

Supplementary Information S1:

Possibilities and limitations of TOF-SIMS for porous solid oxide cells:

The analysis of porous solid oxide cells with TOF-SIMS is not straightforward. Several aspects of the data evaluation procedure must be taken into consideration to assure accuracy and to avoid over- or misinterpretation of the obtained data.

During a TOF-SIMS analysis a sample surface is bombarded with a primary ion beam followed by a mass spectrometry analysis of the emitted secondary ions. TOF-SIMS is a powerful technique to study qualitatively low levels of impurities and changes in the matrix structure in solid oxide cells, manifested in detection limits for most trace elements in the ppm and ppb range. For large scale production of solid oxide cells typically chemicals with low purity grades (e.g. “purified” or “technical”) are used. Consequently, a large number of elements are already present in the raw materials and most elements considered as impurities can be readily detected by TOF-SIMS in the untested cells. Therefore, the challenge in this study is the rather high background level of impurities compared to the observed changes in concentration of impurities, rather than the detection limit itself. Absolute values for the concentration of the impurities or the matrix elements are not given for the following reasons:

In general, the ionization process is poorly understood and no quantitative model currently exists that can accurately predict the secondary ionization process. The sensitivity towards an element is strongly dependent on the composition of the matrix (here Ni-YSZ or LSM-YSZ) and the type of primary beam used and in order to obtain reliable quantitative information a suitable standard close to the composition of the investigated samples has to be used and empirical corrections have to be applied. For dense samples, homogenous in structure and composition, the use of such

standards gives accurate results, but for the investigated Ni-YSZ or LSM-YSZ composites such results could be inaccurate or even invalid. Firstly, the samples have a porous structure (apart from the dense YSZ electrolyte) and a relatively rough surface. For the preparation of the cross sections the open pores are filled with epoxy glue, and consequently the investigated surface has an organic-inorganic hybrid structure. Even if the surface of these samples was mechanically smoothed, such hybrid structures can lead to non-uniform sputter processes/rates. Secondly, the matrix is a composite material consisting of equal amounts of Ni (or NiO for the non-reduced cell) and YSZ or of LSM and YSZ in the case of the anode. It can be assumed, that the same impurity with an identical concentration in a metallic Ni matrix can give different results than in an YSZ matrix. Since it is not obvious whether impurities have a preference to enrich one of the two matrix elements, the use of a standard would be extremely difficult and could be misleading for the here investigated samples.

Also the estimation of the sputter rate and therewith the sputter depth is difficult. Due to the surface roughness and the porous structure of the sample, it is difficult to give accurate values and to correlate the sputter times with depth. After the experiments, the sputtering area is visible by the naked eye due to changes in contrast compared to the rest of sample (Fig. 1Sa). Figure 1Sb shows the surface morphology obtained by an optical laser profilometer after sputtering. No differences were found in the surface structure of the sputtered area (blue rectangle in Fig. 1Sb) compared to the non-sputtered area, indicating that the sputter depth is small compared to the height differences in the surface topology of the SOECs. For estimating the sputter depth, measurements on dense YSZ/CGO/LSM (CGO = $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_2$) films with the same TOF-SIMS equipment under similar experimental conditions can be used. In these experiments a sputter rate of ~ 400 nm/h, corresponding to a depth of $2.5\text{ }\mu\text{m}$ for the 6 h of sputter time, was obtained. A

comparison of the sputter rates for dense YSZ and porous Ni-YSZ is not straightforward and therefore a sputter rate of 400 nm/h may only be used as a very rough estimate.

Nevertheless, the reproducibility of the TOF-SIMS data is excellent. Several measurements at different locations in the same sample give similar results as shown for the surface (Fig. 2Sa depth profiles) and for the cross section of the reduced cell (Fig. 2Sb). This accuracy allows a comparison of the samples among each other; the development, local enrichment, depletion and redistribution of impurities can be studied in detail and the influence of different operating conditions on the impurity distribution can be investigated. The 2-dimensional structure of the samples can be reconstructed from the TOF-SIMS data, the lateral resolution can be as high as 200 nm (one the instrument in question). Different particles like Ni, YSZ or LSM can be resolved by their specific elements. Examples of mapping of the sample surface and of a cross section are given in Figures 3Sa and 3Sb, respectively.

Figures for supplementary information:

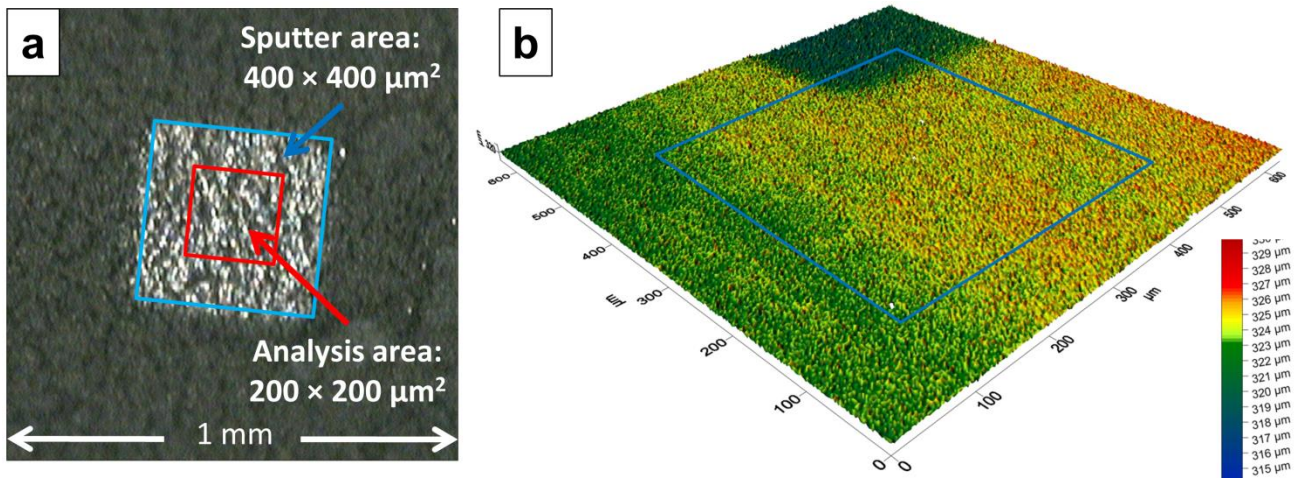
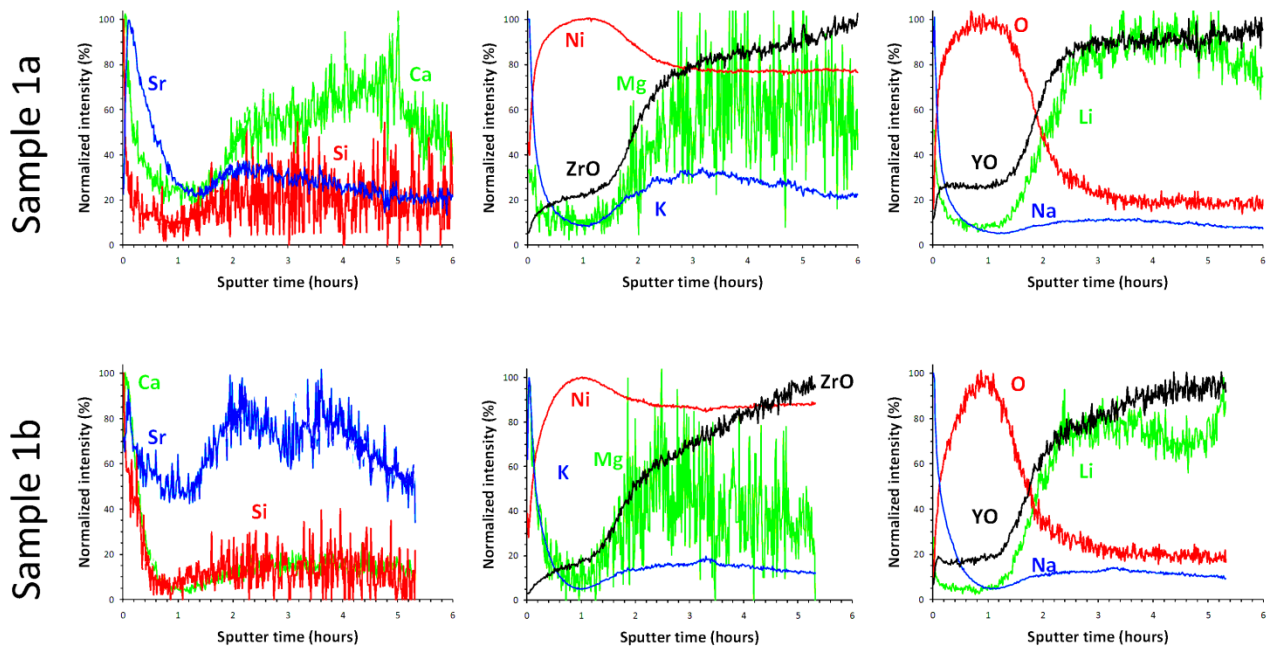


Figure 1S: a) Optical image of the sputtered and analyzed area of the Ni-YSZ surface b) topology of the sputtered area was obtained by optical laser profilometry. The blue rectangle marks the sputtered area, the red one in a) the analyzed area for depth profiling.

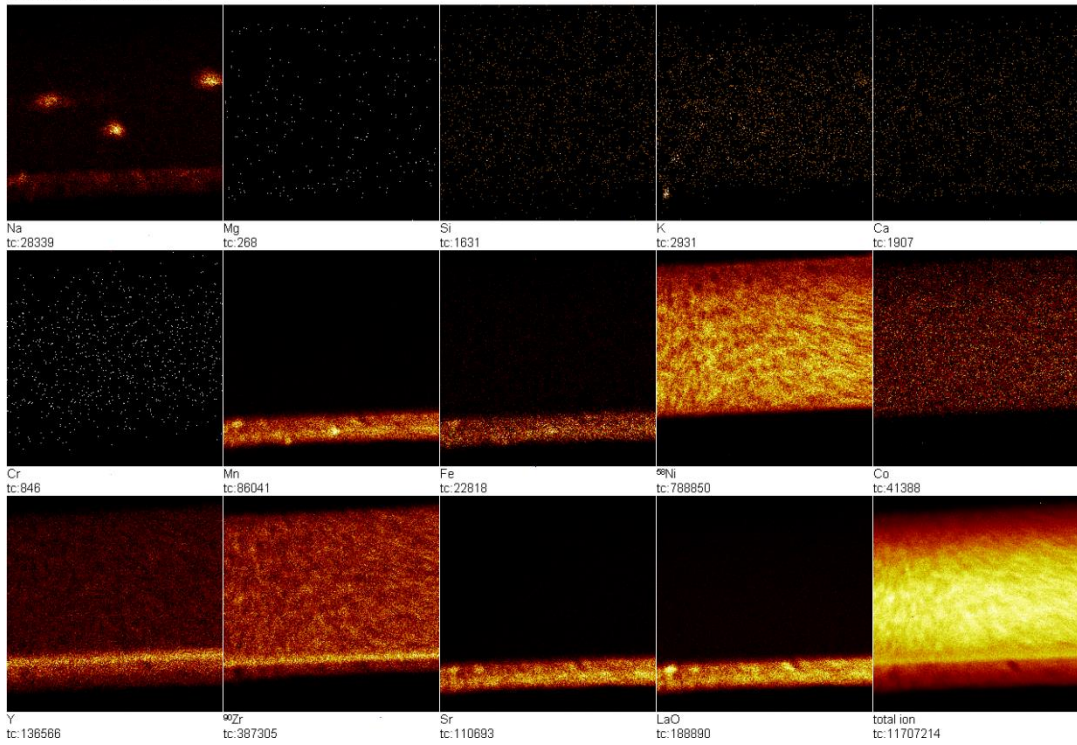
Depth profiles for selected elements – Positive ions



The depth profiles are normalized against the total ion intensity
and then individually normalized to 100%

Figure 2Sa: Depth profile for selected elements in sample 1 obtained two different locations on the cell. The profiles for the different elements in the two locations are similar.

Field of view: 500.0 x 500.0 μm^2



Field of view: 500.0 x 500.0 μm^2

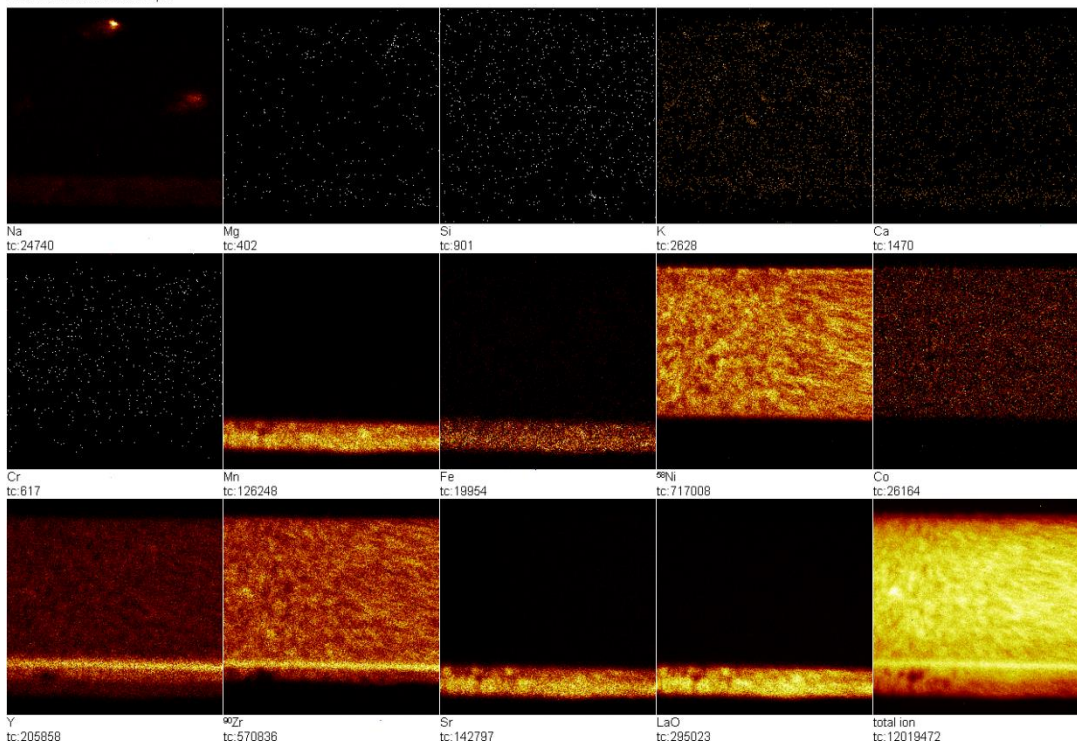


Figure 2Sb:

TOF-SIMS overview images of the different elements obtained at two different locations (cross section) in the reduced cell C2.

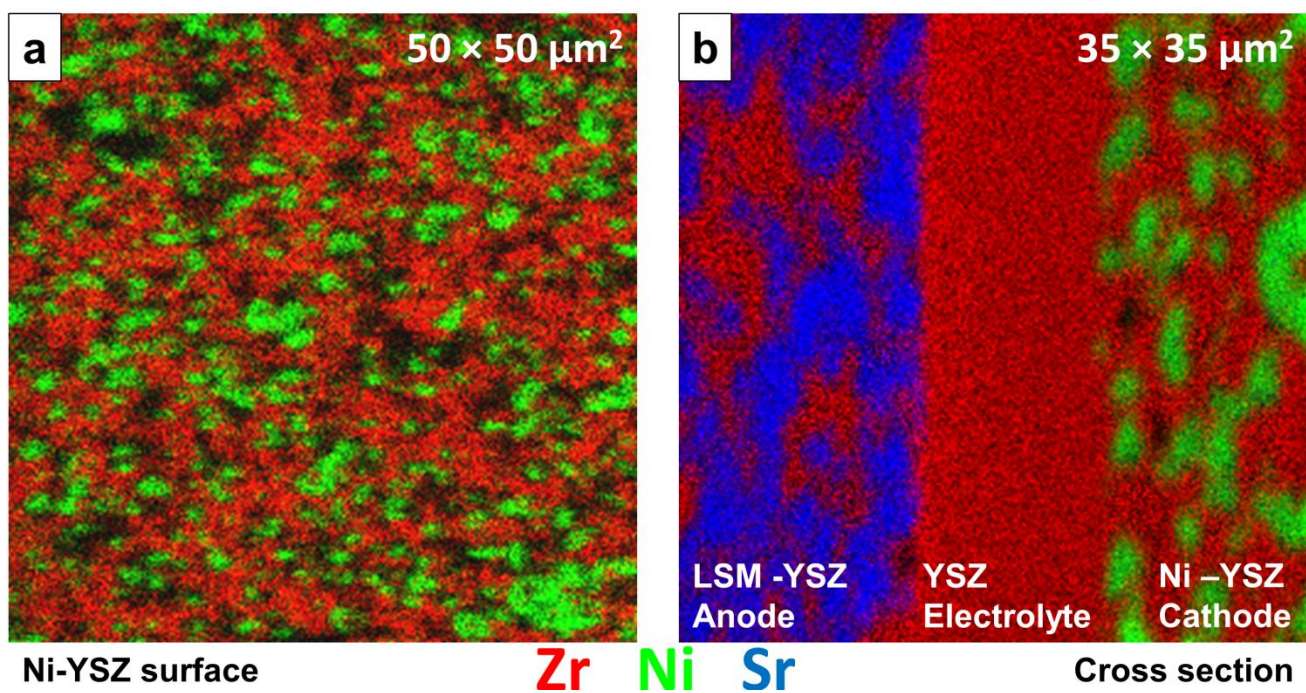


Figure 3S: High resolution: TOF-SIMS images of state-of-the-art solid oxide electrolysis cells; a) Ni-YSZ surface of a reduced cell (S1) b) cross section of the electrochemical active part of an as fabricated cell (C1).