## The effect of Ni doping on the performance and electronic structure of LSCF cathodes used for IT-SOFCs

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We investigated the effect of nickel doping on the electronic structure and performance of nanostructured La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8-0.03</sub>Ni<sub>0.03</sub>O<sub>3-8</sub> prepared by the one pot sol-gel method. The undoped La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub> (LSCF0.8) provided by PRAXAIR was used as reference. Moreover, for comparison, Ni (3 mol%) was deposited by wetness impregnation over the La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub>. We show by in-situ X-ray absorption spectroscopy (XAS) at 900°C under air flow that nickel enters the B perovskite site of the material and favors the stabilization of the cobalt oxidation state, as evidenced by the delay in the decrease of the average Co valence with respect to undoped samples. Our results are further supported by in-situ X-ray Raman spectroscopy (XRS) that allowed us to monitor the temperature evolution of the O K-edge. XRS evidences that nickel-doped LSCF shows unmodified O2p-TM3d density of states, which proves that the Co oxidation state is preserved. Electrochemical impedance spectroscopy (EIS) measurements were carried out over halfcell systems consisting of LSCF-based materials deposited onto a Ce<sub>0.8</sub>Gd<sub>0.2</sub>O<sub>2-8</sub> electrolyte. The improvement of the electrochemical performances of the Ni-doped La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8-0.03</sub>Ni<sub>0.03</sub>O<sub>3-δ</sub> sample with respect to a reference Ni-impregnated LSCF is attributed to the stabilization of the TM-O6 structural units, which were recently proposed as the functional units for oxygen reduction.