Supporting Information

Outstanding oxygen reduction kinetics of $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ surfaces decorated with platinum nanoparticles

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1. Characterization of LSF64 target and LSF64 thin film by means of X-ray diffraction

Figure S1 shows a diffractogram of a LSF64 thin film decorated with platinum particles, measured in gracing incidence geometry, and the LSF64 target used for the deposition of the thin films measured in Bragg-Bretano geometry. Owing to their small amount and size, it was not possible to detect any signal from the platinum particles on the surface of LSF64 by means of the lab-based diffractometer.

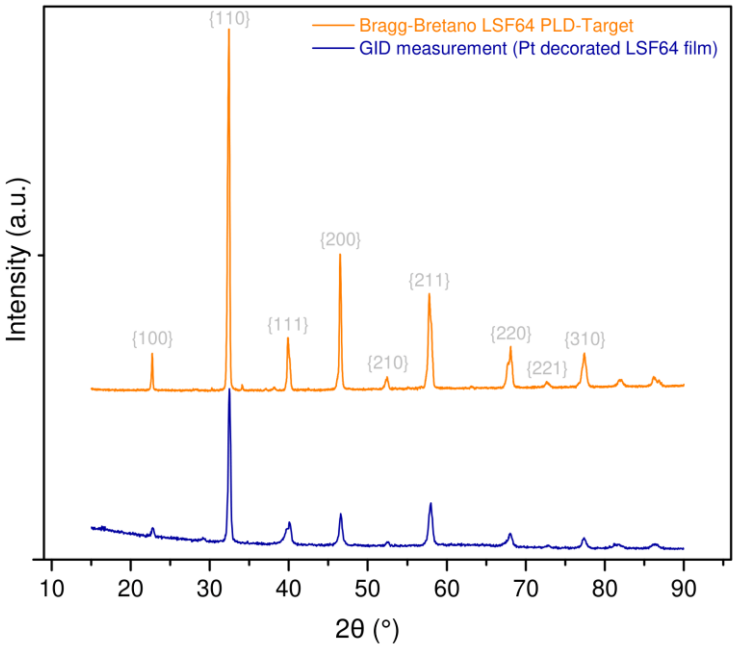

Figure S1: Diffraction pattern of LSF64 thin film decorated with Pt particles, measured in gracing incidence geometry (GID); LSF64 target measured in Bragg-Bretano geometry.

2. Effect of the deposited platinum amount on the resistance: SEM images

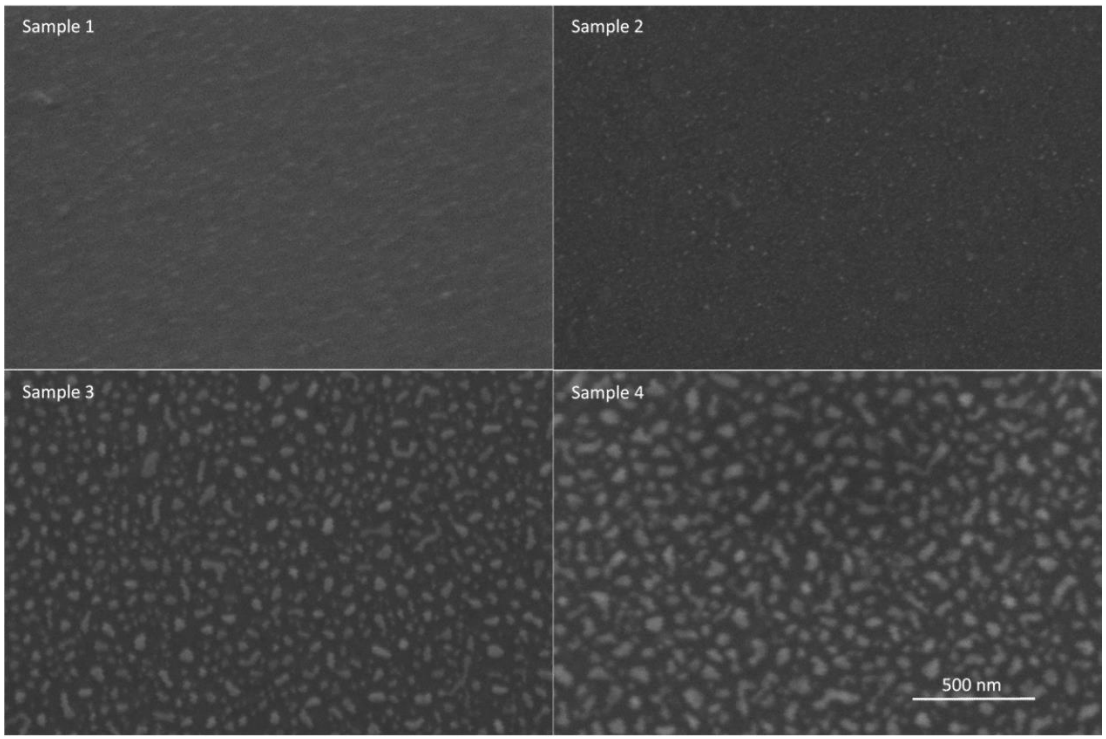

Figure S2: BSE images of all samples decorated with different amounts of platinum.

3. Effect of the deposited platinum amount on the resistance: XPS results

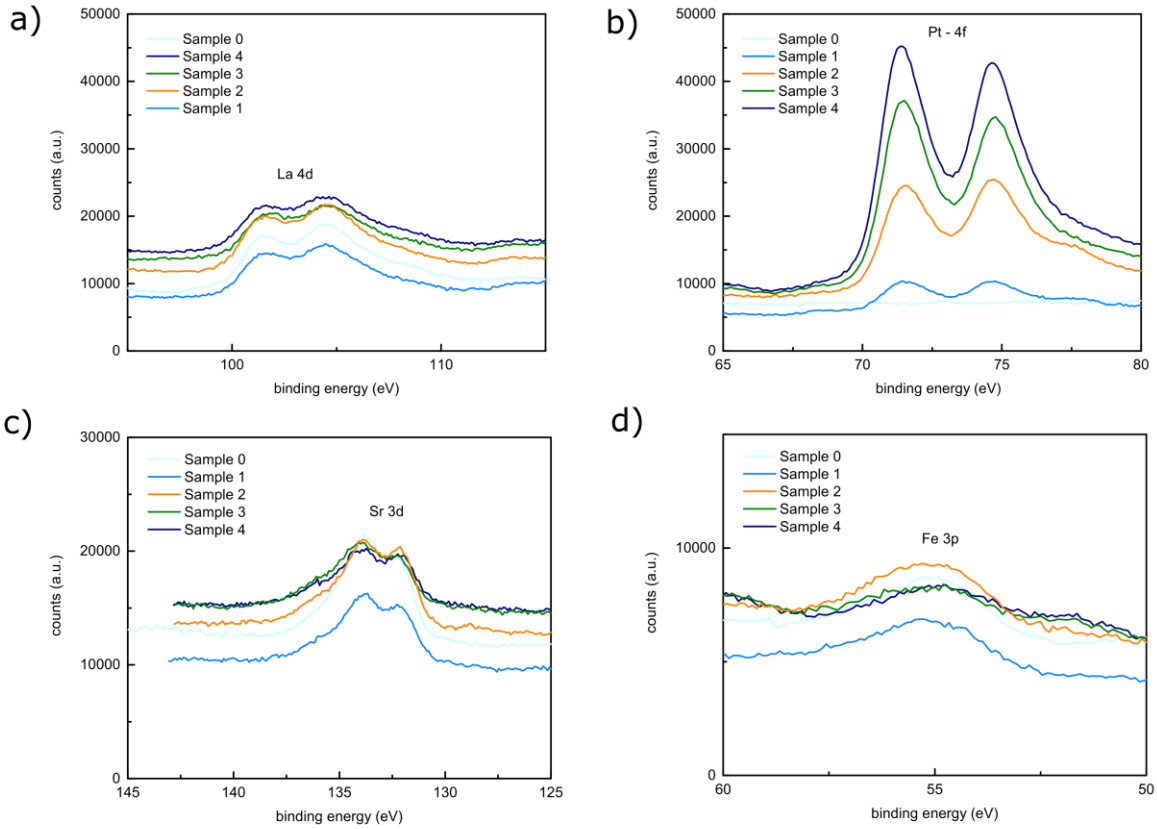

Figure S3: Results of XPS measurements on LSF64 electrodes decorated with different amounts of Pt. a) XPS spectra of La, b) XPS spectra of Pt, c) XPS spectra of Sr, d) XPS spectra of Fe

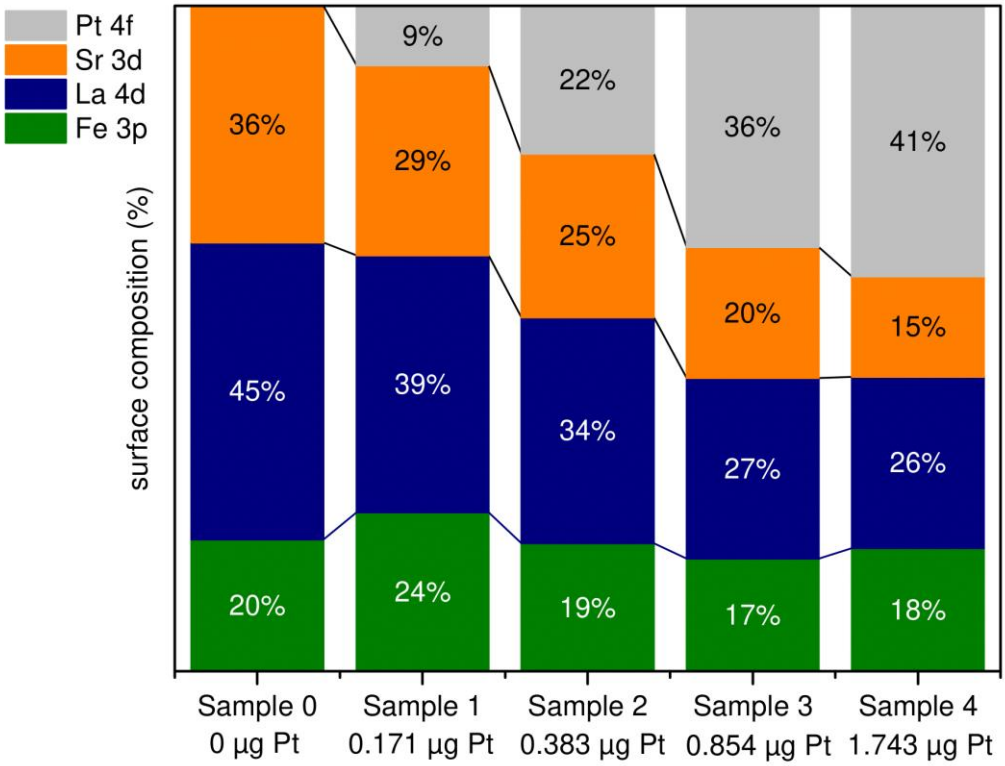

Figure S4: Surface composition of samples with LSF64 electrodes decorated with different amounts of platinum determined by XPS measurements.

4. Effect of platinum nanoparticles on other MIEC materials and in humidified H_2

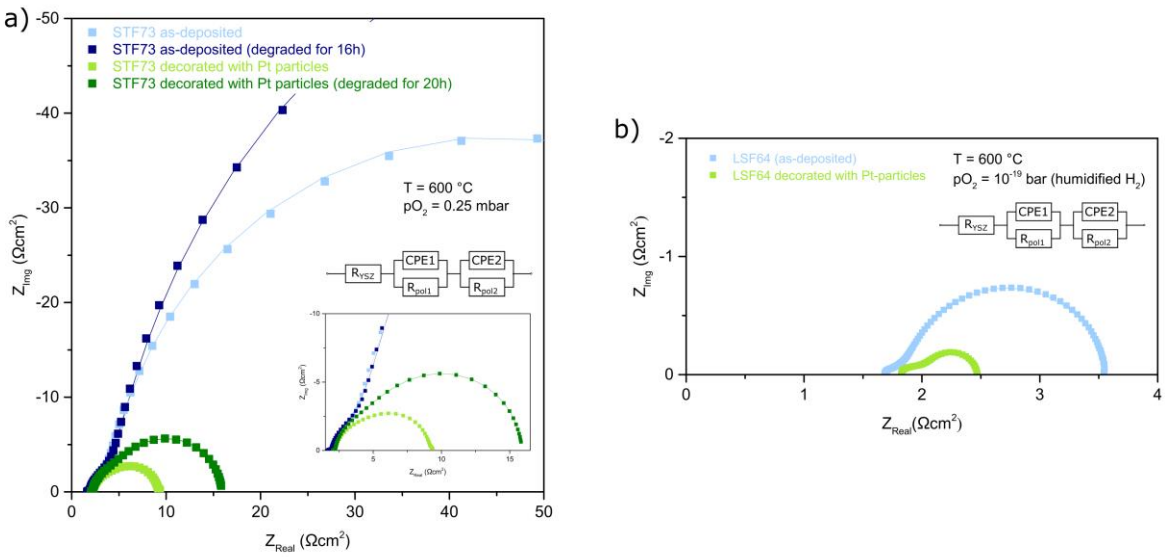

Figure S5: EIS spectra of a) a sample with STF73 electrodes in 0.25 mbar and b) with LSF64 electrodes in humidified H_2 measured in 600 °C before and after Pt decoration.

The accelerating effect of Pt nanoparticles is not restricted to LSF64 in oxidizing conditions. Figure S5 a) displays the same type of measurements for $SrTi_{0.7}Fe_{0.3}O_{3-\delta}$ thin film electrodes with and without Pt, before and after degradation. A symmetrical sample with STF73 electrodes was prepared according to reference [S1] and measured in 0.25 mbar O_2 at 600 °C. The area specific resistance of the pristine STF73 electrode was 86 Ωcm^2 and reached 150 Ωcm^2 after 16 h of measurement. The freshly Pt decorated sample exhibited an ASR of 6.5 Ωcm^2, which increased to 15 Ωcm^2 after 20 h at 600 °C. Owing to an additional impedance feature, the spectra of both the undecorated and the decorated sample were fitted with a resistance in series with two R-CPEs. It was observed that due to platinum decoration the low frequency resistance (R2) and capacitance (C2) changed, while the intermediate frequency resistance (R1) and capacitance (C1) stayed constant. The latter was therefore assigned to the STF73-YSZ interface. Considering only the surface-related resistance, we find a change by Pt decoration from 85 Ωcm^2 to 5 Ωcm^2, clearly showing that again much faster oxygen exchange is found with Pt (though the effect is not as pronounced as for LSF64 with Pt).

In addition to measurements under oxidizing conditions, a symmetrical sample with LSF64 electrodes was investigated under reducing conditions (2.4% humidified H_2 in Argon, pO_2 = 10^{-21} mbar at 600 °C). The obtained spectra (figure S5 b)) were fitted to two R-CPE element, one to describe the rather pronounced shoulder in the mid frequency range and another R-CPE to describe the semicircle in the low frequency range. Under these conditions, where already

pristine LSF64 thin films exhibit fast kinetics, the effect of platinum decoration was smaller, but still observable, with about a factor of 2 faster surface reaction. This result is similar to the promoting effect of metallic Fe particles exsolved from LSF64 electrodes under reducing conditions [S2] thus indicating that the deposited particles may act via a similar mechanism as the exsolved ones. The obtained spectra were fitted to two R-CPE element, one to describe the rather pronounced shoulder in the mid frequency range and another R-CPE to describe the semicircle in the low frequency range. The degradation process of the sample was not investigated, but earlier studies had shown that LSF64 exhibits very little degradation in humidified H_2.[S3] Accordingly we conclude that the beneficial effect of Pt nanoparticles is not restricted to the oxygen reduction reaction.

5. References

[S1] A. Nenning, L. Volgger, E. Miller, L. V. Mogni, S. Barnett, J. Fleig, *Journal of The Electrochemical Society*, 2017, **164**, 364–371.

[S2] A. K. Opitz, A. Nenning, C. Rameshan, R. Rameshan, R. Blume, M. Hävecker, A. Knop-Gericke, G. Rupprechter, J. Fleig, B. Kloetzer, *Angewandte Chemie International Edition* 2014, **54**, 2628–2632.

[S3] S. Kogler, A. Nenning, G. M. Rupp, A. K. Opitz, J. Fleig, *J. Electrochem. Soc*. 2015, **162**, 317–326.