

# Characterization of (La,Sr)(Ti,Co)O<sub>3</sub> oxides for symmetrical solid oxide fuel cell electrodes

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The Symmetrical Fuel Cells (SSOFC's) concept has been reported as a particular SOFC configuration where the same compound is used as anode and cathode [1]. This design has inherent benefits over traditional SOFC since it could solve two of their main problems, sulfur poisoning and carbon deposits (when hydrocarbons are used as fuel), by simply inverting the gas flux and, improving the long term stability. Another benefit is the design and manufacturing simplicity. In the other hand, requisites on SSOFC electrode compounds are more restrictive than in normal cathode or anode materials since it has to fulfill both requirements simultaneously.

Although (La,Sr)TiO<sub>3</sub> oxides (LST) have been reported as a possible SOFC anode materials [2], and (La,Sr)CoO<sub>3</sub> is considered as a SOFC cathode with excellent properties [3], the possible solid solution LST-LSC remained mostly unexplored. In this work, this solid solution is studied in the search of a possible SSFOC electrode. In particular, a complete characterization on La<sub>0.4</sub>Sr<sub>0.6</sub>Ti<sub>1-y</sub>Co<sub>y</sub>O<sub>3±δ</sub> (LSTC) oxides is presented.

LSTC structural properties were obtained from synchrotron powder X-ray diffraction (XPD) at room temperature. A slight distortion from ideal cubic perovskite Pm-3m due to the rigid rotation of oxygen octahedral around transition metals (TM) was observed on all samples, being related to the freezing of an only one symmetry mode (R5') and leading to the rhombohedral R-3c space group. Structural properties at electrode working environment were also evaluated, a reversible R-3c to Pm-3m second order phase transition was found on all samples, both in synthetic air and diluted H<sub>2</sub> atmospheres. A direct correlation between transition temperature and structural distortion was noted. Also, the compound charge compensation through perovskite A-site vacancies was found to be the main process for charge compensation for low cobalt content (y < 0.3). This was followed by the Sr occupancy factor ranging from [Sr] = 0.4 for y = 0.0, expected for a low temperature synthesized LST [4], to the stoichiometric [Sr] = 0.6 for y = 0.3. Complementary, Neutron Powder Diffraction has been also performed on selected samples to confirm oxygen atom positions and thermal parameters.

The local environment around the perovskite B-site was studied by Extended X-ray Absorption Fine Structure spectroscopy (EXAFS) in order to compare it with the atomic ordering observed at longer scales by X-ray and neutron diffraction. This analysis confirmed the model of the oxygen octahedra rigid rotation around the

TM. Additionally, Ti-O distance was found to maintain a stable value as Co content was increased, but a difference between Ti-O and Co-O distances was noted for low cobalt content being greatest (~0.1 Å) for y = 0.1 and decreasing down to be almost zero for y = 0.5.

Electronic structure was also evaluated through the analysis of Absorption Near Edge Spectroscopy (XANES) on Ti and Co K-edge data, combined with EXAFS results and Density Functional Theory (DFT) calculations. Oxidation states of TM could be inferred from their absorption edge energy followed by a calibration with well-known standards having the same symmetry. In this way, Ti oxidation state was found to be +4, remaining stable in all the compositional range. On the other hand, Co XANES spectra have a strong influence from Co-O distance variation for y ≤ 0.5 which affects the crystal field and, therefore, the atomic orbitals splitting. DFT calculations, coupled with XPD and EXAFS results, successfully modeled the samples XANES spectra, even though they show a remarkable energy shift. In this sense, a more qualitative approach leads to identify Co valence state as +3 in that compositional range.

Electric transport properties were evaluated through conductivity measurements on LSTC samples for y ≤ 0.5 as a function of oxygen partial pressure (pO<sub>2</sub>) at several temperatures (T = 600, 800 and 1000°C). An improvement on electric conductivity of several orders of magnitude was found as Co content was increased in the sample. Additionally, a change in pO<sub>2</sub> dependence was observed as Co was added to the structure: while conductivity in LST sample is improved at lower pO<sub>2</sub>, the opposite behavior is observed in Co-doped samples.

Lastly, LSTC oxides performance as a fuel cell electrode were studied with an electrolyte supported symmetrical single cell measurement.

The correlation between all these complementary measurements and analysis is also discussed, aiming to understand the origin of the LSTC electrochemical properties as a SSOFC electrode.

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