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XPS on Mixed Conducting Perovskites at Elevated Temperatures and Close-to-Ambient Gas Pressure

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XPS is a valuable technique for surface-sensitive materials characterization. The usual lab XPS setups have the severe drawback to operate only under UHV conditions, which is, *e.g.*, far from the relevant conditions of solid oxide fuel cell (SOFC) cathode materials. These disadvantages can to a large extent be overcome with a "high pressure" XPS setup installed at the BESSY II synchrotron [1]. It allows sample temperatures up to 700 °C, depth profiling over 2 nm without sputtering (*i.e.* without sputtering artifacts) by variation of the excitation energy, and most importantly measurements under a residual gas pressure in the mbar range. Thus *in situ* measurements close to actual SOFC operation conditions become possible. A positive side effect of measuring samples at elevated T and in mbar O_2 pressure is that the surface becomes "self-cleaning", *i.e.*, organic contaminations and even carbonate groups decompose.

Here we report on SOFC cathode model systems, thin films (100 nm) of nominally identical $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ composition which were prepared by PLD on single-crystalline YSZ substrates under different deposition conditions. Electrochemical investigations prove that the different films indeed have a different electrocatalytic activity for the oxygen incorporation reaction [2], which raises the question of the actual surface composition.

Fig. 1 shows the O1s spectra under $p(O_2)$ = 0.1 mbar, T = 300 °C for $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ films deposited at substrate temperatures of 450 °C (M01) and 650 °C (M02). The peak at highest binding energy (red) corresponds to a surface-related oxygen species; for M02 also the blue peak decreases for higher depths. Fig. 2 demonstrates that also the relative contributions of different La species (green and blue doublets) close to the surface depend on PLD deposition conditions, while they become more similar at higher sampling depth. The different surface composition is also reflected in the different changes of the O1s spectra upon exposure to ≈ 0.05 mbar H_2O (Fig. 3). The detailed assignment of the different peaks to certain environments as well as a quantitative depth-resolved analysis of elemental composition is under way.

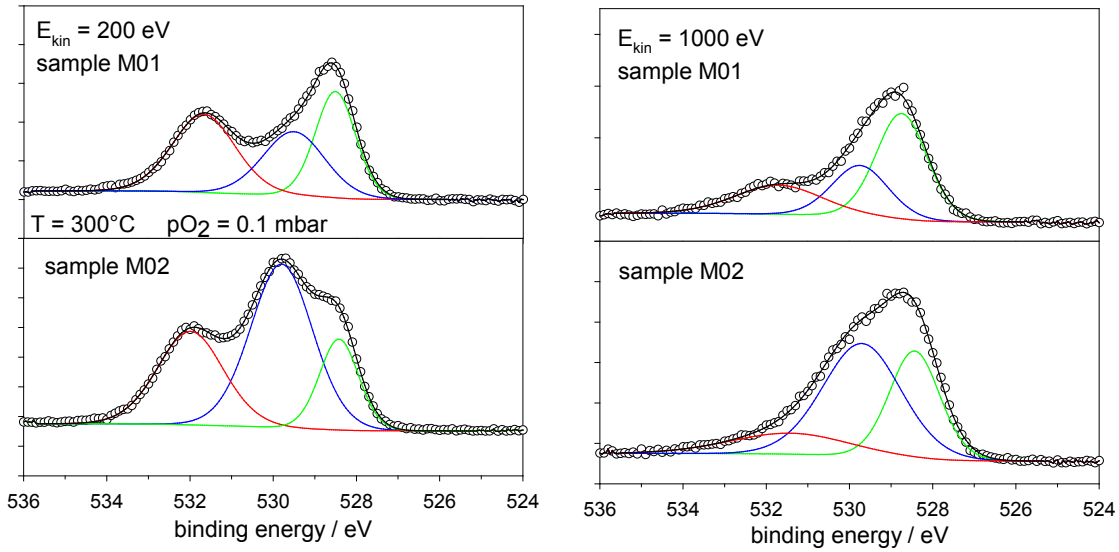

Fig. 1 O1s spectra of samples M01 and M02 recorded at kinetic energies of 200 eV (sampling depth ≈ 0.7 nm) and 1000 eV (≈ 2 nm).

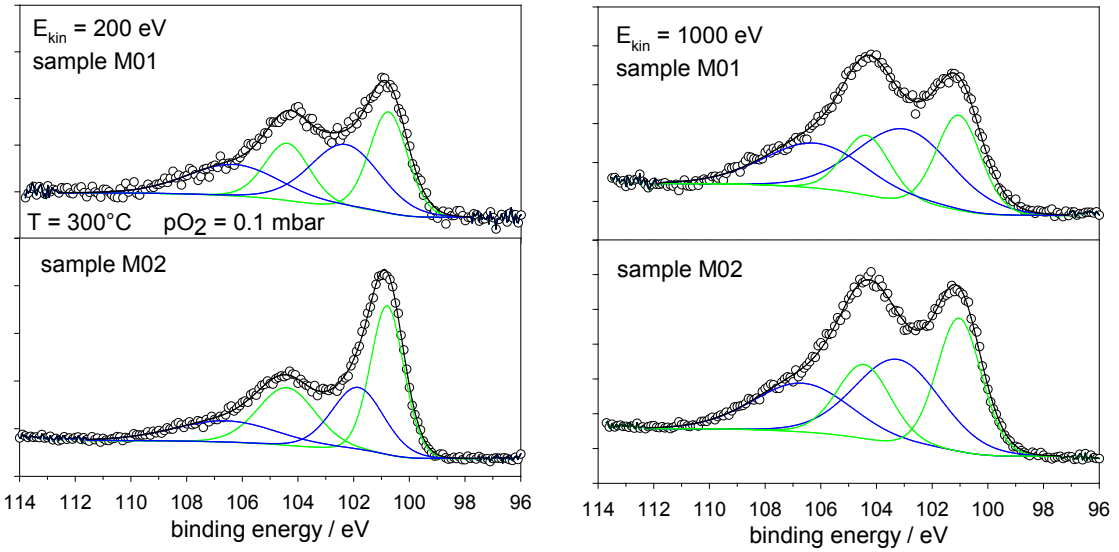

Fig. 2 La4d spectra of samples M01 and M02 recorded at kinetic energies of 200 eV and 1000 eV.

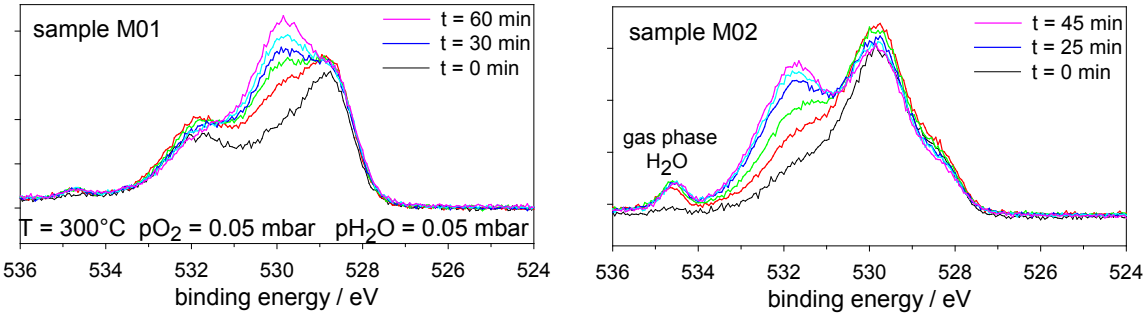

Figure 3: O1s spectra (E_{kin} = 200 eV) for M01 and M02 samples during exposure to 0.05 mbar H_2O.

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