

## Operation of Ni-YSZ Anode Supported Solid Oxide Fuel Cell on Different Simulated Syngases

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Ni-YSZ anode supported solid oxide fuel cells (ASCs) were tested under various simulated syngas. There was no voltage degradation of the cell operated on 41% $H_2$ -7% $CH_4$ -6% $CO$ -11% $CO_2$ -35% $H_2O$  fuel condition for nearly 450 hours. However, the high vapor content reduced the open circuit voltage (OCV) and discharge voltage. The cells run steadily with most dry syngas until the simulated reforming temperature reduced to 500°C and steam to carbon ratio (S/C) reduced to 3. The corresponding composition of this syngas was 49% $H_2$ -24% $CH_4$ -8% $CO$ -14% $CO_2$ -5% $H_2O$ . In this case, the voltage dropped quickly and the cell failed within 5 hours. The microstructure analysis showed that the failed cell had a carbon deposit layer of approximately 10  $\mu m$  thickness close to the anode surface. The results indicated that carbon deposited quickly on Ni surface when there was no adequate carbon dioxide or vapor to avoid methane cracking.

### Introduction

High temperature solid oxide fuel cells have been demonstrated to be promising clean energy technologies due to their high efficiencies and flexibility of fuel types (1). The natural gas which mainly contains methane is one of the most attractive fuels for SOFCs. The Ni-YSZ anode supported cells (ASCs) had been successfully operated directly on methane and natural gas fuel without coke buildup (2, 3). However, the results were only achieved under some special operation conditions, including low operation temperature and high current density. More attention had been paid to internal reforming of methane, and high steam to carbon ratio ( $> 3$ ) was found to be necessary for preventing the carbon deposition (4-7). In addition, the endothermic internal reforming reaction led to large temperature drops in anode and hence resulted in decreased cell performance. In practical application, external reforming of natural gas is still preferred. The methane can be reformed to syngas by different methods, including steam reforming, partial oxidation reforming, carbon dioxide reforming and autothermal reforming. The steam reforming, which is the most mature technology in industry, is also used in household SOFC system, because the water and pipeline natural gas is low-cost and readily available in the dwelling. It should be noticed that the risk of carbon deposition still exists even using the reforming syngas. The solid carbon may come from cracking of residual methane and disproportionation of carbon monoxide.

The syngas derived from steam reforming of methane consists of  $H_2$ ,  $CH_4$ ,  $CO$ ,  $CO_2$  and  $H_2O$ . The ratio of these compositions was determined by the reforming condition, including pressure, steam to carbon ration and reforming temperature. The possibility and

rate of carbon deposition on SOFC vary with syngas fuel. In this study, Ni-YSZ anode supported solid oxide fuel cells were tested with various simulated syngas under different operation conditions. The syngas were simulated by mixing  $H_2$ ,  $CO_2$ ,  $CO$ ,  $CH_4$  and  $H_2O$  according to thermochemical calculation of methane steam reforming. The steam to carbon ratio and reforming temperature for calculation were from 2 to 4 and  $500^\circ C$  to  $800^\circ C$ , respectively. Calculations showed that more than 30% water vapor existed in most syngases. The high vapor reduced the terminal voltage and may have a harmful impact on cell performance in long term test (8). In practical applications, the water could be removed easily by cooling the syngas. Hence, both the syngas with high vapor content (wet syngas) and the syngas containing only 5% water (dry syngas) were used for tests in this study.

## Experimental

The Ni-YSZ anode supported cells used in this study were manufactured by NIMTE. The ASCs consist of a Ni-YSZ support layer of 0.4~0.6 mm, an anode functional layer of  $10\ \mu m$ , an 8YSZ electrolyte of  $10\ \mu m$ , a LSM-YSZ functional cathode of  $20\ \mu m$  and a LSM buffer layer of 40~50  $\mu m$ . The ASCs were cut into pieces of  $5 \times 5.8\ cm^2$  by laser for single cell test. The active area of the cells is  $4 \times 4\ cm^2$ , as determined by the area of cathode which exposed to air in the test. An alumina test house was used to hold the cells and sealed by glass sealant. The current collector consisted of a nickel mesh on the anode side and a silver mesh on the cathode side, respectively. After assembly, the testing house was heated to  $850^\circ C$  at  $1^\circ C/min$  and 7 kg pressure was applied to the test house to improve the sealing. The cells were reduced under 3%water-97% hydrogen condition at  $850^\circ C$  for 3 hours, and then the temperature and fuel were adjusted according to the experiment requirements. The tests were carried out with a commercial SOFC test system supplied by Ningbo Bate Technology. As shown in Figure 1, the test system consists of several sub-systems: temperature system, gas supplying system, humidifying system; DC electronic load system, and data acquisition system.

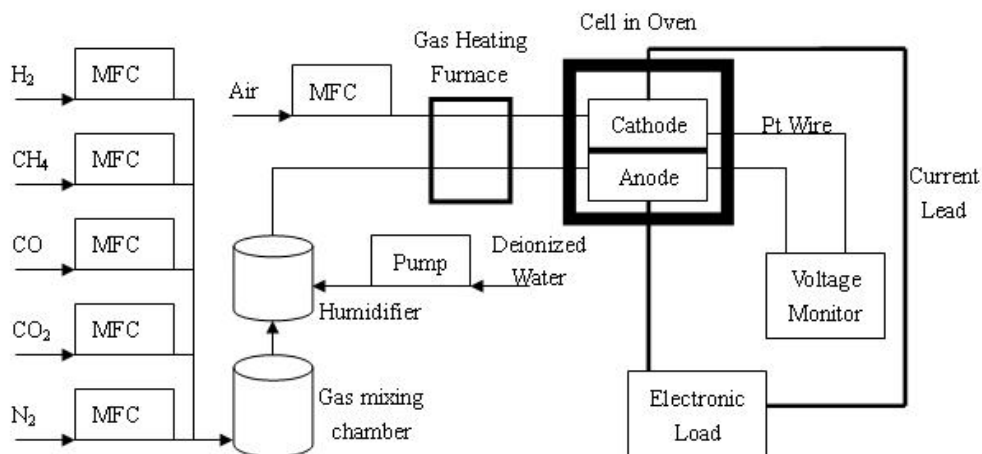


Figure 1. Schematic of single cell test equipment.

The performance of the cells was characterized by measuring IV curves and the cell voltage in time under various gas compositions. After test, the microstructures of the cells were examined using FE-SEM. The carbon deposition on anode was detected by electron dispersion spectroscopy (EDS).

The syngases used in the tests were mixtures of H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>O. The gas flow rates of H<sub>2</sub>, CO, CO<sub>2</sub> and CH<sub>4</sub> were adjusted by mass flow controllers. The steam was added to the gas mixture using the humidify facility of the test system. Before feeding the fuel to the cell, the gas was heated to 400°C by a preheating furnace. The total flow was controlled to 500 sccm to simulate low fuel utilization (10%~30%) in the practical application.

Since only small amount of vapor was in the dry syngas, the risk that the carbon deposited on anode under dry syngas is more remarkable. Hence, more attention was paid to the cell performance under the dry syngas to investigate mechanism of carbon deposition in this study. The compositions of dry syngas and the simulated conditions of steam reforming are shown in Table I.

**Table I.** The Composition of Dry Syngas

S/C	Temperature (°C)	CH <sub>4</sub> (%)	CO(%)	CO <sub>2</sub> (%)	H <sub>2</sub> (%)	H <sub>2</sub> O(%)
4	800	0.02	10.77	19.00	65.22	5.00
4	700	0.26	9.05	18.95	66.74	5.00
4	600	3.23	5.98	18.35	67.44	5.00
4	500	15.09	1.91	15.98	62.01	5.00
3	800	0.05	12.57	18.99	63.39	5.00
3	700	0.59	10.85	18.88	64.68	5.00
3	600	5.51	6.88	17.90	64.72	5.00
3	500	23.64	7.60	14.27	49.48	5.00
2	800	0.15	15.08	18.97	60.80	5.00
2	700	1.64	13.25	18.67	61.44	5.00
2	600	9.80	7.93	17.04	60.23	5.00
2	500	27.04	2.19	13.59	52.17	5.00

## Results and Discussion

### Wet Syngas

The voltage and power density versus current density of an ASC operated on wet syngas and corresponding dry syngas were plotted in Figure 2. The 5% humidified H<sub>2</sub> was employed as reference gas. The methane and carbon monoxide in syngas increased the polarization loss due to the slower reaction rate (9). And the anode polarization further increased because of the slower overall diffusion to reaction site. A certain amount of carbon dioxide could reduce the polarization loss resulting from the electrochemical oxidation of carbon monoxide. However, the overdose of carbon dioxide can dilute the fuel, lower the cell performance. The high content of vapor in wet syngas further dilutes the fuel, reducing the OCV and power output.

Figure 3 showed the aging test result of the cell operated under 41%H<sub>2</sub>-7%CH<sub>4</sub>-6%CO-11%CO<sub>2</sub>-35% H<sub>2</sub>O fuel condition at 850°C for nearly 450 hours. The corresponding parameters for thermochemical calculation of this syngas were 600°C and S/C 2. No voltage degradation could be observed. The result indicated that the high vapor and carbon dioxide content could effectively prevent the coke formation occurring on anode. However, the voltage increased significantly when the vapor content reduced slightly from 35% to 30%. This implied that high humidity could reduce the discharge voltage.

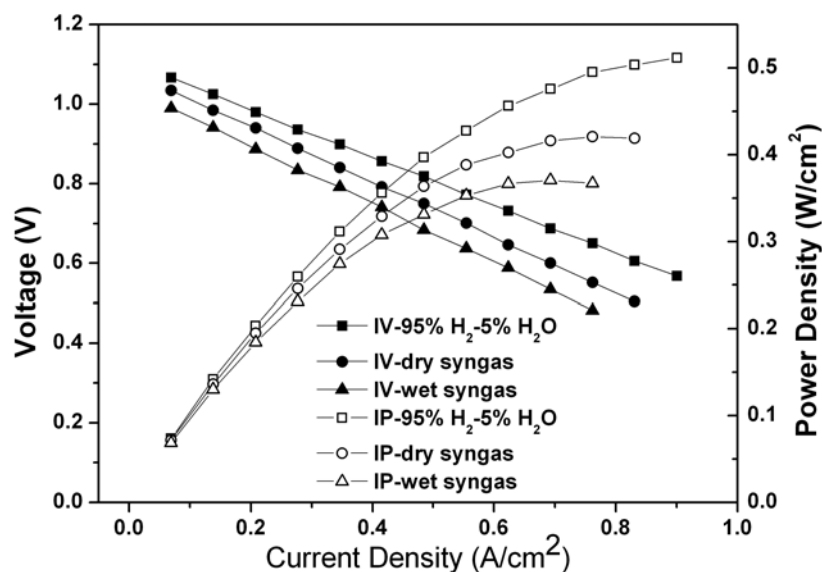


Figure 2. Voltage and power density versus current density of an ASC operated on humidified hydrogen and syngas at 850°C. The composition of wet syngas and dry syngas are 41% $H_2$ -7% $CH_4$ -6% $CO$ -11% $CO_2$ -35% $H_2O$  and 60% $H_2$ -10% $CH_4$ -8% $CO$ -17% $CO_2$ -5% $H_2O$ , respectively.

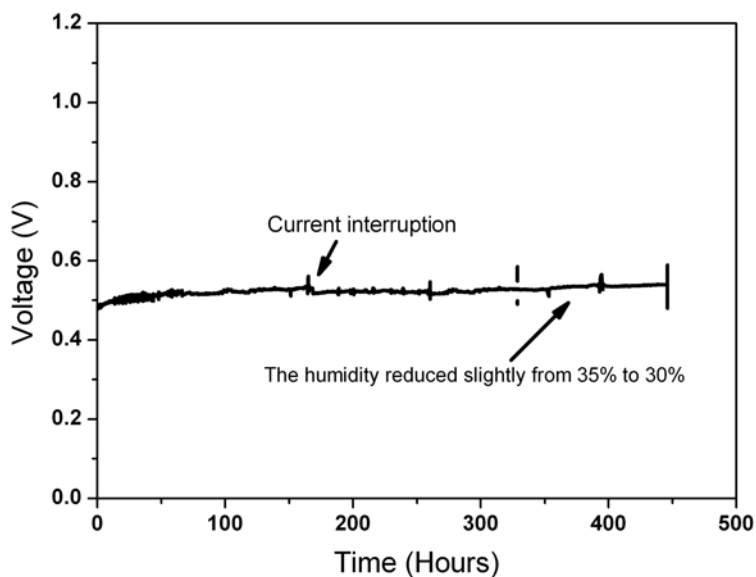


Figure 3. Voltage versus time for SOFC operated at 850°C with a current density of 0.62  $A/cm^2$ . Fuel condition is 41% $H_2$ , 7% $CH_4$ , 6% $CO$ , 11% $CO_2$  and 35% $H_2O$ .

### Dry Syngas

To test the stability of cell under different dry syngases, each syngas was fed to the cell for at least 24 hours. As shown in Figure 4, the cell run steadily with most dry syngases at 850°C until the simulated reforming temperature and steam to carbon ratio decreased to 500°C and 3, respectively. The corresponding composition of dry syngas was 49% $H_2$ -24% $CH_4$ -8% $CO$ -14% $CO_2$ -5% $H_2O$ . In this case, the voltage dropped quickly and the cell failed within 5 hours. The content of  $CH_4$  in this syngas was more than the total amount of  $CO_2$  and  $H_2O$ . This indicated that the carbon deposited rapidly when there was no sufficient vapor and carbon dioxide to avoid methane cracking.

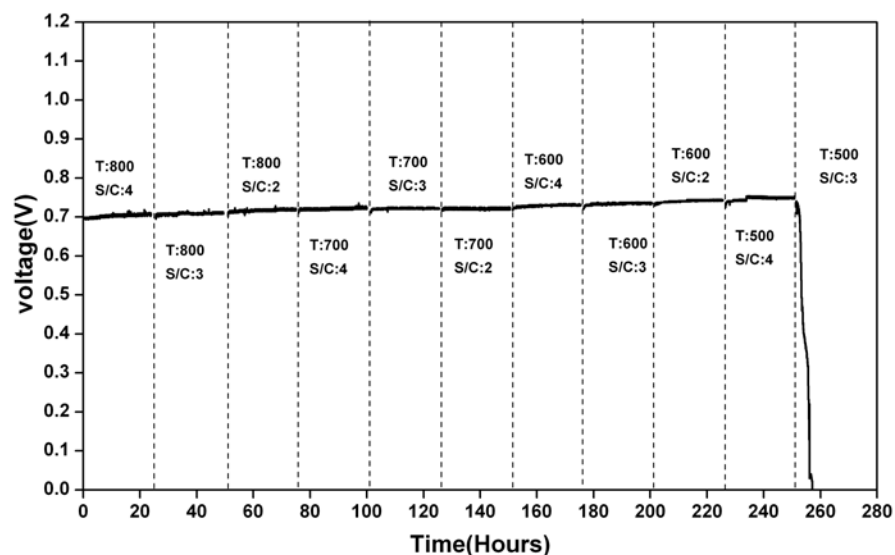


Figure 4. Voltage versus time for SOFC operated in different dry syngas at 850°C with a current density of 0.62 A/cm<sup>2</sup>

### Carbon Deposition

Carbon deposition can cause the cell performance degradation by several mechanisms. For instance, the coke may block anode pores, resulting in fuel shortage in anode functional layer. Alternatively, the carbon may deposit on the three phase boundaries to stop the electrochemical reactions of fuel.

Figure 5 showed the SEM pictures of the failed cell. There was an approximately 10µm carbon deposition zone near the anode surface. However, the carbon couldn't be observed on the other area of the anode. The result indicated that reason of cell performance degradation was the clogging of fuel diffusion channel caused by carbon deposition. The Ni in anode would be electrochemically oxidized into NiO when fuel remained in anode was exhausted, especially the Ni in anode functional layer. The re-oxidation of Ni brought seriously volume expansion and might further crack the cell.

The result of EDS line scan was shown in Figure 6. The C signal intensity increased where the Ni signal intensity decreased. But the intensity of Zr signal kept constant all the time. This revealed that the carbon deposition only occurred on the surface of Ni particle.

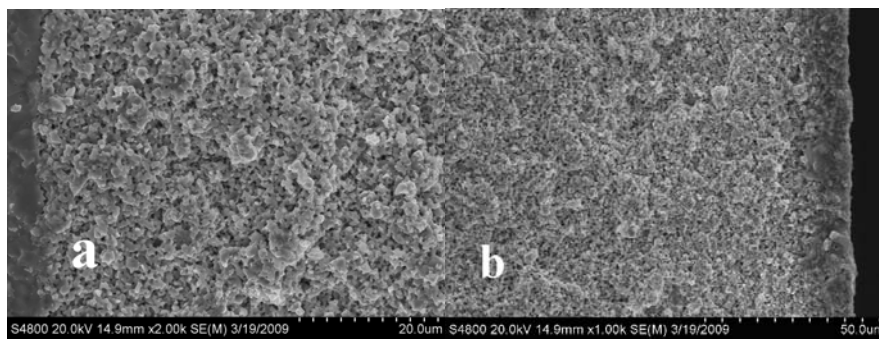


Figure 5. Cross-sectional SEM picture of failed cell anode (a. the section approaching to electrolyte, b. the section near the anode surface).

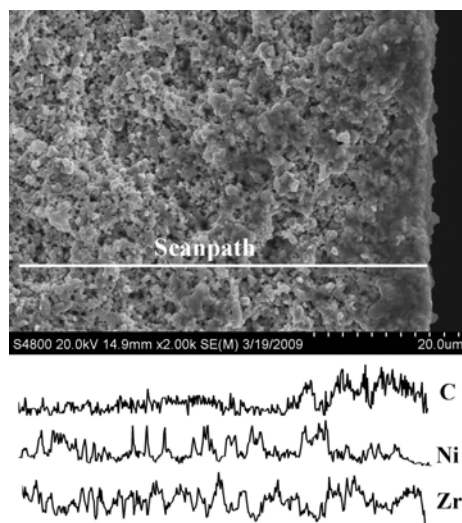


Figure 6. EDS line scan of the failed cell.

### Conclusions

The ASC run steadily under 41% $\text{H}_2$ -7% $\text{CH}_4$ -6% $\text{CO}$ -11% $\text{CO}_2$ -35% $\text{H}_2\text{O}$  fuel condition for nearly 450 hours without any voltage degradation. The high vapor and carbon dioxide content in this wet syngas could effectively prevent the coke buildup. However, reducing the content of vapor significantly increased the power output of cells. The terminal voltage of ASCs remained stable under most dry syngas fuel. The result suggests that the carbon dioxide and vapor in most dry syngases are adequate to restrain carbon deposition. Solid carbon was only found on the surface of the failed cell's anode. This indicated that the rate of carbon deposition is quite rapid if there was no sufficient carbon dioxide or vapor to avoid methane decomposition. The voltage decreasing and cell failing can be attributed to the clogging of anode pores and re-oxidation of Ni.

### Acknowledgements

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