



Redox dynamics of sulphur with Ni/GDC anode during SOFC operation at mid- and low-range temperatures: An *operando* S K-edge XANES study

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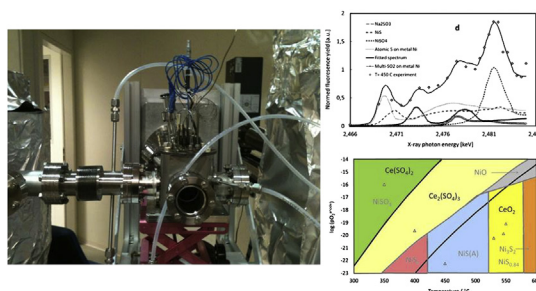
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HIGHLIGHTS

- An *operando* SOFC anode S-poisoning XAS experiment at 550 °C to 250 °C was performed.
- S K-edge XANES spectral information at Ni/GDC outer surface was collected.
- Intermediates with different sulphur oxidation states (6+, 4+, 0, 2−) were observed.
- Proportion of oxidation states changed as a function of temperature.
- Differences between TD calculations and XAS information were observed and discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

Sulphur poisoning of nickel-based solid oxide fuel cell (SOFC) anode catalysts is a well-documented shortcoming, but not yet fully understood. Here, a novel experiment is demonstrated to obtain spectroscopic information at *operando* conditions, in particular the molecular structure of sulphur species in the sulphur K-shell X-ray absorption near edge structure (XANES) region for a SOFC anode under realistic *operando* conditions, thus, with the flux of O^{2-} from cathode to anode. Cooling from $T = 550$ °C stepwise down to 250 °C, 5 ppm H_2S/H_2 reacting with Ni-gadolinium doped ceria (GDC) anode resulted in several sulphur species in different oxidation states (6+, 4+, 0, −2) and in amounts being at a minimum at high temperature. According to sulphur speciation analysis, the species could either relate to $-SO_4^{2-}$ or SO_3 (g), $-SO_3^{2-}$ or SO_2 (g), S_2 (g) or surface-adsorbed S atoms, and, Ni or Ce sulphides, respectively. The coexistence of different sulphur oxidation states as a function of temperature was analysed in the context of thermodynamic equilibrium calculations. Deviations between experimental results and calculations are most likely due to limitations in the speed of some intermediate oxidation steps as well as due to differences between stoichiometric CeO_2 used in calculations and partially reduced $Ce_{0.9}Gd_{0.1}O_{2-\delta}$.

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1. Introduction

Solid oxide fuel cells (SOFC) are promising energy converters with high electrical efficiency (from 45 to 65% based on lower heating value), fuel flexibility (can oxidise virtually any fuel from

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hydrogen to hydrocarbons up to carbon) and environmental friendliness. To reduce thermal degradation of system components, system costs and radiative heat transfer and to increase the speed of start-up and shut-down cycles, attempts have been made to decrease the operating temperature of SOFC from high temperature at $T = 900\text{ }^{\circ}\text{C}$ to intermediate temperature (IT) between $T = 500\text{--}750\text{ }^{\circ}\text{C}$ [1,2] and even to temperatures as low as $T = 350\text{ }^{\circ}\text{C}$ [3,4]. In addition to systems doped with noble metals such as Pt and Pd, until now the best electrocatalytic performance for IT-SOFC application was achieved with Ni-based catalysts. But Ni-based SOFC anode catalysts have some weaknesses when operating at intermediate temperature region such as coke formation (when operating on hydrocarbon fuels) and intolerance against some inorganic impurities [5–8]. Particular attention has been paid to sulphur poisoning, because most fuels contain sulphur and the complete removal of it is a costly process. The majority of sulphur poisoning studies have been carried out on Ni–YSZ (yttrium stabilized zirconia) SOFC anode at elevated working temperatures ($T = 700\text{--}900\text{ }^{\circ}\text{C}$) [9–18]. Only few studies examine sulphur poisoning of Ni-gadolinium doped ceria (GDC) anodes at intermediate temperature region [13,19–23] and the influence of chemical composition of ceramic phase on the poisoning process of Ni-cermet electrodes [24–26]. In good agreement with thermodynamics [9,20] and calculations based on density functional theory (DFT), [27] it has been demonstrated in several electrochemical studies that the extent of sulphur poisoning is a function of temperature, oxygen partial pressure and sulphur concentration as well as chemical nature of fuel and anode material [28–30]. Several studies have demonstrated that there is an initial reversible (or partially reversible) degradation step during the very first minutes when the anode is exposed to H_2S [9,12,31], followed by a slow, but continuous, non-reversible decrease of electrode performance [9,12,31]. First, rapid decrease of electrochemical performance is likely caused by adsorption of sulphur species at electrode and concomitant blocking of the so-called three-phase-boundary (TPB) for hydrogen oxidation [9,12]. There is some consensus about the first step of poisoning, but there are several significantly different if not controversial views about the second, slower step. Some authors are supporting the idea that slow degradation is caused by the formation of volatile Ni_xS_y phase, which causes restructuring and degradation of electrode structure [14,15,27]. Sasaki et al. proposed that blocking of hydrogen diffusion to the TPB caused by sulphur adsorption leads to the oxidation of Ni at TPB interface, causing depletion of active sites [9]. Slow decline in performance might also be caused by adsorption of sulphur on nickel surface grains which are more difficult to access, such as pores with bottlenecks [14], or, because of surface reconstruction or recrystallization of nickel grains from catalytically more active into catalytically less active crystallographic form [14], or, because of bulk phase diffusion of sulphur penetrating into Ni grains [14]. One possible reason of slow degradation could be the formation of $\text{Ce}_2\text{O}_2\text{S}$ as well as $\text{Ce}(\text{SO}_4)_2$ at relatively low H_2S concentrations in reaction with non-stoichiometric CeO_n ($n < 2$), because reduced or doped ceria exhibits significantly larger affinity for H_2S compared to CeO_2 used in theoretical calculations [20,32]. Thus, while there is some information about changes in electrical performance and degradation of electrode structure caused by sulphur at different conditions, there is no comprehensive explanation of the physico-chemical mechanisms which ultimately constitute sulphur poisoning.

1.1. Motivation and goal

Different studies have proposed and supported experimentally the idea that the release of sulphur from SOFC electrode might

take place through the oxidation of sulphur [10,18,22,23,29], which premises the presence of oxidised particles or intermediates at the anode surface. But, up to now, spectroscopic measurements with X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS), or, Raman microspectroscopy either obtain information from SOFC anode surface in the presence of H_2S , H_2 , and, possibly even heat, or *ex-situ* and under *post-mortem* conditions [14,15,22,33]. The molecular structure of sulphur compounds has been studied with sulphur K-shell edge X-ray absorption spectroscopy in various fields of application, particularly in relation to fossil fuels, such as sulphur in coal [34], sulphur in residual oil fly ash [35] and heterogeneous catalysis [36]. High temperature oxidation and reduction studies [34] and catalysis studies [36] have also been made recently with *in-situ* or *operando* sulphur XAS, for example. Sulphur as the ligand ion is also of interest in connection with metal ions [37] and could in future studies open up new opportunities for the understanding and quantification of electronic transport processes in SOFC anodes, where newly formed Ni–S compounds are subject to exchange interactions, in analogy to 3d metal oxides at SOFC cathodes, for example [38,39]. Latter would constitute an extension of sulphur XAS from molecular structure and chemical speciation of sulphur motifs towards electronic structure, valence band and electronic transport properties of aged SOFC anodes. However, so far, there are no spectroscopic experiments made *operando* under realistic SOFC anode operation conditions with oxide ion flux from cathode to anode or under electrochemical polarization of the anode. And, when it comes to study of the nickel–sulphur chemistry in detail, we realize that Ni K-edge XAS is less informative than S K-edge XAS [40], particularly because the sulphur K-edge spectra provide a very detailed picture about the molecular structure of the various sulphur species being formed on the anode during typical SOFC operation. Therefore, the present study demonstrates a novel powerful approach with sulphur-sensitive XAS under *operando* SOFC conditions for studying processes during sulphur poisoning of an IT-SOFC dedicated electrochemical element.

2. Experiments and methods

2.1. Preparation of SOFC single cell assembly

The SOFC single cell assemblies tested in this study were typical electrolyte (GDC) supported planar fuel cells with rectangular shape, which were made befitting with the XAS cell compartments. Supporting electrolyte pellets were made from $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}$ (GDC) powder with $S_{\text{BET}} = 19.9\text{ m}^2\text{ g}^{-1}$ (NexTech Materials) pressed at 20 MPa cm^{-2} and sintered at 1773 K for 10 h. The electrolyte supported cell configuration was used because of better compatibility with the gas sealing concept used. The anode layer was screen printed onto the sintered electrolyte pellet by applying commercial NiO–GDC ink (Fuel Cell Materials) through 200 mesh screen and fired at $1350\text{ }^{\circ}\text{C}$ for 3 h with heating and cooling rates of 2.5 K min^{-1} . The choice of sintering temperature was based on the results of our previous studies [41]. Cathode powder was prepared by nitrate solution thermal combustion method using $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (both from Aldrich, 99.9%) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98%, Riedel de Haën) as precursors for $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ cathode powder and glycine (99.9%, Sigma–Aldrich) as a reducing agent. A detailed description of the experimental procedure can be found from Lust et al. [41]. Finally the cathode paste was deposited onto a GDC electrolyte pellet by screen printing followed by 5 h sintering at $1110\text{ }^{\circ}\text{C}$ with heating and cooling rates of 2.5 K min^{-1} [42].

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