Chemical and structural modifications of electrochemically deposited cermet precursor of Ni/NiO/CeO$_2$, for the realization of solid oxides fuel cells (SOFC), were studied by conventional and in situ transmission electron microscopy (TEM). These cells are devices for effective conversion of chemical energy into electricity and heat, with low environmental impact. Cermet offer high ionic and electronic conductivity and high reforming and electrocatalytic activity. There is considerable interest in lowering the operating temperature of such devices, and doped cerias represent one possible materials choice. Doping ceria with oxides of lanthanides (Dy and Tb) improves the ionic and electronic conductivity and also increases the electrocatalytic activity of cerments [1-2]. In this work, the following CeO$_2$-NiO samples were studied: (i) pure, (ii) Dy-doped, (iii) Tb-doped and (iv) co-doped with Dy and Tb. High spatial resolution in situ TEM techniques were used to monitor the changes in chemical/physical properties of these materials at the nanoscale [3], during thermal treatments employed to fabricate active cerments. High spatial resolution TEM observations were performed in a JEOL 2010F, an aberration corrected ARM200F and an environmental FEI Tecnai F20 transmission electron microscopes, with the combined use of TEM analytical techniques. The materials were initially analyzed in their as deposited form, then after ex situ heat treatments at 600°C for 1 hour in a furnace. After assessing the general modifications of the materials, they were subjected to in situ cycles of aging (temperature up to 700°C for maximum 300 minutes in an oxygen atmosphere) and the changes of their structural properties were monitored. Fig. 1(a) shows a typical high resolution image obtained from the pure and untreated sample, consisting of CeO$_2$ nanograins (size < 5nm) apparently laying over a polycrystalline NiO layer, with much larger grain size. The insets show the Fast Fourier Transform (FFT) from the areas marked in the figure. CeO$_2$ in the cubic phase was detected; evidence for the rhombohedral NiO phase was found. Upon ex situ heat treatment, coarsening of the grains occurs, the CeO$_2$ ones reaching sizes up to 10-20 nm. Large NiO crystals can be observed, as shown in figure 1(b). Doping results in an amorphization of the samples. Fig. 1 shows the images from the co-doped sample, before (c) and after (d) ex situ annealing. The images of the same sample after the in situ treatment are shown ((e) and (f)). The details of the ex situ and in situ treatments will be compared and discussed.


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Fig. 1: High resolution images of: pure untreated a) and treated b) samples and FFTs from marked areas, with zone axis identification and attribution to the CeO$_2$ (1, 2,...labels) and NiO (1', 2'...labels); co-doped untreated c) and treated d) samples and relevant diffraction patterns; co-doped sample untreated e) and in situ treated d) at 700°C for 170 min.