

## High performance anodes with tailored catalytic properties for $\text{La}_{5.6}\text{WO}_{11.4-\delta}$ based proton conducting fuel cells

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### EXPERIMENTAL DETAILS

$\text{La}_{0.85}\text{Sr}_{0.15}\text{CrO}_{3-\delta}$  (LSC) and  $\text{La}_{0.75}\text{Ce}_{0.1}\text{Sr}_{0.15}\text{CrO}_{3-\delta}$  (LSCCe) powders were prepared by citrate reaction route as described elsewhere, with a final sintering temperature of 1200 °C. <sup>1</sup>  $\text{La}_{5.6}\text{WO}_{11.4-\delta}$  (LWO) powder was commercial powder provided by Cerpotech (Norway). Crystalline phases were identified by X-ray diffraction (XRD) performed in a PANalytical Cubix fast diffractometer, using  $\text{CuK}\alpha_1$  radiation and an X'Celerator detector in Bragg-Brentano geometry. XRD patterns were analysed using X'Pert Highscore Plus software.

Total conductivity measurements were carried out by standard four-point DC technique on sintered rectangular bars (1500 °C) by using silver contacts and wires. The constant current was supplied by a programmable current source (Keithley 2601), and the voltage was measured by a multimeter (Keithley 3706). The measurements were performed in cooling down (after two hours stabilization at 800 °C) under different wet atmospheres (5%  $\text{H}_2$  and  $\text{D}_2$  saturated with  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  at 20 °C, respectively)

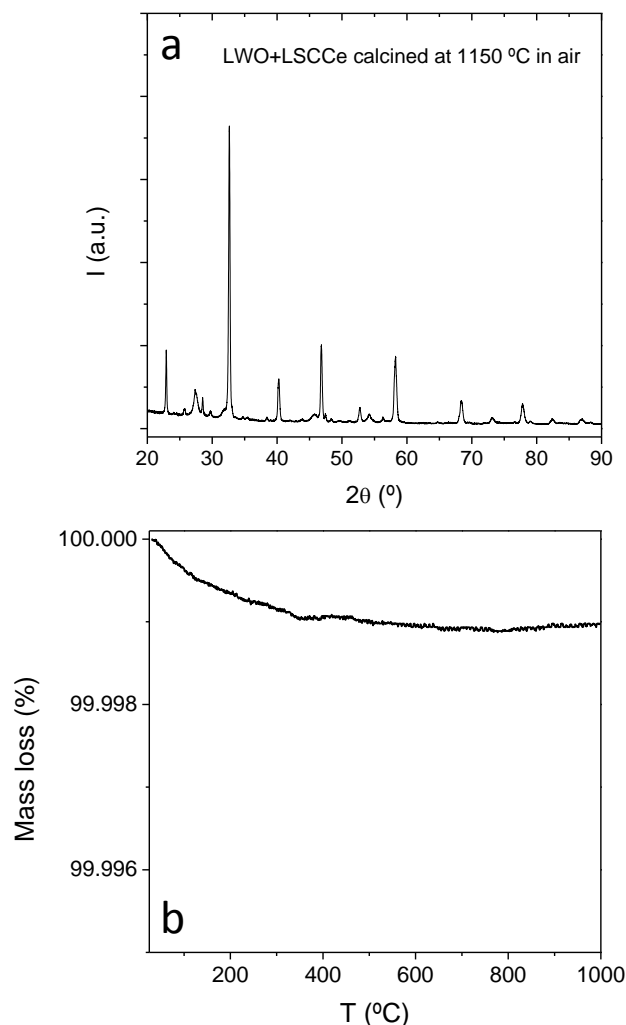
Dense ~1 mm-thick LWO disks were obtained by uniaxially pressing the ball-milled LWO powder at ~120 MPa and final firing at 1500 °C for 5 h. Porous ~15  $\mu\text{m}$  electrodes were obtained by screen-printing the chromite inks on both sides of LWO electrolyte disks. Firing temperature of the screen-printed cells was 1150 °C for 2 h. The infiltration procedure was made by using 1 M and 5 M water solution of Ni Nitrate ( $\text{LSCe}+1\text{Ni}$  and  $\text{LSCe}+5\text{Ni}$ , respectively). The solutions were dropped on the surface of the electrodes and allowed to penetrate into the electrodes pores for 30 min. The infiltration step with the 5 M solution was repeated 4 times. Each infiltration step was followed by calcination at 300 °C to decompose the nitrates. The final size of symmetrical cells was 15.5 mm in diameter, whereas anodes were ~9 mm in diameter. Symmetrical cells were tested by electrochemical impedance spectroscopy (EIS) in two-point configuration. Input signal was 0 V DC – 20 mV AC in the 0.01 –  $3 \cdot 10^5$  Hz frequency range. This signal was generated by a Solartron 1470E and a 1455A FRA module equipment. EIS measurements were performed in the 650-900 °C range, under moistened atmospheres (2.5% vol.  $\text{H}_2\text{O}$ ) at different  $p\text{H}_2$  (100%, 50% and 5%  $\text{H}_2$ ) and in wet 5%  $\text{D}_2$  (2.5% vol.  $\text{D}_2\text{O}$ ). In all the cases, the total flow remained constant (100  $\text{mL} \cdot \text{min}^{-1}$ ). All the impedance spectra were corrected by removing the contribution of the LWO electrolyte, i.e, the high frequency real axis cut-off in the Nyquist diagrams.

The microstructure was investigated using scanning electron microscopy (SEM) (Zeiss Ultra 55), and elemental analysis was carried out with energy-dispersive X-ray spectroscopy (EDS) (INCA, Oxford). Ni particles prepared by using similar procedure as for infiltration but on a Si single crystal substrate were analysed by transmission electron microscopy (TEM) in a Philips CM10 microscope, after a heating treatment at 800 °C in  $\text{H}_2$ .

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1 V.B. Vert, F.V. Melo, L. Navarrete, J.M. Serra, *App. Catal. B*, 2012, **115-116**, 346

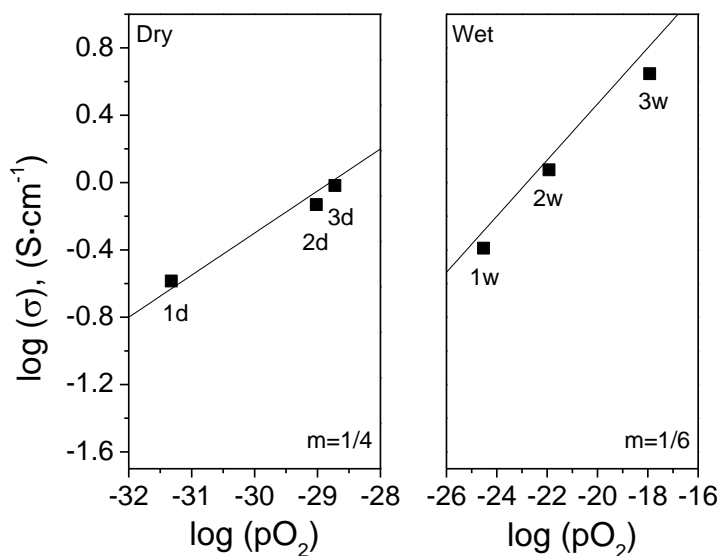
**Supporting Figure S1:** XRD pattern of the LWO+LSCCe after calcination together at 1150 °C, 2 h (a) and TG analysis of the LSCCe in Ar (85%)-CO<sub>2</sub> (15%) (b)



XRD pattern (Fig S1a) of the mixture of LWO and LSCCe (50 wt.%) after being sintered together at 1150 °C for 2 h shows peaks that can be ascribed to the LWO phase and to the chromite phase. Also small amount of SrCrO<sub>4</sub> and CeO<sub>2</sub> that disappear in reducing conditions at high temperatures as is showed in the main text (Figure 1a) and as it is reported elsewhere (ref. 9). It is also possible that some Ce ions form traces of Ce<sub>2</sub>O<sub>3</sub>, in reducing atmospheres. This new phase is stable and may also work as a catalyst that would not be detrimental for the anode performance, especially in such a small quantities.

The thermogravimetric curve (Fig S1b) shows a slight weight loss at temperatures below 400 °C while at higher temperatures the mass remains practically constant. This fact indicates that lack of carbonation processes/reactions (CO<sub>2</sub> uptake) at temperatures below 800 °C and the associate carbonate decomposition (CO<sub>2</sub> release) at temperatures above 800 °C.

**Supporting Figure S2:**  $pO_2$  dependence of the total conductivity at 700 °C of LSCCe measured in dry atmospheres and wet atmospheres

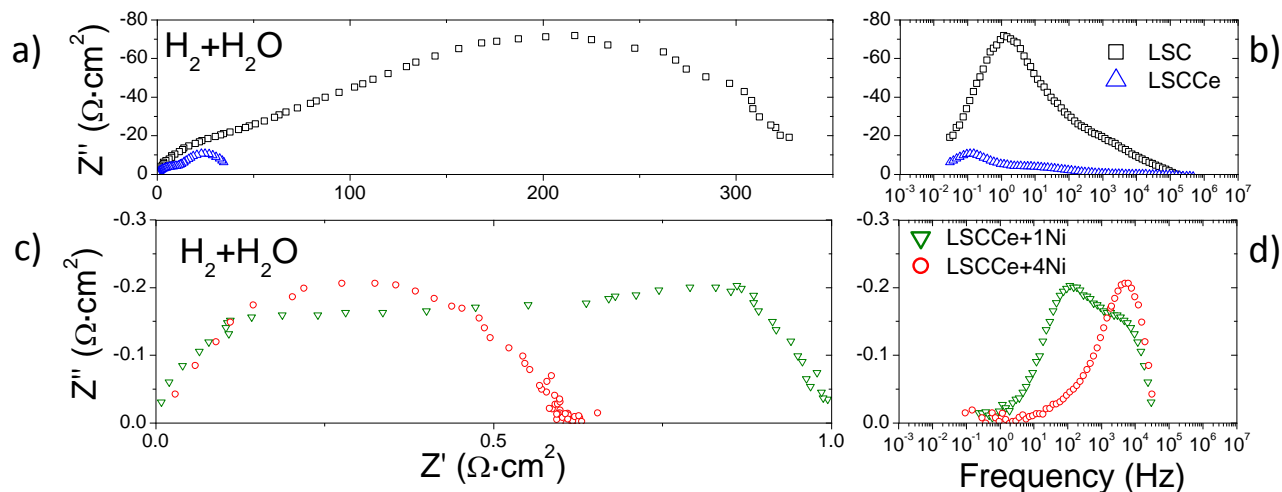


Dry conditions				Wet conditions			
$pH_2O=1 \cdot 10^{-5}$ atm		$pO_2$ (atm)	$\sigma_T$ ( $S \cdot cm^{-1}$ )	$pH_2O=0.025$ atm		$pO_2$ (atm)	$\sigma_T$ ( $S \cdot cm^{-1}$ )
1d	100% $H_2$	$5 \cdot 10^{-32}$	0.26	1w	0.05% $H_2$	$3 \cdot 10^{-25}$	0.41
2d	5% $D_2/Ar$	$1 \cdot 10^{-29}$	0.74	2w	5% $H_2/Ar$	$1 \cdot 10^{-22}$	1.19
3d	5% $H_2/Ar$	$2 \cdot 10^{-29}$	0.96	3w	0.05% $H_2/Ar$	$2 \cdot 10^{-18}$	4.43

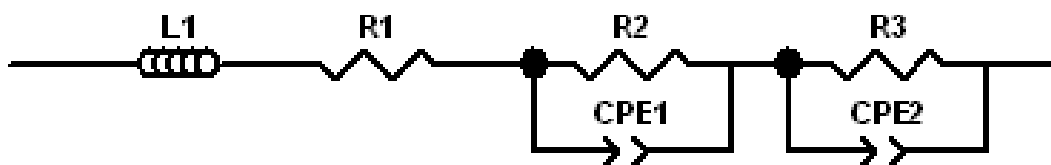
The 1/4 slope (where the conductivity increases by increasing the  $pO_2$ ) is expected for a predominant p-type electronic conductivity in dry atmospheres, as it is the case of the chromite (as reported elsewhere, see references 7 of the main text). In wet atmospheres there is a decrease of the  $pO_2$  slope (1/6) as a consequence of the mixed electronic-protonic character, due to the introduced protonic carriers. The protonic conductivity is deduced from the observed isotopic effect (conductivity in hydrogen is higher than in deuterium).

**Supporting Figure S3:** EIS spectra at 700 °C in H<sub>2</sub> of LSC and LSCCe anodes, Nyquist a) and Bode b) plots and of LSCCe infiltrated with 1Ni and 5Ni c) and d)

The comparison between spectra at 700 °C can be observed in Supporting Figure 1a and b of LSC and LSCCe anodes and c and d of LSCCe+1Ni and LSCCe+5Ni (a and d Nyquist and b and d Bode plots, respectively). LSC and LSCCe anodes present similar behaviour.

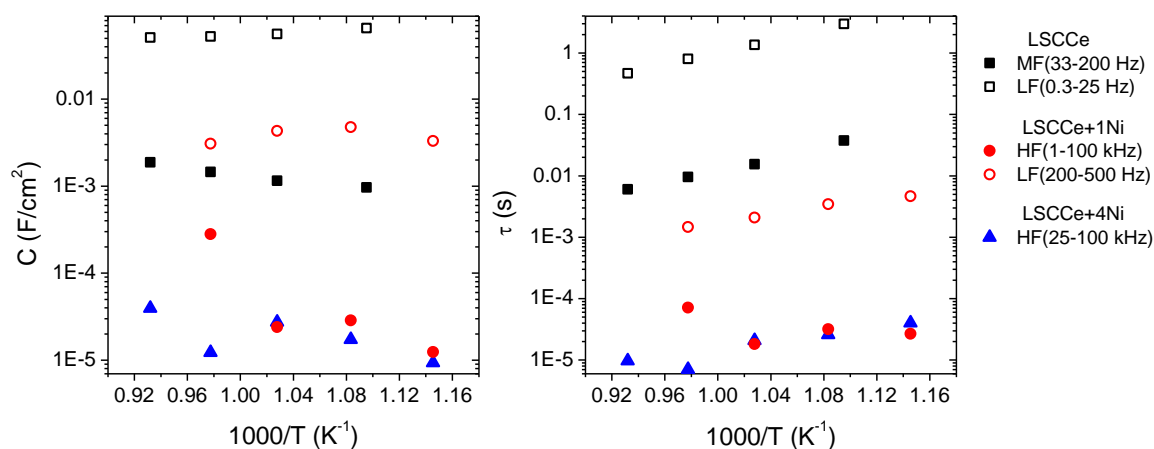


**Supporting Figure S4:** Equivalent circuit used for EIS impedance modeling



The 2 serial RC elements is a very simple equivalent circuit that was selected because it was the best to analyze the spectra and enough for a simple but complete interpretation of the results. With the two arcs interpretation we are able to distinguish different processes occurring in a very different range of frequencies, low, medium and high.

**Supporting Figure S5:** Associated capacitances and relaxation times of the LSCCe, LSCCe+1Ni and LSCCe+5Ni anodes.



The equivalent circuit modeling requires two depressing arcs that need the use of CPE instead of C and, in this case, correspond to the porous structure of the electrode. The impedance of a CPE can be expressed as:

$$Z = A^{-1}(j\omega)^{-n} \quad (1)$$

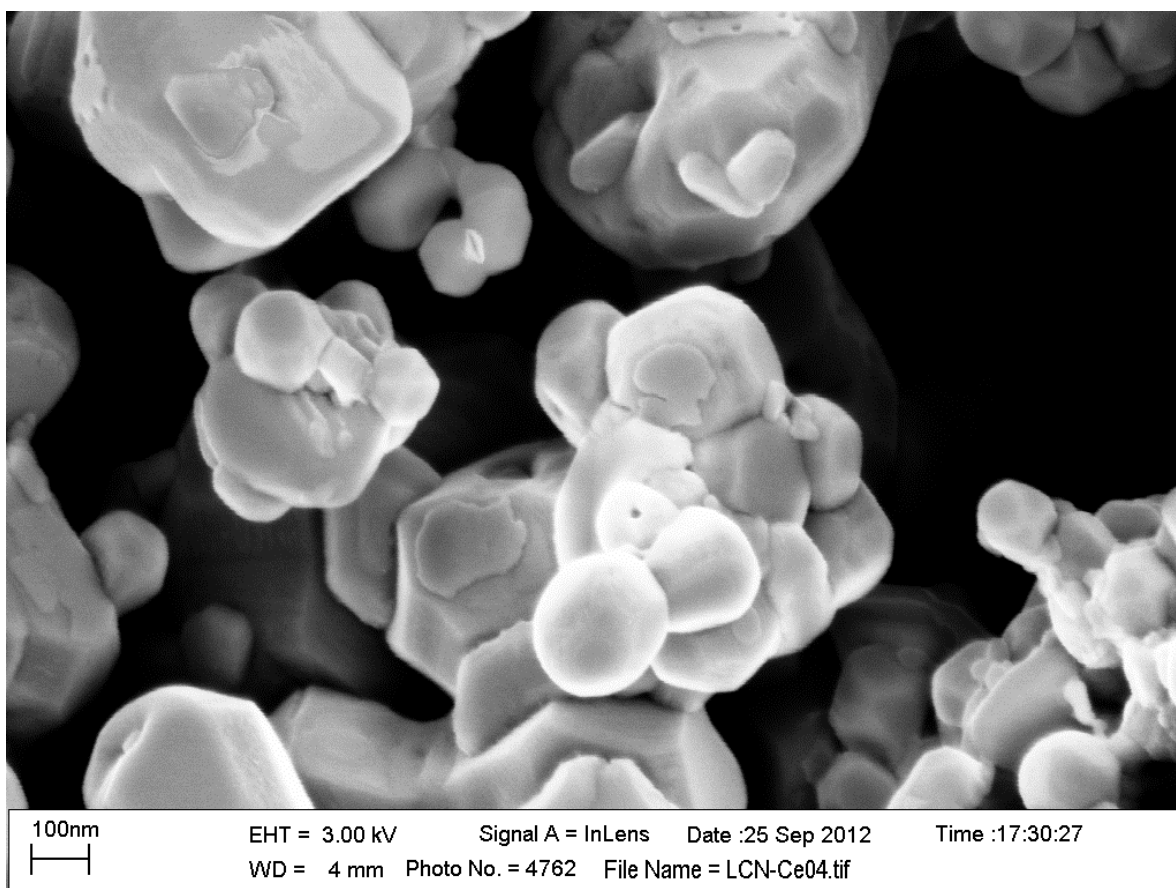
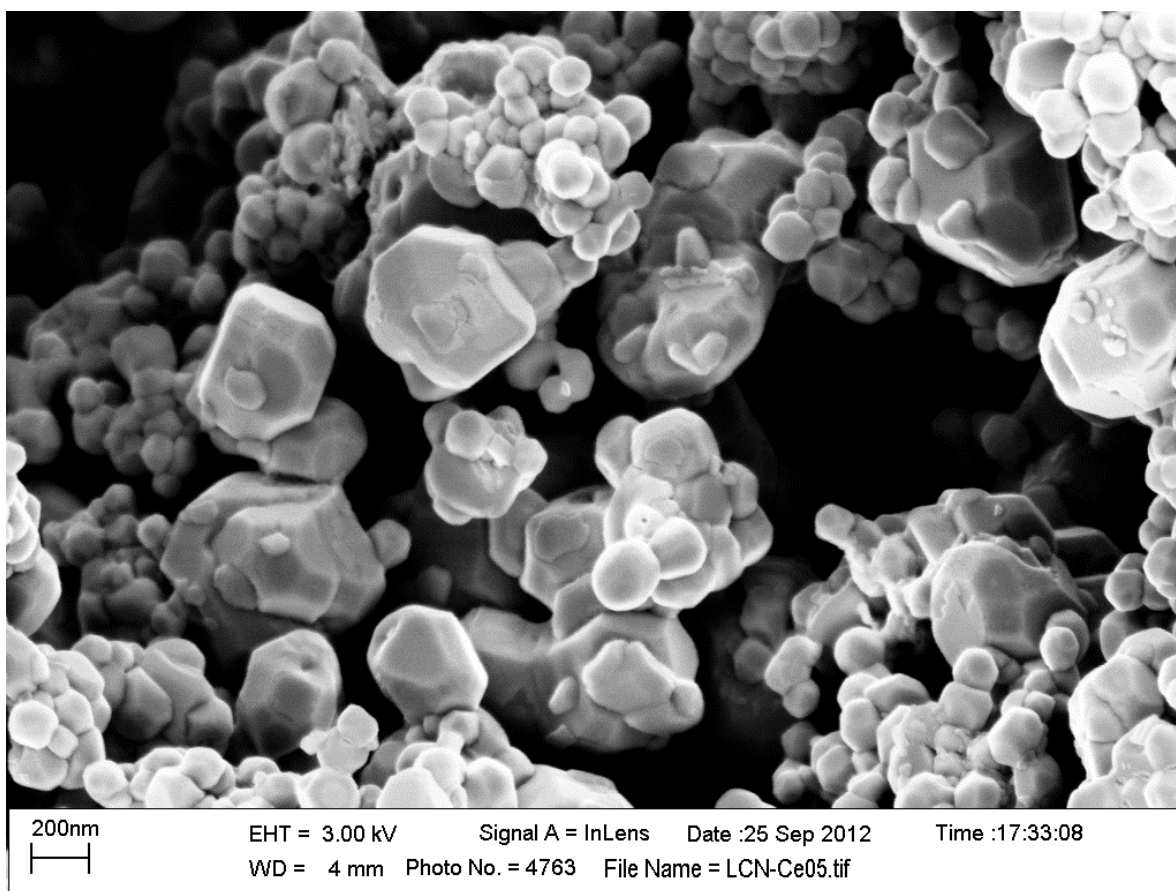
where  $A$  is a constant that is independent of frequency,  $\omega$  is the angular frequency and  $j = \sqrt{-1}$ . Note that there are two limiting cases, first when  $n = 1$ , the CPE operate as an ideal capacitor and second when  $n = 0$ , the CPE acts as a pure resistor.<sup>[2]</sup> The equivalent capacitance of the CPEs can be calculated according to the following equation.<sup>[3]</sup>

$$C_{CPE} = R^{(1-n)/n} A^{1/n} \quad (2)$$

<sup>2</sup> J.R. Macdonald, Impedance Spectroscopy, John Wiley & Sons, New York, 1987.

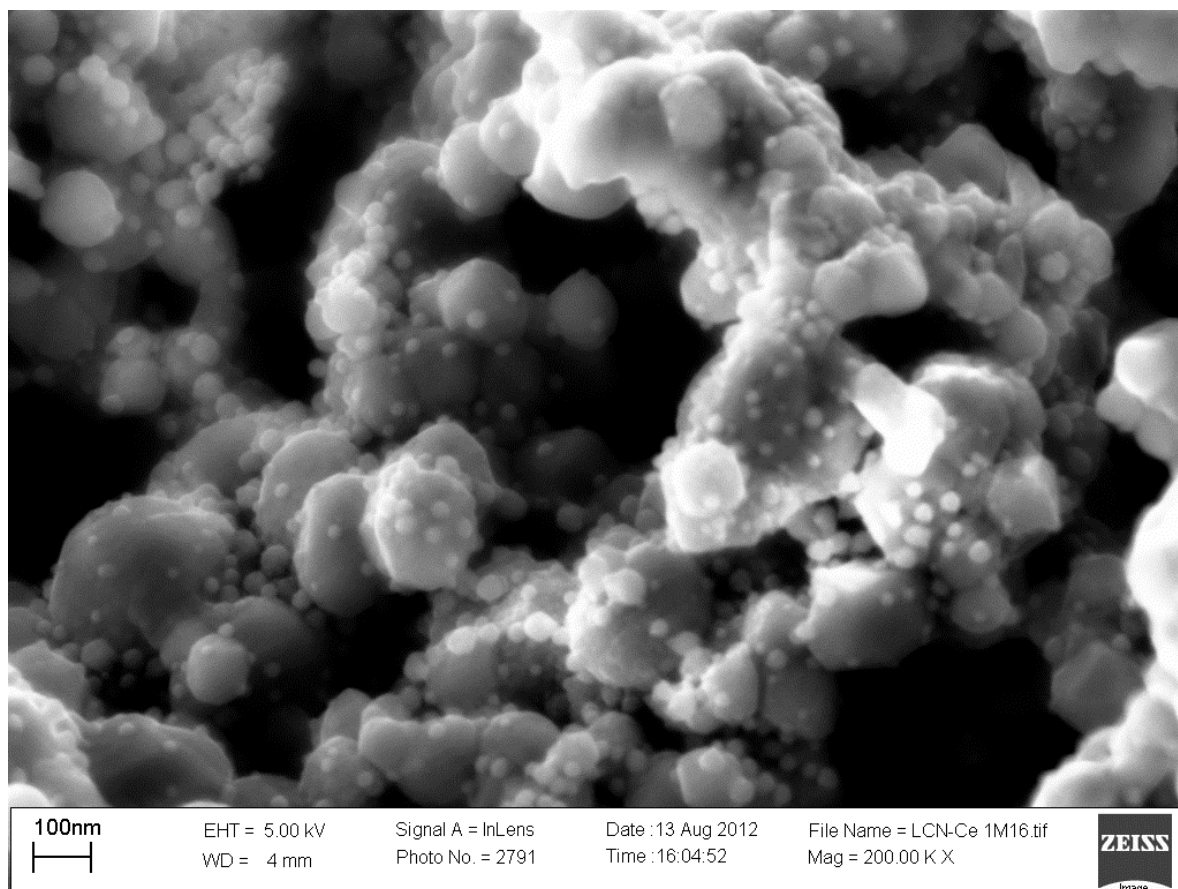
<sup>3</sup> C.H. Hsu and F. Mansfeld, Corrosion **2001**, 57, 747.

**Supporting Figure S6:** SEM images of LSCCe electrode sintered at 1150 °C

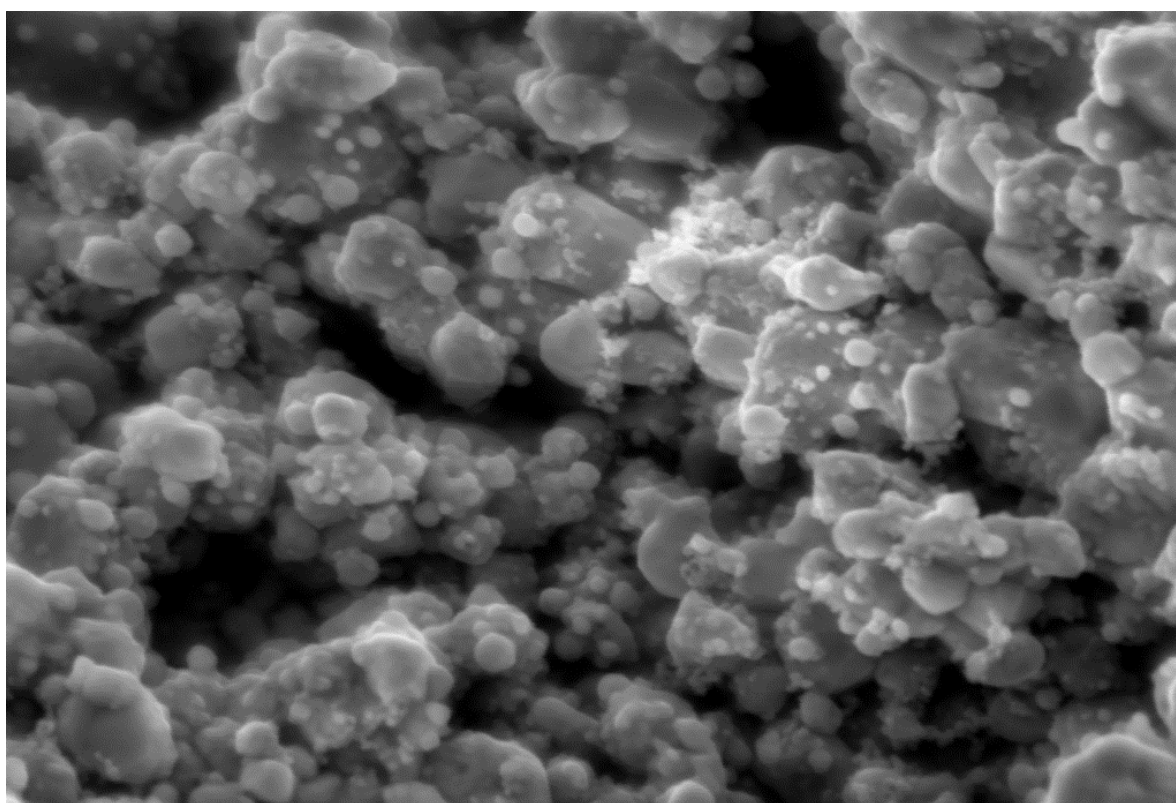




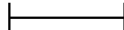
**Supporting Figure S7:** SEM image of LSCCe+1Ni electrode sintered at 1150 °C



**Supporting Figure S8:** SEM images of LSCCe+5Ni electrode sintered at 1150 °C



200nm

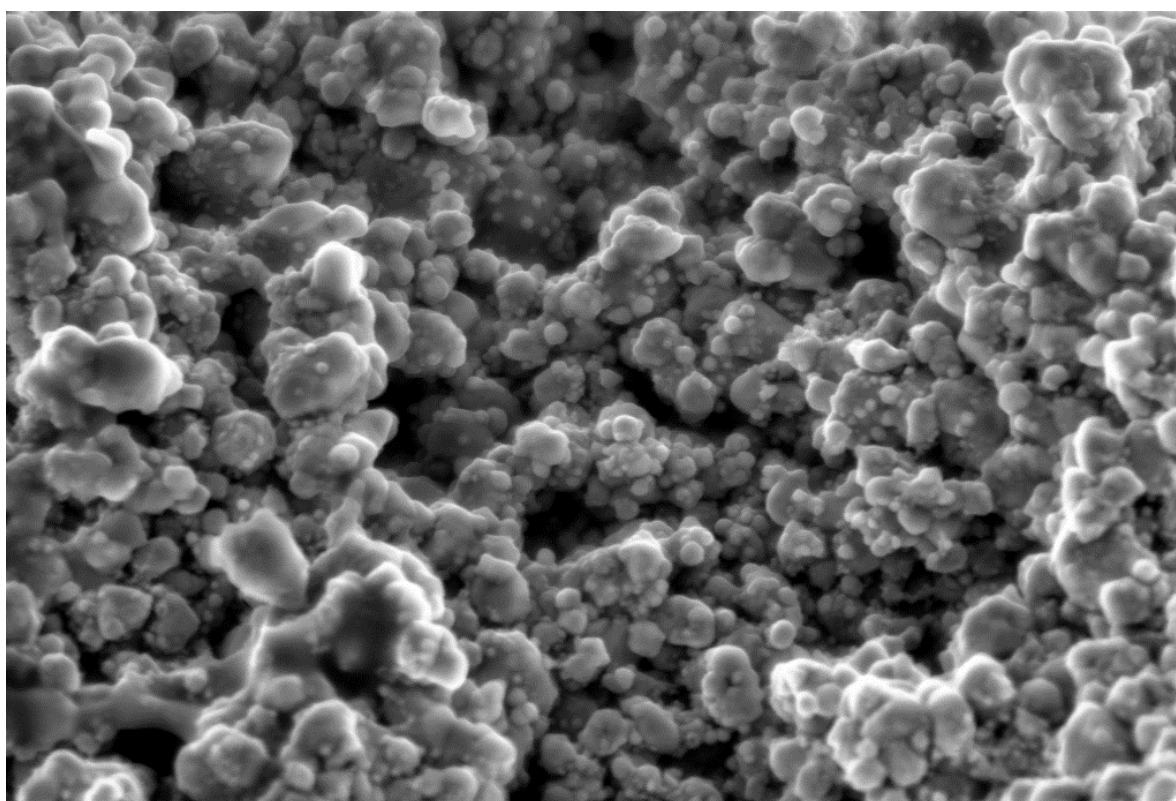


EHT = 3.00 kV  
WD = 3 mm

Signal A = InLens  
Photo No. = 4133

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Time : 15:35:50

File Name = LSCCe-4x5M35.tif  
Mag = 200.00 K X



200nm



EHT = 3.00 kV  
WD = 3 mm

Signal A = InLens  
Photo No. = 4134

Date : 11 Sep 2012  
Time : 15:41:12

File Name = LSCCe-4x5M36.tif  
Mag = 100.00 K X

