Experimental report

08/09/2015

Proposal: 5-24-542 **Council:** 4/2014

Title: Evolution of the crystal structureof novel SOFC cathode materials SrCo1-xMxO3 (M= V,Nb,Ti): unveiling the oxygen diffusion pathway

Research area: Materials

This proposal is a new proposal

Main proposer: **Jose Antonio ALONSO**

Experimental team: Vanessa CASCOS
Jose Antonio ALONSO

Local contacts: Maria Teresa FERNANDEZ DIAZ

Samples: SrCo0.95M0.05O3 (M= V,Nb,Ti)

Instrument	Requested days	Allocated days	From	To
D2B	3	3	10/10/2014	13/10/2014

Abstract:

The novel perovskites Sr1Co1-xMxO3-delta (M= V,Nb,Ti) have been evaluated as superior cathodes for solid-oxide fuel cells (SOFC); tests in single fuel cells yield output powers higher than 800 mW/cm2 at 850 C with H2 as a fuel. In this experiment we aim to unravel the oxide-ion diffusion path of this family of MIEC (mixed ionic-electronic conductor) oxides. We plan to study the thermal evolution of the crystal structure in order to get information about the actual crystal symmetry, the thermal vibrations and oxygen contents as well as the order-disorder of the oxygen vacancies and their evolution at the actual working conditions in a SOFC cell, in air at temperatures between 600 and 900 C.

The stabilization of a 3D perovskite-like framework in the $SrCoO_{3-\delta}$ system has been a widely used strategy in order to obtain an adequate mixed ionic-electronic conductor to be used as cathode in intermediate temperature solid oxide fuel cells. For this purpose, several chemical substitutions have been performed in either the Sr (Ba, La, Sm) [1] or in the Co (Sc, Fe,Ni,etc) [2,3] positions or in both. In this work we have stabilized a perovskite phase by doping the $SrCoO_{3-\delta}$ system with low M = V, Nb and Ti contents in $SrCo_{1-x}M_xO_{3-\delta}$ (x = 0.05). The stabilization of a tetragonal *P4/mmm* structure was obtained in all cases. The doped compounds present high thermal stability without abrupt changes in the expansion coefficient and a great enhancement of the electrical conductivity compared to the pristine $SrCoO_{3-\delta}$ at low and intermediate temperatures (T ≤ 800 ºC). The sample $SrCo_{0.95}Ti_{0.05}O_{3-\delta}$ displayed the highest conductivity value over 80 $S \cdot cm^{-1}$[4].

In this experiment we have measured the in-situ structural evolution of the SrCo1-xMxO$_{3-\delta}$ system (M = V, Nb and Ti, x= 0.05) in the usual working conditions of a cathode in a SOFC (in air from 200 ºC to 800 ºC). Neutron powder diffraction (NPD) data were collected in the diffractometer D2B. The high intensity mode ($\Delta d/d \approx 5 \cdot 10^{-4}$) was selected, with a neutron wavelength λ= 1.594 Å within the angular 2θ range from 8° to 155°. About 2 g of the sample was contained in a quartz tube open to the ambient atmosphere, placed in the isothermal zone of a furnace with a vanadium resistor operating under vacuum ($P_{O2} \approx 10^{-6}$ Torr). The measurements were carried out in air at 200, 400, 600 and 800ºC. The collection time was of 3 h per pattern. The irregular background coming from the quartz container was interpolated from points devoid of reflections.

Fig. 1 illustrates the example of $SrCo_{0.95}Ti_{0.05}O_{3-\delta}$ at 400 ºC and 800 ºC. The crystal structure can be Rietveld-refined in the tetragonal *P4/mmm* space group till 400 ºC (Fig. 2). At this temperature a tetragonal (*P4/mmm*) to cubic (*Pm-3m*) phase transition takes place. Fig. 2 shows the crystal structures of the tetragonal and cubic phases. The thermal evolution of the lattice parameters and the oxygen content can be seen in Fig. 3. The tetragonal superstructure is due to the long-distamnce ordering of the vacancies along the c-axis. The occupancy factors of O atoms strongly decrease (Fig. 3b) as temperature

increases, which favours the oxygen ion mobility, as required in SOFC cathodes. Similar behaviours have been observed in the remaining materials.

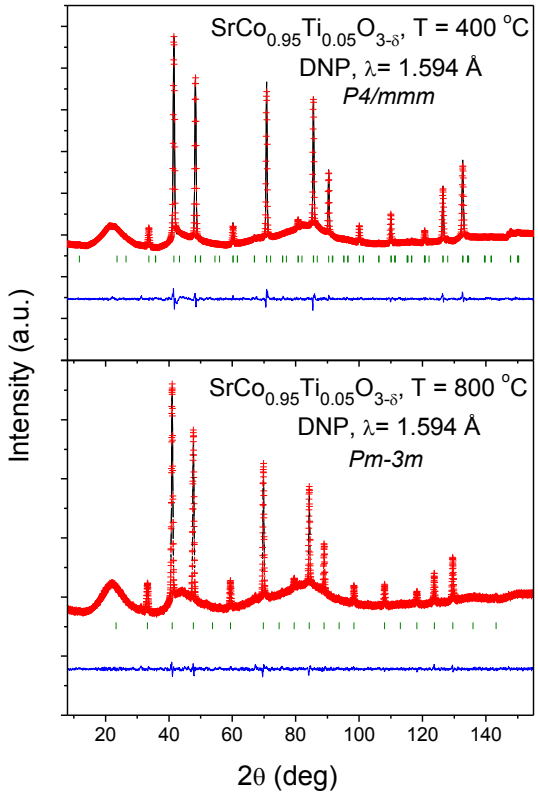

Fig. 1. *Observed (crosses), calculated (full line) and difference (at the bottom) NPD profiles for $SrCo_{0.95}Ti_{0.05}O_{3-\delta}$ at 400 ºC and 800 ºC. The vertical markers correspond to the allowed Bragg reflections.*

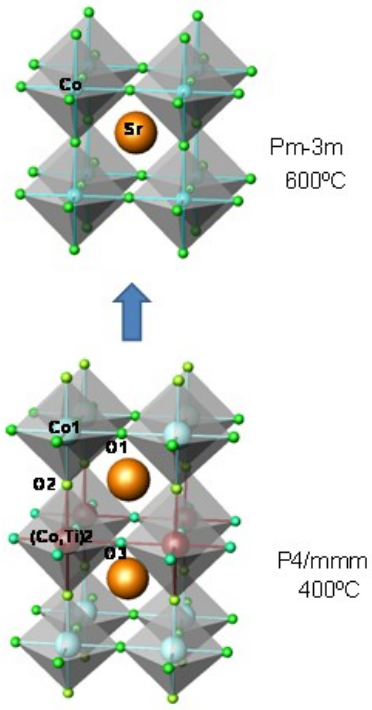

Fig. 2. *Crystal structures of the tetragonal and cubic phases*

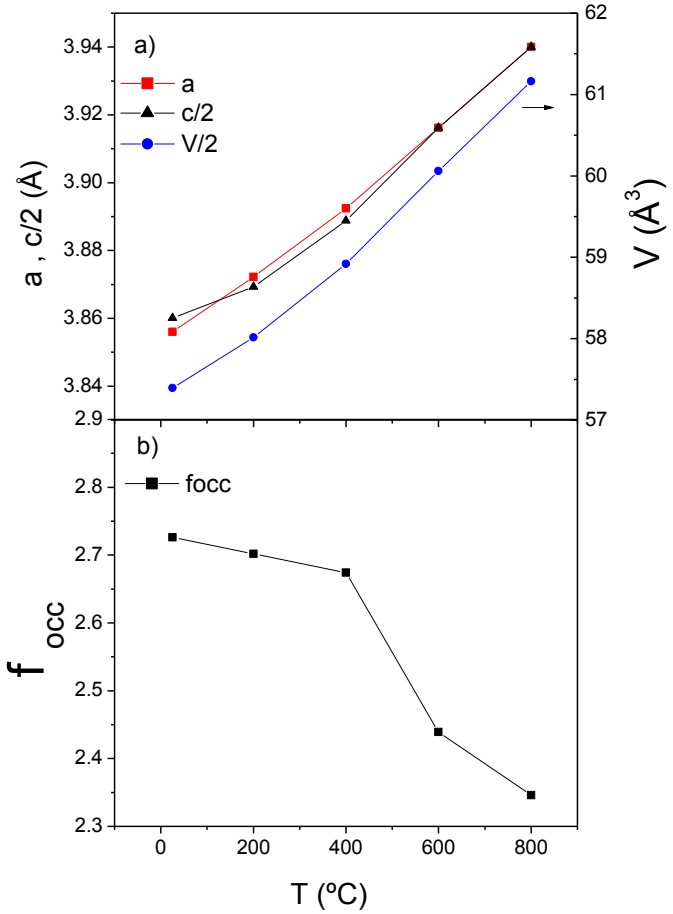

Fig. 3 *Therrnal evolution of structural parameters and oxygen content.*

References

[1] T. Nagai, W. Ito, TR. Sakon, Solid State Ionics 177 (2007) 3433.

[2] Z. Q. Deng, W. Liu, C. S. Chen, H. Lu, W. S. Yang, Solid State Ionics 170 (2004) 187.

[3] P. Zeng, R. Ranj, Z. Chen, W. Zhou, H. Gu, Z. Shao, S. Liu, J. Alloys and Comp., 455 (2008) 465-470.

[4] V. Cascos, L.Troncoso, J.A. Alonso, International Journal of Hydrogen Energy, 40 (2015) 11333-11341