Enhancing electrochemical water-splitting kinetics by polarization-driven formation of near-surface Fe^0: An in-situ XPS study on perovskite-type electrodes[**]

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Abstract: In the search for optimized cathode materials for high temperature electrolysis, mixed conducting oxides are highly promising candidates. This study deals with fundamentally novel insights into the relation between surface chemistry and electrocatalytic activity of lanthanum ferrite based electrolysis cathodes. For this means, near-ambient pressure x-ray photoelectron spectroscopy (NAP-XPS) and impedance spectroscopy experiments were performed simultaneously on electrochemically polarized $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ (LSF) thin film electrodes. Under cathodic polarization the formation of Fe^0 on the LSF surface could be observed, which was accompanied by a strong improvement of the electrochemical water splitting activity of the electrodes. This correlation suggests a fundamentally different water splitting mechanism in presence of the metallic iron species and may open novel paths in the search for electrodes with increased water splitting activity.

Solid oxide electrochemical cells are highly promising devices for efficient conversion of chemical into electrical energy (solid oxide fuel cells, SOFCs) as well as vice versa (solid oxide electrolysis cells, SOECs). SOFCs are already commercialized and a Ni/yttria stabilized zirconia (YSZ) cermet is successfully employed as anode material.[1] In contrast, SOECs are still lagging behind and often SOFCs are simply used in “reverse mode” for running electrolysis, which may cause severe degradation of the Ni/YSZ electrode.[2, 3] A possible solution is to replace Ni/YSZ by mixed ionic and electronic conductors (MIEC). MIECs are already used as electrodes in oxidizing atmosphere and mixed conducting oxides such as $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ (LSF) are also interesting candidates for future SOEC cathodes, since large parts of the electrode surface may become electrochemically active[4-8] rather than just the triple phase boundary region as in Ni/YSZ.[9, 10] However, little is known about the surface chemistry of mixed conducting perovskite-type electrodes in reducing atmosphere and its relation to the electrochemical properties. Especially knowledge on the changes in near-surface composition and cation valence states upon electrochemical polarization is rare.

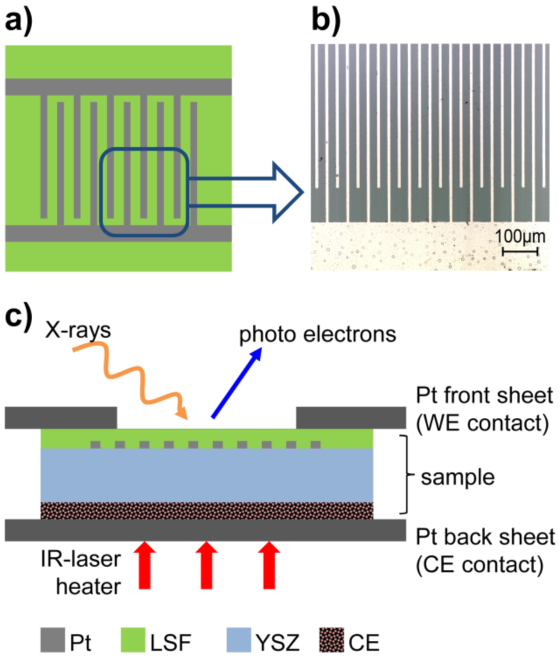

Figure 1. a) Sketch and b) optical micrograph of a sample with thin film LSF electrode and buried current collector. c) Sketch (cross section) of a sample mounted for NAP-XPS measurements (WE – working electrode, CE – counter electrode).

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Near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) offers a powerful tool for the investigation of MIECs under electrochemical polarization, providing information on adsorbed species as well as on near-surface cations of a polarized electrode.[11-13] In-situ NAP-XPS studies were performed on perovskite-type electrodes in oxidizing atmosphere [14-16] and on ceria-based electrodes under reducing conditions.[17-19] However, establishing a well-defined polarization state of a perovskite-type mixed conducting electrode in H_2/H_2O atmosphere and simultaneously probing the electrochemical surface activity as well as performing NAP-XPS measurements has – to the best of our knowledge – not been achieved yet. Especially the attainment of a well-defined and rather homogeneous polarization of the LSF electrode (despite being a poor electronic conductor under reducing conditions) allows the relation of changes in the electrochemical surface activity to the observed changes in surface chemistry.

In the present study, synchrotron-based NAP-XPS and impedance spectroscopy were performed simultaneously, enabling one to investigate changes in surface chemistry and in water splitting kinetics of the perovskite-type mixed conductor $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ (LSF) under electrochemical polarization in humid H_2 atmospheres. An issue complicating such measurements on LSF is its low electronic conductivity under reducing conditions.[20, 21] This can be overcome by a micro-structured metallic thin film, which acts as a current collector and may provide virtually homogeneous polarization of the working electrode[8, 22] and thus a homogeneous driving force of the electrochemical surface reaction; see also supporting information. Here, homogeneous polarization was realized by interdigitated Pt fingers buried beneath the 200 nm LSF layer. This model-composite working electrode was deposited on single-crystalline yttria stabilized zirconia (YSZ) with a porous counter electrode – see Fig 1. Details on the preparation of LSF working electrodes with embedded current collectors and of porous counter electrodes are given in the supporting information.

NAP-XPS measurements were conducted at the ISISS beam line of synchrotron HZB/BESSY II in Berlin.[23] NAP-XPS experiments under electrochemical polarization were realized by mounting the samples between two platinum sheets (top one with a hole), which served as mechanical fixation and as electrical contacts of the two electrodes – cf. Figure 1c. This novel setup allows a simultaneous measurement of the electrochemical reaction rate and surface activity (via dc current and impedance spectroscopy, respectively) as well as of the chemical surface composition and the near-surface cation valence states (by means of XPS). For experimental details the reader is referred to the supporting information.

In Figure 2 the measured current-overpotential characteristic of an LSF working electrode is shown. Three selected Fe2p spectra, corresponding to three different polarization states, are depicted as insets and reveal that already at relatively low cathodic overpotentials a metallic iron species evolves. Upon formation of this Fe^0 species the electrochemical water splitting activity of the LSF surface strongly increased, leading to a highly asymmetric current-voltage curve, which does not follow an exponential function (e.g. Butler-Volmer's equation; see Figure s1, supporting information) with electrochemically meaningful parameters. This indicates a mechanistic change of the reaction kinetics of $H_2O + 2e^- \rightleftharpoons H_2 + O^{2-}$ at the LSF surface. The cathodically formed Fe^0 was quickly re-oxidized after removing the polarization (within the time between two simultaneous XPS/impedance measurements of about 200 to 600 seconds). Accordingly, the current voltage curve in Figure 2 is highly reversible. Owing to this reversibility an observation of the cathodically formed metallic Fe species is clearly only possible by means of in-situ experiments as employed in the present study.

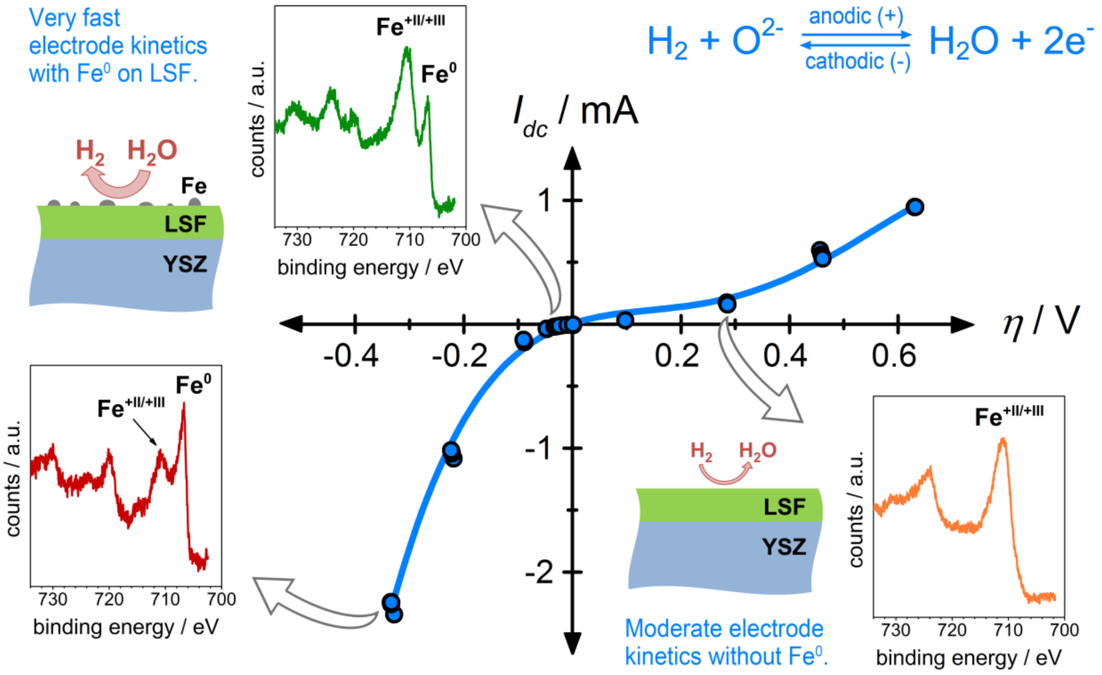

Figure 2. Current-overpotential curve (I_{dc} vs. η) of LSF in humid reducing atmosphere (0.25 mbar H_2 + 0.25 mbar H_2O); the symbols show measured values, the line is not a fit but a guide for the eye. The reaction proceeding on the surface of the LSF working electrode is given top right. For selected points of the curve (indicated by arrows) Fe2p XPS spectra are shown as insets. The sketches indicate the respective situation of the LSF surface and the resulting reactivity.

At each point of the current voltage curve (i.e. for distinct reaction rates) NAP-XPS and impedance measurements were performed simultaneously. The main results of the impedance measurements are as follows (details regarding data analysis are given in the supporting information): From the recorded impedance spectra (cf. Figure s2, supporting information) a surface resistance ($R_{surface}$) was extracted. The area(A)-related inverse surface resistance $1/(R_{surface}\times A)$, which is a measure of the electrochemical activity of the LSF surface for the water splitting/hydrogen oxidation reaction, is plotted versus the overpotential η in Figure 3a. In this plot, the strong asymmetry – especially at small overpotentials – is even better visible: A strong anodic overpotential (η = +285 mV) causes an increase of $1/(R_{surface}\times A)$ by a factor of about three to four, whereas already a small cathodic polarization (η = –47 mV) leads to approximately the same change. A 70 mV increase of the cathodic overpotential (from –20 to –90 mV) improves the surface activity – quantified by $1/(R_{surface}\times A)$ – by about one order of magnitude. In Figure 3a this strong asymmetry is reflected by an almost step-like non-linearity of the water-splitting activity in the cathodic regime and finds its counterpart in the XPS results, see below.

The measured Fe2p XPS spectra were analyzed using a simplified peak model with the main objective to quantify the relative proportions of metallic and oxidic iron and thus only the Fe2p$_{3/2}$ peak was considered in the fit (for details see Sec. 3.3 of the supporting information,). In Figures 3b and 3c the resulting peak areas of both Fe species (metallic and oxidic) and the fraction of Fe^0 (with respect to the total Fe amount) are plotted versus the overpotential η, respectively. Amount and fraction of metallic iron abruptly increases for cathodic polarizations exceeding ca. –20 mV. In the same voltage range also the water splitting activity of the LSF electrode – i.e. $1/(R_{surface}\times A)$ – increases strongly. This correlation suggests a fundamental difference in the water splitting mechanism on LSF with and without Fe^0.

From the data available the exact structural morphology of the Fe^0 species cannot be identified yet. Surface iron might be reduced to an atomic species while still being part of the perovskite lattice but formation of metallic iron particles on the LSF surface appears more likely. The formation of a Fermi-edge in the valence band spectra (cf. Figure s3b) strongly indicates formation of a metallic phase and thus strongly suggests the latter mechanism – i.e. the electrochemically driven evolution of metallic Fe particles on the LSF surface sketched in Figure 2. This is also supported by the observation that the total iron (i.e. oxidic and metallic) peak area strongly decreases upon formation of Fe^0 – see Figures 3b and s3a. Assuming particles being significantly larger than the mean free path of photoelectrons (which is ca. 0.5 nm), a significant amount of near-surface iron would become inaccessible for XPS measurements after Fe^0 particle formation. Evolution of metallic iron particles already for small cathodic polarization is also in agreement with the fact that under these experimental conditions LSF is rather close to its thermodynamic stability limit.[21] Moreover, chemically driven formation of metal particles from perovskite-type SOFC anode materials under reducing conditions as well as the fully reversible reintegration of these particles under oxidizing conditions was reported recently.[24, 25] Also similar chemically driven formation of metallic Pd particles on Pd-doped LaFeO$_3$ catalysts under reducing conditions was found.[26] The observed stability of the LSF electrodes under reducing conditions may be due to the near-surface formation of Ruddlesden-Popper like phases upon Fe^0 particle evolution.[24]

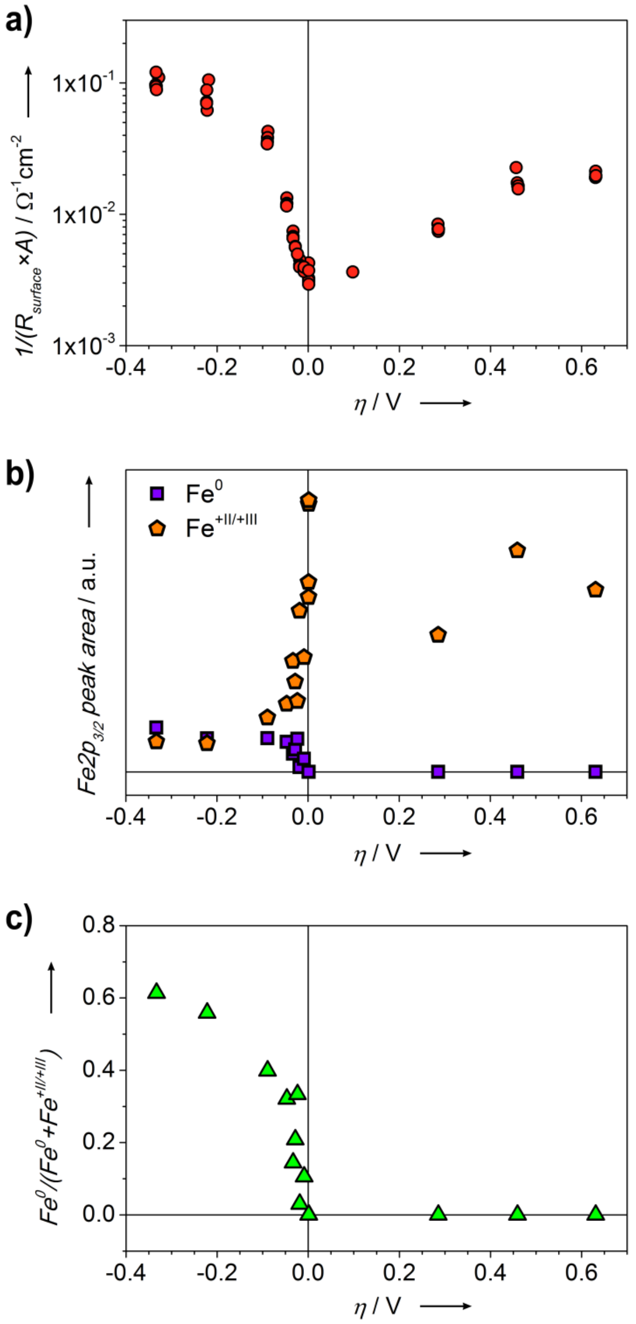

Figure 3. a) Area related inverse surface resistance from impedance spectra vs. overpotential η. b) Fe2p$_{3/2}$ peak areas of the different Fe species (obtained by fits of XPS spectra) as a function of η. c) Fraction of Fe^0 calculated from the peak area values in (b) plotted vs. overpotential.

High chemical stability of such phases in hydrogen atmosphere was reported for Cr/Ni containing Ruddlesden-Popper oxides.[27] The strongly enhanced electrochemical kinetics even for small cathodic overpotentials may be caused by the presence of Fe^0 particles at the surface promoting the kinetics of the water splitting reaction. However, also the remaining Fe-depleted oxide surface (of unknown crystal structure) may offer significantly faster electrode kinetics – e.g. by a drastically changing Fe^{+II}/Fe^{+III} ratio at the oxide surface upon Fe^0 formation. Furthermore, a complex mechanistic interplay of both a metal and an oxide phase is conceivable; two phase promoted electrochemical kinetics has been reported for perovskite-type electrodes in oxygen.[14, 28, 29]

Only further measurements can reveal details regarding the Fe^0 containing phase, the rather complicated mechanistic reasons for the uncommon I-V curve, and the possibilities to realize such highly active SOEC cathodes also by chemical preparation rather than by polarization. In any case, the measured almost step like improvement of the electrode performance by Fe^0 exsolution emphasizes the high complexity of such a system but provides new directions in the search of novel oxide based electrodes for high temperature electrochemical water splitting.

Keywords: electrocatalysis, heterogeneous catalysis, mixed ionic electronic conductor, perovskite-type electrode, solid oxide electrolysis cell

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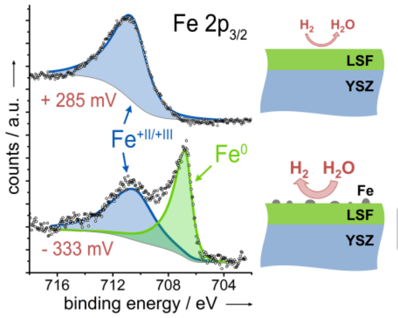
Water splitting activity and surface chemistry of perovskite-type $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ thin film electrodes were simultaneously investigated by impedance spectroscopy and synchrotron based near-ambient XPS. Upon cathodic polarization the formation of metallic iron on the electrode surface could be observed, accompanied by a strong improvement of the electrochemical water splitting activity.



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