Effect of H_2S on Ni-YSZ SOFC anodes: a combined in situ Raman spectroscopy-impedance spectroscopy study

Hai Ha MAI THI, Nicolas SERGENT, Thierry PAGNIER
LEPMI, CNRS – Grenoble-INP – Univ. de Savoie – UJF, BP75, F-38402 Saint Martin d'Hères France

SOFC offers a low-cost opportunity to use directly (or through internal reforming) gasified biomass, coal gas, hydrocarbons as fuels due to its high temperature functioning nature (500-800°C for intermediate temperature SOFC) [1]. However these fuels often contain sulfur compounds to some extent. Hydrogen sulfide is known to deactivate Ni-YSZ (yttria-stabilized zirconia) or Ni-CGO (gadolinium-doped ceria) anodes [2, 3]. The oxidation mechanisms in the presence of H_2S is still not clear.

Impact of H_2S was investigated first on the most H_2S-sensible component of anode Ni. Exposure of Ni pellet to H_2S was carried in two different ways: 1) only at working temperatures (200-800°C) and 2) during heating up to working temperature. *In situ* Raman spectroscopy showed that H_2S reacts fast with Ni at low temperatures, and violently at 500°C which cause dramatic change of the pellet morphology. Above 500°C no Raman spectra of Ni_3S_2 can be obtained although the development of various crystals which correspond to nickel sulfide can be seen by *in situ* optical microscope. A complete breakdown of the beginning morphology of the pellet was seen clearly through *in situ* optical camera when it was subjected to H_2S during the heating period.

For the fact that no Raman spectrum of Ni_3S_2 can be obtained at higher than 500°C and that the poisoning effect is most severe at 500°C, 500°C was chosen first to combine *in situ* Raman spectroscopy and impedance spectroscopy in order to study the poisoning mechanism of H_2S. Experiments were performed with half-cell Y-TPZ/Ni-YSZ from Kerafol on which counter and reference electrodes were added with Pt paste. The sample was kept first in a clean atmosphere of 3%H_2, 3%H_2O in Ar, then with 200 ppm H_2S added at 500°C under open circuit and polarizing conditions.

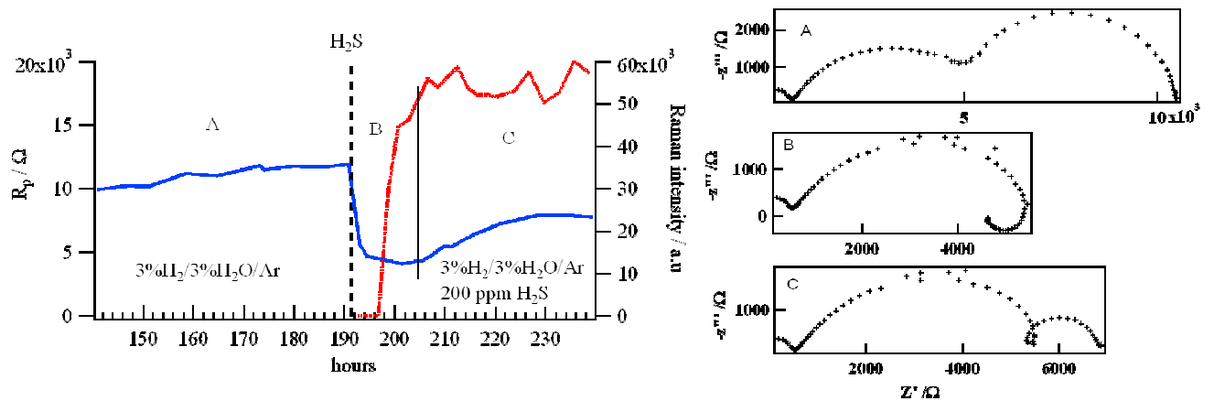

Figure: Evolution of polarization resistance (solid line), quantity of Ni_3S_2 (dotted line) in function with time and representative impedance of three zones A, B, C.

In OCP condition, the polarization resistance R_p increased slightly during 50 hours in clean fuel, with a predominant enlargement of the low frequency (LF) arc (A). *In situ* Raman spectra of the anode surface were taken every 30 minutes after the introduction of 200 ppm H_2S. The quantity of Ni_3S_2 was determined using the integrated area of characteristic peaks in the spectrum, as shown by the dotted line in the Figure. During the first 10 hours of accumulation of Ni_3S_2, R_p decreased and the LF arc changed from capacitive to inductive behavior (from A to B). The saturation of Ni_3S_2 corresponded with the increase of R_p due to a change from inductive LF arc to a capacitive arc with a loop (from B to C).

Under a permanent polarization of 500 mV, an abrupt decrease of the current and an increase of the impedance were observed few minutes after addition of H_2S with the formation of a loop in the LF arc. The amount of Ni_3S_2 was much less than in the case of OCP conditions.

The shape of the electrode impedance is consistent with a Volmer-Heyrovsky mechanism, such as the one proposed by Vogler et al. [4]. The high frequency semicircle arc could be attributed to charge transfer, while the low frequency impedance can be fitted with second order impedances characteristic of concentration impedances. It is clear from impedance spectra that H_2S strongly and immediately interferes with the absorption of others species on the anode surface. The formation of Ni_3S_2 and the apparent absence of reaction between H_2S and the electrolyte surface suggest that the mechanism proposed by Vogler et al. [4] should be modified in order for the Ni surface to play a more important role. From a technological point of view, the high reaction of Ni with H_2S at low temperatures indicates that H_2S should be avoided during heating of the SOFC at start.
Studies with lower H_2S concentrations and a higher temperature of 715°C are in progress.

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