Evolution of Yttria Stabilized Zirconia in SOFC Operated Using Fuel of H_2, Syngas, and Syngas Containing PH_3

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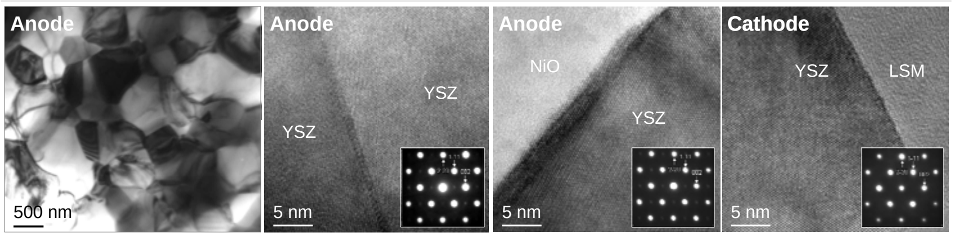
Background and Motivation

- In Solid Oxide Fuel Cells (SOFC), electrode reactions take place on the triple phase boundaries (TPBs) between electrolyte, electrode and air/fuels. During operation of SOFCs, some impurities and dopants could segregate/ precipitate to grain boundaries (GBs). Therefore, the microstructure and chemistry of electrolyte/electrodes interfaces change, and both affect the subsequent electrochemical reactions occurring near those interfaces. Understanding how performance depends on the microstructural and chemical changes of TPBs is critical to the application of SOFCs.
- The performance of the Ni-YSZ anode is known to degrade during operation. The suggested degradation mechanisms are generally attributed to microstructure failure including phase transformation and formation of secondary phase at GBs. However, so far, very limited experimental work has been done on studying the structure and defects inside YSZ and particularly the defect evolution in the SOFC anode upon cell operation.

➢ Current study: Microstructure and chemistry analysis of anode of SOFCs operated using various fuels.

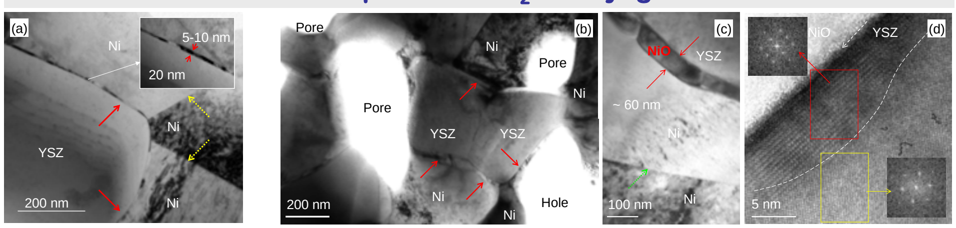
As-received MSRI button cell



TEM Cross section view of interfaces and the diffraction patterns of YSZ grains in the as-received cells

Highlight: All interfaces are free of impurity phases. The cubic phase dominates in YSZ grains in the cathode, anode and electrolyte of an as-received cell. Kinematically forbidden spots are observed in diffraction patterns only from YSZ in the anode and the electrolyte. The phenomena are interpreted as nanoscale irregularly-shaped tetragonal-YSZ (*t*-YSZ) domains distributed in the cubic YSZ matrix in the anode and the electrolyte, but not in the cathode.

Cells operated in H_2 and syngas

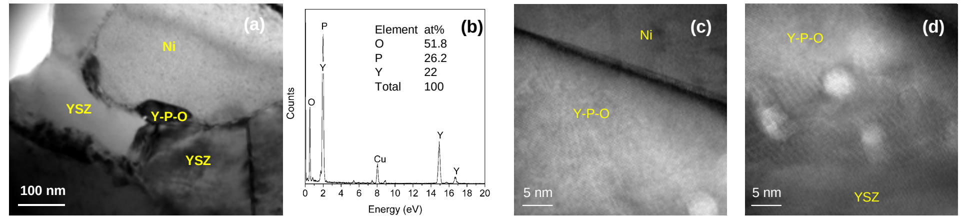


TEM Cross section view of the button cells after operated in H_2 (cell I) and syngas (cell II)

(a) Forrmation of NiO for the cell operated in H_2 at 800ºC for 24 h (cell I); **(b)** TPB areas for the Cell operated in syngas at 800ºC for 540 h (cell II); **(c)** Close view of a NiO interface phase (cell II); (d) HRTEM shows the formation of *t*-YSZ layer (cell II).

Highlight: NiO is present at the Ni/YSZ interface for cells operated in H_2 or syngas. In addition to NiO, ribbon shaped *t*-YSZ domains with 10 nm widths and 30 nm lengths are observed to form at the Ni/YSZ interface of the cell operated in syngas for 550 h.

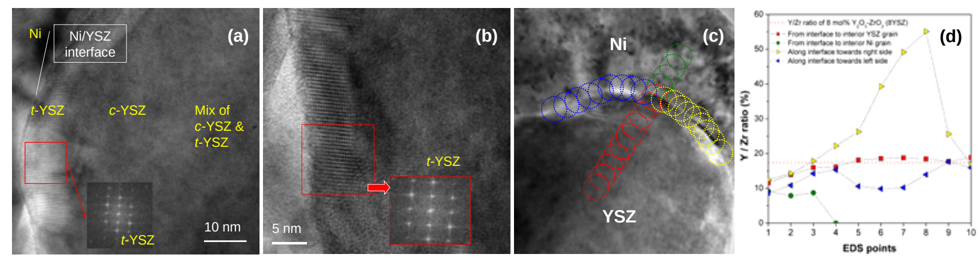
Button cells operated in syngas containing 10 ppm PH_3



Y-P-O precipitate at Ni/YSZ/YSZ triple grain junctions for the cell operated in syngas containing PH_3 for 110 h.

(a) Precipitates sitting at Ni/YSZ/YSZ interfaces. **(b)** EDS data indicates the precipitate is composed of Y, P and O. **(c)** No lattice matching between Ni grain and Y-P-O grain. **(d)** Y-P-O grain seems to grow epitaxially aligning to the neighboring YSZ grain.

Highlight: After operation, Y-P-O precipitates of ~100 nm were found to form at Ni/YSZ/YSZ triple grain junctions. HRTEM images show that Y-P-O precipitates have a coherent interface with the neighboring YSZ grain matrix, implying that the YSZ grain is the parent phase and that the Y-P-O precipitates grew epitaxially aligning to the YSZ matrix during the solid state phase transformation.



Microstructure and chemistry near Ni/YSZ interface for the cell operated in syngas containing PH_3 for 110 h.

(a) and (b) A distinct *t*-YSZ interfacial layer in a YSZ grain by the Ni/YSZ interface. **(c)** The circles schematically indicate where the EDS spots were taken and the size of the electron beam. **(d)** Y/Zr ratios along the Ni/YSZ boundary and into the Ni and YSZ grains. EDS point 1 for all measurement was from a spot sitting at Ni/YSZ interface.

Highlight: A distinct and long *t*-YSZ ribbon layer with ~5-10 nm in thickness developed along the original Ni/YSZ boundary. The distinct t-YSZ layer is accompanied by the adjacent cubic YSZ region. In addition, a high Y concentration region in YSZ could be found near Ni/YSZ boundaries with Y/Zr ratio up to 0.55.

Summary points

- Tetragonal YSZ nano-domains are scattered randomly within the bulk cubic YSZ phase in the anode and electrolyte.
- Ribbon-shaped tetragonal YSZ domains, with length scales that are significantly larger than the intragranular *t*-YSZ domain, are observed at the Ni/YSZ interface of the cell operated in the syngas for 550 h.
- The presence of PH_3 in syngas results in the formation of new precipitate Y-P-O.
- Distinct tetragonal YSZ interfacial ribbon layers can be found everywhere at Ni/YSZ boundaries in the anode active layer for the cell operated in syngas containing PH_3.

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