

Supplementary Informations

Materials and Methods

The synthesis of $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3\pm\delta}$ was based on the citrate complex sol-gel route.

- 5 Stoichiometric amounts of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99% *ChemPur*), $\text{Sr}(\text{NO}_3)_2$ (99% *Alfa Aesar*) and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98.5% *Alfa Aesar*) were dissolved in ethylene glycol. The mixed nitrate solution was added to a mixture of $\text{MnN}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$ (98% *Alfa Aesar*), citric acid and ethylene glycol in the ratio 1:4:3:99.
- 10 The solution was stirred and heated up to 90 °C for one hour. For further concentration the mixture was heated up to 150 °C then forming a homogeneous brown gel which was finally calcinated at 600 °C for five hours.
- The powder was characterized by X-ray diffraction (XRD) and inductively coupled plasma mass spectrometry (ICP-MS, $\text{La}_{0.73}\text{Sr}_{0.27}\text{Mn}_{0.3}\text{Cr}_{0.59}\text{O}_3$) to verify the formation of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3\pm\delta}$ perovskite phase
- The calcined powder was wet milled in isopropanol, isostatic pressed into pellets and sintered at 800 °C for three hours.
- 20 sintered pellets were used as targets for the laser ablation process.
- For the pulsed laser deposition process a KrF excimer laser with a wave length of 248 nm was used. The laser power was fixed at 300 mJ/pulse with a pulse frequency of 5 Hz. The oxygen partial pressure in the chamber was held constant at $1 \cdot 10^{-2}$ mbar in order to avoid film cracking and the temperature of the substrate was 450 °C during the deposition for 60 minutes. The as-grown films were annealed at 800 °C for 3 h in oxygen atmosphere to obtain the perovskite phase.
- 25 oxygen partial pressure in the chamber was held constant at $1 \cdot 10^{-2}$ mbar in order to avoid film cracking and the temperature of the substrate was 450 °C during the deposition for 60 minutes. The as-grown films were annealed at 800 °C for 3 h in oxygen atmosphere to obtain the perovskite phase.
- 30 The samples were characterized by X-ray diffraction (XRD) and Scanning electron microscopy (SEM).

In situ XPS

- The beamline at ELETTRA/Sincrotrone Trieste, Italy allows two modes of operation: imaging and spectroscopy from a small dot. For our experiments we used a photon energy of approximately 650 eV, the instrumental broadening is about 0.35 eV. The spatial resolution of the instrument approximates to 100 nm. The samples were heated up to 600 °C by a Boraelectric heating element at a residual oxygen partial pressure of 10^{-6} mbar. To obtain the element distribution on the surface two dimensional maps were recorded by scanning the sample and collecting the photoelectrons of a selected element. For detailed informations of the surface composition on a local scale we used the spatially resolved photoelectron spectroscopy. All spectra and images were fitted by using XPSPeak4.0 and standardized (Intensities) with IGOR Pro 6.0.

In situ SIMS

- The used TOF.SIMS⁵ machine (IonTOF, Münster, Germany) is equipped with a Bismut cluster primary ion gun and with two sputter guns for depth profiling (Oxygen and Caesium). Always positive ions were analyzed. A special designed sample holder (Fig. S1) (ION ToF GmbH, Münster) enables to investigate *in situ* the diffusion processes of the different species at elevated temperatures under electrochemical

polarization. Images were recorded at the YSZ/LSCrM interface with a magnitude of $500 \times 500 \mu\text{m}^2$ and a resolution of 3.9 μm . To achieve a greater significance each area were scanned for 50 times, each with two shots per pixel.

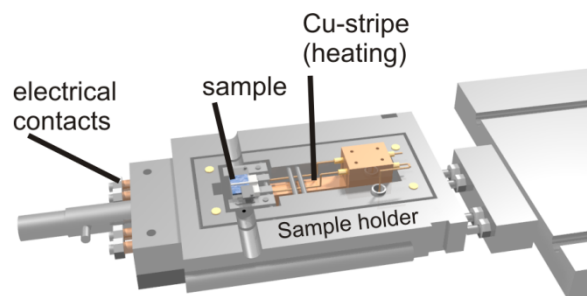


Fig S1 Sample holder for the *in situ* SIMS measurements

60

Before the electrochemical experiments were performed, all samples were annealed in the SIMS chamber at 600 °C for 30 minutes and then analyzed to test if any changes occur during the annealing process. This procedure was repeated around three times until no further changes could be detected.

The *in situ* polarization measurements were again performed at 500 °C with an oxygen partial pressure of 10^{-6} mbar and different applied voltages for 30 minutes. After electrochemical polarization the samples were cooled down to 200 °C in 30 minutes. It is not possible to perform the SIMS measurements at elevated temperatures due to the high background of thermal emitted ions. This procedure (heating/polarization/cooling/measurement) were repeated for three times (cathodic polarization ($V_{\text{WR}} = -2.5$ V)/anodic polarization ($V_{\text{WR}} = +2.0$ V)/cathodic polarization ($V_{\text{WR}} = -2.5$ V)) to check the reproducibility of the observed segregation phenomenon.

70

75

Results

80 Sample Preparation

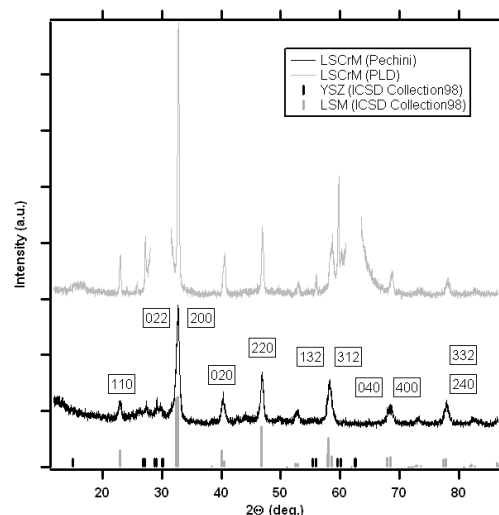


Fig. S2 XRD of the as prepared LSCrM powder and the thin film electrode after annealing at 800 °C for 3 hours. The XRD of the LSCrM powder (black line) and the deposited LSCrM film (gray line) shows the pure perovskite phase with no impurities phases.

85

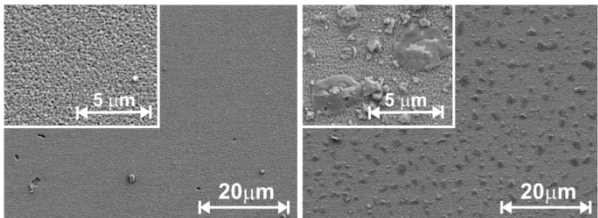
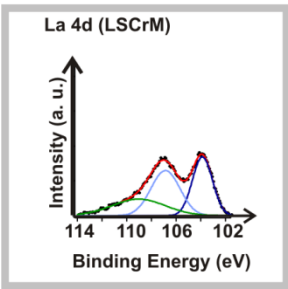


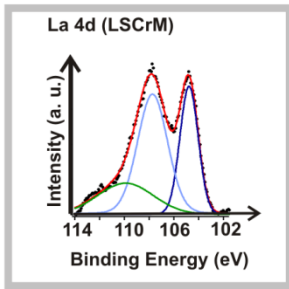
Fig. S3 HSEM image of a LSCrM electrode surface after annealing at 800 °C for 3 hours (left) and after electrochemical polarization (cathodic and anodic) (right). The HSEM characterization of the annealed electrode surface shows a covering film. After polarization the film is covered with small dots which were identified as SrO_x by EDX.

In situ XPS

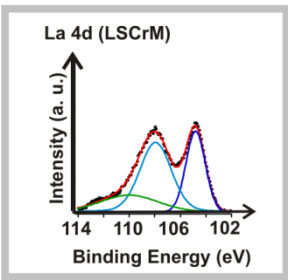
a) without polarization



b) cathodic polarization (V_{WR} = -2.5 V)



c) anodic polarization (V_{WR} = 2.0 V)



d) cathodic polarization (V_{WR} = -2.5 V)

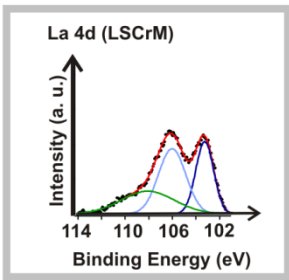
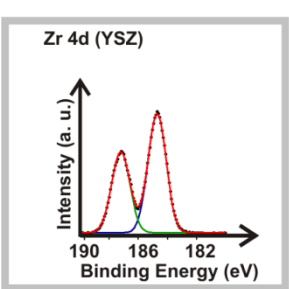
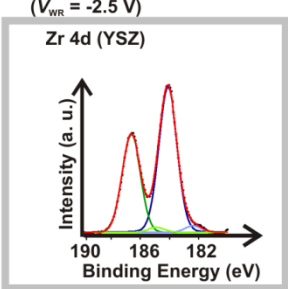


Fig. S4 La 4d spectra monitored *in situ* on the LSCrM surface at 600 °C under different applied voltages. The La 4d peak consists of a doublet and a satellite peak on the high binding energy side. During cathodic polarization the LSCrM surface become enriched in La and anodic polarization causes a depletion of the surface. A segregation of La on the YSZ surface could not be observed for any time.

a) without polarization



b) cathodic polarization (V_{WR} = -2.5 V)



c) anodic polarization (V_{WR} = 2.0 V)

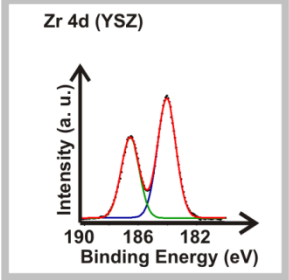


Fig. S5 Zr 4d spectra monitored *in situ* on the electrolyte surface at 600 °C under different applied voltages. The Zr 4d peak reveals as a good resolved doublet^{S1,S2}. Additionally, under cathodic polarization a second doublet at lower binding energies appears. The reason for this additional component is an initiating reduction of Zr(IV+) to Zr(III+).

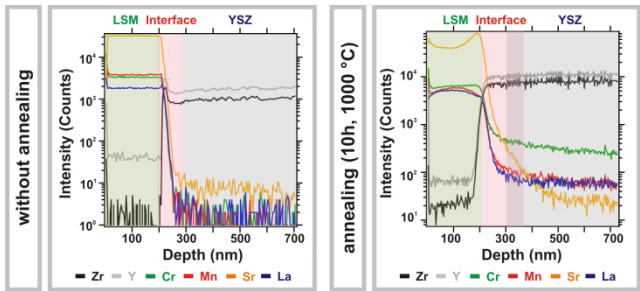


Fig. S6 SIMS depth profiles before and after cathodic polarisation. Diffusion of strontium in the bulk of the electrode after cathodic polarization is visible.

30

Literature

S1 M. Matsuoka, S. Isotani, J. F. D. Chubaci, S. Miyake, Y. Setsuhara, K. Ogata, N. Kuratani, Journal of Applied Physics, 88, (2000), 6, 3773
35 S2 J. C. Ruiz-Morales, J. Canales-Vasques, D. Marrero-Lopez, J. Pena-Martinez, A. Tarancon, J. T. S. Irvin, P. Nunez, Journal of Materials Chemistry, 18, 2008, 5072