

# Study on Degradation of Solid Oxide Fuel Cell With Pure Ni Anode

Zhenjun Jiao<sup>1</sup>, Naoki Shikazono<sup>1</sup> and Nobuhide Kasagi<sup>2</sup>

<sup>1</sup> IIS, the University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo. 153-8505, Japan

<sup>2</sup> Department of Mechanical Engineering, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan

## Abstract

Current popular SOFC anode is made by composite cermet of Ni and yttria stabilized zirconia (YSZ). The interaction between Ni and YSZ at triple phase boundary (TPB) must be studied intensively to investigate anode degradation mechanism. In this study, the degradation phenomena at the interface between Ni and YSZ have been investigated by using screen-printed pure Ni anode sintered on YSZ pellet. The time depended microstructural evolution of Ni-YSZ interface in long time galvanostatic polarization is studied in hydrogen with different humidities. Compared with normal composite cermet anode experiments, this method provides easy observation of the Ni-YSZ interface where degradation takes place. The microstructural changes were characterized by scanning electron microscopy (SEM). The influence of humidity on sintered pure Ni anode is investigated and the degradation mechanism at Ni-YSZ interface is discussed.

## Introduction

Normal SOFC Ni cermet anodes degradation includes many complicated processes, parameters and phenomena, the dominating kinetics of Ni phase morphological changes cannot be explained only by a simple Ostwald ripening mechanism. There is thus a complex interplay between Ni grain growth (e.g. by surface diffusion) [1], volatilization [2] and microstructural reorganization [3]. In order to simplify the problems, Jiang et al. [4] has studied hydrogen oxidation for pure Ni porous electrode for different hydrogen/humidity ratios at 1000°C in SOFCs using galvanostatic current interruption and electrochemical impedance spectroscopy, which clearly indicated that the mechanism and kinetics of the hydrogen oxidation reaction are strongly dependent on the catalytic activities of electrode materials, electronic conductivity of the electrolyte surface, and the humidity in hydrogen. In this paper, similar method was applied and the microstructural changes of Ni upon long time discharge within different humidities were studied. High purity NiO slurry was screen-printed onto commercial YSZ electrolyte pellet and then sintered at 1400 °C for 3 hours, after which it was reduced and employed as anode and operated in humidified hydrogen at 800 °C. The study focuses on the microstructural changes of Ni phase at both the interface between Ni and YSZ and in bulk. The detachment process of Ni from YSZ is also studied in this paper, while the same phenomena happens to normal composite Ni-YSZ anode to cause structural degradation. Comparing to normal Ni-YSZ composite anode, the new method has the advantage of easy observation of the reaction sites at Ni-YSZ interface, which facilitates the correlation of phase changes to cell performances.

## Experiments

NiO powder used in this study has an average particle diameter of 1.1 μm. The powder was mixed with terpineol solvent and the ethylcellulose binder in agate mortar to obtain anode screen-printing slurry. The slurry

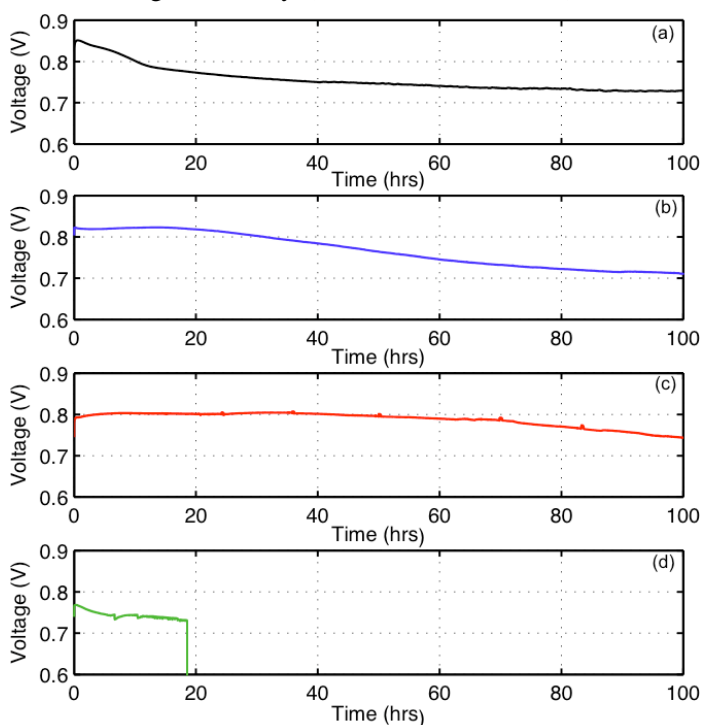
was screen-printed onto commercial dense YSZ pellet (diameter 20 mm, thickness 0.5 mm) with a diameter of 10 mm and then sintered at 1400°C for 3 hours to obtain a strong bonding between YSZ and NiO.  $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.97}\text{MnO}_3$  (LSM) powder (0.4  $\mu\text{m}$ ) mixed by YSZ powder (0.1  $\mu\text{m}$ ) in a mass ratio of 1 : 1 was used as cathode material. The cathode was sintered at 1200°C for 3 hours. The details of SOFC performance measurement setup has been introduced in last paper [2].

## Results and Discussions

Four humidity conditions, dry, 3%  $\text{H}_2\text{O}$ , 10%  $\text{H}_2\text{O}$  and 30%  $\text{H}_2\text{O}$ , were applied at anode side in discharging processes. Fig. 1 shows the transient performances of the four cells with a discharging time of 100 hours. It can be seen that the all the performances of the cells within dry, 3%  $\text{H}_2\text{O}$  and 10%  $\text{H}_2\text{O}$  hydrogen conditions present different degradation rates from the beginnings of the discharging and last through 100 hours. The degradation rates in dry hydrogen and 30%  $\text{H}_2\text{O}$  hydrogen are larger than in 3%  $\text{H}_2\text{O}$  hydrogen and 10%  $\text{H}_2\text{O}$  hydrogen. For the cell tested in dry hydrogen, the anode degradation rate decreases with time and the performance tends to stable state after about 80 hours discharging. For the cell tested in 30%  $\text{H}_2\text{O}$  hydrogen, there was a sudden failing of the cell anode before 20 hours from the initial discharging. Cells tested in 3%  $\text{H}_2\text{O}$  hydrogen and 10%  $\text{H}_2\text{O}$  hydrogen present a relative stable discharge performance from the initial discharging and the stable stage lasting time increase with the increase of humidity. After the initial stable stage, a relatively slower degradation followed for both cases. In addition, the performances of the cells tested in high humidity (10%  $\text{H}_2\text{O}$ , 30%  $\text{H}_2\text{O}$ ) show some irregular pulse signals in the degradation process, comparing to the smooth degradation process within low humidity (dry, 3%  $\text{H}_2\text{O}$ ).

The YSZ-Ni interfaces of different circumstances after cooling down, with Ni peeled off, are shown in Fig. 2. From the comparison, it is clearly shown that the anode discharging has obvious influences on the interaction between Ni and YSZ. Because of the thermal expansion coefficient matching between Ni and YSZ, Ni phase was always partially (completely for 30%  $\text{H}_2\text{O}$ ) delaminated from YSZ substrate after cooling down the samples to room temperature, which facilitates the direct observation of Ni-YSZ interfaces. It was found that no bonding effect was formed right after reduction and kept anode with OCV for 100 hours

within 3%  $\text{H}_2\text{O}$ . With discharging, Ni was found to be bonded strongly onto YSZ with different morphologies when bulk gas humidity was changed from dry to 30%  $\text{H}_2\text{O}$ . It is found that with the increase of the bulk gas humidity,



**Fig. 1 Anode galvanostatic performances within  $\text{H}_2$  humidified by (a) dry, (b) 3% (c) 10% and (d) 30%  $\text{H}_2\text{O}$ .**

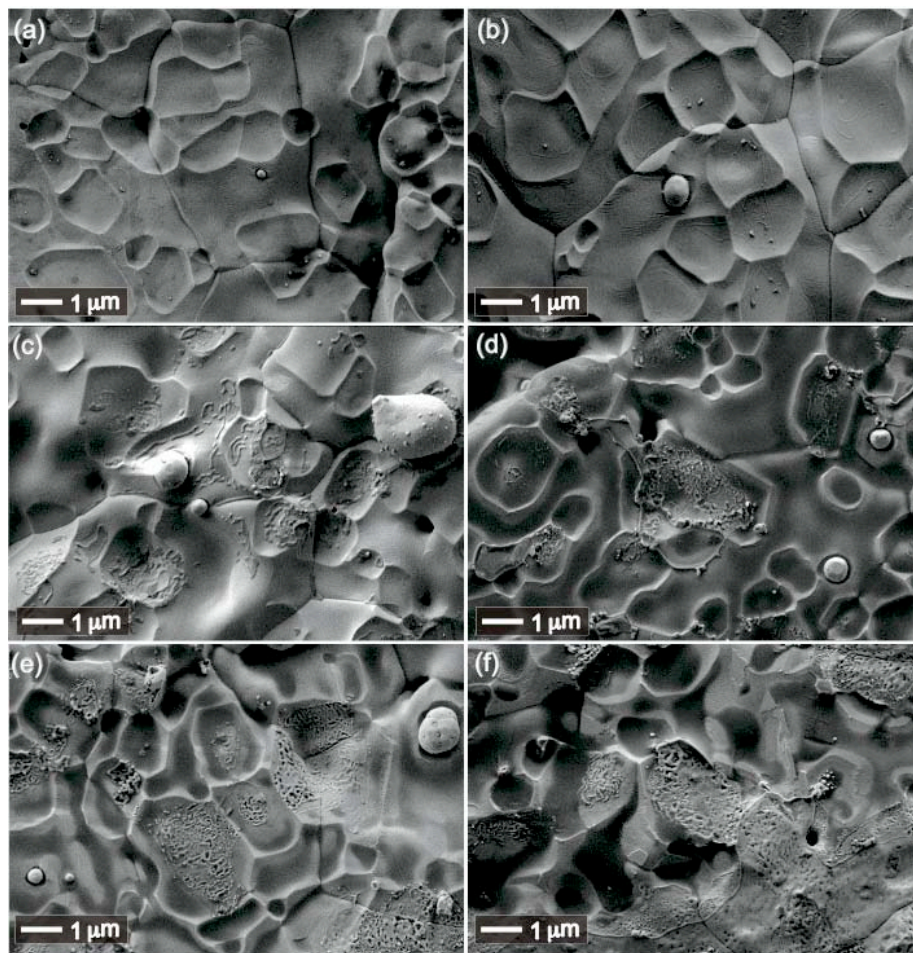
more Ni was bonded to YSZ surface and especially for 30% H<sub>2</sub>O case that the discharging time is only one fifth of the other three cases. The porous bonding Ni phase may have large influence on the local TPB density in the discharging process which finally determinate the anode performances.

The edge microstructural morphologies of the anode samples corresponding to Fig. 2 were also observed by SEM. Comparing to the sample right after reduction, Ni aggregation phenomena found for all the other cases when the time is 100 hours.

But the Ni phase along the edge of anode presents totally morphologies with discharge taking effects. The spreading of Ni was found when the bulk gas humidity is low. With the increase of humidity, bulk Ni phase become more coarse but the spreading of Ni is prohibited.

This effect can be explained by the modeling of the vaporization-deposition mechanism driven by humidity gradient proposed by Jiao et al. [2]. In the central part of anode, this kind of Ni redistribution also took place which enhancing the bonding of Ni to YSZ, at the same time reducing the active TPB density by merging the porous Ni phase around TPB. With the increase of bulk gas humidity, the humidity gradient from TPB outwards to bulk gas is reduced so that no obvious Ni spreading phenomena can be observed within 10% and 30% H<sub>2</sub>O situations. The redistribution of Ni was confined in the very vicinity of TPB at contacting points, which explains the large amount of bonded Ni after discharge as shown in Fig. 2 (c), (d). The vaporization mechanism consumed the Ni phase and reduced the Ni-YSZ contacting area, with the bulk Ni sintering enhanced by humidity greatly [1], the shrinkage of bulk Ni finally delaminated Ni from YSZ and caused sudden failing of the anode as shown in Fig. 1 (d). The competition of the local Ni phase redistribution and the shrinkage of the bulk Ni finally decided the anode performances.

Pure Ni anode method facilitates the observation of Ni-YSZ interface with a fast revolution of Ni phase. Compared to normal Ni-YSZ composite anode, the new method has the advantage of easy observation of the

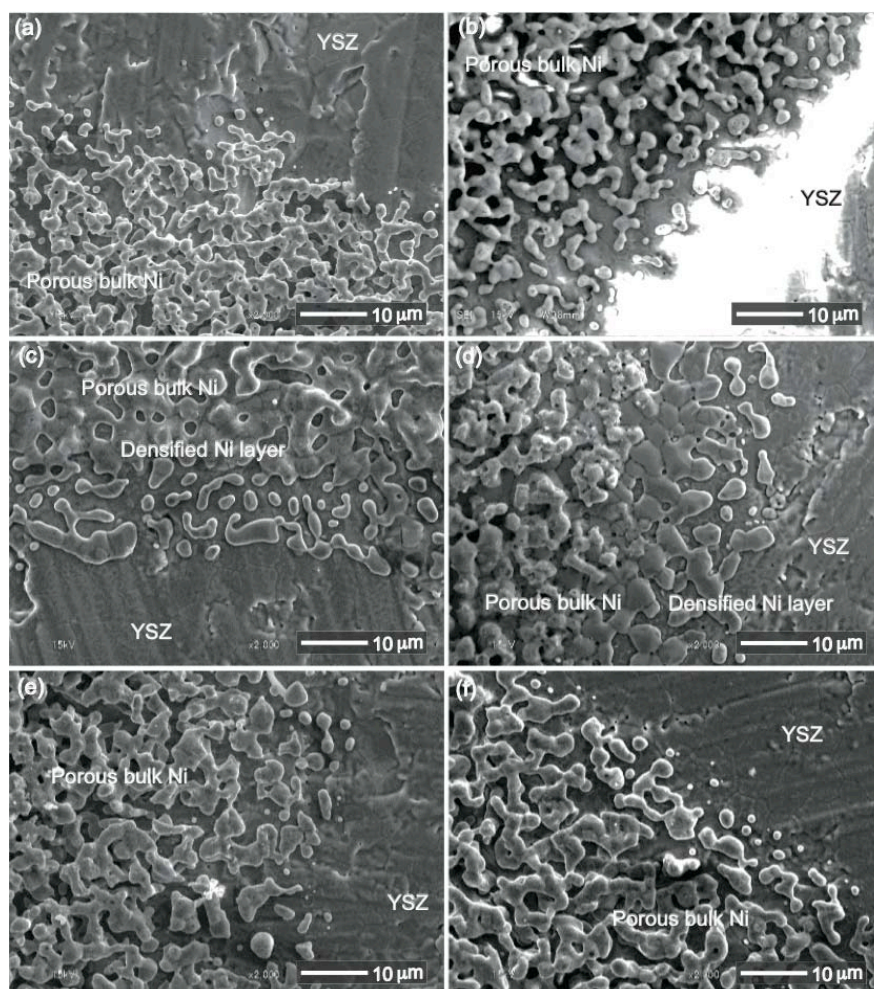


**Fig. 2 YSZ-Ni contacting interfaces, with Ni peeled off, after cooling the samples of anode (a) after reduction, (b) after OCV for 100 hours and (c)-(f) after discharge tests corresponding to Fig. 1.**

reaction sites at Ni-YSZ interface, which facilitates the correlation of phase changes to cell performances. In further study, the Ni phase evolution will be systematically and quantitatively investigated.

## Conclusion

Pure Ni anode method was used to study the degradation phenomena at the Ni-YSZ interface. The time evolution of Ni-YSZ interface in long time galvanostatic polarization is studied in hydrogen with different humidities. Compared with normal composite cermet anode experiments, this method provides easy observation of the Ni-YSZ interface where degradation takes place. The microstructural changes were characterized to be correlated to anode performances.



**Fig. 3 Anode edges microstructures after cooling the samples corresponding to Fig. 2.**

## Reference

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