Evolution of Nickel Microstructure during Methane Reforming over Ni-YSZ Anodes

DL King, JJ Strohm, X Wang, KP Recknagle, P Singh, Y Wang
Pacific Northwest National Laboratory
Richland, WA 99352

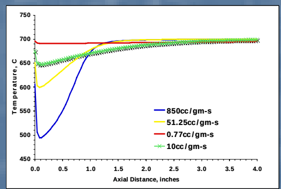
Goal

Control activity of methane reforming over Ni-YSZ anodes for endotherm management through Ni microstructure control

Introduction: On-Anode Reforming

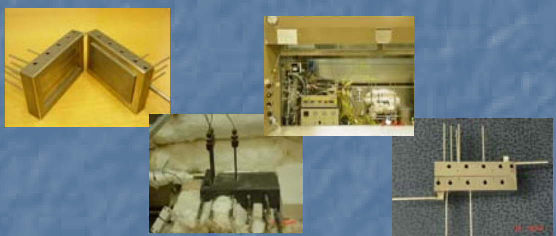
- Thermal management through balancing endothermic steam reforming with exothermic electrochemical oxidation of hydrogen and carbon monoxide
- Significantly different rates of methane reforming and reformate electrochemical oxidation can result in significant temperature gradients leading to mechanical failure of the anode

Estimated temperature gradients as a function of methane reforming activity. Tailoring of reforming activity is critical to prevent excessive enodtherms from developing due to either high reforming activity or instability in the reforming activity



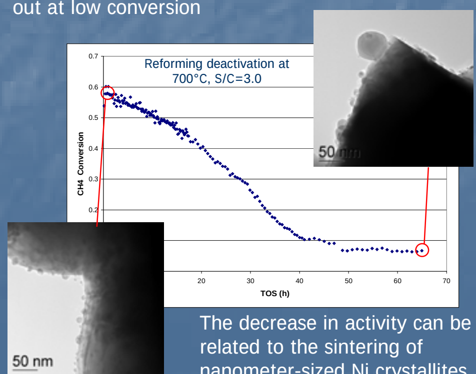
Novel Anode Plate Reformer

Developed to study the thermal gradients that develop during methane reforming over anode plate materials with modified Ni microstructures to prevent such gradients while the net methane conversion is maximized



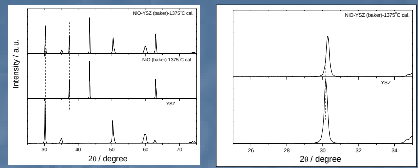
Methane Reforming

Methane reforming activity slowly declines and lines-out at low conversion

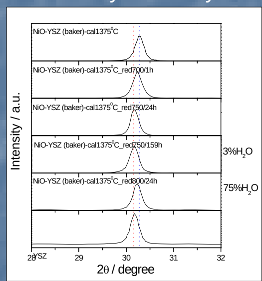


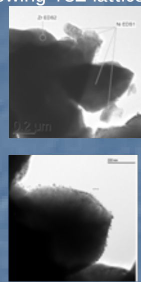
The decrease in activity can be related to the sintering of nanometer-sized Ni crystallites

Evolution of Active Ni Sites: Ni Solubility in YSZ



During anode firing at 1375°C, NiO dissolves into YSZ structure, as evident by XRD analysis showing YSZ lattice expansion



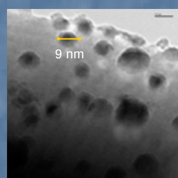


Hydrogen reduction Ramp of 5°C/min from room temp. to 700°C and a final hold of 1 hour

Hydrogen reduction results in Ni crystallite evolution from YSZ giving rise to nanometer-sized Ni crystallites that are highly active for steam reforming of methane

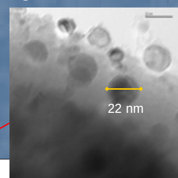
Sintering Studies

Increased time results in crystallite sintering



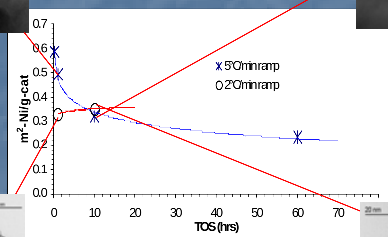
10 hours in hydrogen flow at 700°C with heating ramp of 5°C/min

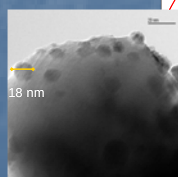
Ni crystallite size:
8-11nm (1hr) → 10-22nm (10 hrs)



Decrease in ramp rate results in lower Ni surface area after 1 hour reduction

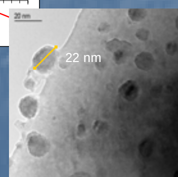
Decrease in number of Ni crystallites with decrease in ramp rate





10 hours in hydrogen flow at 700°C with heating ramp of 2°C/min

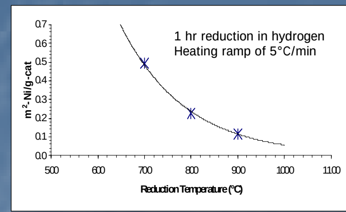
Ni crystallite size:
10-18nm (1hr) → 10-22nm (10 hrs)
But an increase in Ni surface area!
Due to increased Ni evolution

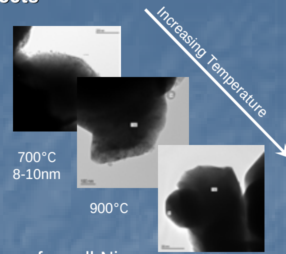


Amount and size of Ni crystallites is also dependent upon heating ramp

Under high heating rates the rate limiting step for Ni crystallite formation and stabilization is Ni crystallite sintering, while at low heating rates the rate limiting step is Ni extraction from YSZ

Temperature Effects





As temperature is increased, the number of small Ni crystallites decrease and the size of the crystallites increase

Activity and Microstructure Relationships to Thermal Gradient Control

	Activity	Ni Crystallite size	Comments
700°C (initial) Ni-YSZ	850 cc/gm*s	8-10nm	Temperature gradient is unacceptable
700°C (lineout) Ni-YSZ	51.25 cc/gm*s	12-50 nm	Temperature gradient is unacceptable
700°C (initial) Sintered Ni	0.77 cc/gm*s	No crystallites	Methane utilization across plate is only 73%
Desired	~10 cc/gm*s	???	Minimum rate for 100% methane utilization

Pretreatments including high temperature reduction over extended times may allow for fine tuning of the Ni microstructure for improved thermal management of the anode

Summary

- Ni evolution from YSZ gives rise to highly active Ni crystallites for the steam reforming of methane
- Sintering of the Ni crystallites reduces methane reforming activity
- Parameters such as heating rate, temperature, and time on stream effect the size and quantity of Ni crystallites
- Adjusting pretreatment parameters may allow for tailored reforming activity over Ni-YSZ anodes

Future Work

- Determine parameters that effect NiO solubility in YSZ and Ni evolution from NiYSZ solutions and develop Ni solubility models
- Develop pretreatment methods to control and stabilize the activity of Ni-YSZ towards methane reforming
- Experimentally measure the impact of microstructure control on reforming activity and the prevention of thermal gradients across anode plates using the newly developed anode plate reformer

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