Microstructural Evolution of Nickel-Zirconia SOFC Anode During Methane “On-Anode” Reforming

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Introduction
The conversion of methane and natural gas over the anode of a solid oxide fuel cell followed by electrochemical oxidation of the produced H$_2$ and CO is of interest as a means to increase the overall efficiency of power generation [1,2]. On-anode steam reforming is attractive, since the heat required to drive the endothermic reforming reaction can be provided by the exothermic heat generated through the electrochemical oxidation of H$_2$ and CO. Linking the reforming reaction with electrochemical oxidation also provides a driving force for equilibrium CH$_4$ conversion [3]. It has been reported that the activity of the Ni-YSZ anode for steam reforming is significantly higher than the electrochemical activity for the conversion of H$_2$ and CO. Fast methane conversion at the leading edge of the anode can result in endothermic thermal gradients that can potentially warp or even crack the anode during operation of the cell [4]. This study was initiated to address the thermal mismatch issue.

Materials and Methods
Ni-YSZ bulk anode samples were tested as powders in a small fixed bed reactor. We utilized Ni-YSZ samples that had been prepared by milling (in isopropanol, Al$_2$O$_3$ as grinding media) nickel oxide (Baker) and 5Y YSZ (Unitec) powders, followed by co-sintering in air at a maximum temperature of 1375°C for 1h. Ni-YSZ powders were mechanically mixed with YSZ diluent in a weight ratio of 1:10. Typically 20mg of Ni-YSZ and 200mg YSZ were added to a tubular quartz reactor. The sample was then pre-reduced, typically at 700°C, for 1 h using undiluted H$_2$. The gas feed then switched to a methane steam reforming mixture, which comprised H$_2$O, CH$_4$, H$_2$, and in some cases a diluent (He or N$_2$). Product analysis was carried out by micro GC. TEM analysis employed a JEOL JEM 2010 microscope. The elemental composition of the particles was analyzed by energy-dispersive X-ray spectroscopy (EDS). X-ray diffraction data was collected on a Philips X'Pert MPD instrument.

Results and Discussion
Our initial focus was to measure the Ni-YSZ powder for methane steam reforming, a first step in predicting methane conversion activity over the entire anode and thermal profiles along the anode. We discovered that it took a substantial period of time to achieve a linearized activity, and during this line-out period methane conversion decreased monotonically. Figure 1 shows a typical plot of methane conversion vs. time, operating at a S/C/H/He ratio of 3/1/1/5 at 700°C with a space velocity of 667,000 cc/g-h. We were able to dismiss the possible contribution of carbon formation, as a similar trend of declining activity was observed when carrying out the reaction at a S/C ratios as high as 15.

![Figure 1](image1.png)

Figure 1. Time dependence of methane conversion by steam reforming over Ni-YSZ anode powder material

TEM characterization of the as-reduced and spent Ni-YSZ samples indicates the presence of small Ni crystallites that appear to be attached to the surface of YSZ. These small Ni particles appear to sinter during reaction, consistent with the loss of catalytic activity with time on stream, as shown in Figure 1. Detailed XRD analysis indicates that the small Ni crystallites come from NiO that is present in the YSZ at a low concentration due to the sintering process.

![Figure 2](image2.png)

Figure 2. Nickel crystallites on surface of YSZ following 700°C reduction (left) and 65 h steam reforming reaction [S/C/H/N = 3/1/1/5, 700°C, 200,000 cc/g-h] (right).

Significance
Understanding the structure and morphology of Ni in the solid oxide fuel cell anode is critical to predicting and matching its reforming and electrochemical activity.

References