
IV.B.6 Modification of Nickel-YSZ Anodes for Control of Activity and Stability from Carbon Formation during SOFC Operation

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Objectives

- Quantify and evaluate microstructural evolution as a function of time and pretreatment conditions. Correlate the catalytic activity with Ni microstructure.
- Develop methods to adjust and control Ni-YSZ anode activity to provide good thermal management and efficiency for methane on-anode reforming.
- Determine the activity and thermal profile of Ni-YSZ anode wafers under steam methane reforming and compare results with previous powder test results and computational modeling calculations.
- Determine what factors and conditions influence NiO solubility into yttria-stabilized zirconia (YSZ) and formation of Ni crystallites from the NiO/YSZ solution.

Approach

- Complete construction and installation of plate reactor system.
- Measure thermal profiles and conversion levels over a Ni-YSZ anode plate, under open circuit conditions, i.e., in the absence of electrochemistry.
- Carry out supporting work in catalytic micro-reactor powder testing.
- Utilize surface area measurements, X-ray diffraction, transmission electron microscopy (TEM) and scanning electron microscopy (SEM) microscopy to characterize catalysts before and after reforming.
- Develop understanding of Ni dissolution into/exolution from YSZ.

Accomplishments

- Brought on-line anode plate reactor and measured activity and thermal profiles of Ni-YSZ anode wafers with time at 700°C and 750°C.
- Demonstrated leading edge to back edge migration of endotherm in plate reactor tests, consistent with Ni microstructural sintering, and showed that the magnitude of the endotherm migration decreases as it migrates down the cell.
- Demonstrated that the Ni anode, following initial activity lineout, is sufficient to fully convert methane, but insufficient to generate an endotherm that would lead to destructive thermal gradients during long-term operation.
- Brought on line, and utilized, new powder testing capability to support activity evolution and plate reactor studies of Ni-YSZ anodes.
- Designed, and implemented, a multi-tubular reactor to study effects of steam and hydrogen treatment on evolution of Ni microstructure; obtained and tabulated initial sintering data.
- Identified possible role of NiO dissolution in YSZ on enhancing the presence of the ZrO₂ monoclinic phase.

Introduction

During FY 2007, the Solid State Energy Conversion Alliance (SECA) Core Technology Program in Fuel Reforming at Pacific Northwest National Laboratory (PNNL) moved to completion of its work on Ni/YSZ internal reforming of methane. A major focus was to carry out plate reactor tests and analyze the test results. The focus of this work was on anode activity and activity maintenance, to determine their effect on the magnitude and positioning of any endotherm encountered on the anode. This is of interest because it is believed to be necessary to bring the reforming activity into balance with electrochemical (H₂ and CO oxidation) activity, in order to avoid excessive and damaging thermal gradients, along the anode during reformation.

The activity of the anode toward methane reforming depends substantially on the nickel microstructure that develops. We reported previously that NiO dissolves into YSZ and exolves during the reduction procedure, generating small Ni crystallites at the surface of YSZ. These small crystallites generate high initial catalyst activity, but activity declines as these crystallites sinter.

In our current work, we are investigating the effect of pretreatment procedures and conditions on development of the Ni microstructure, and have seen important differences, depending upon pretreatment. Thus, pretreatment can provide a method to control anode activity, which may be important in operating the overall fuel cell.

Approach

Our approach has been to measure thermal profiles and conversion levels over a Ni-YSZ anode plate under open circuit conditions, i.e., in the absence of electrochemistry. A plate reactor was constructed and described (had not been used) in the previous annual report. In FY 2007, the reactor was brought on line, and several experiments were carried out, under a variety of conditions. Temperatures were measured at various positions on the anode wafer as a function of time, to obtain an estimate of the extent of endotherms and possible thermal gradients. Methane conversion was measured simultaneously to verify that anode activity was sufficient to assure that no unconverted methane could exit the anode compartment of the fuel cell.

In addition to the plate reactor tests, supporting work was carried out through catalytic micro-reactor powder testing, surface area measurements via chemisorption, X-ray diffraction, TEM and SEM, and other methods. These data were used to gain a better understanding of Ni exsolution from YSZ, and the fate of the exsolved Ni by either sintering or other interaction with the YSZ.

Results

Ni-YSZ Anode Plate Tests

A first catalytic test was carried out for approximately 130 hours, operating the plate reactor at a nominal temperature of 700°C. The conditions of the test were: S/C/H (steam/methane/hydrogen) = 3/1/2; weight hourly space velocity (WHSV) $\text{gCH}_4/\text{gNi-YSZ-h}$ = 0.8; wafer dimensions 10 cm (length) x 5 cm (width) x 0.45 mm (thickness). During the test, temperatures were monitored by thermocouples placed at various locations along the flow axis. Figure 1 provides a visual summary of the thermal profile during the test at the different distances from the front edge of the wafer. There is a sharp endotherm produced immediately at the front edge of the cell and at 2 mm from the leading edge. This indicates that the majority of the reforming is carried out at the leading edge. With time, however, the temperature at those locations increases and a temperature lowering is observed, at progressive distances from the front edge. This behavior is indicative of a “wave” of activity that propagates with time, consistent with progressive sintering of the anode along

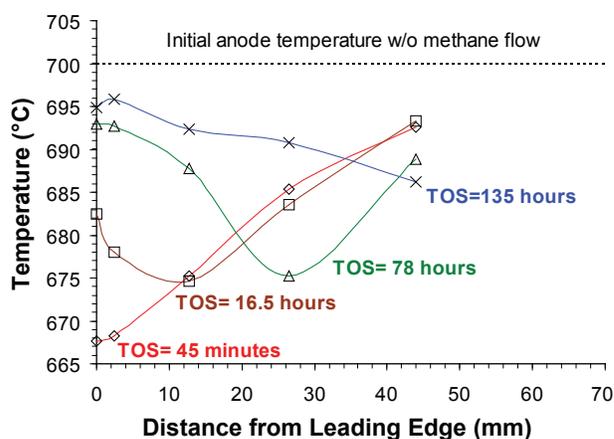


FIGURE 1. Thermal Profile along Anode Wafer as a Function of Time for First Methane Steam Reforming Plate Test at 700°C

the flow axis. As the sintering takes place at a given distance from the leading edge, the primary conversion is carried out farther down the anode. We monitored the methane conversion and product distribution during the run, and equilibrium conversion of methane was achieved. However, we were seeing indications that, if the endotherm migration had continued, conversion below equilibrium most likely would have occurred. Post analysis of the anode was carried out to determine Ni surface area. As seen in Table 1 the leading edge had a substantial decrease in Ni surface area, compared with the back edge, indicative of significant sintering occurring at the leading edge.

TABLE 1. Post analysis of Ni-YSZ wafer following 700°C steam reforming test, indicating significant Ni particle sintering at the leading edge.

	H ² Uptake (umol/g)	Surface Area m ² Ni/gcat	Surface Area m ² Ni/gcat	Particle Size (nm)	Active Ni (umol/g)
Leading Edge	1.1	0.086	0.194	3481	2.2
Back Edge	2.7	0.211	0.475	1418	5.4

A second reforming plate reactor test was carried out, this time at 750°C, S/C/H = 3/1/4 and WHSV = 1.12 $\text{g CH}_4/\text{gcat-h}$. The temperature profile measured during this test is provided in Figure 2. There is a clear migration of the endotherm maximum down the flow axis with time, and the extent of the endotherm decreased as it migrated down the flow axis. After approximately 50 hours on stream, we saw evidence of CH_4 conversion decreasing below equilibrium values, indicating that under these conditions the anode was insufficiently active to achieve full conversion after the full sintering of the anode occurred. Post analysis showed some mechanical damage to the front edge of

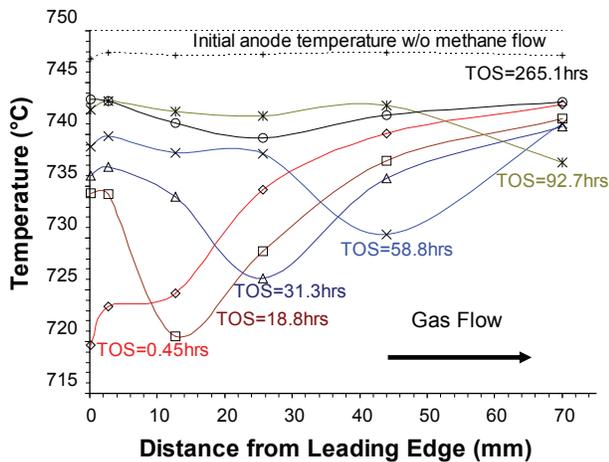


FIGURE 2. Thermal Profile along Anode Wafer as a Function of Time for Second Methane Steam Reforming Plate Test at 750°C

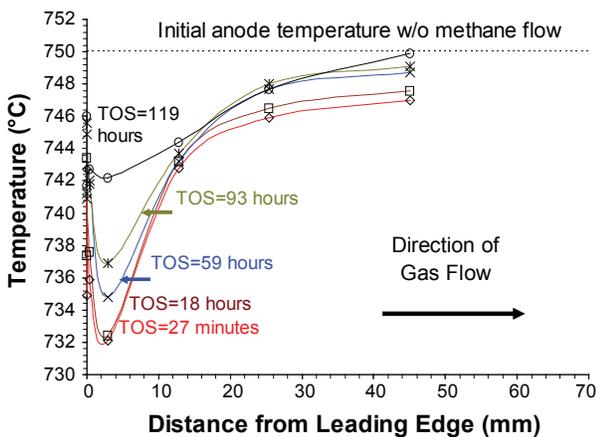


FIGURE 3. Thermal Profile along Anode Wafer as a Function of Time for Third Methane Steam Reforming Plate Test, Also at 750°C

the anode plate because of the rather severe operating conditions. A third run, also carried out at 750°C but at a lower flow rate (more typical of anticipated fuel cell operating conditions) showed very slow migration of the endotherm, although it decreased in intensity with time (Figure 3), and under these conditions we expect full conversion of methane at long reaction times.

Ni Dissolution into and Exolution from YSZ

We previously described the appearance of small Ni crystallites on the surface of YSZ that are generated following a reduction procedure. We have asserted that NiO must be present in the YSZ, possibly because of NiO migration during the sintering procedure (calcination in air at 1,375°C). Supporting evidence and additional information is provided in Figure 4. This shows X-ray diffraction traces of the Ni-YSZ material,

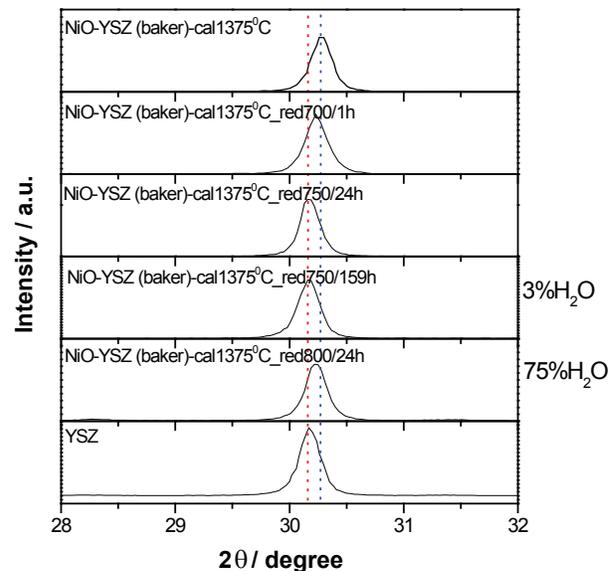


FIGURE 4. X-ray Diffraction Traces of Primary YSZ Peak, Showing Effect of NiO Dissolution into the YSZ Structure and the Effect of Various Pretreatments on Exolution of NiO from the YSZ

following a series of different treatments. The figure focuses on the specific location of a characteristic YSZ line at around $30.15^\circ 2\theta$. Following sintering, NiO dissolution into YSZ is evidenced by the change in peak location to 30.3° , indicative of a change in lattice spacing caused by NiO. Following reduction in H_2 at 750°C, the peak moves again close to 30.15° , however at 800°C, in high quantities of steam, only partial shift of the peak is observed, indicating that NiO remains in the YSZ. It appears that water vapor plays a role in dictating the ease of reduction and exolution of the Ni from YSZ. Pretreatment, therefore can have a strong effect on Ni-YSZ activity, by modulating the amount of small crystallite Ni available for reaction with CH_4 .

Conclusions

Ni-YSZ methane reforming activity is a result of two contributions: the activity from the bulk Ni in the structure, and the activity arising from small Ni crystallites that are contained in the YSZ and migrate to the surface, under reduction pretreatment. Both have been found to sinter during methane steam reforming, the extent a result of several factors, including steam content in the feed and overall flow rate. Our studies have indicated that understanding the pretreatment process allows some flexibility in controlling the anode activity for methane steam reforming. In general, we have found that initial activity of the Ni-YSZ can generate a substantial endotherm and thermal gradients across the anode. However, as the Ni component of the anode undergoes sintering, lined out activity is substantially reduced, and does not appear to be a

danger from strong endotherm, or thermal gradients, under normal operating conditions.

Future Directions

- Evaluate the effect of NiO present within the YSZ on facilitating possible phase changes in the YSZ.
- Begin studies of diesel reforming.

FY 2007 Publications/Presentations

1. Y-H. Chin, D. L. King, H-S. Roh, Y. Wang, and S. M. Heald. Structure and Reactivity Investigations on Supported Bimetallic Au-Ni Catalysts Used for Hydrocarbon Steam Reforming; *J. Catalysis* 244 (2006) 153-162.