Fuel Dependence of Interfacial Nanostructure from the Anode of Solid Oxide Fuel Cells

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U.S. DEPARTMENT OF ENERGY

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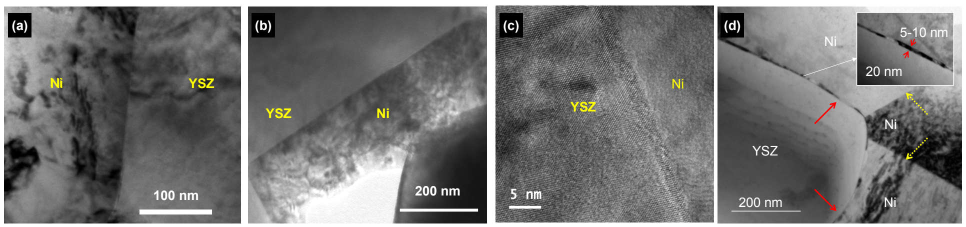
Background and Motivation

- During operation of SOFCs, impurities and dopants could segregate/precipitate to interfaces.
- Nanostructure and chemistry of electrolyte/electrodes interfaces change affecting the subsequent electrochemical reactions occurring near those interfaces.
- Limited experimental work has been reported on the structure and defects in YSZ, particularly with regard to the defect evolution in the Ni/YSZ anode upon cell operation.

Current study: microstructure and chemistry analyses of anode for SOFCs operated using various fuel conditions.

1. Explore the growth of NiO interface layer at Ni/YSZ phase boundaries governed by the over potential applied on anode during the operation at 800°C. The control of over potential was executed by changing the hydrogen partial pressure in fuel while the loading current kept constant at 0.3 A/cm^2.
2. Effect of PH3 contained fuels on the NiO thickness and cell cooling condition on the thickness of NiO layer.
3. Effect of PH3 contained fuels on the YSZ interface structure.

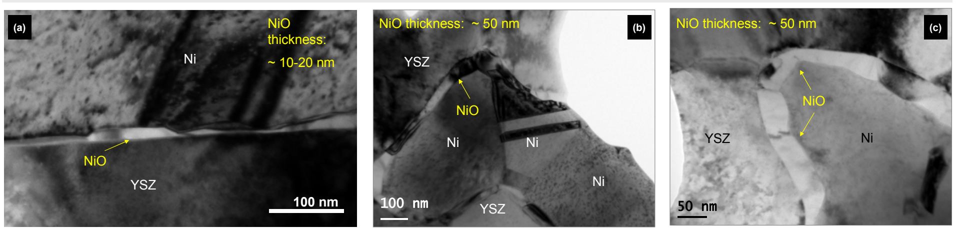
Nanostructure evolution of Ni/YSZ upon operation : NiO interface layer



TEM cross sectional view of: **(a), (b) and (c)** Fully reduced button cells; and **(d)** Cell operated in hydrogen for 24 h (with 0.7 V of terminal voltage). Both cells were cooled down in nitrogen.

Highlight: Ni/YSZ interface is free of secondary phase in the fully reduced cell. On the other hand, NiO is present at the Ni/YSZ interface for the operated cell, but the Ni/Ni boundaries are free of NiO.

Impact of over potential change (via changing H_2 partial pressure) on NiO



At a constant current of 0.3 A/cm^2, **(a)** Cell operated in the 97% H_2 (with 3% H_2O) for 196 h; and **(b) and (c)** Cell operated in the 24% H_2 (with 3%H_2O and 73% N_2) for 196 h. Both cells were cooled down nitrogen.

Highlight: NiO layer thickness increases as the overpotential applied at Ni/YSZ interfaces increases.

Summary points

- When operated cells cooled down in N_2, the NiO presents at the Ni/YSZ interfaces, but not along the Ni/Ni grain boundaries.
- Operated at 0.3 A/cm^2 for 196 h, NiO thickness varies as hydrogen partial pressure changes. The thickness is ~50 nm in fuel with 24% hydrogen, while it reduced to ~10-20 nm for the cell operated in 97% hydrogen.
- NiO layer increases for the cell operated using the fuel with PH3 contamination; NiO layer can be fully reduced to Ni, when the cell is cooled down in nitrogen containing 1% hydrogen.
- YSZ along the Ni/YSZ interface is with alternating *t*-YSZ and *c*-YSZ nano domains for cell operated in hydrogen/phosphine fuel for 120 h. *t*-YSZ layer at the Ni/YSZ interface and the formation of Y-P-O phase were observed for the cell operated in the syngas with 10ppm phosphine for 100 h.

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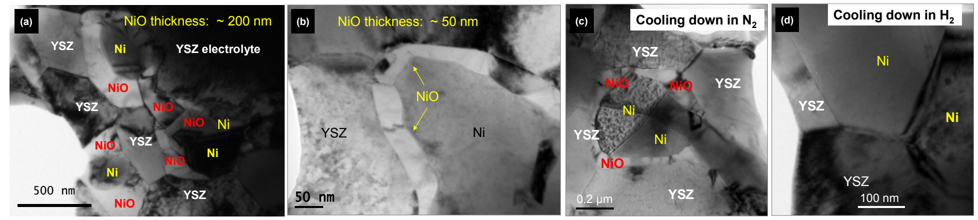
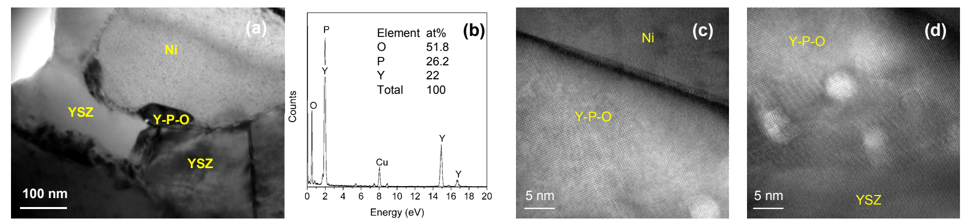
Contamination of phosphine and cooling condition on NiO interface layer



(a) Anode/Electrolyte interface of cell operated in H_2 containing 10 ppm PH_3 for 120 h. **(b)** Ni/YSZ interface of cell operated for 200 h. **(c)** Ni/YSZ interface of cell operated for 120 h cooled down in N_2 **(d)** cell operated for 120 h cooled down in N_2 with 1%H_2.

Highlight: NiO thickness increase in the cell operated in hydrogen/phosphine fuel. The NiO layer could be reduced during cooling.

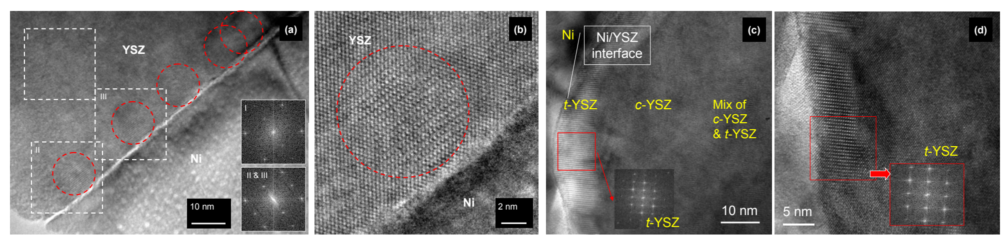
Phosphine contamination on the nanostructure of YSZ



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

(a) Precipitates sitting at Ni/YSZ/YSZ grain junctions; **(b)** EDS data indicates the precipitate is composed of Y, P and O; **(c)** Interface between Y-P-O grain and Ni grain; and **(d)** Interface between Y-P-O grain and neighboring YSZ grain.

Highlight: Y-P-O precipitates (~100 nm in size) 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 epitaxial aligning to the YSZ matrix during the solid state phase transformation.



Nanostructure and chemistry near Ni/YSZ interface for the cell operated in fuels containing phosphine for 120 h.

(a) and (b) Nanostructure of near Ni/YSZ interface region for cell operated in **hydrogen/phosphine** fuel; **(c) and (d)** Nanostructure of near Ni/YSZ interface region for cell operated in **syngas/phosphine** fuel.

Highlight: Alternating *t*-YSZ and *c*-YSZ domains along Ni/YSZ interface of cell operated in hydrogen/phosphine fuel. By contrast, for the cell operated in syngas/phosphine fuel, a distinct and long *t*-YSZ ribbon layer with ~5-10 nm in thickness developed along the original Ni/YSZ phase boundaries.

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