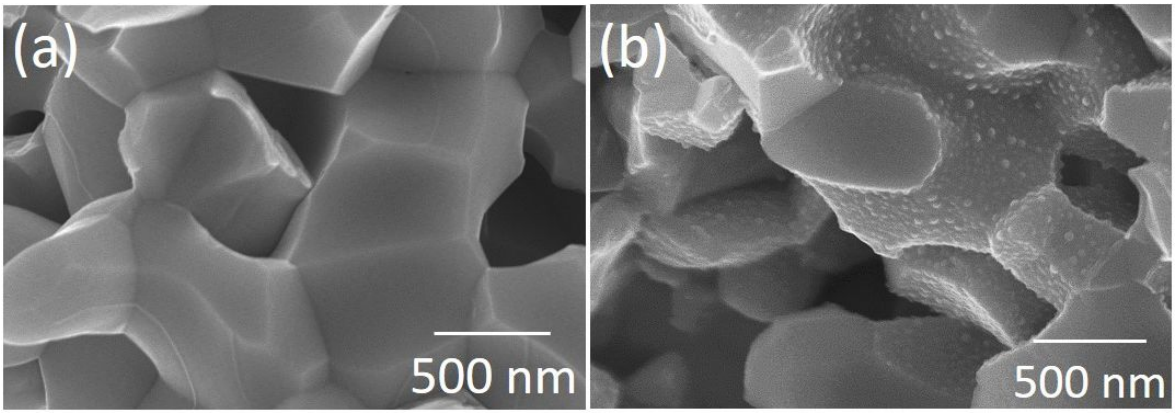

Figure S3. Cross-sectional SEM images for the electrodes of the un-tested (a) Ni–YSZ and Ni–YSZ:GDC cells.

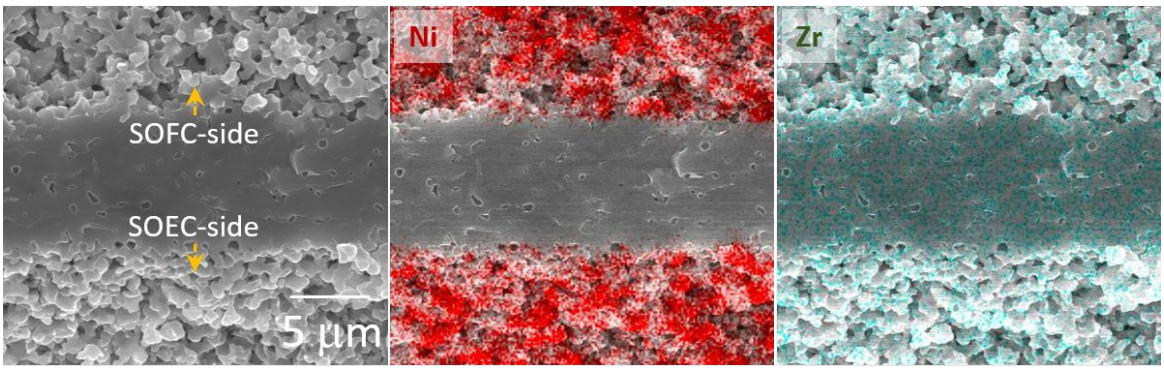

Figure S4. EDS elemental distribution of Ni and Zr for the Ni–YSZ symmetric cell after the life test.

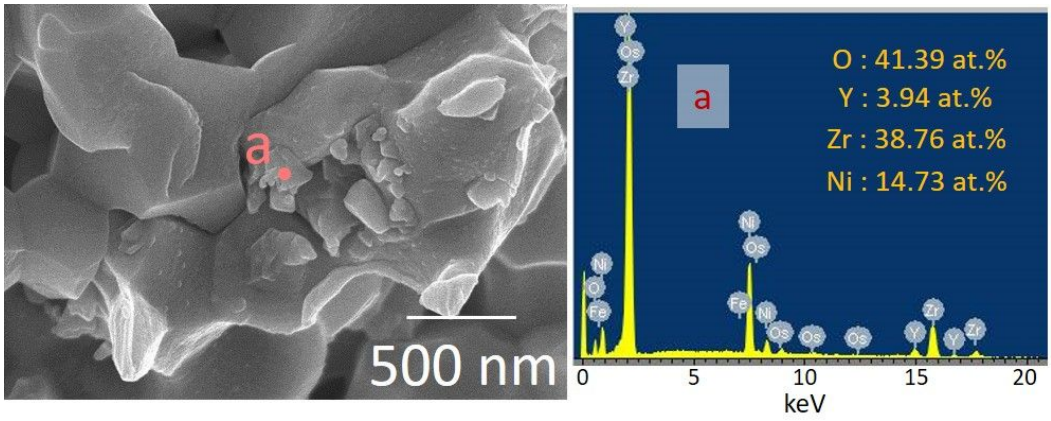

Figure S5. A cross-sectional SEM image of SOEC-side Ni–YSZ electrode for the tested Ni–YSZ symmetric cell, and EDS spectrum measured on (a).

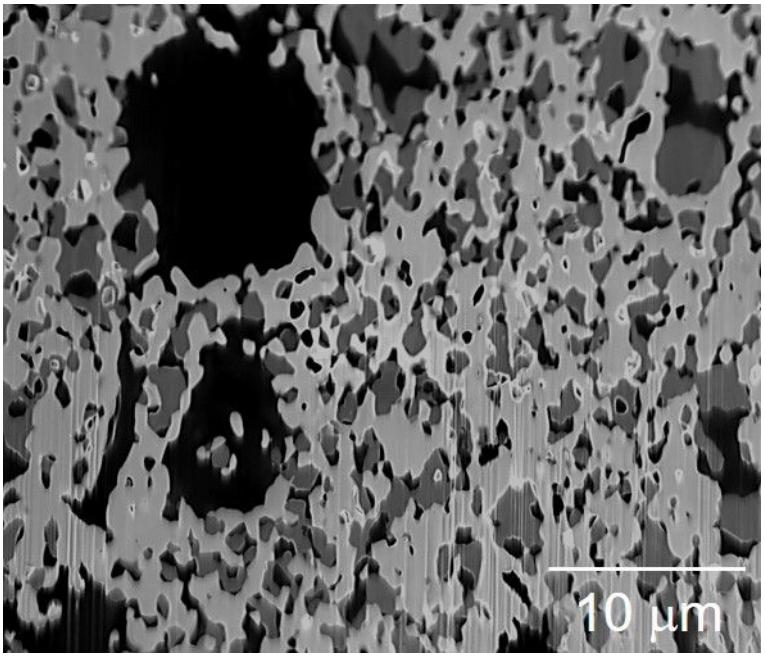

Figure S6. Polished cross-sectional SEM images of the anode support layers (ASLs) of Ni–YSZ supported symmetric cell (ASC) after electrochemical characterization.

The sample was polished up to a 1 µm polishing solution on the top and imaging sides, then a high current Ga beam was used to rough cut the surface, leaving behind the curtaining. A low current beam was then applied as a cleaning cut to remove the large curtaining. While the black color indicates the pore, the bright and dark gray colors indicate the Ni and YSZ, respectively.

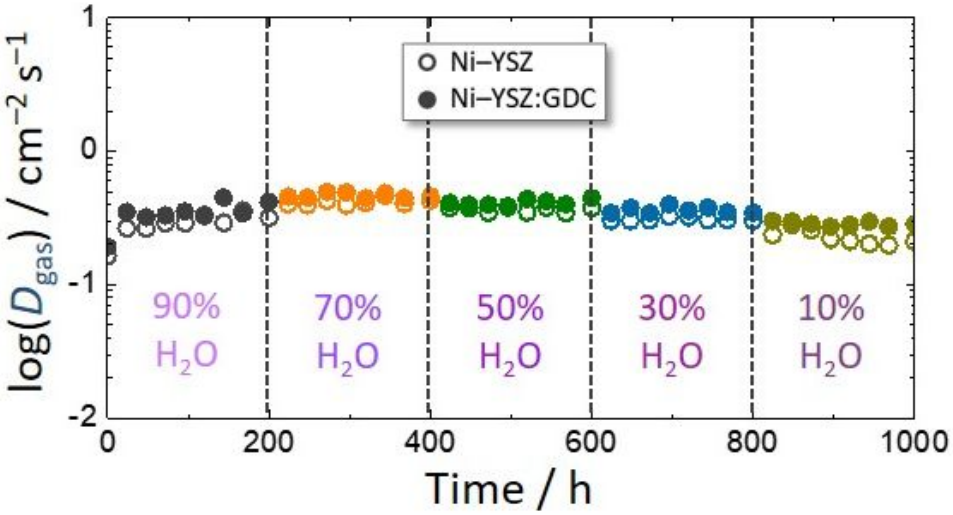

Figure S7. D_{gas} values as a function of time for the different steam contents.

Stereological Analysis

2D stereological analyses of the Ni–YSZ support microstructures were performed to obtain specific surface area and porosity. Polished epoxy-infiltrated samples were milled and imaged at 8000× magnification using an FEI Helios FIB-SEM. Images of the electrode were taken in a manner to avoid biasing the results: there was no overlap in images in the x–y plane and milling depth in the z direction was greater than the largest particle size to ensure independence of the sampled areas.

Using in-house MATLAB code, the SEM images (Figure S6) were binaried into solid and pore phases and the total length of interface of the two phases in each 2D image was calculated. Porosity and specific surface area were estimated using the equations:

$$\varepsilon = \varepsilon_A \qquad \text{(S1)}$$

$$a = (4L_A)/\pi \qquad \text{(S2)}$$

Where ε_A is the 2D porosity of the image and L_A is the interface length divided by the area of the image.[5] Values obtained for each image were averaged within the composition dataset. To verify the method, the stereological calculations were performed on previously obtained full 3D reconstruction datasets. It was found that 10 independent images (no particle overlap between images) of the 300 image datasets was sufficient to ensure that 3D porosity and surface area values fell within the error of stereological measurement.

This section of the supplemental materials provides experimental details done in this work.

Cell fabrication

The cell fabrication process here utilizes the reduced sintering temperature by adding sintering aids into the YSZ through which the resultant Ni–YSZ is expected to have a smaller particle size, higher TPB density, and lower polarization resistance compared to typical 1400 ^{o}C fired electrodes [1]. The symmetric cell has a thin YSZ sandwiched between identical Ni–YSZ electrodes, each of which is composed of an electrode functional layer and a thick support layer (Figure S1). The cells were fabricated through tape casting and lamination using 45 wt.% NiO–45 wt.% YSZ–10 wt.% starch (as a support), 50 wt.% NiO–50 wt.% YSZ (as an electrode functional layer), and YSZ with 1 mol.% Fe_2O_3 sintering aid (as an electrolyte). Each layer was cast on a carrier film from its slurry containing the desirable amounts of ethanol/xylene (as solvent), fish oil (as dispersant), polyvinyl butyral (as binder), and plasticizers, as reported elsewhere [1-3]. Then, the lamination was performed at 70 ^{o}C for 5 minutes under a pressure of ~22 atm. The resultant specimens were co-sintered at a reduced temperature of 1250 ^{o}C for 4 h. The final fired thicknesses of electrolyte, electrode functional layer, and support layer were found to be ~8, 20, and 350 μm.

GDC infiltration

The GDC solutions were prepared by dissolving desired amounts of $Gd(NO_3)_3{\cdot}6H_2O$ and $Ce(NO_3)_3{\cdot}6H_2O$ in distilled water, followed by adding Triton X-100 and citric acid as a surfactant and a chelating agent, respectively. In order to fully impregnate the GDC precursor with the Ni–YSZ electrode surface, the sufficiently porous Ni–YSZ structures were derived through pre-reduction at 700 ^{o}C for 5 h in 3 vol.% H_2O-humidified H_2. Note that while the symmetric cells were pre-reduced in a tube furnace, the fuel electrode parts of full cells were reduced in the cell test setup in which the cell could be removed for infiltration followed by resealing into the testing rig. Similarly to the literature [3-5], the GDC nanoparticles resulted from infiltration of 10 μl of GDC solution into the porous scaffold, followed by in situ thermal conversion during the cell startup – heating in 3 vol.% H_2O–humidified H_2 at 5 ^{o}C/min to 800 ^{o}C.

Electrochemical characterization

For the symmetric cell testing, Ni-meshes were first attached to both Ni–YSZ support by using Ag paste (DAD-87, Shanghai Research Institute of Synthetic Resins) to enhance current collection. The life tests were carried out at 800 ^{o}C for 1000 h in various H_2O–H_2 mixtures by using a constant current density of 0.8 A cm^{-2}. Starting with 90 vol.% H_2O, the steam content decreased by 20 vol.% every 200 h. The fuel composition was carefully controlled by getting H_2 flowing to the H_2O-containing bubbler where the H_2O temperature was adjusted on purpose. The electrochemical impedance spectroscopy (EIS) was periodically conducted with an IM6 Electrochemical Workstation (ZAHNER) by using a 20 mV ac signal in the frequency range of from 0.1 Hz to 100 kHz. The complex nonlinear least squares fitting of the EIS data and simulations of the individual circuit elements were performed using software programmed in Python that relies on the scientific Python stack [6].

References

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[6] Pyeis: A Python-Based Electrochemical Impedance Spectroscopy Analyzer and Simulator, ECS Meeting Abstracts, (2019).