

Supporting information

***In situ* characterization of Ni and Ni/Fe thin film electrodes for oxygen evolution in alkaline media by a Raman-coupled scanning electrochemical microscope setup**

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ABSTRACT

In this file a detailed characterization of the synthesized thin film electrodes is given. Deposition curves and cyclic voltammograms of the thin film electrodes are presented. The chemical composition of all samples and the ITO electrode determined by ICP-OES analysis is shown and discussed. For morphological characterization, a scanning electron microscopic image of the 30 % Fe containing sample is shown as an example for determination of the film thickness. Additionally, the approach curve of the 25 μm Pt ultramicroelectrode (UME) to the substrate is given as well as theoretical approach data. Those Raman spectroscopic results which are not in the main text can be found in this file. Finally, all the electrochemical and spectroscopic data of the bare ITO electrode is presented and discussed.

To demonstrate the essential features of the Raman-coupled scanning electrochemical microscope, Ni and Ni/Fe thin film electrodes were prepared by chrono-potentiometric electrodeposition. A cathodic current of $50 \mu\text{A cm}^{-2}$ was applied over a period of 1000 s. The corresponding E/t-curves are displayed in Figure S1a. The atomic ratios of the respective metal sulfates (10 mM deposition solution) were adjusted as shown in Table S1.

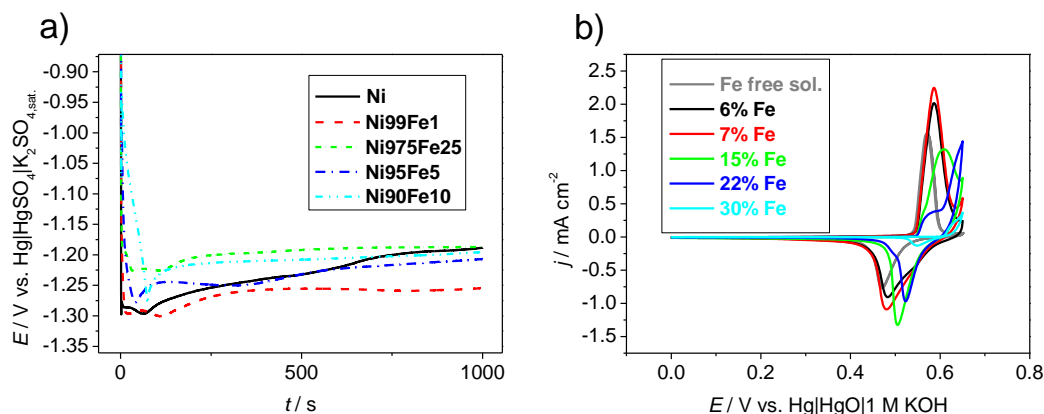


Figure S1: Chrono-potentiometric curves of the deposition in the respective metal salt solution (a) and cyclic voltammograms of all prepared thin film electrodes in 0.1 M KOH, scan rate 5 mV s^{-1} (b).

The composition of the thin film electrodes determined via ICP-OES (Table S1) showed high amounts of Fe in all samples which (in accordance to other work, see main text) is in all cases higher than the relative proportion in the deposition solution. Additional Fe incorporation into the films is likely caused by the presence of Fe in the 0.1 M KOH solution. To exclude an influence of the substrate on the Fe content, X-ray photoelectron spectroscopy (not displayed) of the bare indium-doped tin oxide (ITO) electrode was performed without finding any traces of Fe. The surface composition was found to be 10.3 wt% Sn in Sn/In (evaluating the areas of In $3p^{3/2}$ and Sn $3p^{1/2}$ peaks). This value correlates to the bulk composition of Sn/In that was additionally determined using ICP-OES (Table S1).

Table S1: Composition of the deposition solutions and the ICP-OES results of the composition of the Ni and Ni/Fe thin film electrodes determined after dissolving them in 5 ml concentrated HNO₃.

atomic ratio of the deposition solution	[Fe] / mg L ⁻¹	[Ni] / mg L ⁻¹	wt% Fe
Ni*	< LOD	0.284	0
Ni**	0.032	0.496	6.1
Ni99Fe1	0.036	0.503	6.7
Ni975Fe25	0.063	0.345	15.4
Ni95Fe5	0.121	0.433	21.8
Ni90Fe10	0.133	0.316	29.6

* used in Fe free solution, **Additionally, in this solution 1.89 mg L⁻¹ indium and 0.223 mg L⁻¹ tin were found resulting in 10.6 wt% Sn in Sn/In (m/m).

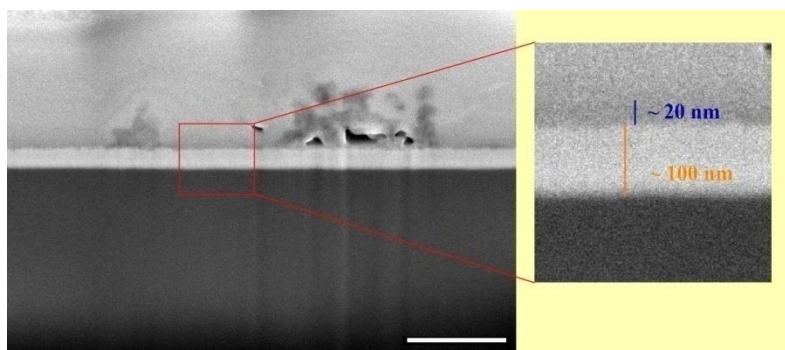


Figure S2: Electron microscopy image of the sample containing 30 % Fe sample after the electrochemical characterization procedure, the thin film is visible with dark shadow-like appearance above the bright ITO layer, the white scale bar represents 500 nm.

To get an impression of the morphology of the prepared thin films individual samples were studied with scanning electron microscopy. As displayed in Figure S2, on top of the non-conductive quartz substrate (dark) a bright layer of ~100 nm thickness can be found. This layer is likely composed of ITO and the thickness is in accordance to the manufacturer information. An additional darker region on top of the ITO with a thickness of 20 – 50 nm on the average is attributed to the deposited thin film layer containing also larger agglomerates.

Raman spectra were corrected by subtracting the initial spectrum at OCP potential. As shown in Figure S3a broad Raman features at ~500, 600 and 800 cm⁻¹ can be observed that are attributed to the conductive indium-doped tin oxide layer.

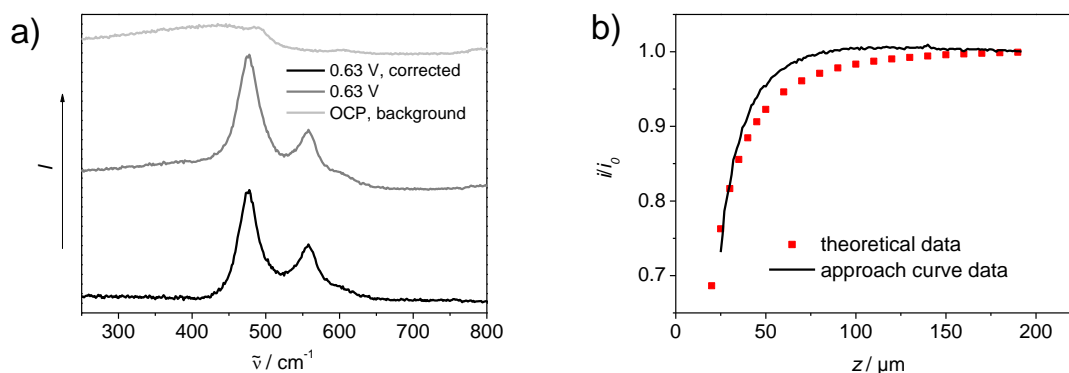


Figure S3: *In situ* Raman spectra of the Fe free Ni sample in 0.1 M KOH at OCP and at 0.63 V and the resulting corrected spectrum (a) and an example of an approach curve to the ITO substrate as well as theoretical approach data of a 25 μm UME (b).

As mentioned in the experimental part, the UME was positioned by an approach curve measurement bringing the UME to the ITO substrate while a constant reductive potential (-0.6 V) was applied. An example of such an approach curve which is representative for all other curves can be found in Figure S3b showing the normalized current (i/i_0) plotted against the relative tip-to-sample distance. The obtained curve sufficiently matches with theoretical data of a negative feedback.

The *in situ* Raman spectra of the 6 % and 22 % Fe containing samples are displayed in the main text (Figure 4). All the other spectra that were obtained during the coupled experiments are shown in Figure S4. As stated in the main text, the 30 % Fe sample shows a shift of the 557 cm^{-1} band to lower wavenumbers (550 cm^{-1}). Additionally in this sample, a third weak band can be found as a shoulder of the 475 cm^{-1} band at $\sim 500 \text{ cm}^{-1}$.

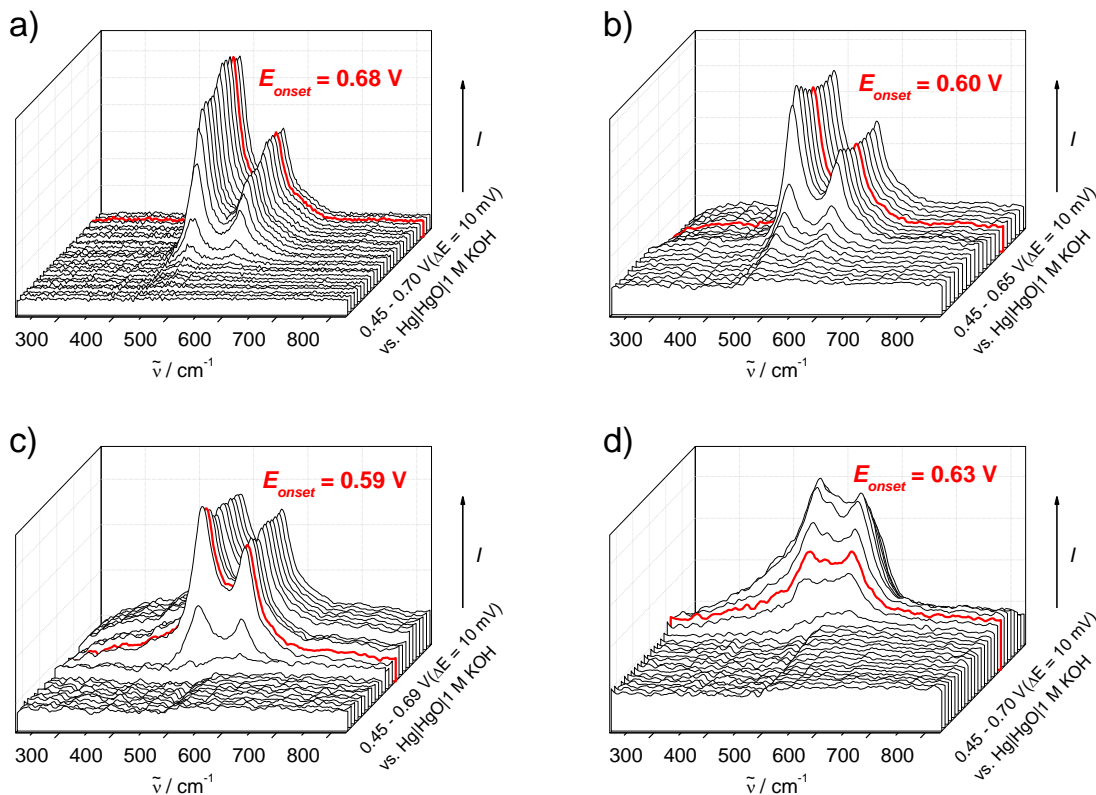


Figure S4: *In situ* Raman spectra of Ni thin film electrodes in Fe-free solution (a) and with 7 % (b), 15 % (c) and 30 % Fe content (d) in dependence of the applied potential, the *onset* potential detected by the UME is highlighted for every sample; all spectra are background corrected by subtracting the initial spectrum at OCP.

To exclude any effects from the transparent conductive substrate, the bare ITO electrode was examined by the very same procedure as the Ni and Ni/Fe thin film electrodes. The results can be found in Figure S5a where the current densities of the electrode and the UME response are plotted against the applied potential. Here, the UME response shows a starting oxygen evolution at potentials > 0.69 V, but the current density increase of the electrode as well as the UME response are magnitudes lower than in Figure 3. It can be concluded that the activity for the OER of the bare ITO is significantly lower than those of the Ni and Ni/Fe films. Also the Raman spectra are not affected by the ITO substrate which can be concluded from Figure S5b. The substrate shows Raman bands as already mentioned at ~ 300 , 600 and 800 cm^{-1} which do not change during potential modulation. By subtracting the initial spectrum at OCP as in Figure S3a

these peaks can be removed. As a result, other raising bands are only attributed to the structural changes in the Ni and Ni/Fe thin film electrodes.

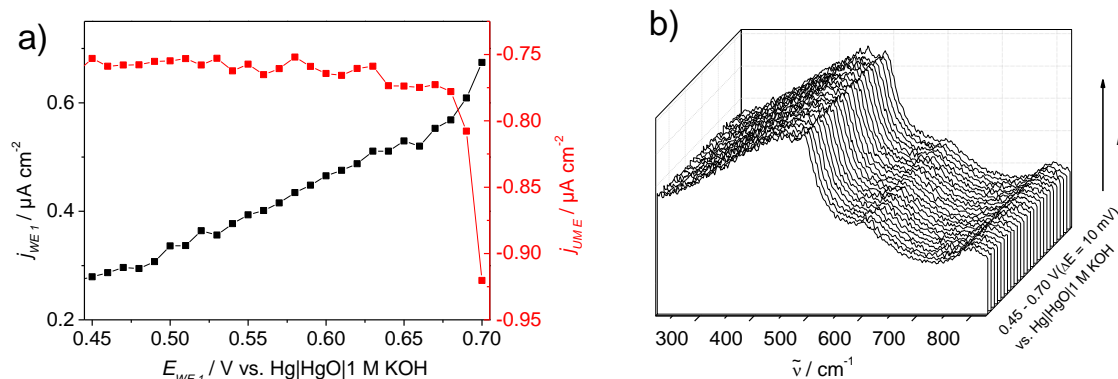


Figure S5: Current densities measured at the bare ITO electrode as well as the UME response (red) at -0.6 V for oxygen detection (a) and corresponding uncorrected *in situ* Raman spectra in 0.1 M KOH (b), please notice that the current densities are magnified by a factor of 1000 in comparison to the results in Figure 3 showing Ni and Ni/Fe thin film electrodes, lines connecting the data points are intended as a help for the eye.

Thus, indium-doped tin oxide on quartz glass can be used as adequate transparent and conductive material, which can be applied as electrode in such *in situ* experiments.