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In situ Raman and optical characterization of H_2S reaction with Ni-based anodes for SOFCs

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ABSTRACT

In this paper, we re-assess the use of Raman spectroscopy as an *in situ* method to monitor the sulfidation of SOFC (solid oxide fuel cell) anode-based materials. The technique allows studying *in situ* kinetics of the sulfidation of nickel at low temperature (up to 500 °C). A severe poisoning happens at 500 °C with a layer of Ni_3S_2 covering the entire pellet surface. At higher temperatures, optical microscopy helps to observe *in situ* the formation and growth of nickel sulfide crystals for the first time. The crystals' growths observed *in situ* strongly suggest the diffusion of nickel toward sulfide species. A reaction between H_2S and CGO was clearly observed at 750–790 °C.

1. Introduction

Hydrogen sulfide H_2S is known as a poison for solid oxide fuel cells (SOFCs) fueled with hydrocarbon sources: natural gas, LPG, syngas, biogas, … [1–6]. The effect of H_2S on Ni-based SOFC anodes has been widely studied. Thermodynamic calculations [6,7] allow the determination of the stability of nickel sulfides as a function of temperature, oxygen partial pressure (or $P(H_2)/P(H_2O)$), and H_2S content. At low H_2S concentrations (~10 ppm or less), sulfides are not observed [8–10] but changes in the Ni microstructure were determined by *ex situ* SEM and TEM examinations [11]. For higher (ca 100 ppm or more) H_2S concentrations, nickel sulfides are generally observed. Harris et al. have determined the 3D-structure of Ni-YSZ submitted to 100 ppm H_2S in H_2 at 800 °C and during cooling by X-ray nanotomography. They observed sulfide scales at the surface of most, but not all Ni grains [12]. Lussier et al. [13] have studied *ex situ* by XAS, XPS and XRD techniques the effect of 200–500 ppm H_2S in a H_2/N_2 atmosphere on Ni-yttria stabilized zirconia (YSZ) and Ni-cerium gadolinium oxide (CGO) anodes at 750 °C under an applied voltage of 0.5 V. The post mortem inhomogeneity of Ni distribution was attributed to the presence of a liquid Ni–S at 750 °C in spite of a theoretical instability of sulfide compounds at such temperature. Dong et al. [14] studied Ni-YSZ composites submitted to various H_2S contents at high temperatures by *ex situ* Raman spectroscopy and X-ray diffraction (XRD). Their *ex situ* results suggested that nickel sulfide was formed for tests operated with H_2 containing 100 ppm H_2S at 727 °C after 5 days although it is not thermodynamically stable. Cheng et al. [15] studied the reaction of Ni-YSZ cermets with 50 ppm H_2S at elevated temperatures and *in situ* during cooling from 570 °C. They showed that nickel sulfides were observed only during cooling below ~350 °C. These reports highlight the importance of *in situ* techniques to study the sulfidation process.

In recent years, *in situ* Raman spectroscopy has been applied successfully to study the adsorption of oxygen on Pt, the oxidation/reduction of Ni/NiO, the formation/disappearance of graphite and the redox state of the YSZ electrolyte [16–20]. For the study of Ni–H_2S reaction, Cheng et al. [18] showed that the Raman peaks of Ni_3S_2 disappear at temperatures higher than ~567 °C due to a phase transition. This fact clearly inhibits the real time detection of Ni_3S_2 (if any) by Raman spectroscopy at SOFC operating temperatures (700–1000 °C). It has therefore been impossible, up to now, to observe *in situ* the formation of nickel sulfides at temperatures higher than about 500 °C. Since there had been no attempt to use Raman spectroscopy at conditions in which nickel sulfides are stable at temperatures above 500 °C, it was necessary to re-assess the use of this technique as an *in situ* method to determine the presence of sulfides. Above 500 °C, as we will see, this is not the case therefore we observed the formation and growth of nickel sulfide crystals by optical microscopy, using the low (<500 °C) Raman spectra to confirm the nature of the observed features. At low temperatures (500 °C and below), Raman spectroscopy helps in understanding

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the kinetics of the sulfidation process. Moreover, the technique allows studying *in situ* samples during the heating process and is a useful tool for understanding thermal stability of nickel sulfides.

2. Experimental

2.1. Preparation of pellets

The reactions between H_2S and Ni or Ni-CGO were evaluated by passing a flow of H_2S-containing gas to Ni and Ni-CGO pellets at different temperatures from 200 °C to 800 °C. Ni pellets were prepared from NiO commercial powder (Alfa Aesar). The powder was pressed at 290 MPa into pellets 7.85 mm in diameter and 0.76 mm thick. The pellets were sintered in air at 800 °C for 3 h. The heating and cooling rate was 60 $°C\ min^{-1}$. NiO was then reduced in 3%H_2/Ar for 9 h at 715 °C.

Ni-CGO pellets were prepared from a mixture (supplied by CEA-Grenoble) of NiO (Alfa Aesar) and CGO (Praxair). The initial mixed powder was ball-milled for 20 h in ethanol with zirconia balls. The mixture was then put in an ultrasonic bath at 60 °C to remove ethanol. The resulting paste was finally dried at 75 °C. Pellets were obtained by uniaxial and isostatic pressure at 19.5 MPa. The pellets were then sintered in air at 715 °C for one hour with heating and cooling rate of 2 $°C\ min^{-1}$. NiO was finally reduced in a 3%H_2/Ar atmosphere at 715 °C for 3 h, time sufficient to make the pellet electronically conducting.

2.2. Investigation procedure by Raman spectroscopy and optical imagery

The sample, *i.e.* Ni or Ni-CGO pellet, was placed in a lab-made furnace allowing temperature and atmosphere control [21]. The desired atmosphere was obtained by mixing 3%H_2/Ar with 500 ppm H_2S/3%H_2/Ar from Air Liquide through mass flow-meters. The overall flow was of the order of 30 $cc\ min^{-1}$ in standard conditions of temperature and pressure. When an inert atmosphere was needed, Ar was used, with a residual oxygen content of about 10 ppm.

For measurements at a constant temperature, the sample was heated at 120 °C/min to the working temperature in 3%H_2/Ar. The heating rate was the maximum allowed by the apparatus, in order to avoid any possible reaction. After 30 min, H_2S (concentration of 300 or 500 ppm) was added to the flowing gas. Raman spectra and optical images were recorded at regular time intervals. At the end of the experiment, the gas was switched to Ar for 1 h to clean the system and prevent any sulfidation during the cooling. Then, the sample was cooled down to 50 °C (in about 50 min) in Ar.

Raman spectra were obtained with an InVia Renishaw Raman spectrometer. The excitation light was the green light of an Ar laser (514.53 nm). Raman spectra were collected in micro Raman configuration with a ×50 objective having a long working distance (8 mm). Spectra were generally collected using a line configuration of ca $45 \times 4\ \mu m^2$. The rejection of the Rayleigh line was done with dielectric filters and the Raman photons collected on a Peltier-cooled CCD.

Optical images were obtained with an Olympus Camedia C5050 optical camera working in manual mode to prevent any modification of the images due to changes in optical appearance. The camera was fixed on the ocular of the microscope used for Raman spectroscopy through an Olympus C3040-ADU adaptor. Images were taken at constant intervals using the Cam2com software.

3. Results

3.1. Raman spectra of Ni submitted to H_2S at various temperatures between 200 and 800 °C

Fig. 1 shows the Raman spectra measured at the Ni pellet surface at 200 °C as a function of time in 300 ppm H_2S/3%H_2/Ar atmosphere. Broad bands appear first at 0.8 h and resolve quickly at 6.6 h into band characteristic of Ni_3S_2 [18,22]. From 7.3 h, a new band appears at 367 cm^{-1} (arrow in Fig. 1). This band increases gradually while the Ni_3S_2 bands disappear. After 14.2 h, the spectra are characteristic of NiS. The $Ni_3S_2 \rightarrow NiS$ transformation involves an intermediate species which could be Ni_6S_5 according to Rosenqvist [23] or Ni_9S_8 according to Waldner and Pelton [24]. In any case, the similarity between the high

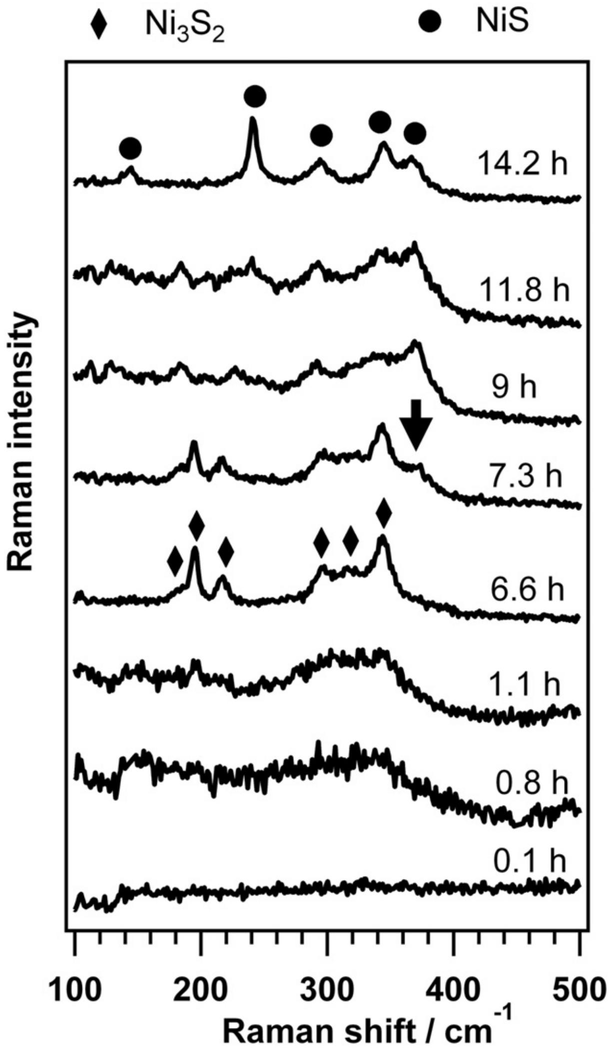

Fig. 1. Raman spectra recorded from Ni pellet surface exposed to flowing 300 ppm H_2S/3%H_2/Ar as a function of time at 200 °C.

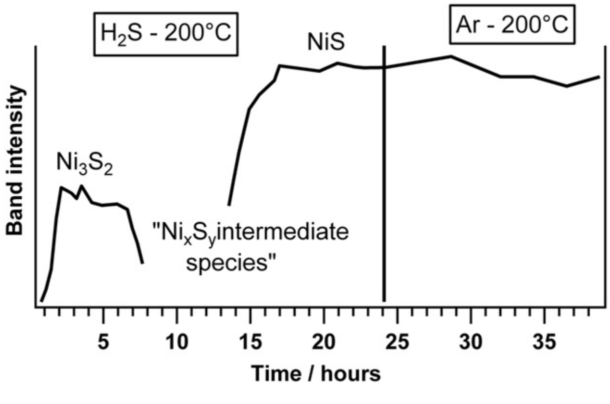

Fig. 2. Evolution of the integrated intensities of the bands characteristic of Ni_3S_2 and NiS respectively, as a function of H_2S-exposure time at 200 °C. The 300 ppm H_2S/3%H_2/Ar atmosphere was switched to Ar after 24 h (black vertical line). Notice the gap between Ni_3S_2 band intensity decrease and NiS band intensity increase.