

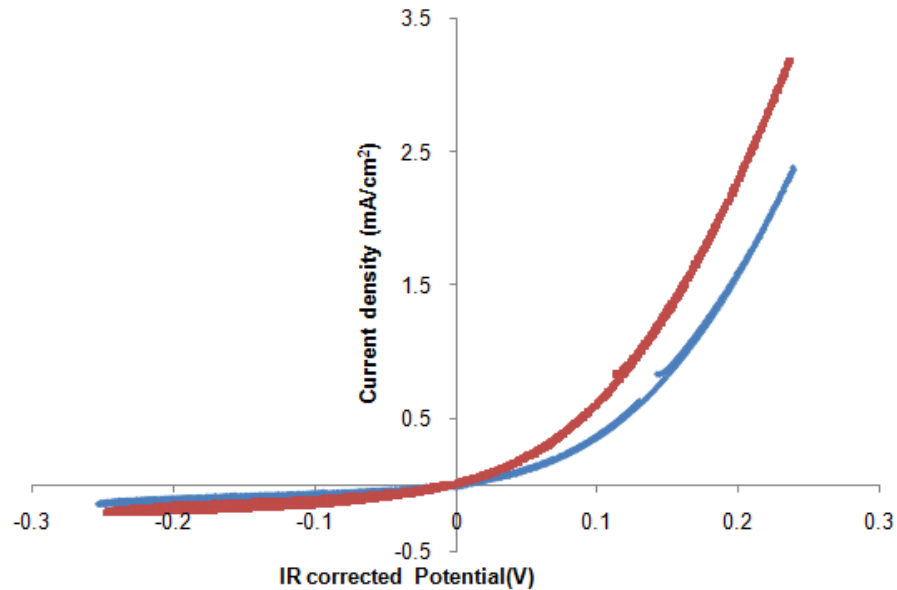
## Supporting Information

### **Activation of H<sub>2</sub> Oxidation at Sulphur-Exposed Ni Surfaces Under Low Temperature SOFC Conditions**

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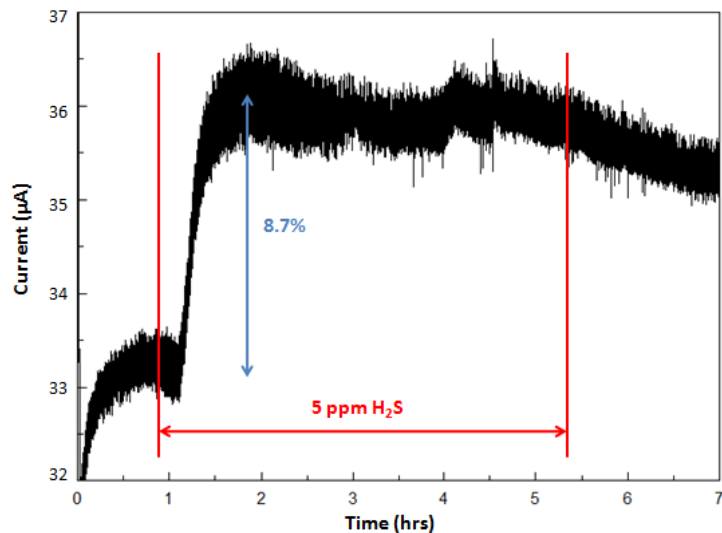
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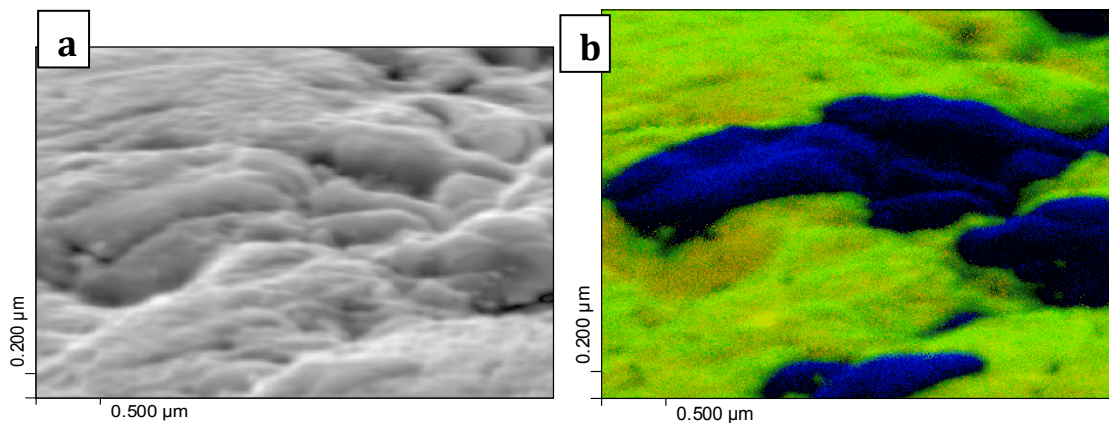
**Fig. S1 – Cyclic voltammetry response of Ni-YSZ anode with/without H<sub>2</sub>S.** Cyclic voltammetry ( $\pm 250$  mV at 5 mV/s) in humidified H<sub>2</sub> (blue) and after the addition of 5 ppm H<sub>2</sub>S (red), all for cell PR4 at 500 °C.

As shown in Fig. S1, higher current densities were observed throughout the full scanned potential range ( $\pm 250$  mV) when humidified 5 ppm H<sub>2</sub>S was added to the 95:5 H<sub>2</sub>:N<sub>2</sub> gas mixture, compared to the cyclic voltammetry (CV) obtained in the absence of H<sub>2</sub>S, all at 500 °C. This shows that, in the presence of ppm levels of H<sub>2</sub>S, the catalytic activity of the hydrogen oxidation reaction (HOR) on Ni-YSZ is enhanced. The anodic transfer coefficient ( $\alpha$ ) is close to 1 in both cases, with the extrapolated exchange current density increased by approximately a factor of two for the CV obtained in the presence of 5 ppm H<sub>2</sub>S.



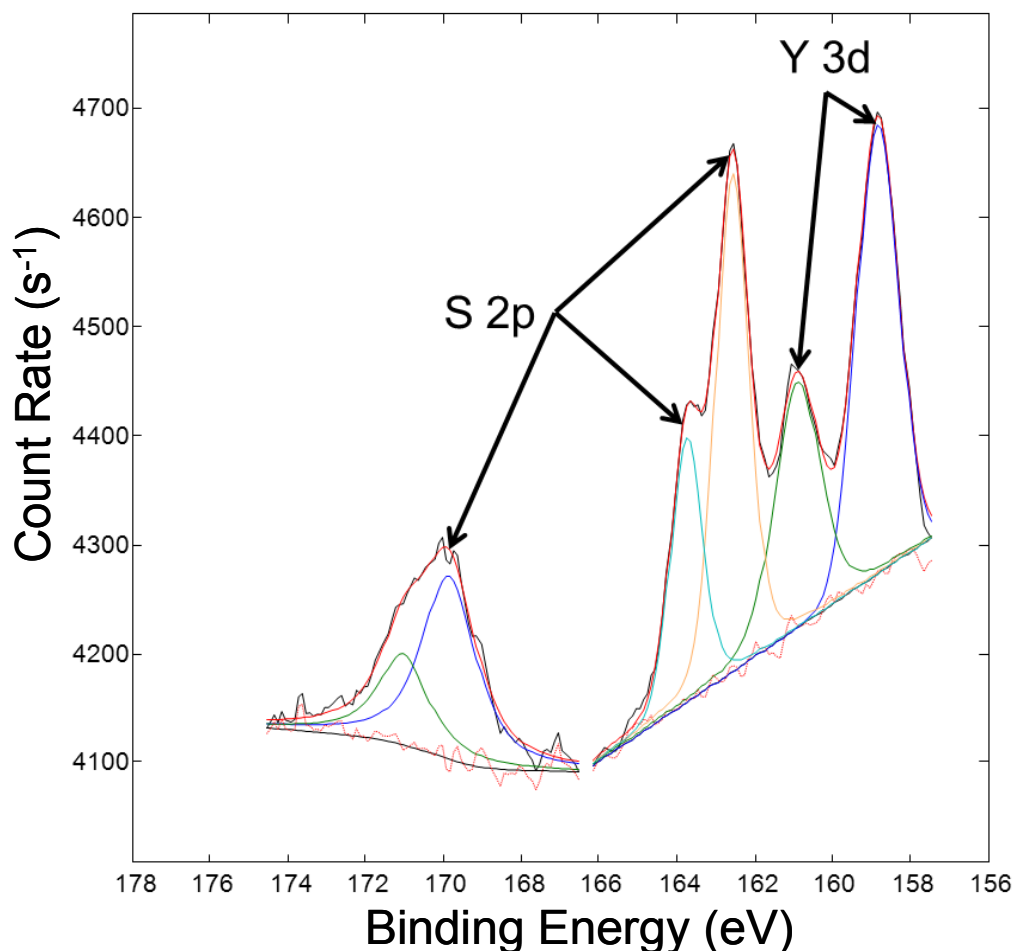
**Fig. S2 – Response of 2-electrode FC1 full cell to H<sub>2</sub>S exposure and removal.** i/t transients seen during introduction and removal of 5 ppm H<sub>2</sub>S in humidified H<sub>2</sub> at a 0.1 V vs. full cell OCP, at 500 °C, 5 ppm H<sub>2</sub>S in humidified H<sub>2</sub> for full cell (FC1).

As seen in Fig S2, the 2-electrode electrolyte-supported full cell (FC1) test showed a ca. 9% increase in current when 5 ppm H<sub>2</sub>S in humidified H<sub>2</sub> was introduced to the anode at 500 °C under a constant potential (0.1 V vs. full cell OCP). This demonstrates that both full cells and half cells exhibit the unexpected activation of the H<sub>2</sub> oxidation reaction by exposure to low levels of H<sub>2</sub>S at relatively low operating temperatures, in this case being 500 °C.



**Fig. S3: Auger Electron Spectroscopy (AES) analysis of the Ni-YSZ cermet after exposure to 5 ppm H<sub>2</sub>S.** AES analysis of Ni-YSZ sample exposed to 5 ppm H<sub>2</sub>S at 500 °C for 72 hrs and then rapidly cooled to room temperature. (a) SEM image and (b) the combined Ni (green), S (yellow) and Zr (blue) elemental maps.

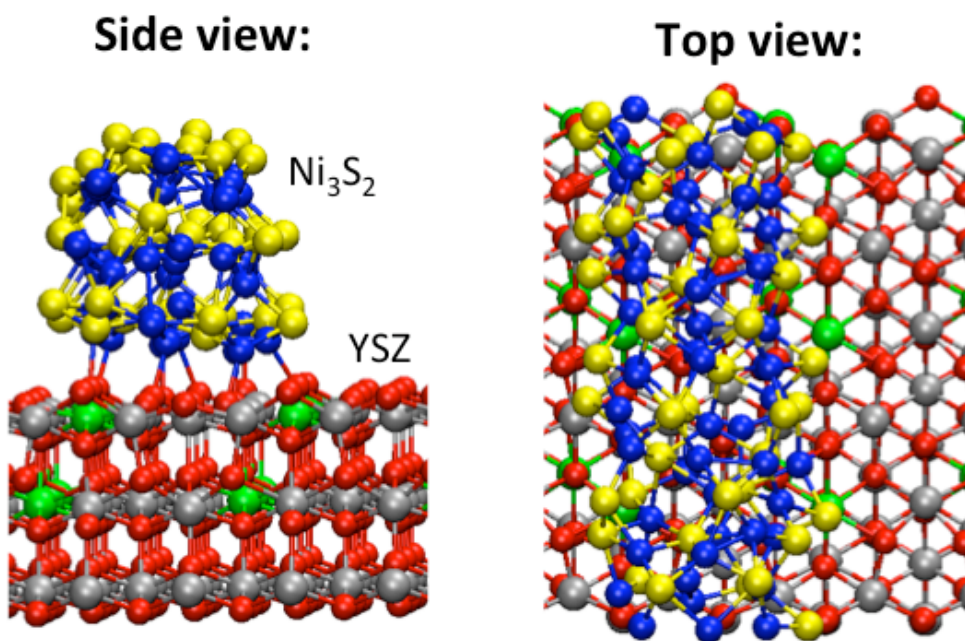
AES mapping, shown in Fig. S3, indicates that there is sulphur present on the Ni particles, consistent with the results from XPS analysis (Fig. S4), with no evidence seen for any sulphur on the YSZ phase.



**Fig. S4 – XPS analysis of Ni-YSZ anode layer after exposure to H<sub>2</sub>S at 500 °C.** XPS analysis of the Ni-YSZ anode layer surface (SS8, after removal of porous Ni current collector) following electrochemical studies at 500 °C and at an anode overpotential of 250 mV in 5 ppm H<sub>2</sub>S in humidified H<sub>2</sub> (half-cell cooled down in H<sub>2</sub>). Deconvolution (156-175 eV) of the XPS pattern confirms the presence of sulphur (S 2p) as a sulphate (169.9 and 171.1 eV), sulphide (162.6 and 163.8 eV) and yttrium (Y 3d, from YSZ) on the sample surface.

The S 2p (3/2) X-ray photo-electron spectroscopy (XPS) peaks seen in Fig. S4 confirm the presence of sulphur (as a sulphide) and sulphate at the surface of the SS8 sample after electrochemical testing (last at 500 °C in H<sub>2</sub>). Analysis of the curve fits suggests that the sulphide:sulphate ratio is 6:4, whereas the total sulphur is only 3% of the

amount of Ni observed (with the signal coming from roughly 15-25 atomic layers into the Ni substrate). Sulphate has been reported as the surface sulphur species observed in at Ni surfaces exposed first to  $\text{H}_2\text{S}/\text{H}_2$  and then to air at room temperature during specimen transfer<sup>38</sup>, as well as at the surface of bulk  $\text{Ni}_3\text{S}_2$  after air exposure. Therefore, if the sulphate detected in Fig. S4 represents the sulphur species only in the outer monolayer of the sample, then the sulphide signal must arise from underlying layers, likely one or two monolayers in thickness, at most. Overall, the results in Fig. S3 suggest that a multiple layer of a Ni sulphide may be present under the conditions of our experiments.



**Figure S5.** The model of the  $\text{Ni}_3\text{S}_2/\text{YSZ}$  system ( $\text{Ni}_3\text{S}_2$  is exposed by the S2 termination to the gas phase). Ni and S atoms are denoted as yellow and blue balls, whereas Zr, Y and O atoms are denoted as grey, green and red balls, respectively. In the employed model of  $\text{Ni}_3\text{S}_2/\text{YSZ}$ , the  $\text{Ni}_3\text{S}_2$  is exposed to the gas phase by S2 termination. The model has been used for the study of hydrogen oxidation with the help of interfacial oxygen atoms of YSZ, bonded to  $\text{Ni}_3\text{S}_2$ . Using this model, the evaluation of vacancy formation energies (Fig. 7) and the electronic structure analysis (Fig. 8) have been performed.

**Table S1. Effect of anode overpotential on Ni-YSZ activity in 5 and 10 ppm H<sub>2</sub>S in humidified H<sub>2</sub> at 500 °C**

<b>Overpotential (mV)</b>	<b>% Change in Current</b>	
	<b>Sample SR2 (5 ppm H<sub>2</sub>S)</b>	<b>Sample PR2 (10 ppm H<sub>2</sub>S)</b>
-50	-	6.1
OCP	34	-
+50	30	9.7
+100	20	-
+250	22	-

To further understand the impact of polarization on the observed activation phenomena, overpotentials of -50 to +250 mV were applied at 500 °C for comparison (Fig. 2a, b), as well as over a range of anodic and cathodic overpotentials (Table S1). The two cells considered in Table S1 gave differing extents of activation during H<sub>2</sub>S exposure. While some variability is normally seen in the percentage activation between cells, the H<sub>2</sub>S concentrations also differed in these two experiments (10 ppm H<sub>2</sub>S for PR2 and 5 ppm H<sub>2</sub>S for SR2).



**Table S2 - Compiled Half-Cell H<sub>2</sub>S Exposure Results at 500 °C**

<b>Cell Name</b>	<b>Preparation method</b>	<b>H<sub>2</sub>S conc. (ppm)</b>	<b>Potential (mV)</b>	<b>ASRp (Ω cm<sup>2</sup>) (OCP at 800 °C)</b>	<b>% current increase at 500 °C</b>
SS1	NiO-YSZ was painted on both sides of a 0.5 mm thick dense 8YSZ (Ceraflex) electrolyte disc to form the WE, RE and CE.	5	+250	0.8	24, 12
SS8	NiO-YSZ was painted on both sides of a 0.5 mm thick dense 8YSZ (Ceraflex) electrolyte disc to form the WE, RE and CE.	5	+250	6	4
SS9	NiO-YSZ was painted on both sides of a 0.5 mm thick dense 8YSZ (Ceraflex) electrolyte disc to form the WE, RE and CE.	5	+250	5.2	17, 35, 28, 32
JS1	NiO was painted onto a 0.5 mm thick 3YSZ (Ceraflex) electrolyte disc to form the WE. The CE was formed by sputtering Pt onto the opposite of the electrolyte. No RE was used.	5	+250 (vs. OCP)	1900 (2 electrode)	0
SR1	NiO-YSZ was painted on both sides of a 1 mm thick dense 8YSZ (Tosoh) electrolyte disc to form the WE, RE and CE.	5	+50	0.2	11, 25
PR2	Ni was infiltrated into a porous YSZ scaffold, spray-coated on a 1 mm thick dense 8YSZ (Tosoh) electrolyte to form the WE. The NiO-YSZ RE and CE were painted on the opposite side of the dense YSZ disc.	10	-50, +50	1.3	19,10, 10, 6, -8
SR2	NiO-YSZ was painted on both sides of a 1 mm thick, dense 8YSZ (Tosoh) electrolyte to	5	+50, +100,	0.7	30, 20, 22

	form the WE, RE and CE.		+250		
SR3	NiO-YSZ was painted onto both sides of a 1 mm thick, dense 8YSZ (Tosoh) electrolyte to form the WE, RE and CE.	5	+250	0.8	14, 21, 35, 39, 38
PR3	Infiltration of Ni into porous YSZ scaffold, spray-coated on a 1 mm thick dense 8% mol YSZ (Tosoh) electrolyte to form the WE. The NiO-YSZ RE and CE were painted on the opposite side of the dense YSZ.	5	+250	1.1	22
FC1	NiO-YSZ was screen printed on a 1 mm thick dense 8% mol YSZ (Tosoh) electrolyte to form the anode. LSM-YSZ was screen printed at the opposite side to from the cathode	5	100 mV (vs. OCP)	4.1 (2 electrode)	9

Table S2 details the preparation methods employed in the manufacturing of each Ni-YSZ half-cell and full-cell exposed to low ppm H<sub>2</sub>S concentrations (in H<sub>2</sub>) at 500 °C. Additionally, the electrochemical activity of each working electrode (WE), as determined by electrochemical impedance spectroscopy (EIS) at the open circuit potential (OCP) at 800 °C in humidified H<sub>2</sub>, prior to exposure to H<sub>2</sub>S, is provided. Cells SS1, SS8 and SS9 consisted of painted Ni-YSZ anodes on a 0.5 mm thick 8 mol% YSZ disc (Ceraflex), while Cells SR1, SR2, and SR3 were made identically, but using 1 mm thick YSZ discs from Tosoh. The anode of FC1 (full-cell) is identical to the WE of these half-cells (SR-series). Cells PR2 and PR3 involved Ni-YSZ deposition on the 1 mm YSZ discs as used in the SR-series cells, but included Ni infiltrated into a pre-deposited porous YSZ scaffold. Cell JS1 was made by painting the Ni anode on a 0.5 mm thick 3 mol% yttria-

doped zirconia disc. Table S2 also details the % current change seen at each overpotential and H<sub>2</sub>S concentration (in 5 and 10 ppm H<sub>2</sub>S) at 500 °C, where multiple entries indicates replicate exposures to H<sub>2</sub>S.