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| ESRF | **Experiment title: Structural stability upon cycling of the extremely good materials $Sr_2CoNb_{1-x}Ti_xO_6$ ($0 \leq x \leq 1$) for hydrogen production by thermal water splitting at moderate temperature.** | **Experiment number**: A25-2-1017 |
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| **Shifts:** | **Local contact(s)**: Juan Rubio | *Received at ESRF:* |


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**Report:**

The aim of the experiment was to perform a structural study of materials $Sr_2CoNb_{1-x}TixO_6$ for compositions x = 0.7 and 1.0 under water splitting cycles to assess their stability in real operando conditions to get knowledge about the evolution of their crystal structure when submitted to significant number of cycles, in the range of 200 to 500. In previous XAS experiments, we determined the formal oxidation state of cobalt in these compounds (3) at different $pO_2$, which confirmed the results obtained by thermogravimetric analysis (TGA) and electron energy loss spectroscopy (EELS).

Oxides for water splitting application should fulfil, among other requirements, the presence of metal ions, which can change its oxidation state at a rate as fast as possible, being this associated to a loss/gain of oxygen while the material suffers small structural changes. NPD (2) (neutron power diffraction) data of $Sr_2CoTiO_{6-\delta}$ obtained at different $pO_2$ that the material retains the structure of a simple cubic perovskite with a volume increase of 1.7% in the Ar-reduced sample (oxygen content 5.18) compared to the as-prepared in air (oxygen content 5.54). These values suggest a theoretical production of ca. 24 $cm^3$ STP $H_2$/g (standard temperature and pressure) material which is more than double the yield of the best material reported so far, $La_{1.6}Sr_{0.4}MnO_{3-\delta}$ (3). Our previous TGA and thermal water splitting studies revealed that both materials show good cyclability and stability. The oxide $Sr_2Co^{+3.28}Nb_{0.3}Ti_{0.7}O_{5.79}$ which contains more oxygen and Co ions in a higher oxidation state than $Sr_2Co^{+3.08}TiO_{5.54}$ behaves clearly worse: the amount of $H_2$ produced is much lower (3).

Samples of the two above commented compositions were prepared as previously reported in (1,2) and bring to the MB25 Spline line as powders and as pellets. The in-house setup shown in Fig. 1 to feed the Anton Paar reaction cell available in the line with pure and water saturated (at 80 ºC) $N_2$ streams in alternating cycles of 10 minutes. The experiment was conducted at 700 ºC and the exhaust was analyzed after drying in a Peltier trap.

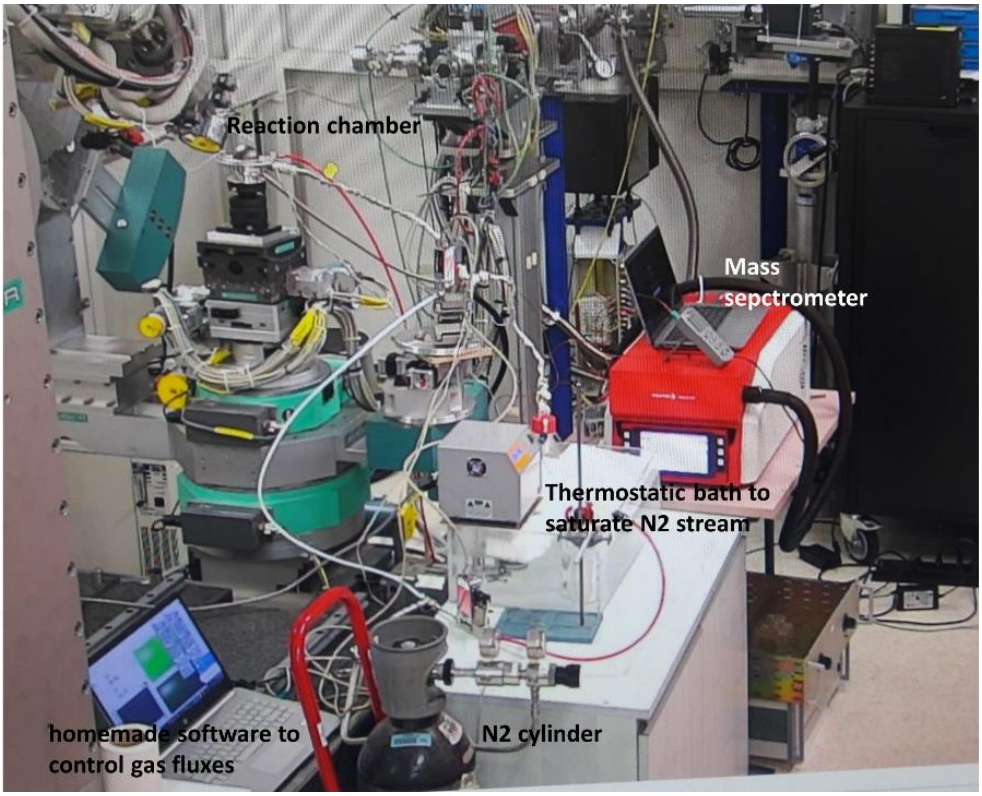


**Figure 1**. Experimental setup.

The structurla changes obesrved in $Sr_2CoTiO_{5.54}$ upon cycling are very subtle, but detectable. The material is stable up to 25 cycles (Fig. 2). Unfortunately, mass spectrometry does nor provide conclusive evidence about the hydrogen production in the applied conditions. This can be explained due to the very little amount of $H_2$ produced, sine just a few milligrams are used in each experiment. Besides, only the material close to the surface of the pellet is in contact with the gases.
Indirect confirmation of the reaction of water with the oxide (and hence providing support to the WS process) can be obtained by XAS measurements during cycling. Such kind of experiments are planned.

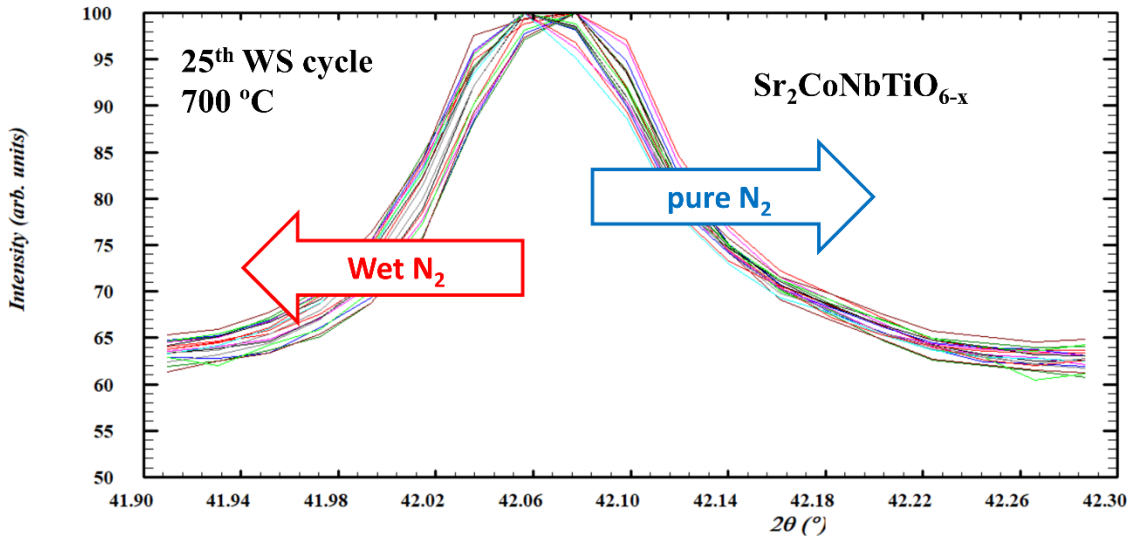


**Figure 2**. Evolution of the (123) peak of $Sr_2CoTiO_{5.54}$ during cycle 25. Small but detectable displacements are evident, as a signature of the contraction/expansion of the cell. The material is stable in the applied conditions.

1. M.T. Azcondo et al, *ChemSusChem.*, **2019**, 12(17), 4029
2. M.T. Azcondo et al, *ChemSusChem.*, **2017**, 10(14), 2978
3. A. Steinfeld, *Solar Energy* **2005,** 78, (5), 603-615