

## Report of proposal no. 2013\_2\_130382

### Objectives

We investigated the near-surface chemistry of the mixed electronic/ionic conductors  $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{(3-x)}$  (LSF) and  $\text{SrTi}_{0.7}\text{Fe}_{0.3}\text{O}_{(3-x)}$  (STF) under anodic and cathodic polarization at  $600^\circ\text{C}$  in 0.5 mbar oxygen and 0.5 mbar hydrogen/water atmospheres. Depending on gas phase and polarization, AP-XPS shed new light on the MIEC surface state associated with the oxygen reduction/evolution reactions (ORR, OER), the hydrogen evolution (HER) reaction and its reversal (HOR) under realistic SOFC conditions. Reduction stable perovskite-type electrodes represent promising candidates for future SOFC anodes, as the entire electrode surface can be electrochemically active, but spectroscopic studies on their polarization behavior under reducing conditions are rare. The in-situ analysis of near-surface composition and cation valence chemistry upon electrochemical polarization represents a novel field of research. The adaptation of a working MIEC electrode to the thermodynamic boundary conditions was studied in-situ, comparing the effect of cathodic polarization or an equivalent reducing atmosphere. Kinetically, a steady state on a working electrode is only reached with a current flowing via the electrolyte which is not the case when only the atmosphere is changed. By simultaneously measuring the surface exchange kinetics via impedance spectroscopy, and the associated near-surface chemical state by XPS, in-operando information about the active surface state was obtained.

### Achievements

- 1) Electrochemical in situ-characterization of LSF and STF was perfectly feasible both under oxidizing and reducing conditions using the AP-XPS setup at the ISS beamline endstation.
- 2) A pronounced initial activation effect (increase of surface exchange rate) was observed on LSF upon the first polarization cycles, associated with XPS-monitored surface dehydroxylation.
- 3) XPS at the LSF-electrode in 0.5mbar  $\text{O}_2$  under variation of the electrochemical potential showed changes of the Sr 3d signal, appearing qualitatively stronger as compared to changes in the Fe 2p region.
- 4) XPS at the LSF-electrode in 0.25mbar  $\text{H}_2$ / 0.25mbar  $\text{H}_2\text{O}$  showed that the Sr-component at lower BE is more strongly pronounced as compared to  $\text{O}_2$  atmosphere. Yet, the main and most interesting redox effect is the appearance of metallic Fe species in the Fe2p region under cathodic electrochemical polarization (Figure 1).
- 5) Fe metal formation was shown, by switching back and forth between anodic and cathodic polarization, to be perfectly reversible with minor hysteresis effects. No irreversible decomposition of the LSF even under HER conditions was observed, showing the high reduction stability of LSF.
- 6) The near surface distribution of Fe metal under cathodic polarization in  $\text{H}_2/\text{H}_2\text{O}$  was studied by depth profiling using variable photon energy/ kinetic energies of the photoelectrons. Fe0 exhibits a clear enrichment at the electrode surface, as shown in Figure 2.
- 7) Formation of metallic Fe is also observable under cathodic polarization/ reducing conditions on STF. Spectroscopic effects on Sr and Ti are markedly less pronounced.

Captions of Figures:

Figure 1: Fe2p and Sr3d regions monitored on LSF in 0.5 mbar hydrogen/water atmosphere (1:1) under both cathodic and anodic polarization. The buildup of metallic Fe can be clearly seen under cathodic conditions.

Figure 2: Depth profiling of metallic Fe on LSF under cathodic conditions in 0.5 mbar hydrogen/water.

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Figure 1 / report 2013\_2\_130382

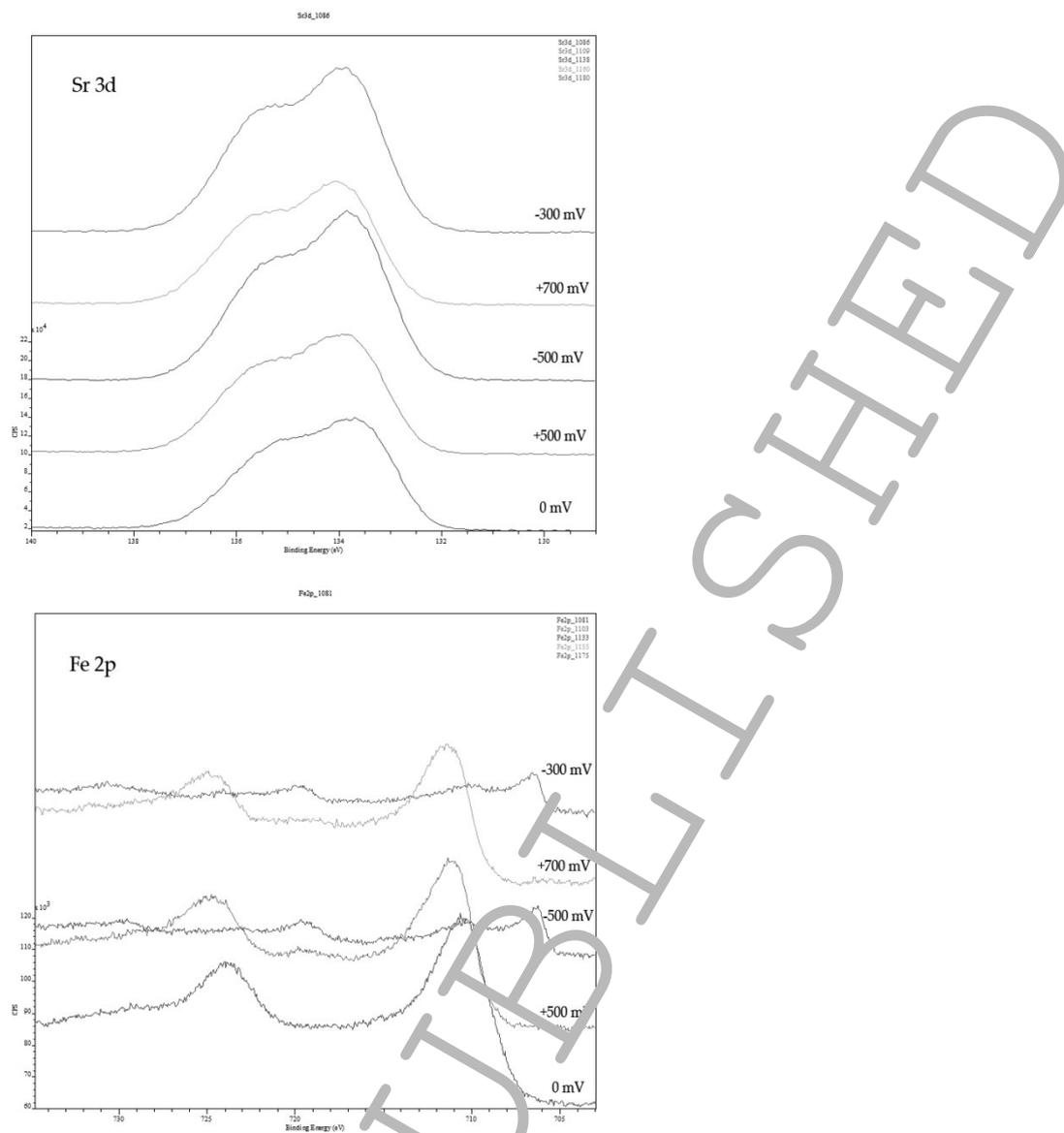


Figure 1: XPS spectroscopic effects under cathodic polarization in H<sub>2</sub>/H<sub>2</sub>O atmosphere

Figure 2 / report 2013\_2\_130382

