

## The boosting effect of metal particles exsolved from perovskite-type electrodes on the electrochemical H<sub>2</sub>O splitting reaction in solid oxide electrolysis cells

Alexander K. Opitz<sup>a</sup>, Andreas Nenning<sup>a</sup>, Vedran Vonk<sup>b</sup>, Sergey Volkov<sup>b</sup>,  
Florian Bertram<sup>b</sup>, Andreas Stierle<sup>b</sup>, Jürgen Fleig<sup>a</sup>

<sup>a</sup> TU Wien, Institute of Chemical Technologies and Analytics, Getreidemarkt 9/164-EC,  
1060 Vienna, Austria

<sup>b</sup> Deutsches Elektronen-Synchrotron (DESY), Notkestraße 85, 22607 Hamburg,  
Germany

Precipitation of metallic nanoparticles from perovskite-type oxides under sufficiently reducing conditions is a very promising approach to obtain highly dispersed oxide-supported catalysts. Performing this so-called exsolution process from mixed ionic/electronic conducting (MIEC) oxide electrodes offers the very attractive possibility of tailoring the catalyst by electrochemically switching between different activity states.

In this study, the exsolution process and the re-oxidation of iron particles exsolved from mixed conducting La<sub>0.6</sub>Sr<sub>0.4</sub>FeO<sub>3-δ</sub> (LSF) thin film electrodes was monitored by X-ray diffraction (XRD) on an electrochemically operating cell at 625 °C in H<sub>2</sub>/H<sub>2</sub>O atmosphere. These synchrotron-based *in-situ* experiments revealed the formation of α-Fe on the LSF electrode surface under sufficiently reducing conditions (i.e. cathodic polarization), accompanied by a strong improvement of the electrode's catalytic activity. Under sufficiently high anodic polarization (i.e. oxidizing conditions), the oxidation of α-Fe to Fe<sub>1-x</sub>O and Fe<sub>3</sub>O<sub>4</sub> could be observed, accompanied by a drastic drop of the catalytic activity. Moreover, it was possible to reversibly switch between these two states by applying the corresponding electrochemical polarization even in atmospheres where Fe-oxides are thermodynamically unstable. A complete re-integration of exsolved Fe into the perovskite – as often stated in literature – is thus not required for an electrochemical switching between high and low catalytic activity.

Based on these results, a mechanism is discussed how the surface decoration by metallic particles can affect the H<sub>2</sub> oxidation and H<sub>2</sub>O splitting reaction by introducing a novel reaction pathway that bypasses the rate limiting step on the bare oxide electrode surface.