New insights into sulfur poisoning behavior of Ni-YSZ anode from long-term operation of anode-supported SOFCs

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The performance characteristics of high-performance Ni-YSZ (yttria-stabilized zirconia) anode-supported solid oxide fuel cells (SOFCs) are examined under typical fuel cell operating conditions over a period of ∼3000 h when hydrogen contaminated with different concentrations of H_2S was used as the fuel. Analyses reveal some new insights into the sulfur poisoning behavior of a Ni-YSZ anode. First, an initial drop in power output upon exposure to H_2S-contaminated fuels is more dramatic in an anode-supported cell (with small cell resistance) than in electrolyte-supported cell (with large cell resistance), creating an illusion that a high-performance cell appears to be less sulfur tolerant than a low-performance cell. Second, the transition time for this rapid performance drop to cease is much longer for an anode-supported cell (with a thicker anode) than an electrolyte-supported cell (with a thinner anode). Third, the degree of sulfur poisoning (or the cell resistance increase due to sulfur poisoning) diminishes with operating cell current density, suggesting that the water produced at the active sites on anode surface from electro-oxidation of hydrogen (or oxygen ions) may promote the oxidation and removal of adsorbed sulfur. This effect becomes less pronounced at higher concentration of H_2S, but still significant at ∼1 ppm of H_2S. Fourth, the subsequent slow degradation in performance after the rapid performance drop upon initial exposure to H_2S can be avoided, indicating that the previously reported slow degradation is unlikely the inherent behavior of a Ni-YSZ anode, but associated with other complications. This further implies that sulfur poisoning may be reversible and the performance drop could be fully recovered when the fuel is switched back to clean hydrogen.

1. Introduction

One of the unique advantages of solid oxide fuel cells (SOFCs) over other types of fuel cells is their potential for direct (or through internal reforming) and cost-effective utilization of a wide variety of fuels, including hydrocarbons and gasified coal or different types of ample carbonaceous solids.[1–5] Unfortunately, many low-cost, readily available fuels contain sulfur to some extent. For example, sulfur concentration in pipeline natural gas is usually several ppm by volume while jet fuels, even when desulfurized using cost effective processes, still contain ∼10 ppm of sulfur species.[6,7] In reforming, the sulfur compounds are converted to gaseous hydrogen sulfide (H_2S), which readily deactivates Ni-yttria-stabilized zirconia (Ni-YSZ) anodes of existing SOFCs, leading to dramatic reduction in cell performance and even operational life.

While the detrimental effect of hydrogen sulfide in the fuel stream for SOFCs is well known, a complete understanding of the sulfur poisoning behavior of a Ni-YSZ anode in a high-performance anode-supported SOFC under typical

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Broader context

Solid oxide fuel cells (SOFCs) offer great prospects for the most efficient utilization of a wide variety of low-cost fuels such as hydrocarbons, coal gas, and gasified biomass. However, the conventional Ni-YSZ anode is highly susceptible to deactivation by sulfur contaminants. In this work, we report some new insights into the poisoning behavior of the state-of-the-art anode-supported SOFCs tested in H_2S-contaminated H_2 for ∼3000 h. An initial drop of significant magnitude in power output upon exposure to H_2S prevails in all cells with Ni-YSZ anodes. The degree of sulfur poisoning diminishes with increasing current density, more so at lower H_2S concentration. After the initial drop in power output, nevertheless, the performance of Ni-YSZ anodes are stable under the testing conditions for over 3000 h, suggesting that the previously reported slow degradation after the initial H_2S poisoning can be avoided. Understanding the poisoning behaviors is important to the development of new and potentially simpler solutions towards sulfur tolerance, thereby advancing the possibility for cost-effective conversion of readily available fuels to electricity with minimum emissions. For example, SOFCs powered by gasified coal are twice as efficient as today's coal-fired power plants, potentially reducing CO_2 emission by 50%.

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operating conditions is yet to be determined. Many previous studies indicate that sulfur poisoning behavior is characterized by two stages.[8–11] Since bulk sulfide would not be formed under the operating conditions,[12,13] it is well accepted that the rapid drop in power output upon initial exposure to several ppm H_2S is caused by the dissociative adsorption of sulfur species around three-phase boundaries (the active sites for electrochemical oxidation of the fuel), leading to an increase in anodic polarization. However, the mechanism of the slow degradation in performance during continuous exposure to H_2S over a long period of time (hundreds to even thousands of hours) as observed in some studies[9–11] is still not clear. One hypothesis is that the continuous sulfur exposure leads to surface reconstruction of nickel.[9] Another hypothesis is that H_2S results in migration of nickel in the anode, thereby degrading the distribution of the percolating Ni phase in the anode.[10]

Furthermore, the relevant reports are primarily based on the investigations of electrolyte-supported cells in a short period of time ($\sim$100 h).[8–11,14] Because of the large electrical resistance of the electrolyte, the drops in performance (current density or voltage) due to sulfur poisoning of an electrolyte-supported cell (typically with electrolyte thicker than 300 μm) are much smaller than those for an anode-supported cell (typically with electrolyte of $\sim$10 μm thick). In other words, the electrolyte-supported cell "appears" to be more sulfur tolerant than the anode-supported cell. This is because the power output of an electrolyte-supported cell is dominated by the resistance of the electrolyte; the dramatic change in anodic polarization resistance due to sulfur poisoning has little effect on the cell power output. In addition, the discrepancies in the microstructure and thickness of the Ni-YSZ anodes as well as in the anode/electrolyte interfaces for the two kinds of cells may also contribute to their different electrochemical behaviors in H_2S. Moreover, operation of cells in H_2S-contaminated fuels for a short period of time ($\sim$100 h) may be inadequate to the examination of the subsequent degradation with much slower deterioration rate (the so-called second-stage poisoning). Thus, it is essential to study the poisoning behavior of high-performance anode-supported cells in H_2S-containing fuels for a longer period of operation.

Here, we report our new insights into the poisoning behavior of the state-of-the-art anode-supported SOFCs fueled with H_2S contaminated hydrogen for up to $\sim$3000 h under different operating conditions. Compared with electrolyte-supported cells, these anode-supported cells show more severe drop in power output upon exposure to sulfur-containing fuels over a longer period of transition time. It was also found that the subsequent slow degradation in performance can be eliminated when a new sealant was used.

2.   Experimental

The diameter of the anode and electrolyte of the anode-supported cells (from Delphi) was 9 mm while the cathode was smaller, with an active area of 0.28 cm^2. The thicknesses of the Ni-YSZ anode, the YSZ electrolyte, and the LSCF cathode layers were $\sim$500, $\sim$10, and $\sim$30 μm, respectively. To make electrical connection, two Pt lead wires were bonded to the current collector on both the anode and the cathode. To seal a button-cell on the test fixture, a Ceramabond® 552VFG

sealant (Aremco, abbreviated as C552), which has been widely used in single cell testing, was applied to the edge of the cell. The composition of C552 glass, as determined using an Inductively Coupled Plasma–Optical Emission Spectrometer (ICP-OES), can be specified as SiO_2-Al_2O_3-MgO-CaO with mole ratio of 70 : 36 : 1 : 1. For direct comparison, a new sealant developed by Pacific Northwest National Laboratory in the US, G18 glass (BaO-CaO-Al_2O_3-SiO_2-B_2O_3 with mole ratio of 35 : 15 : 5 : 35 : 10[15,16]), was also used in this study. After cell assembling/sealing, all cells were dried in air at room temperature for $\sim$24 h. They were subsequently inserted into a multi-cell testing furnace capable of simultaneously testing 12 button cells under various electrochemical (e.g., potentiostatic, galvanostatic, or potentiodynamic) conditions at a temperature up to 1050 °C. The gas distribution system can deliver gas mixtures from humidified inert gas, H_2, and H_2 with different concentrations of H_2S. It can supply up to four different fuel mixtures with H_2S concentration varying from 0.05 to 100 ppm by volume. For a typical 3,000 h long-term testing, all cells were first operated in 50%H_2−48.5%N_2−1.5%H_2O for $\sim$300 h, before the fuel was switched to H_2S-contaminated H_2. The flow rate of H_2 was $\sim$7.5 mL/min for each cell. The fuel utilization was $\sim$11% at a current density of 400 mA/cm^2.

While anodic overpotential is often directly measured in a well-designed electrolyte-supported cell to characterize the sulfur poisoning effect,[14] it is impossible to do the same in an anode-supported cell with electrolyte thickness of $\sim$10 μm.[17] Any attempts to do 3-electrode measurements on such a cell could result in substantial errors in estimation of half-cell overpotential. Accordingly, the relative changes in cell voltage or current density were measured to examine indirectly the electrochemical behavior of the Ni-YSZ anode in H_2S-containing fuels.[8–11] The cell voltages and current densities were recorded continuously using an Arbin fuel cell testing system (12 channels). During the test, impedance spectra as well as I–V curves were also collected periodically for some cells. Impedances were measured in the frequency range from 0.01 Hz to 100 K Hz with an EG&G Potentiostat/Galvanostat (Model 273A) and lock-in amplifier (5210).

3.   Results and discussion

3.1.   High-performance anode-supported SOFCs

Anode-supported structures are widely employed in the state-of-the-art SOFCs because of the high power output. Fig. 1 shows the current–voltage characteristics and the corresponding power densities at 750 °C for a typical YSZ-based anode-supported fuel cell using G18 sealant. This cell produced a peak power density of 844 mW/cm^2 at 750 °C when humidified hydrogen (50% H_2, 1.5% H_2O, and 48.5% N_2) was used as the fuel and ambient air as the oxidant. The power outputs of this anode-supported cell (with $\sim$10 μm thick YSZ electrolyte) is much higher than those of a typical electrolyte-supported cell (with $\sim$300 μm thick YSZ electrolyte) due primarily to the dramatic reduction in electrolyte thickness and the superior anode-electrolyte interface resulted from co-firing of the Ni-YSZ anode and the YSZ electrolyte. Meanwhile, the OCV (1.06 V at 750 °C) of this anode supported cell is as high as that of an electrolyte-supported cell, indicating
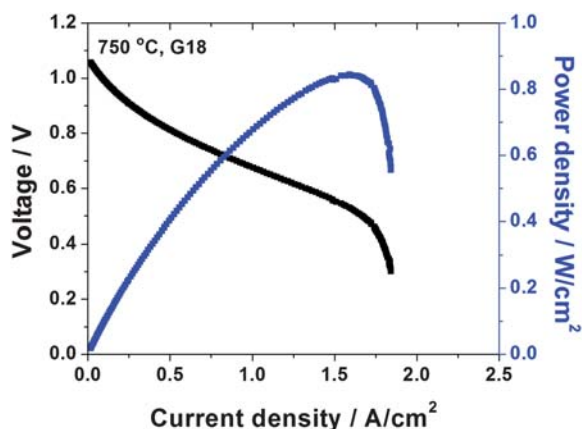
Fig. 1 Typical cell voltages and power densities as a function of current density at 750 °C for the anode-supported fuel cells in this study using G18 sealants when humidified hydrogen (50% H_2, 1.5% H_2O, and 48.5% N_2) was used as fuel and ambient air as oxidant.

that the thin electrolyte is sufficiently dense. These anode-supported cells are extremely stable; they were operated in H_2 for up to ~3500 h with negligible degradation in performance.

Fig. 2 shows the terminal voltages for cells with G18 sealant before and after the fuel was switched from clean hydrogen to hydrogen containing 0.8 and 10 ppm H_2S. As expected, the cell terminal voltages experienced rapid drops upon initial exposure to H_2S in all cases. The cell voltages further decreased when the concentration of H_2S was changed from 0.8 ppm to 1.1 ppm, indicating that Ni-YSZ anode is very sensitive to minuscule concentration of H_2S. More importantly, unlike what was observed in previous studies,[9,10] there was no observable subsequent degradation in performance (*i.e.*, the so-called second-stage poisoning) in these cells up to ~3000 h after the rapid drop in performance due to the initial exposure to H_2S.

3.2 The initial drop in performance due to sulfur poisoning

To examine how operating conditions influence the degree of initial degradation in performance due to sulfur poisoning, we recorded the cell voltage drops as a function of H_2S concentration and current density. Fig. 3 shows some typical cell voltage drops of test cells upon initial exposure to fuels containing H_2S. While there were some small differences in performance between the cells using the C552 sealant and those using the G18 sealant (due probably to slight variations in cells and H_2S concentration), the general trends are similar for both anode-supported cells, indicating that an initial drop of significant magnitude in power output is unavoidable for a Ni-YSZ anode. In contrast, the magnitude of this initial performance drop appears less dramatic in an electrolyte-supported cell (with large cell resistance) than an anode-supported cell (with small cell resistance). For example, a terminal voltage drop of ~5.1% and ~7.2% were observed in electrolyte-supported cells under a constant current density of 241 mA/cm² as the fuel was switched from clean hydrogen to hydrogen containing ~1 and 10 ppm H_2S, respectively; but the voltage drops in an anode-supported cell were ~8% and ~11% under similar conditions, as seen in Fig. 3. This is expected partially because the anode polarization resistance
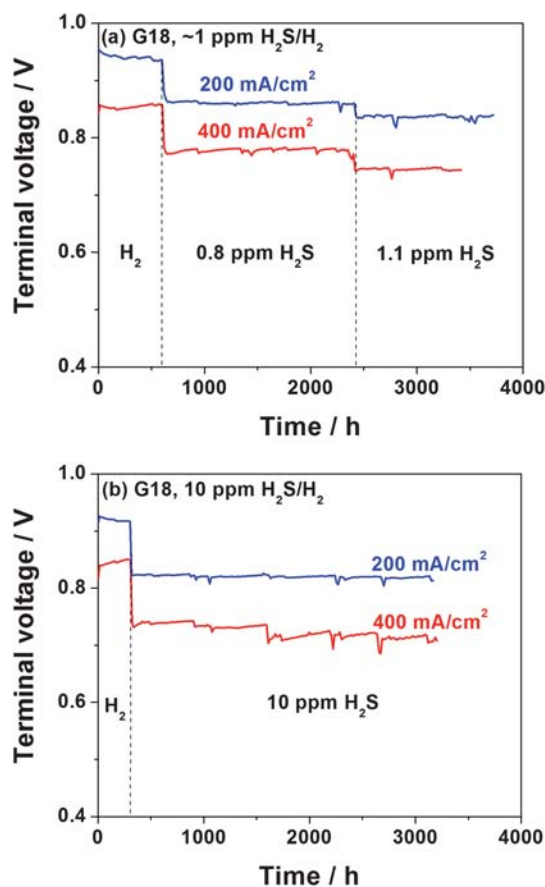
Fig. 2 (a) Performances of the test cells using G18 sealant operated at 750 °C at a constant current density of 200 and 400 mA/cm² in hydrogen for the first ~600 h and then in hydrogen with 0.8 ppm H_2S. The concentration of H_2S in the hydrogen was changed from 0.8 ppm to 1.1 ppm at ~2400 h (change of gas cylinder); the effect of H_2S concentration is clearly seen. (b) Performances of the test cells (with G18 sealant) operated at 750 °C at a constant current density of 200 and 400 mA/cm² in hydrogen for the first ~300 h and then in hydrogen with 10 ppm H_2S.

constitutes a smaller portion of the total resistance for an electrolyte-supported cell (with thicker electrolyte) than for an anode-supported cell (with much thinner electrolyte). The
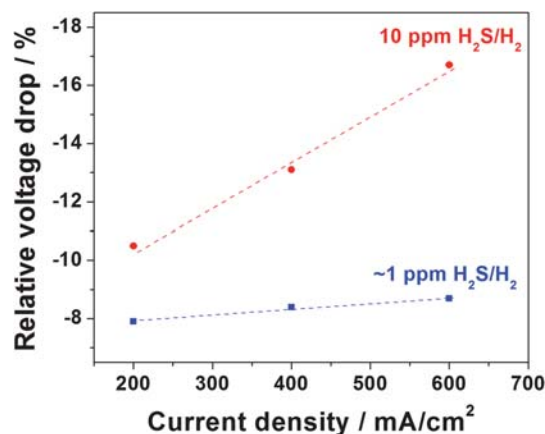
Fig. 3 Typical drop in cell voltages for test cells using G18 sealant upon initial exposure to H_2 containing ~1 and 10 ppm H_2S at 750 °C.

discrepancy in anode structures for electrolyte- and anode-supported cells may also contribute to the different degrees of degradation in performances.

In general, the immediate drop in cell performance upon exposure to H_2S increases with the concentration of H_2S, regardless of the types of cells or electrochemical testing conditions.

However, the rates of poisoning (or degradation in performance) are much slower in anode-supported cells (with much thicker Ni-YSZ anodes) than in electrolyte-supported cells (with much thinner Ni-YSZ anodes). For instance, anode-supported cells usually took ~32 and ~15 h to reach relatively steady state in hydrogen containing ~1 and 10 ppm H_2S, respectively. In contrast, it took only a few minutes for electrolyte-supported cells to reach a steady state.[8,10] This seems to be consistent with the mechanism of sulfur poisoning. Since the sulfur levels used in the present study will not lead to formation of bulk sulfides,[12,13] the sulfur poisoning is most likely caused by the strong adsorption of the elemental sulfur on Ni surface and the three-phase boundaries (TPB) between Ni, electrolyte, and the fuel. Sulfur would then block the active site for fuel oxidation in a Ni-YSZ anode and increase the polarization resistance.[13,18] Thus, for an anode-supported cell with a thick anode (~500 μm), it takes longer for all Ni surfaces to be saturated with sulfur. The adsorption of sulfur on Ni may propagate from the outer layer to the inner active layer of anode. In contrast, for an electrolyte-supported cell with a thin anode (~30 μm), it takes less time for the Ni surfaces to be saturated with sulfur.

Similar to a previous study on electrolyte-supported cells,[8] the relative increase in cell resistance for an anode-supported cell operated under galvanostatic (constant current) mode can be expressed as

$$\Delta R_{cell\_r} = \frac{\Delta R_{cell}}{R_{cell\_0}} = \Delta P_r \frac{U_0}{E_0 - U_0}$$

where E_0 is the open circuit voltage, U_0 is the cell terminal voltage before exposure to H_2S, and ΔP_r is the relative drop in cell power output (or cell voltage). Thus, the relative increase in cell resistance for anode-supported cells can be calculated from the relative cell voltage drop, as shown in Fig. 4. An anode-supported cell (with thin electrolyte) displayed a larger relative increase in cell resistances than an electrolyte-supported cell (with thick electrolyte).[8] In addition, the relative increase in cell resistances is smaller when the cell current is higher, indicating that the water produced at the active sites on anode surface from fuel oxidation may promote the oxidation and removal of adsorbed sulfur.[1]

Furthermore, it seems that the degree of sulfur poisoning (or the relative drop in voltage) was more sensitive to cell current density when the H_2S concentration was higher, as seen from the slopes of the relative voltage drop *versus* the cell current density shown in Fig. 3. For example, the observed relative drop in cell voltage was less sensitive to cell operating current density when the concentration of H_2S was ~1 ppm: −7.9% at 200 mA/cm², −8.4% at 400 mA/cm², and −8.7% at 600 mA/cm². In contrast, the relative drop in cell voltage increased with operating current density when the concentration of H_2S was 10 ppm: −10.5% at 200 mA/cm², −13.1% at 400 mA/cm², and −16.7% at 600 mA/cm². Because cell resistance is inversely proportional to
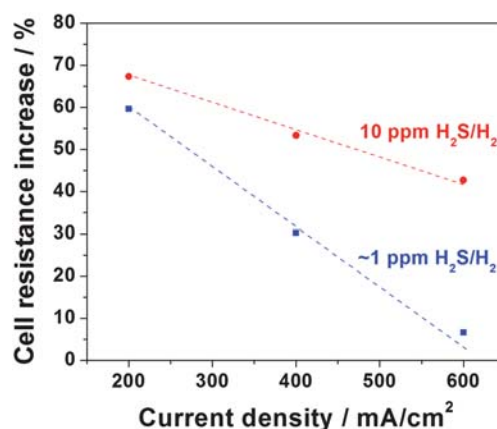
Fig. 4 Calculated relative cell resistance increase as a function of cell current density upon exposure to hydrogen containing ~1 and 10 ppm H_2S at 750 °C under the galvanostatic conditions for the test cells (with G18 sealant).

cell performance, consequently, the relative cell resistance change due to sulfur poisoning would change more dramatically with cell current density when the H_2S concentration was ~1 ppm than 10 ppm, as seen from the slopes of the relative cell resistance change *versus* cell current density shown in Fig. 4. This can be explained as follows: at lower H_2S concentration, less reaction sites in the Ni-YSZ anode are occupied by adsorbed sulfur. Under the same current density, the percentage of adsorbed sulfur atoms removed by oxidation is more significant in ~1 ppm H_2S than that in 10 ppm H_2S. In other words, the water-mediated oxidation and removal of adsorbed sulfur becomes less effective at higher concentration of H_2S, but still considerable at ~1 ppm of H_2S.

Fig. 5 shows several typical impedance spectra for cells before and after initial exposure to ~1 ppm H_2S at different operating current densities. Clearly, the increase in cell polarization resistances after exposure to H_2S (or the degree of sulfur poisoning) diminished with the increase in current density. This is consistent with the trend of calculated relative increase in cell resistance shown in Fig. 4 for the case with hydrogen containing ~1 ppm H_2S, indicating that the effect of sulfur removal by oxygen ion or water produced at the active sites is more pronounced when the concentration of H_2S is relatively low.

3.3 The subsequent degradation after the initial exposure to H_2S

Exposure of cells to H_2S-contaminated fuels for an extended period of time (up to ~3000 h) was carried out to investigate the subsequent behavior of Ni-YSZ anodes after the initial drop in performance. Shown in Fig. 6 (a) and (b) are normalized changes in cell voltage (in percentage) after the large, initial drop in cell voltage due to exposure to hydrogen containing ~1 ppm H_2S for cells sealed with C552 and G18 sealants, respectively. Obviously, the subsequent degradation in performances for all the cells were relatively small when the concentration of H_2S was ~1 ppm, although there was indeed a gradual decline in terminal voltage for the cell with C552 sealant at a current density of 200 mA/cm². It is worthy of note that a voltage step at ~500 and ~1800 h
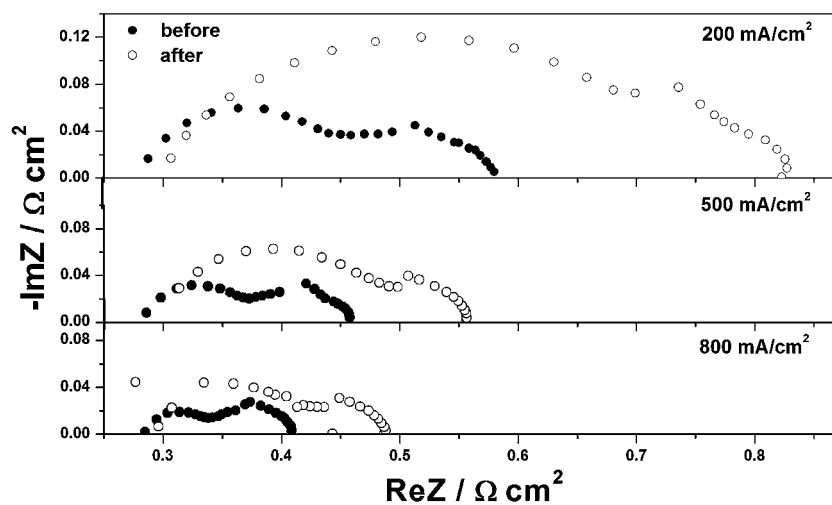
Fig. 5 Impedance spectra of anode-supported cells (with C552 sealant) operated at a constant current density of 200, 500, and 800 mA/cm^2 before and after ~1 ppm H$_2$S was introduced into the fuel at 750 °C.
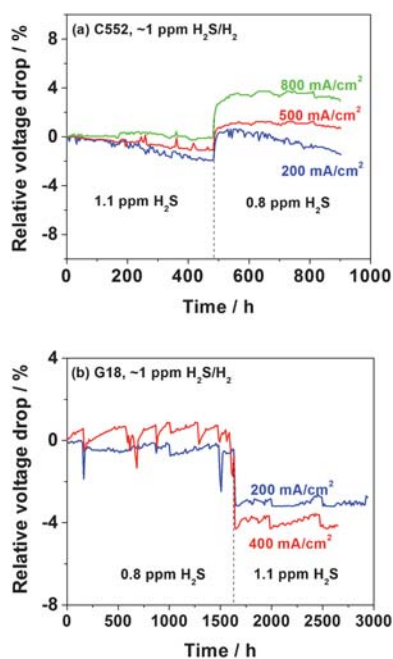

voltage were −9.6%, −14.2% and −15.6% at 200, 500 and 800 mA/cm^2, respectively. The accumulated relative cell voltage drop over the period of testing was as much as the initial drop in performance upon initial exposure to H$_2$S. It is troublesome to note that this degradation continued even after 1000 h of exposure to H$_2$S, suggesting the severity of the degradation effect. This subsequent degradation was also observed by others[9–11] and attributed to continuous sulfur poisoning of anode. In contrast, when G18 sealant was used in the anode-supported cells, there
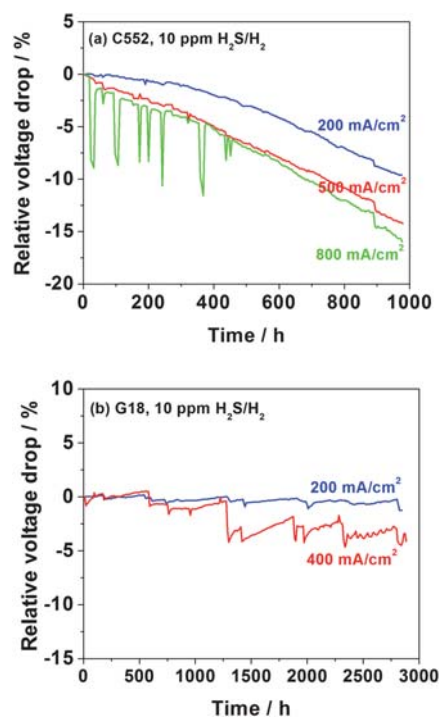

Fig. 6 Normalized voltage changes (in percentage) after the large initial voltage drop due to switching from clean H$_2$ to H$_2$ containing ~1 ppm H$_2$S for cells with (a) C552 sealant, (b) G18 sealant. These variations in cell voltage correspond to additional degradation under a steady operating condition. Note: H$_2$S gas cylinders were changed at ~500 and ~1600 h for (a) and (b), respectively.

occurred for cells with C552 and G18 sealants, respectively, which was caused by replacement of H$_2$S gas cylinders with different concentrations of H$_2$S (0.8 ppm and 1.1 ppm). These slight voltage changes further suggest that Ni-YSZ anode is susceptible to sulfur poisoning even under minuscule concentration of H$_2$S.

When the concentration of H$_2$S was increased to 10 ppm, significant degradation in performance was observed for the cells with C552 sealant under constant current densities, as shown in Fig. 7a. After ~1000 h operation, the relative drops in cell

Fig. 7 Normalized voltage changes (in percentage) after the large initial voltage drop due to switching from clean H$_2$ to H$_2$ containing 10 ppm H$_2$S for cells with (a) C552 sealant (b) G18 sealant. These voltage drops correspond to a continued degradation in performance.

was little observable degradation in performance under the steady testing conditions, as shown in Fig. 7b (the fluctuations in cell voltage are believed to be originated primarily from unstable flow of the H_2-H_2S-N_2 fuel mixtures). For cells run at 200 and 400 mA/cm^2, the degradations were only $\sim$0.2% and $\sim$2.2% after $\sim$3000 h operation, respectively. Therefore, the continuous degradation in performance is most likely not inherent to Ni-YSZ and can be eliminated in properly designed experiments.

There are two possibilities which might cause the continuous degradation in cells sealed by C552 sealant. First, segregation of impurities from glass sealant onto YSZ electrolyte is well known to take place.[19] It is possible that the diffusion of detrimental elements in C552 sealant could lead to continuous poisoning of the anode when the sealant interacts unfavorably with H_2S, while the G18 sealant might prevent such undesirable diffusion and/or interactions. Second, the leakage of H_2S in the anode through the C522 sealant might also cause the performance degradation of cathode. It has been reported that sulfur species could poison the cathode performance.[20] In comparison, the G18 sealant demonstrated excellent chemical and thermal compatibilities with other fuel cell components,[15] thereby it might inhibit the performance drop by preventing the leakage of sulfur species through the sealant. Further experiments are required to clarify this point.

4. Conclusions

In conclusion, some new insights have been revealed from long-term ($\sim$3000 h) testing of the-state-of-the-art, high-performance, anode-supported SOFCs. An inevitable drop in power output upon exposure to small amount of H_2S appears more dramatic in a high-performance anode-supported cell than in a low-performance electrolyte-supported cell, thus creating an illusion that a low-performance cell is more sulfur tolerant than a high performance cell. Also, the time it takes for the cell to reach a steady state upon exposure to H_2S is much longer for an anode-supported cell than for an electrolyte-supported cell, mostly because the Ni-YSZ anode in an anode-supported cell is much thicker than that in an electrolyte-supported cell. Impedance spectroscopy and equivalent circuit analysis suggest that the degree of sulfur poisoning (or the increase in cell resistance due to sulfur poisoning) can be alleviated by the water produced at the active sites from electro-oxidation of hydrogen; this effect is more pronounced at lower concentration of H_2S. Furthermore, the previously observed continuous degradation in performance after initial exposure to H_2S may be associated with other possible complications, including contamination of Ni-YSZ anode by the sealant or sulfur poisoning of cathode due to leaking through the sealant. With proper sealant (*e.g.*, G18 glass), stable power output (without continuous degradation in performance) has been demonstrated by anode-supported cells fueled with hydrogen containing up to $\sim$10 ppm H_2S for $\sim$3000 h operation.

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