



Short communication

# Sulfur-poisoned Ni-based solid oxide fuel cell anode characterization by varying water content

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## ABSTRACT

The 0.2% hydrogen sulfide (H<sub>2</sub>S) poisoning of Ni/YSZ anode-supported solid oxide fuel cells (SOFCs) is investigated by varying water content in fuel. The degradation extent of the cell voltage decreases with increasing water content (from 0% to 10%). Water can be generated at the anode side through an electrochemical reaction, and the content of water product augments upon the addition of fuel. However, our results indicate that an increase in fuel utilization significantly aggravates H<sub>2</sub>S poisoning behavior. The results of X-ray analysis suggest that the presence of water in fuel cannot affect the final forms of nickel sulfides, but microstructural inspection reveals different attack modes upon the injection of vapor (from 0 to 10%) into fuel containing 0.2% H<sub>2</sub>S.

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## 1. Introduction

The effect of H<sub>2</sub>S addition to fuel on solid oxide fuel cell (SOFC) performance has been widely evaluated under various SOFC operating conditions [1–4]. The mechanism of H<sub>2</sub>S poisoning of Ni/YSZ based SOFC anodes has been attributed to the formation of nickel sulfides [5–7], which results in anodic active site loss and cell performance degradation. Dong et al. [5] indicated that Ni<sub>3</sub>S<sub>2</sub> and Ni<sub>7</sub>S<sub>6</sub> were detected in small amounts using an XRD technique, when a sample was exposed to 100 ppm H<sub>2</sub>S at 727 °C for 5 days. Ni<sub>7</sub>S<sub>6</sub> was also detected by the authors, with a small amount of Ni<sub>3</sub>S<sub>2</sub> formed by exposing the sample to 10% H<sub>2</sub>S at 950 °C for 5 days. Cheng and Liu [6] reported that nickel surfaces underwent significant sulfidation when Ni–YSZ cermet was slowly cooled below 500 °C to room temperature, using an *in situ* Raman microspectroscopy technique.

The influence of fuel composition on the interaction of H<sub>2</sub>S and nickel-based anodes for SOFCs was studied [8,9]. Our previous work revealed that the presence of 10% water in fuel promotes performance recoverability to a large extent [9]. Wang and Liu [10] predicted the regeneration of sulfur-poisoned nickel by O<sub>2</sub> and H<sub>2</sub>O (as described by the Eqs. (1) and (2)), and they also pointed out that sulfur adsorption on

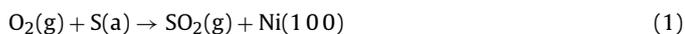
the nickel surface can only be cleaned with water. Therefore, the introduction of water to fuel may reduce the degree of H<sub>2</sub>S poisoning of SOFCs and improve the performance to a recoverable extent.

In the present study, we tested the performance of SOFCs with both dry and wet gas containing 0.2% H<sub>2</sub>S and analyzed the materials that had been poisoned in each operational condition using XRD and SEM/EDS techniques. In addition to the relationship between degradation and the format of nickel sulfide, microstructural changes were also analyzed.

## 2. Experimental

The cells tested in this study were typical anode supported planar fuel cells produced at NIMTE [11]. The cells had a 10 μm thick anode of Ni/YSZ, a 400 μm thick supported layer of Ni/YSZ, a 10 μm thick electrolyte of YSZ, a 25 μm thick composite cathode of LSM/YSZ and a 20–30 μm thick cathode current collecting layer of LSM. The specific description of cell configuration and testing procedures has been previously reported [11,12].

Current–voltage curves were characterized with 0.5 SLM H<sub>2</sub> (as the anode fuel) and 2 SLM air (as the cathode gas) at 750, 800 and 850 °C. The cells were then galvanostatically operated at 0.25 A cm<sup>−2</sup> at 800 °C, and each condition was held constant at least 10 h to avoid abrupt electrochemical activation [13] before the cells were exposed to 0.2% H<sub>2</sub>S for 60 min. Microstructural analyses were carried out for each sample after electrochemical tests using a Hitachi S4800 field emission scanning electron microscope (FE-SEM/EDS). XRD data were collected using Bruker D8 Advance with Cu Kα radiation at a step of 0.02° S<sup>−1</sup> in the range of 2θ from 20° to 70°.



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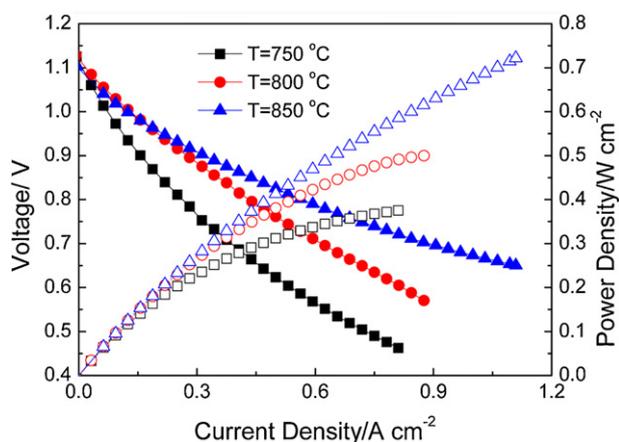


Fig. 1. Cell voltage and power density vs. current density recorded at 750–850 °C.

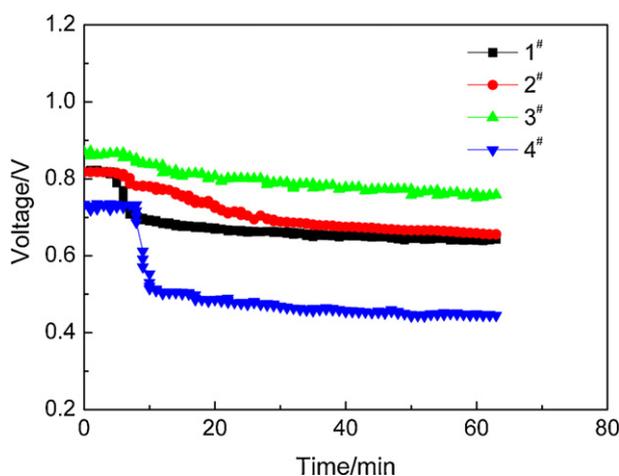


Fig. 2. The variation of cell voltage vs. time when the cells were exposed to 0.2% H<sub>2</sub>S at 800 °C.

### 3. Results and discussions

Fig. 1 displays both cell voltage and power density as a function of current density for a typical SOFC single cell. Because the cells used for the test were manufactured in series, with relatively large active areas, the cell performance shown in Fig. 1 represents an average level of the manufactured cells. The cells were first stabilized in pure hydrogen fuel with a flow rate of 0.3 SLM for 60 min at 850 °C to convert NiO to Ni, and then a steady open circuit voltage (1103 mV) was reached at 850 °C. The maximum power density measured for the cell arrived at 0.72 mW cm<sup>-2</sup> at 850 °C, 0.50 mW cm<sup>-2</sup> at 800 °C and 0.38 mW cm<sup>-2</sup> at 750 °C. For comparison, the cell fabrication and operating conditions, including operation temperature, current density and fuel flow, were kept identical.

Fig. 2 displays the variation of cell voltage vs. elapsing time. The detailed explanations of numbers 1–4# are listed in Table 1. A sharp drop in cell voltage was observed once 0.2% H<sub>2</sub>S was injected, and

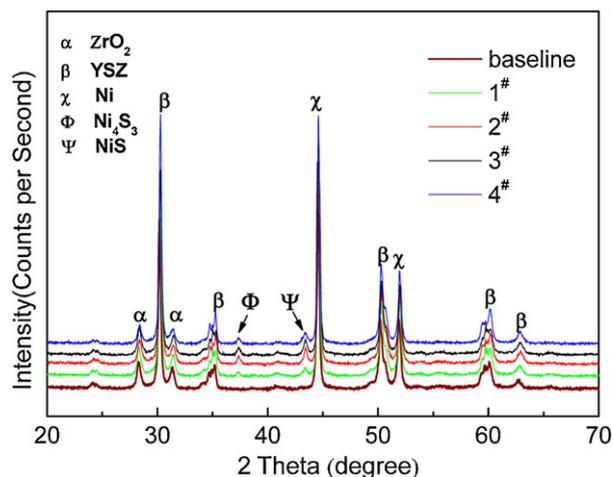


Fig. 3. XRD spectrum of a Ni/YSZ anode material on a tested cell, with 0.2% H<sub>2</sub>S exposure at various conditions.

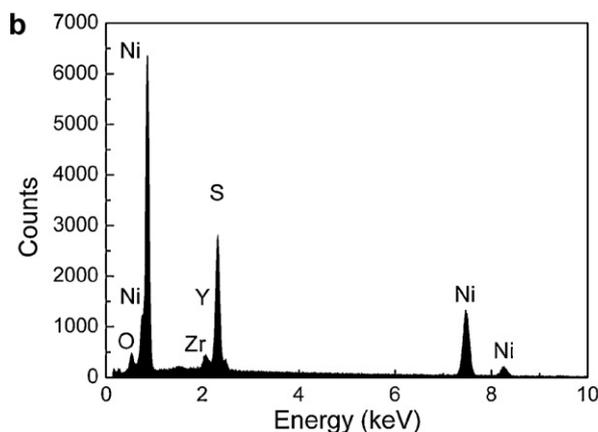
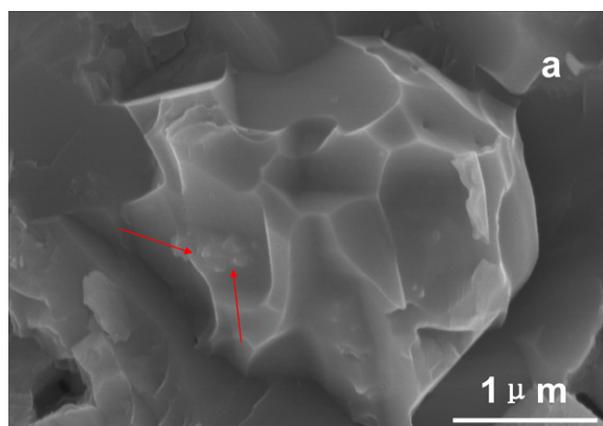


Fig. 4. Microstructure of the cell anode after operating in dry gas containing 0.2% H<sub>2</sub>S at 0.25 A cm<sup>-2</sup> (a), and elemental analysis (b).

Table 1

The values of the drop in cell voltage at various testing conditions.

	T (°C)	i (A cm <sup>-2</sup> )	Water content	H <sub>2</sub> S/period (%/h)	Fuel utilization	Voltage drop (mV)
1#	800	0.25	0%	0.2/1.0	11%	180
2#	800	0.25	3%	0.2/1.0	11%	161
3#	800	0.25	10%	0.2/1.0	11%	108
4#	800	0.50	0%	0.2/1.0	22%	287

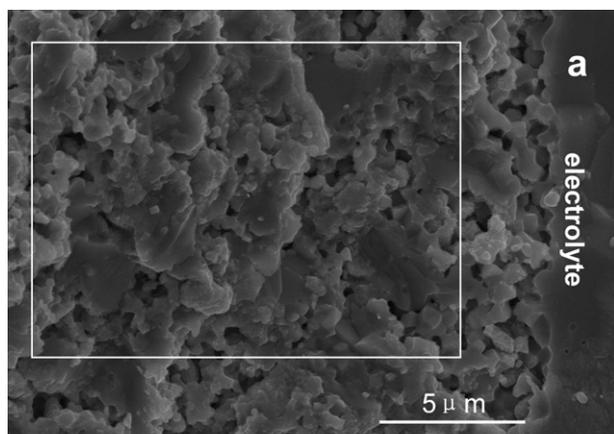


Fig. 5. Microstructure of the cell anode after operating in dry gas containing 0.2%  $\text{H}_2\text{S}$  at  $0.50 \text{ A cm}^{-2}$  (a), and elemental analysis (b).

then a saturation status seemed to be achieved in a subsequent test as shown in data labeled 1<sup>#</sup> [14]. However, the rate and extent of degradation dramatically declined upon addition of water (from 3% to 10%) to fuel, as shown in data 2<sup>#</sup> and 3<sup>#</sup>. When hydrogen gas is oxidized on the active sides of the anode, water is produced, and the amount of water increases with current load, which can be calculated by Faraday's law of electrolysis [15]. Therefore, we also tested the degradation by increasing the current density to  $0.50 \text{ A cm}^{-2}$ , as shown in 4<sup>#</sup>. In this experiment, a large, sharp drop in cell voltage was recorded and then a sluggish deterioration followed, in accordance with the trend that was revealed by data 1<sup>#</sup>, which implies that the effect of direct current (DC) polarization load on  $\text{H}_2\text{S}$  poisoning behavior is dominant to the impact of water produced at the anode.

Fig. 3 shows the XRD pattern for the fresh sample and the samples after exposure to 0.2%  $\text{H}_2\text{S}$  at  $800^\circ\text{C}$  for 60 min. A strong reflection of  $\text{Ni}_4\text{S}_3$  (located at  $37.42^\circ$ ) and  $\text{NiS}$  (at  $43.47^\circ$ ) was observed for both the poisoned samples, and no other peaks corresponding to nickel sulfides in XRD spectra were observed. The final forms of nickel sulfide may be thoroughly dependent on  $\text{H}_2\text{S}$  concentration and operating temperature [5]. Therefore, the different effect of water content on  $\text{H}_2\text{S}$  poisoning in SOFC cannot be related to the reaction between a Ni catalyst and a  $\text{H}_2\text{S}$  contaminant.

Nickel sulfide agglomeration, with a diameter of nearly  $3 \mu\text{m}$ , was detected after the cell was operated at  $0.25 \text{ A cm}^{-2}$  in dry fuel containing 0.2%  $\text{H}_2\text{S}$ , as shown in Fig. 4(a) and in the elemental analysis in Fig. 4(b). It can be seen that the morphology of the contaminated particles appeared to remain the same as the surrounding regions, which was similar to observations from our

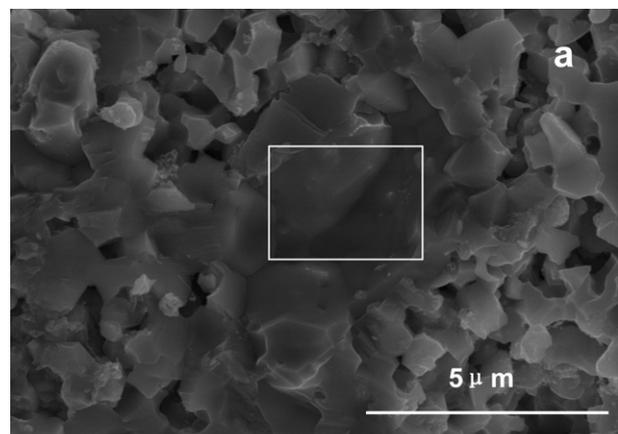


Fig. 6. Microstructure of cell anode after operating in 10% wet gas containing 0.2%  $\text{H}_2\text{S}$  at  $0.25 \text{ A cm}^{-2}$  (a), and elemental analysis (b).

previous test [12]. The result of EDS analysis showed that nickel and sulfur coexist in the bulk phase, which confirms the possible formation of nickel sulfide.

The anode area attacked by  $\text{H}_2\text{S}$ , when the cell was loaded with a current density of  $0.50 \text{ A cm}^{-2}$  in dry gas, seemed to be more extensive, as displayed in Fig. 5(a) and (b). The reaction between nickel and sulfur at the anodic layer can definitely reduce the length of triple phase boundary (TPB), resulting in an immediate drop in cell performance. However, the preferred formation of sulfur compounds shifting to the anode-supported domain will decrease electrical conductivity, which may account for the sluggish degradation that follows a rapid decline in cell voltage. At high levels of fuel utilization,  $\text{H}_2\text{S}$  may be completely oxidized to  $\text{SO}_2$  at the anodic layer [16], and sulfur dioxide will be converted to sulfur by  $\text{H}_2\text{S}$  flow. When this type of conversion occurred at the interface of the anode active layer and supported layer, it can aggravate the degradation because the resistance of hydrogen diffusing to TPB will be increased.

The structure shows that sulfur incorporates at the surface, as shown in Fig. 6(a) and (b). The diameter of embedded sulfur bulk was about  $2\text{--}3 \mu\text{m}$ . The EDS analysis revealed that nickel and sulfur elements comprised the main species of the agglomeration, verifying the possible formation of sulfur compounds. Compared to the result in Fig. 4(a), the presence of 10% water in fuel cannot change the poisoned microstructure, which is reasonable because the water can only shift the sulfur adsorption on the surface of nickel [10]. Small particles, with the diameter of several hundredths of a nanometer, dotted the surface of the poisoned cluster as shown in Fig. 4(a), which faded with the introduction of 10% water, as observed in Fig. 6(a). Therefore, these fine grains appeared to be

the result of sulfur element adsorption on the surface of the nickel sulfides, which can be removed according to the above discussion and a previous report [10].

#### 4. Conclusions

The effect of water content on H<sub>2</sub>S poisoning of SOFCs was studied. The extent of degradation decreased with increasing vapor content in fuel, but increasing current load seemed to aggravate the poisoning degree. The deterioration rate was independent of the forms of the final nickel sulfides, according to XRD analyses. The poisoned samples were analyzed in terms of microstructure and element distribution, and the results indicated that the different attack modes for H<sub>2</sub>S in each testing condition may cause a difference in the extent of the decrease in cell performance.

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