Supporting Information

Dynamic behavior of impurities and native components in model LSM microelectrodes on YSZ

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Figure S1. Line profiles extracted from the TOF-SIMS Sr and LaO ion images $(150 \times 150 \ \mu m^2)$ of an LSM microelectrode with a diameter of 100 μ m and a thickness of ~500 nm. The purple arrow in the inset indicates from where the line profile was created. All ion images and thus line profiles were normalized against the total ion image in order to remove possible instrument effects.

Line profiles can be extracted from the ion images. Figure S1 displays Sr and LaO line profiles extracted from the corresponding ion images. The purple arrow in the inset indicates from where the information was obtained from. The line profiles are displayed on a logarithmic intensity axis in order to enhance the rather weak Sr and LaO signals on the YSZ surface, which are not visible in the ion images due to the very high intensity originating from the LSM microelectrode surface area.



Figure S2. (a) TOF-SIMS silicon ion image $(31 \times 31 \ \mu\text{m}^2)$ of an LSM microelectrode with a diameter of 20 μm and a thickness of ~500 nm for the ASM electrode. The ion image was normalized against the total ion image in order to remove possible instrument effects. (b) SEM image of a different 20 μm LSM microelectrode showing the position of the silicon containing particles.

The silicon edge area (part of the LSM edge area) with a width of ~3 μ m (Figure S2a) is observed on all microelectrodes for the ASM electrode, and not on any of the microelectrodes that were subjected to high temperatures in the CAHT-2. The width (~3 μ m) is the same for all sizes of microelectrodes, *i.e.* 20, 50, and 100 μ m in diameter. Figure S2b is a SEM image of a 20 μ m LSM microelectrode (not the same as in Figure S2a) showing that the silicon containing particles (black arrows pointing at them) occupy only the outer part of the LSM edge area.



Figure S3. TOF-SIMS depth profiles for selected markers obtained from four different LSM surface areas on the TAL electrode. The depth scales for the profiles were modified in order to compensate for the missing sputter cleaning. All ion profiles were normalized against the total ion intensity in order to remove possible instrument effects.

Four different LSM surface locations for the TAL electrode were subjected to TOF-SIMS depth profiling in order to map the point-to-point variation with respect to the depth profiles. As is evident three out of four surface locations produced very reproducible depth profiles, with only one (Figure S3d) deviating somewhat at a depth of ~30 nm, which is associated with a relatively high concentration of manganese.



Figure S4. XPS depth profiles (La, Sr, Mn, Zr) obtained on the LSM surface of the TAL electrode. (a) The entire LSM electrode and some of the YSZ. The depth window between the dashed lines represents where the element composition was determined. (b) Narrow depth window showing the quantitative changes induced by heat treatment near the gas/LSM interface.

In order to confirm that the observed intensity variations in the presented TOF-SIMS depth profiles in Figure S3 are not a consequence of matrix effects caused by changed material properties induced by the elevated temperature, XPS depth profiling was employed as matrix effects do not exists in this technique. As is evident from Figure S4 the TOF-SIMS depth profiles indeed reflect changes in concentration. The qualitative shapes of the profiles unfortunately resemble the depth profiles shown in Figure S3d, which suggests that a somewhat non-representative surface spot was chosen. However, the goal was to confirm that changes in the TOF-SIMS depth profiles reflect changes in concentration, which was indeed confirmed. The depth window between the two dashed lines in Figure S4a has parallel profiles, so it is an obvious choice to determine the element composition. The element composition was measured to $(La_{0.75}Sr_{0.27})_{0.95}Mn_{0.86}O_n$, which is in fair agreement with the expected composition $(La_{0.75}Sr_{0.25})_{0.95}MnO_3$ except for manganese, which is believed to be caused by partial dissolution in YSZ. The sputter process is known to deplete oxygen, so it is usually underestimated and therefore disregarded in this context. So why not use XPS for all the microelectrodes? XPS has (compared to TOF-SIMS) inferior sensitivity, inferior surface sensitivity, inferior spatial resolution, and a relatively long acquisition time.



Figure S5. TOF-SIMS depth profiles for selected markers obtained from four different LSM surface areas on the TAL electrode. All ion profiles were normalized against the total ion intensity in order to remove possible instrument effects.

Four different LSM surface locations for the TAL electrode were subjected to TOF-SIMS depth profiling in order to map the point-to-point variation with respect to the depth profiles. As is evident from the depth window in question all four surface locations produced very reproducible depth profiles.



Figure S6. TOF-SIMS ion images $(50 \times 50 \ \mu m^2)$ showing the lateral distribution of impurities (Si, K, Na) on YSZ for the OCV electrode.

The impurities (Si, K, Na) exhibit inhomogeneous intensity on the YSZ surfaces surrounding the LSM microelectrodes. This phenomenon is difficult to see in the ion images of the entire 100 μ m microelectrodes, but on a smaller scale (*i.e.* 50×50 μ m² images) it is clearer. This is presented in Figure S6 for the OCV electrode. The phenomenon is believed to be caused by varying crystallographic orientations that presumably will result in different affinities towards different species, which will result in an inhomogeneous distribution in regard to the concentration of surface species between different grains. The work by Stanek *et al.*³² supports this assumption.