ESRF	**Experiment title:** Structural stability upon cycling of the perovskite oxide $Nd_{1/3}Sr_{2/3}CoO_{3-y}$ with outstanding performance for CO2 removal by thermal splitting at moderate temperature.	**Experiment number**: MA-4722
Beamline:	**Date of experiment**: from: 5 July 202 to: 11 Jul 202	**Date of report**: 29/01/2023
Shifts:	**Local contact(s)**: Juan Rubio	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dr Maria Teresa Azcondo* and Dr Ulises Amador*

Univ. CEU San Pablo, CEU Universities, Dpto. Química y Bioquímica, Facultad de Farmacia, Campus de Montepríncipe, Boadilla de Monte, Madrid, Spain

Dr Esteban Climet-Pascual, Departamento de Ingeniería Química Industrial y Medio Ambiente, Escuela Técnica Superior de Ingenieros Industriales, Universidad Politécnica de Madrid, Spain

Dr. María Orfila*, Departamento de Tecnología Química, Energética y Mecánica, Universidad Rey Juan Carlos, Campus de Mostóles (Madrid), Spain

Report:

Oxides for water and CO_2 splitting, like $Nd_{1/3}Sr_{2/3}CoO_{3-y}$, 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 data at different temperatures of this oxide and TG (thermo-gravimetric) experiments, both in air, revealed that the compound losses a significant amount of oxygen but it retains the structure of a simple cubic perovskite. The as-prepared oxide contains 2.94 O p.f.u whereas at 800 ºC the oxygen content is 2.66. These values suggest a theoretical CO_2 splitting (or CO production) of ~1320 μmol CO_2/g material which is almost three times the yield of the best material reported so far, $La_{0.5}Sr_{0.5}Mn_{0.95}Sc_{0.05}O_3$. Our previous TG and thermal CDS studies revealed that this material shows good cyclability and stability. Up to 15 reduction/oxidation cycles have been performed with good and stable yield; about 1500 μmol CO2/g material, slightly higher than the calculated value suggesting that the reduction of the material is deeper upon cycling. Besides, for this limited number of cycles, the structure seems to remain unchanged. The objective of the present proposal is to study the structure of the title perovskite in operando conditions upon cycling, for a significantly large number of thermochemical cycles.

$Nd_{1/3}Sr_{2/3}CoO_{3-y}$ samples prepared by spray pyrolysis (to obtain a high specific area) were transported to the MB25 Spline line as powders and as pellets. The setup shown in Fig. 1 was used to feed the Anton Paar reaction cell available on the line with air and CO_2 streams in alternating 10 min stages. The experiment was performed at 800 °C and the exhaust gases were analysed with a mass spectrometer.

Figure 1 depicts the XRD pattern of peak (321), used to follow the structure evolution, along the cycles air/CO_2 at 800ºC. During the first cycle the sample behaves as expected, with reversible cell evolution (increases under CO_2 and decreases in air). However, from the 10th cycle the material shows large signs of sever decomposition, as revealed the apparition of new peaks (Fig. 2). This behaviour worsens for successive cycles and finally becomes irreversible. Unfortunately, mass spectrometry provides no useful information on the gas composition to elucidate what is happening with the sample. At the end of the experiment (last stage under CO_2) a complete XRD pattern was collected, showing a complex mixture of several phases, among them Nd and Sr carbonates were detected.

As a conclusion, the mateails is not useful for long-term application for carbon diozide splitting.

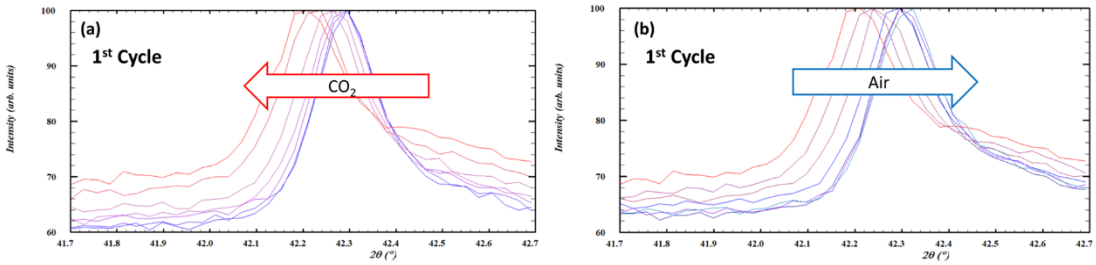

Figure 1. Evolution of the (123) peak upon cycling in CO_2 (a) and air (b).

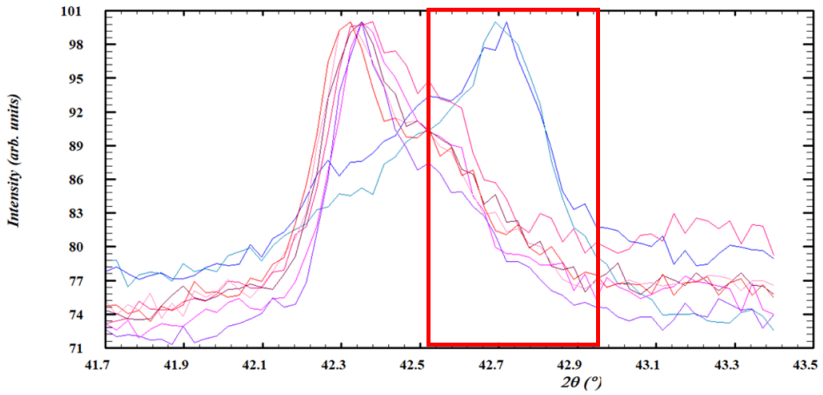

Figure 2. Evolution of the (123) peak in the 10th cycle in CO_2. Note the formation of a secondary phase.

As a contingency plan, other similar samples were taken to the line. Preliminary analysis of some of them was carried out, the best results were obtained with the sample $Sr(Fe_{0.9}Mo_{0.1})O_{3-x}$. The results on this material allow writing a paper whose publication is pending of some minor details. A summary of the main rsults are presented in the asbract below.

Long-term stability and CO production of perovskite $SrFe_{0.9}Mo_{0.1}O_{3-\delta}$ under cycling in thermochemical cycles of carbon dioxide splitting at intermediate temperature in isothermal condition

M. Teresa Azcondo[1], Gloria Anemone[1], Esteban Climent-Pascual[2,3], Juan Rubio Zuazo[2,4,5] Germán Castro[2,4,5] and Ulises Amador[,1]*

ABSTRACT

Reduced $SrFe_{0,9}Mo_{0,1}O_{3-\delta}$ perovskite can be oxidized with carbon dioxide at 800°C producing carbon monoxide. The two-stage reduction/oxidation cycle can be repeated more than one hundred times, without decomposition, segregation, or irreversible structural changes making this perovskite a good candidate for long-term application in real devices for thermochemical carbon dioxide splitting. CO production remains constant upon cycling at 0.177(3) $mol/mol_{perovskite}$ (i.e. 910 $\mu mol/g_{perrovskite}$). Perovskite reduction is a first-order reaction with respect to oxygen content. Oxidation with CO_2 is independent on the oxide vacancies concentration at the beginning of the process when high concentration of vacancies exists, and a constant velocity is observed. When about half of the initial vacancies are consumed a change to first order regimen occurs, so the velocity is dependent on concentration of the remaining oxide vacancies. In any case, reduction is much faster than oxidation by one order of magnitude.

Graphical Abstract