DEACTIVATION AND RECOVERY OF Ni-YSZ ANODE IN H₂ FUEL CONTAINING H₂S

S. J. Xia and V. I. Birss
Department of Chemistry
The University of Calgary, Calgary, AB T2N 1N4, Canada

ABSTRACT

The degradation of Ni-YSZ composite anodes in a single solid oxide fuel cell (SOFC) running on humidified H₂ containing 10 ppm H₂S, at 800°C, has been investigated, both at the open circuit potential (OCP) and under load. With exposure to H₂S at the OCP, the series resistance (electrolyte plus interfacial contacts) and especially the polarization resistance increase with time. Anode degradation is enhanced when exposure occurs under a load, and the higher the current density, the more rapid the loss of performance, without reaching a steady-state. Partial or full recovery of the H₂S-poisoned Ni-YSZ anode, determined by the extent of lowering of the series and polarization resistance, was achieved by exposure to pure H₂, N₂ or air at the OCP. Greater than 90% recovery was obtained in N₂ or air, while only ~75 % recovery could be achieved in H₂. Overall, the results indicate that the reversible component of H₂S poisoning is caused by the blocking of the active Ni-YSZ sites by adsorbed sulfur or H₂S, while the small, irreversible component may be due to the formation of a Ni-S compound in some areas within the anode structure.

INTRODUCTION

Compared to low temperature fuel cells, such as polymer electrolyte (PEM) and alkaline fuel cells, solid oxide fuel cells (SOFCs), which operate at temperature ranging between 650 and 1000°C, can run directly on hydrocarbon fuels without prior reforming. This not only reduces the capital cost of the fuel cell operating system, but it also improves the fuel efficiency. The most convenient hydrocarbon fuel available is natural gas, which can contain relatively high levels of H₂S, ranging from 1 to 30 ppm, depending on its source [1]. Natural gas can also contain sulfur-based compounds added as an odorant. In coal syngas, which is the product of coal gasification, the H₂S level can be as high as 0.2 to 1.3 mol percent [1].

The poisoning of Ni by H₂S and other sulfur-containing species is well known [2-4], although only a few literature reports have focussed on H₂S-poisoning of Ni-based anodes in SOFCs [5-7]. For example, it has been reported that H₂S can severely poison Ni-YSZ anodes at 1000°C, even when its concentration is as low as 2 ppm [7]. However, it was shown in other work that the poisoning of Ni-YSZ anodes by H₂S (<15 ppm at 1000°C) can be reversed when pure H₂ is introduced into the fuel cell [7], although periodic H₂ purges would increase the operating cost of the fuel cell system. Another approach which has been used to prevent poisoning has been to remove H₂S from the fuel cell.
before further fuel processing. However, the addition of a sulfur removal system makes the SOFC system more complex and reduces the overall energy conversion efficiency. Other research directions have involved the development of a sulfur-tolerant anode. For example, it has been reported that some metal oxide perovskites can tolerate the presence of up to 5000 ppm H2S in a H2 fuel at 1000°C, offering an attractive alternative to Ni as the anode material [8]. However, the activity of the perovskite anodes for H2 oxidation is much lower than that of the Ni anode.

Because of the many advantages of Ni-based SOFC anodes, a key research goal is the development of a means of preventing or minimizing their sulfur poisoning and/or of rapidly and fully recovering their performance after exposure to H2S, especially at operating temperatures as low as 800°C. In the present work, the degradation of electrolyte-supported Ni-YSZ anodes in H2 containing 10 ppm H2S + 3% water was investigated, both at open-circuit and under a load, using a range of electrochemical techniques. It was found that the higher the current, the greater the extent of anode poisoning. After deactivation, it was found that the anode could be almost fully recovered by the introduction of various other gases into the anode chamber.

EXPERIMENTAL

YSZ (ZrO2 stabilized with 8% Y2O3, Tosoh, Inc.) discs were prepared in a stainless steel die and then sintered at 1450°C for 4 hours. The diameter and thickness of the sintered YSZ discs were 20 and 0.6 mm, respectively. A mixture of ceramic-grade NiO powder (Aldrich) and YSZ powder (Tosoh, Inc.), at a weight ratio of 50:50, was made into a slurry using glycerol and then screen-printed (ca. 20 μm thick) on one side (0.75 cm²) of the YSZ discs, followed by sintering at 1350°C for 2 hours. On the other side, a slurry, prepared from a mixture of Sr-doped LaMnO3 powder (LSM, supplied from Seattle Ceramics, Inc.) and YSZ powder at a weight ratio of 50:50 and glycerol, was screen-printed on the YSZ and then sintered at 1150°C for 2 hours. A small piece of Pt gauze, attached to the YSZ disc surface about 2 mm from the LSM-YSZ composite cathode, was used as the reference electrode (RE).

The current collectors attached to the Ni-YSZ and LSM-YSZ anode and cathode consisted of a piece of Pt gauze, connected to a Pt wire. The gauze was attached to the cathode layer using LSM slurry, and to the anode with Pt paste (Ferro 482). Then, the single SOFC cell was sintered at 1000°C for 30 min, after which it was sandwiched between two alumina tubes using ceramic power as the sealant. H2, or H2 + 10 ppm H2S, humidified in water at room temperature (3% water), was fed to the anode chamber at a flow rate of 20 ml/min, while the cathode was left in air during operation. All potentials in this paper are given with respect to the Pt RE, exposed continuously to air on the cathode side.

Electrochemical experiments were performed using an EG&G 263A potentiostat, with control and data collection handled by Corrware software. For the impedance analysis, a Solartron 1255 frequency response analyzer was coupled to an EG&G 263A potentiostat. The frequency range employed was 0.05 Hz to 100 kHz and all measurements were made at the open circuit potential (OCP), with an AC amplitude of 10 mV. The impedance measurements were controlled with commercial software (ZPLOT).
RESULTS AND DISCUSSION

Deactivation of Ni-YSZ Anodes in H₂S-Containing H₂

Figure 1 (curve a) shows the area-corrected ac impedance data, in the form of a Nyquist plot, for a freshly prepared Ni-YSZ anode at 800°C when exposed to H₂ + 3% H₂O. The anode impedance is composed of two semicircles and, therefore, a two time constant equivalent circuit, shown in the inset of Fig. 1, was employed to fit the experimental data.

\[ R_s \] represents the series resistance of the anode, \( R_1 \) and \( R_2 \) are related to interfacial or charge transfer resistances, and the CPEs represent constant phase elements, which reflect the dispersion of a capacitive element (e.g., the film dielectric capacitance or interfacial capacitance) around a central value [9], with the relationship between a capacitor (C) and a CPE [9] being \( j \omega \) \( \beta \) (CPE), where \( j^2 = -1 \) and \( \omega \) is angular frequency. For \( n = 0 \), a CPE is a resistor, while for \( n = 1 \), a CPE represents a perfect capacitor. When \( n \) is between 0 and 1, its value can provide information about diffusion phenomena, surface morphology, and other dissipative processes [10,11]. The \( n_1 \) and \( n_2 \) values in H₂ + 3% H₂O, associated with CPE₁ and CPE₂, are 0.55 and 0.8, respectively, obtained from impedance fitting. Based on these \( n \) values, the \( (R_1CPE_1) \) component at high frequencies likely reflects the properties of the porous anode layer (CPE ~0.5) [12], while the \( (R_2CPE_2) \) component at low frequencies likely represents the charge transfer resistance and double layer capacitance.

The impedance data for the Ni-YSZ anode are quite stable in H₂ with time at 800°C. No change was seen for up to 20 hrs, after which the gas fed to the anode side of the cell was switched to H₂ + 10 ppm H₂S, humidified at room temperature. The changes in the anode performance were then tracked with time of exposure to H₂S. Fig. 1 (curves b to d) shows that the total resistance of the anode, obtained from the low frequency intercept on the \( Z' \) axis, increases with time, indicative of the overall degradation of the Ni-YSZ anode performance in H₂ + 10 ppm H₂S.

Fig. 2 shows that all three resistors (\( R_s \), \( R_1 \) and \( R_2 \)) remain almost unchanged in the first 2 hrs, presumably reflecting the time that it takes for H₂S to access and adsorb at the triple phase boundary (TPB). After the initial induction period, the series resistance, \( R_s \), gradually increases from 0.25 to 0.55 ohms.cm² (after 18 hrs). \( R_1 \) and \( R_2 \) both increase.
rapidly in the first 3 hrs, and then increase more slowly with time. Overall, after 18 hrs, Rs and R1 both increased by ~2 times, while R2 increased by ~7 times. Therefore, the parameter which is most affected by H2S exposure is R2, the charge transfer resistance.

Cyclic voltammetry (CV) experiments also revealed (Fig. 3) that, after 18 hrs of exposure to 10 ppm H2S at the OCP, the H2 oxidation currents notably decreased. Fig. 4 shows the IRs compensated Tafel plots of these data, revealing that the Tafel slope, obtained over the potential range of -0.93 to -0.90 V before poisoning and -0.82 to -0.76 V after poisoning, has increased only slightly after H2S exposure, from 120-130 mV to 140 mV.

On the other hand, the exchange current density, obtained from the IR compensated Tafel plot, decreased from ~75 mA/cm² before poisoning to ~10 mA/cm² after 18 hrs of exposure to H2S, similar to the 7-fold increase of the impedance-determined charge transfer resistance (Fig. 2). Together, these data demonstrate that the reaction mechanism (inferred from the Tafel slope) has likely not changed, but that the number of active Ni/YSZ sites has decreased significantly due to H2S exposure. Therefore, the Ni sites located at the TPB are now in one of two states, either free or blocked/poisoned by a sulfur species.
The degradation of the Ni-YSZ anode in H₂ + 10 ppm H₂S + 3% water was also carried out under galvanostatic square wave conditions (Fig. 5), during which the current was cycled between 0.13 A/cm² for 300 s and 0.4 A/cm² for 100 s for 6 hours.

Figure 5. The anode overpotential in a single cycle of galvano-static square wave in which the current density was altered between 0.13 A/cm² for 300 s and 0.4 A/cm² for 100 s in H₂ + 10 ppm H₂S + 3% water at 800°C.

Fig. 6 shows that the anode overpotential remains almost constant in the first ~8 cycles (3200 seconds), and then increases notably.

Figure 6. The change of the anode overpotential at 0.13 and 0.4 A/cm² with cycling of current density between 0.13 A/cm² for 300 s and 0.4 A/cm² for 100 s in H₂ + 10 ppm H₂S + 3% H₂O at 800°C.

The fact that an induction time is seen is reminiscent of what was observed when the Ni anode was H₂S poisoned at the OCP (Fig. 2), demonstrating again that performance loss results only once there are sufficient sulfur-species at the TPB.

Importantly, the time over which the anode remains stable under load is significantly shorter than at the OCP, 3200 vs. 7200 s, indicating that the operation of the fuel cell under load accelerates the adsorption/poisoning of Ni anodes by H₂S. In other preliminary experiments, our data show that the degradation of Ni-YSZ anodes increases more rapidly under a load than at the OCP in an H₂S environment. This may be due to the large local current density which will develop at sites not covered by H₂S when a constant current is applied to the anode.

The results of the poisoning of the Ni anode in H₂ + 10 ppm H₂S at OCP and under load are very reproducible, overall. Indeed, similar data were obtained for five different Ni anodes that were prepared using the same general procedure.
Recovery of H₂S-Poisoned Ni-YSZ Anode

After the Ni-YSZ anodes were H₂S poisoned, several approaches were attempted to recover their performance. First, anodes were simply exposed to pure H₂ at the OCP, shown to be a successful method in previous work [6]. Fig. 7 shows, for a particular anode, that both the diameter of the impedance arcs and the magnitude of the series resistance both decrease with time. Again using the two time constant equivalent circuit (Fig. 1), the change of the three resistive elements (Rs, R₁ and R₂) is shown in Fig. 8.

![Figure 7. The change of impedance data of the H₂S poisoned anode with exposure time in H₂ at OCP and 800°C: a) after poisoning, b) after 6 h, and c) after 20 h.](image)

The values of all three resistors are seen to decrease rapidly in the first 5 hours, and then to decrease more slowly. However, these resistance values are still higher by ca. 40, 50 and 60%, respectively, than their corresponding values before exposure to H₂S (Fig. 2). Recovery of the Ni-YSZ anode by exposure to H₂ was also attempted under load, but it was found that the higher the current, the slower was the recovery rate.

![Figure 8. Rs, R₁ and R₂ obtained from fitting of impedance data shown in Fig. 7 as a function of exposure time in H₂ + 3% H₂O at OCP and 800°C.](image)

These results indicate that the poisoning of the anode by H₂S is only partly reversible through the use of H₂ gas. The change in the series resistance is most likely due to the deterioration and recovery of the quality and area of contact between electrically...
conducting particles in the anode layer and at the anode/current collector interface. Overall, the recovery of the H2S poisoned anode in pure H2 is a relatively slow process, and is therefore not likely to be of practical use.

Recovery of poisoned Ni-YSZ anodes was also attempted by exposing them directly to air for a very short period of time, e.g., 10 min. In these experiments, after 18 hours of exposure to a fuel containing H2 + 10 ppm H2S, the supply of the fuel to the anode was cut off, allowing air to gradually reach the anode through the exit in the anode chamber. Fig. 9 shows that the anode OCP initially decreases, then increases a little, and then decreases continuously to 0 V, indicative of the fact that both electrodes are air-saturated.

Figure 9. Variation of the cell OCP with time. After 30 s, the supply of H2 to the anode was cut off, and after 700 s, the supply of H2 to the anode was resumed.

After 10 min of air exposure, the supply of pure H2 to the anode was resumed. The OCP was seen to increase rapidly from 0 to 1 V, showing that the reduction of any NiO that may have formed during air exposure is rapid.

After the OCP reached 1.05 V, the anode performance was assessed again using the impedance technique. Fig. 10 shows the impedance data collected before H2S poisoning, after 18 hours of exposure to 10 ppm H2S at OCP, and after 10 min of air exposure. These results clearly reveal that the poisoned anode has been almost fully recovered (> 98%) after 10 min of air exposure. The circuit fitting results before, and after recovery in air, are shown in Table 1.

Figure 10. Anode impedance collected at OCP in H2 (+ 3% H2O) before and after poisoning in H2 + 10 ppm H2S, and after 10 min. of air exposure: a) after poisoning, b) after recovery in air, and c) before poisoning.

After 10 min in air, the anode was almost fully recovered. Compared to the recovery process in H2 (Figs. 7 and 8), the use of air has several advantages, including an enhanced recovery rate and simple operation, involving only the cutting of the fuel supply to the anode. However, NiO, which has been detected in other experiments by XRD analyses
[13] at Ni-YSZ anodes after air exposure, may form. This may result in the development of stress in the anode, especially for anode-supported cells, thus ultimately deteriorating the anode performance.

Table 1. Impedance-derived data for Ni-YSZ anode, degraded in H₂ + 10 ppm H₂S + 3% H₂O for 18 h at the OCP, and recovered in N₂ and air.

| Condition          | Rs / ohms.cm² | R₁ / ohms.cm² | R₂ / ohms.cm² |
|--------------------|---------------|---------------|---------------|
| before degradation | 0.35          | 0.53          | 1.11          |
| after degradation  | 0.55          | 1.62          | 5.04          |
| after 1 hr in N₂*  | 0.36          | 0.62          | 1.18          |
| after 10 min in air* | 0.36      | 0.55          | 1.12          |

For this reason, the recovery of H₂S poisoned Ni-YSZ anodes was carried out in an inert gas, specifically N₂. The N₂ gas was passed through a column of hot Cu foil, at 400°C, to remove O₂. After 18 hours of exposure to 10 ppm H₂S at OCP, N₂, which was humidified at room temperature, was fed into the anode chamber. After 1 hr, the N₂ gas was cut off and the supply of H₂ was resumed. After the OCP reached 1.06 V, the anode activity was measured using the impedance technique. Table 1 shows that the three resistive elements have decreased significantly after 1 hr of exposure to N₂. Notably, the extent of recovery estimated from the change in the total resistance is about 90%, much higher than obtained with H₂, but somewhat less than with air. These results show that the exposure of H₂S poisoned Ni-YSZ anodes using N₂ may be an effective and safe approach to use to recover its original activity.

**Mechanism of H₂S Poisoning and Recovery of Ni-YSZ Anodes**

The poisoning of Ni-YSZ anodes by H₂S is shown here to affect primarily the H₂ oxidation charge transfer reaction resistance, with a lesser impact observed on the series resistance. These results, together with the fact that the anode retains some activity even after long times of exposure to H₂S, suggest that the Ni-YSZ triple phase boundary becomes partly blocked by a sulfur species during the poisoning process. Under our experimental conditions (10 ppm H₂S, 800°C rate), the extent of blockage can be as high as 80-90%, exacerbated by exposure to H₂S under a load, vs. at open circuit. Indeed, when Ni is exposed to a mixture of H₂ and 10 ppm H₂S at 800°C, H₂S and S are both expected to adsorb [3], leading to an anticipated blockage of ~80% of the active sites for H₂ oxidation. This prediction is consistent with our present results.

Although adsorbed H₂S and S are the preferred species at Ni at 800°C, the presence of YSZ and the particulate nature of the composite anode, may affect the reaction outcome, allowing other products, e.g., sub-monolayer Ni₅S₂, to form. Notably, those sites that are not blocked by a sulfur species continue to react with H₂, without a change in reaction mechanism, as seen from the fact that the Tafel slope remain essentially unaffected by H₂S poisoning.

The fact that H₂S poisoning is more severe when exposure occurs under a load vs. at the OCP likely arises from the fact that the active surface area is lowered due to sulfur-species adsorption. Thus, the local current density at sites not-blocked by S-species can become quite high. This may enhance the sulfur species adsorption process or induce the
formation of a thin layer of Ni$_3$S$_2$. Alternatively, the higher overpotential generated may result in Ni oxide formation, which in turn, may contribute to anode deactivation.

The partial recovery of the H$_2$S poisoned Ni anode in either H$_2$ and air/N$_2$ environments suggests that poisoning of the Ni anode is due primarily to the adsorption of S or H$_2$S on the surface of Ni. When the H$_2$S poisoned anode is exposed to pure H$_2$ or N$_2$, the adsorbed S-species will gradually be displaced. In air, both the adsorbed S-species and Ni can react with O$_2$, forming SO$_2$ and possibly NiO, resulting in recovery of the poisoned Ni. The very rapid recovery of the poisoned Ni in air would indicate that the oxidation of adsorbed sulfur/H$_2$S is a rapid reaction. The fact that not all of the activity can normally be recovered may support the formation of a thin (sub-monolayer to several monolayers) of a Ni-S compound, e.g., Ni$_3$S$_2$, at some locations within the anode.

ACKNOWLEDGEMENTS

This work has been supported by the National Research Council/Natural Sciences and Engineering Research Council of Canada's Fuel Cell Research Partnership Program and Versa Power Systems, Ltd. (formerly Global Thermoelectric Inc.).

REFERENCES

1. J. Larminie and A. Dicks, Fuel Cell Systems Explained, John Wiley & Sons Ltd., England, 2003.
2. C. H. Bartholomew, Applied Catalysis A: General, 212, 17 (2001).
3. I. Alstrup, J. R. Rostrup-Nielsen and S. Roen, Applied Catalysis, 1, 303 (1981).
4. C. H. Bartholomen and J. R. Katzer, in Catalyst Deactivation, B. Delmon and G. F. Froment, Eds., Proceedings of the International Symposium, Antwerp, (1980).
5. J. Geyer, H. Kohlmuller, H. Landes and R. Stubner, in Solid Oxide Fuel Cells V, U. Stimming, S. C. Singhal, H. Tagawa and W. Lehnert, Eds., PV97-40, p. 585, The Electrochemical Society Proceedings Series, Pennington, NJ, (1997).
6. D. Dees, U. Balachandran, S. Doris, J. Heiberger, C. McPheeter and J. Picciolo, in Solid Oxide Fuel Cells, S. C. Singhal, Editor, PV 89-11, The Electrochemical Society Proceedings Series, Pennington, NJ (1989).
7. Y. Matsuzaki and I. Yasuda, Solid States Ionics, 132, 261 (2000).
8. R. Mukundan, E. L. Brosha and F. H. Garzon, Electrochemical and Solid-State Letters, 7, A5 (2004).
9. B. A. Boukamp, Equivalent Circuit, University of Twente, (1988/89).
10. M. Leibig and T. Halsey, Electrochim. Acta, 38, 1985 (1993).
11. R. D. Armstrong, R. A. Burnham, J. Electroanal. Chem., 257, 72 (1978).
12. A. Lasia, Modern Aspects of Electrochemistry, No. 32, B.E. Conway et al., Eds., Kluwer Academic/Plenum Publishers, New York, (1999).
13. S. J. Xia and V. I. Birss, J. Electrochem. Soc., in preparation.