# Enhanced activity and stability of Pt-La and Pt-Ce alloys for oxygen electroreduction: the elucidation of the active surface phase.

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# **Supporting Information**

## 1. X-Ray Diffraction (XRD)

The XRD profiles of Pt<sub>5</sub>Ce, Pt<sub>5</sub>La and Pt<sub>3</sub>La polycrystalline electrodes are shown in Figure S1. XRD peaks for both Pt<sub>5</sub>Ce and Pt<sub>5</sub>La match with a hexagonal phase which forms a Cu<sub>5</sub>Ca-type structure, with the space group P6/mmm, and the fitted lattice parameters:  $a = b = (0.5378 \pm 0.0005)$  nm,  $c = (0.4187 \pm 0.0008)$  nm for Pt<sub>5</sub>Ce, and  $a = b = (0.5393 \pm 0.0003)$  nm,  $c = (0.4381 \pm 0.0004)$  nm for Pt<sub>5</sub>La, consistent with the literature.<sup>1,2</sup> In the case of Pt<sub>3</sub>La, the XRD peaks match with two different phases, a hexagonal phase and a cubic phase. The hexagonal phase forms a Cu<sub>5</sub>Ca-type structure, with the space group P6/mmm, and the fitted lattice parameters:  $a = b = (0.5416 \pm 0.0009)$  nm,  $c = (0.437 \pm 0.001)$  nm, while the cubic phase forms a Cu<sub>2</sub>Mg-type structure, with the space group Fd-3m and the fitted lattice parameters:  $a = b = c = (0.7780 \pm 0.0009)$  nm. The result found on the Pt<sub>3</sub>La sample is consistent with the presence of a Pt<sub>5</sub>La phase (hexagonal, Cu<sub>5</sub>Ca-type) and a Pt<sub>2</sub>La phase (cubic, Cu<sub>2</sub>Mg-type),<sup>3</sup> instead of a single Pt<sub>3</sub>La phase. This can be explained by the fact that a stable Pt<sub>3</sub>La phase does not exist, as deduced from the La-Pt phase diagram.<sup>4-6</sup>



**Fig. S1.** XRD intensity profile of Pt<sub>5</sub>Ce, Pt<sub>5</sub>La and Pt<sub>3</sub>La polycrystalline electrodes.

# 2. Electrochemical measurements

All glassware was cleaned for 24 h in a "piranha" solution consisting of a 3:1 mixture of 96% H<sub>2</sub>SO<sub>4</sub> and 30% H<sub>2</sub>O<sub>2</sub>, followed by multiple runs of heating and rinsing with ultrapure water (Millipore Milli-Q, 18.2 M $\Omega$  cm) to remove sulphates. The electrochemical experiments were performed with a VMP2 potentiostat (Bio-Logic Instruments), controlled by a computer. The rotating ring-disk electrode (RRDE) assemblies were provided by Pine Instruments Corporation. A standard two-compartment glass cell was used, which was equipped with a water jacket attached to a hot water bath to control the temperature. All electrochemical experiments were carried out at 23 °C.

The electrolyte, 0.1 M HClO<sub>4</sub> (Merck Suprapur), was prepared with Milli-Q water. The counter electrode was a Pt wire and the reference was an Hg/Hg<sub>2</sub>SO<sub>4</sub> electrode, separated from the working electrode compartment using ceramic frits. Following each measurement, the potential of the reference electrode was checked against a reversible hydrogen electrode (RHE) in the same electrolyte. All the potentials in the text are referred to the reversible hydrogen electrode (RHE), and are corrected for ohmic losses. Following each measurement, 0 V vs. RHE was established by carrying out the hydrogen oxidation and hydrogen evolution reactions on Pt in the same electrolyte. The ohmic drop was measured by carrying out an impedance spectrum with a peak-to-peak amplitude of 10 mV, typically from 500 kHz down to 100 Hz. The target resistance was evaluated from the high-frequency intercept on the horizontal (real) axis of the Nyquist plot and further checked by fitting the impedance spectra by using EIS Spectrum Analyser software.<sup>7</sup> The uncompensated resistance came typically to approximately 30  $\Omega$ , and was independent of the potential, rotation speed and the presence of O<sub>2</sub>.

The RRDE was immersed into the cell under a potential control of 0.1 V vs. RHE into a nitrogen (N5, Air Products) saturated electrolyte. The polycrystalline  $Pt_5Ce$ ,  $Pt_5La$  and  $Pt_3La$  electrodes were cycled until stable cyclic voltammograms (CVs) where obtained (100-150 cycles). Figure S2 shows a typical stable CV on sputtered-cleaned  $Pt_5Ce$  and  $Pt_5La$ , compared to the base CV on polycrystalline Pt. The fact that around 100 cycles are needed in order to get the typical (stable) CVs shown in Figure S2 can be explained by the dealloying process occurring at the electrode surface until a thick and stable Pt overlayer is formed,<sup>8</sup> as well as the cleaning of the impurities accumulated on the surface during the transfer from the UHV chamber to the RRDE assembly. Figure S2 also shows substantial differences in the double layer capacitance depending on the polycrystalline alloy. This had been previously observed for sputter-cleaned polycrystalline alloys such as  $Pt_3Co$ ,  $Pt_3Ni$ ,  $Pt_3Y$ ,  $Pt_5Y$  and  $Pt_3Sc$ .<sup>9-12</sup> Cu underpotential deposition (upd) and stripping measurements for alloys of Pt and early transition metals ( $Pt_3Y$ ,  $Pt_5Y$  and  $Pt_3Sc$ ) show that their surfaces are smooth, with the microscopic surface area approximating to the geometric surface area (0.196 cm<sup>2</sup>).<sup>11,12</sup> Notably, for both  $Pt_5Ce$  and  $Pt_5La$  alloys the capacitance does not change, once the stable CVs are obtained.



**Fig. S2.** Cyclic voltammograms at 50 mV s<sup>-1</sup> of  $Pt_5La$ ,  $Pt_5Ce$  and Pt polycrystalline electrodes in a  $N_2$ -saturated 0.1 M HClO<sub>4</sub> solution.

Immediately after the ORR activity tests, we carried out CO-stripping experiments on  $Pt_5La$  and  $Pt_5Ce$ . Notably, the voltammetric currents and charges remained constant during successive measurements on the same surface; this allows us to neglect the possibility that the sputter-treatment followed by acid leaching results in an increase of surface area. The CO adlayer was formed by holding the electrode potential at 0.1 V vs. RHE in a CO-saturated solution until a steady current close to zero was reached (which typically occurs within the first 5 minutes). The solution was then purged with Ar for 15 minutes, after which the CV in Ar was recorded. The integrated charge obtained from the CO-stripping peak were on Pt<sub>5</sub>La is ~310  $\mu$ C cm<sup>-2</sup>. This value is lower than that we obtained on polycrystalline Pt under similar conditions (360  $\pm$ 20 µC cm<sup>-2</sup>), which is in agreement with the literature.<sup>13</sup> This lower CO coverage in comparison with pure Pt had been previously observed for other Pt-alloys with a Pt-overlayer, such as Cu/Pt(111) near surface alloys, both in electrochemical environments<sup>14</sup> and in UHV.<sup>15</sup> This was due to a weaker binding of the Pt-surface to CO.<sup>14</sup> Figure S3 shows the CO-stripping voltammograms of COadsorbed on Pt<sub>5</sub>Ce for dosing potentials ( $U_d$ ) of 0.10 V and 0.45 V vs. RHE. The CV recorded after the CO adlayer was formed holding the potential at 0.10 V presents a higher charge in the first positive-going cycle in comparison with the subsequent cycles in addition to the CO-stripping peak. This makes the interpretation of the CO-stripping measurement very challenging for  $Pt_5Ce$ . The fact that charge is not zero would be an indication that the surface is not completely poisoned by CO. However, this charge is higher than that corresponding to H adsorption, which leads us to the view that it could be due to the absorption of hydrogen after holding the potential at 0.10 V for some minutes. Presumably hydrogen is adsorbed before the CO adlayer is formed and this leads to the absorption of H on the electrode. H absorption may take place on some metals such as Pd and Pd-based alloys<sup>16</sup> simultaneously with H electroadsorption. In order to study whether H is absorbed on polycrystalline Pt<sub>5</sub>Ce, we performed CVs in N<sub>2</sub>-saturated HClO<sub>4</sub> solutions after holding the potential for 5 minutes at 0.10, 0.15, 0.20, 0.30, 0.40 and 0.50. Figure S4 shows the first and second cycles on Pt<sub>5</sub>Ce in a N<sub>2</sub>-saturated solution after holding the

potential at 0.10 V, 0.15 V, 0.30 V and 0.50 V for 5 minutes. As can be observed, the first positive-going cycles present an extra feature when the potential is holded at less positive values and this feature decreases as the holding potential increases. In all cases, the CV was completely recovered in the second cycle. This is an indication that H is absorbed on the Pt<sub>5</sub>Ce, similar to Pd and Pd-based electrodes.<sup>16</sup> The integrated charge obtained from the CO-stripping peak on Pt<sub>5</sub>Ce for  $U_d = 0.10$  V considering both the main peak and the so-called pre-peak that also appears on polycrystalline Pt electrodes<sup>17</sup> (see shaded areas in Figure S3) is ~300  $\mu$ C cm<sup>-2</sup>, very similar to the charge obtained for Pt<sub>5</sub>La and other Pt-alloys.<sup>13,14</sup> When  $U_d$  is 0.45 V (dosing potential at which we do not observe any additional charge corresponding to H absorption), the CO-stripping charge is ~220  $\mu$ C cm<sup>-2</sup>, much lower than that for  $U_d = 0.10$  V. The electrodes as a function of the dosing potentials.<sup>17</sup>



**Fig. S3.** CO-stripping voltammograms at 10 mV s<sup>-1</sup> of CO adsorbed on  $Pt_5Ce$  in 0.1 M HClO<sub>4</sub>. The first cycles are represented by dashed lines while the second ones are represented by solid lines.



**Fig. S4.** Cyclic voltammograms at 10 mV s<sup>-1</sup> of  $Pt_5Ce$  in a N<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> solution after holding the potential for 5 minutes at 0.10 V, 0.15 V, 0.30 V and 0.50 V vs. RHE. The first cycles are represented by dashed lines while the second ones are represented by solid lines.

The behavior of  $Pt_3La$  under acidic conditions is significantly different than that of  $Pt_5La$  and  $Pt_5Ce$ . Figure S5 shows the CV on a sputter-cleaned  $Pt_3La$  polycrystalline electrode after being transferred from the UHV chamber to the RRDE assembly (cycle 1), as well as after 30 and 60 cycles. The ORR activity measurements were performed after cycle 60 and were followed by subsequent CVs in a N<sub>2</sub>-saturated solution (see  $Pt_3La$  after the ORR curve in Figure S5). Notably, the voltammetric current for  $Pt_3La$ increased continuously throughout the measurement and the initially polished surface had become very rough within an hour. This can be attributed to the corrosion of this sample, that is, the dissolution of La to  $La^{3+}$ , and the formation of  $H_2$ . This behavior on  $Pt_3La$  can be explained by the presence of two different metastable phases.



**Fig. S5.** Cyclic voltammograms at 50 mV s<sup>-1</sup> of  $Pt_3La$  (cycles 1, 30 and 60 after transferring the sputtercleaned sample to the electrochemical cell, as well as voltammograms after the ORR) and Pt in a N<sub>2</sub>saturated 0.1 M HClO<sub>4</sub> solution.

The ORR activity measurements were conducted in an electrolyte saturated with  $O_2$  (N55, Air Products), following the attainment of a stable CV in a  $N_2$ -saturated solution. Figure S6 shows typical voltammograms on  $Pt_5La$ ,  $Pt_5Ce$  and Pt in  $O_2$ -saturated 0.1 M HClO<sub>4</sub>. It can be observed that the overpotential for both  $Pt_5La$  and  $Pt_5Ce$  is lower than for pure Pt.



**Fig. S6.** RRDE polarization curves at 1600 rpm and 50 mV s<sup>-1</sup> for the ORR on Pt<sub>5</sub>La, Pt<sub>5</sub>Ce and Pt polycrystalline electrodes in O<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub>.

## 3. Inductively coupled plasma mass spectrometer (ICP-MS)

ICP-MS measurements were performed to gain a better understanding on the electrochemical results obtained on  $Pt_3La$  and  $Pt_3La$  alloys. The measurements were carried out on the electrolyte after the ORR activity testing experiments (see section 2) on the different electrodes, keeping very similar conditions for both  $Pt_3La$  and  $Pt_5La$ . Briefly, CVs in  $N_2$  were taken in the potential region from 0.05 to 1.0 V vs. RHE until stable CVs were obtained. Subsequently, the ORR activity was measured in the potential region from 0.0 to 1.0 V vs. The of electrolyte were extracted from the perchloric acid solution and brought to a Perkin-Elmer 6000 ICP-MS. Internal standards for the calibration were used. For comparison, the spectrum of a clean 0.1 M HClO<sub>4</sub> solution (free of Pt and La) was also taken and showed no La and Pt signals above the background level. Figure S7 shows the appearence of La (atomic mass: 139 amu) and Pt (atomic masses: 194, 195, 196 and 198 amu) signals after the electrochemical experiments. For both  $Pt_3La$  and  $Pt_5La$  electrolytes small Pt signals appear. Very recently, Mayrhofer and co-workers studied the Pt dissolution on pure Pt by combining an electrochemical scanning flow cell and an ICP-MS.<sup>18</sup> They did not observe, however, any significant Pt dissolution in this potential region. Compared to the  $Pt_5La$  electrolyte a much more intense La signal was measured in the case of  $Pt_3La$ . These results support the conclusion that the  $Pt_3La$  sample is corroded.



**Fig. S7.** ICP-MS analysis on the amount of dissolved La and Pt from  $Pt_3La$  and  $Pt_5La$  electrodes in 0.1 M HClO<sub>4</sub> electrolytes. Background La and Pt signals were measured on a clean 0.1 M HClO<sub>4</sub> electrolyte and found to be negligible in comparison with these values.

# 4. Vacuum requirements

The very reactive nature of lanthanide metals sets very strict vacuum requirements if an excessive level of surface contamination has to be avoided. In order to provide an estimate of such requirements a simple model is here introduced. From the kinetic theory of an ideal gas, given a Maxwell-Boltzmann distribution of velocities, the flux of molecules impacting the surface of a catalyst can be estimated by the formula:

$$F(p,T) = \frac{p}{\sqrt{2\pi m k T}}$$

Where *p* is the pressure, *m* is the mass of the single gas molecule, *k* is the Boltzmann's constant and *T* is the absolute temperature (International System of Units). Avoiding a full calculation of the alloy structure and being particularly interested in the lanthanide properties, it is here assumed to have a clean La surface, with a surface density of  $9 \times 10^{14}$  atoms/cm<sup>2</sup>. Totally similar considerations also apply for Ce. The rate of molecule adsorption is the product of the flux and the sticking probability *S* of a molecule on the La surface. The surface coverage is then given by the rate of adsorption multiplied by the total time *t* of gas exposure:

$$\theta = SFt$$

While the sticking probability of a gas molecule on a noble metal (ex. Pt) is generally low, sticking probabilities of reactive gases as oxygen on La or Ce are close to unity at room temperature.<sup>19</sup> Table S1 shows the coverage in monolayers of some reactive gases ( $O_2$ ,  $H_2O$ ,  $H_2$ ) after exposure at different gas pressures and for different times (sticking coefficient *S* is assumed to be unity). A time between 1 and 10 seconds was chosen as the typical time needed for the deposition of one monolayer with standard UHV techniques (electron beam physical vapor deposition, evaporative deposition, sputter deposition, ...). At least one hour is typically needed for most of the typical characterization techniques (ex. XPS, ...).

	p =	= 5×10 <sup>-9</sup> ml	bar	<b>p</b> =	5×10 <sup>-10</sup> m	ıbar	$p = 5 \times 10^{-11} \text{ mbar}$			
	$O_2$	$H_2O$	$H_2$	$O_2$	$H_2O$	$H_2$	$O_2$	$H_2O$	$H_2$	
Typical times	1 s	0.2%	0.2%	0.6%	0.0%	0.0%	0.1%	0.0%	0.0%	0.0%
with vacuum techniques	10 s	<u>1.5%</u>	<u>2.0%</u>	<u>6.0%</u>	0.2%	0.2%	0.6%	0.0%	0.0%	0.1%
Typical time for UHV measurements (ex. XPS)	3600 s	542.2%	723.0%	2169%	54.2%	72.3%	216.9%	5.4%	7.2%	21.7%

**Table S1**. Coverage in monolayers of some reactive gases  $(O_2, H_2O, H_2)$  adsorbed on a clean La surface. For each gas, three different gas pressures and three different exposure times are shown. The coverages above 1% have been highlighted (underlined values) as critical for the purity of the material.

After one hour of gas exposure the adsorbed contaminations always exceed 5% of a monolayer, even at the lowest UHV pressure of  $5 \times 10^{-11}$  mbar. This explains the difficulty of maintaining clean such a reactive surface. It also justifies the need of continuous mild Ar sputtering for keeping a very low level of

contaminations during the XPS measurements of this work on sputter-cleaned alloys. Even on a time scale of 1 to 10 seconds, the contaminations might be relevant at pressures like  $5 \times 10^{-9}$  mbar which are close to UHV conditions. It should be noticed that this model is very simplified and does not take into considerations various complications: for instance it does not consider the variation of the sticking probability as a function of the increasing coverage and the effect of alloying on the sticking coefficient of lanthanides. However, it underlines once more how important physical characterization techniques are for ensuring that the fabricated materials have the expected composition and structure, especially for this kind of alloys.

#### 5. Angle resolved X-Ray Photoelectron Spectroscopy (AR-XPS)

In-depth surface composition information of the Pt-alloys were extracted from AR-XPS spectra recorded using a Theta Probe instrument (Thermo Scientific). The chamber has a base pressure of  $5 \times 10^{-10}$  mbar but it was allowed to reach 5 x  $10^{-9}$  mbar due to degasing from the samples. The instrument uses monochromatized AlK $\alpha$  (1486.7 eV) X-rays, with a maximum resolution estimated from the Ag 3d5/2 full width at half maximum (FWHM) smaller than 0.5 eV at a pass energy of 25 eV. It was operated at a pass energy of 100 eV giving a resolution better than 1 eV. XPS spectra can be recorded from within a diameter of 15 µm but an X-ray beam size of 400 µm was chosen for all measurements. The electron energy analyzer has an acceptance angle between 20° and 80° degrees from the surface normal, corresponding to a total acceptance angle of  $60^{\circ}$ . Angle resolved spectra were acquired in parallel, without tilting the sample, from 16 different channels: each corresponding to a 3.75° wide angle interval. However, the spectra of Figure 3 in the main text, as well as the overview spectra (Figures S8, S9, S10), were acquired summing up the intensities at all angles in order to maximize the signal to noise ratio, ensure the best fits and the maximum sensitivity to possible contaminations. In this mode, the average angle, weighted on the Pt 4f signal intensity of clean Pt(111), is approximately 45°.

#### Overview spectra

Overview XPS spectra were systematically taken before and after all the experiments of this work in order to ensure no contaminations. Overview spectra acquired during sputter-cleaning did not show any impurities, however detailed scans around the O1s region, in some cases, showed small traces of O below 1% of the total atomic composition. The measurements taken after air-exposure only showed the rise of O and C peaks. Following electrochemical measurements, all samples were cleaned from the electrolyte by blowing clean Ar. Figures S8, S9 and S10 show examples of overview spectra acquired after ORR testing of  $Pt_5La Pt_5Ce$  and  $Pt_3La$  respectively. As after all electrochemical measurements minor signals from C, O were found, usually accounting for about 20-30 % of the atomic composition. Advantageous C is expected to appear as a consequence of the air exposure. O can be associated either to the air exposure or oxygenated species of the electrolyte. Traces of Cl from the  $ClO_4^-$  ions of the electrolyte were also identified.



Fig. S8. XPS overview spectrum of Pt<sub>5</sub>La after electrochemical ORR measurements.



**Fig. S9.** XPS overview spectrum of  $Pt_5Ce$  after electrochemical ORR measurements.



Fig. S10. XPS overview spectrum of Pt<sub>3</sub>La after electrochemical ORR measurements

#### XPS fitting procedure

The XPS intensities of La 3d and Ce 3d peaks were fitted after removal of a Shirley-type background. Since this doesn't give a satisfactory description of the background in the case of spin-orbit doublets<sup>20</sup>, the background were independently defined on the  $3d_{5/2}$  and  $3d_{3/2}$  regions. With this choice, the areas of these regions agreed within 5 % to the expected ratio of 2/3. Fitting peaks were defined as the product of a Gaussian and a Lorentzian shape. However, in the case of La, the fitting parameters evolved towards Gaussian-shaped peaks which were found to better describe the experimental data in all cases. For the fit of the metallic peaks during sputter-cleaning and after electrochemical measurements both the position and the full width at half maximum (FWHM) of the  $f^{n-1}$ ,  $f^n$ ,  $f^{n+1}$  components was allowed to vary. In the end, the obtained positions were compared to those measured earlier on similar alloys and found to be qualitatively similar.<sup>21–24</sup> The spectra of the air exposed samples were made by imposing the same peak positions, FWHM and relative intensities of the metallic phase measured on the clean alloys. The resulting peak shape and positions for the oxide phase was also compared to literature in order to check

that a reasonable similarity was achieved.<sup>25</sup> For brevity and for their similarity with  $Pt_5La$ , the fitted spectra of  $Pt_3La$  were not shown in the main text and are presented in Figure S11.



**Fig. S11.** XPS spectra of  $Pt_3La$  at an average emission angle of 45°. The spectra were acquired in three different conditions: during sputter-cleaning (a), after one hour air exposure (b) and after electrochemical measurements (c). The measurements after electrochemical measurements were magnified three times due to the lower signal intensity.

Even after electrochemical measurements the La 3d peak shape is metallic and similar to that of  $Pt_5La$ , despite the strong corrosion. As in the other cases, the La oxide is expected to dissolve from the surface. If the corrosion was simply due to the La dissolution from the bulk of the alloy the La 3d intensity would be much lower than for  $Pt_5La$  and hardly visible after a short electrolyte exposure. This suggests that both Pt and La are dissolving from the surface. Such corrosion will also increase the roughness of the sample possibly influencing the Pt to La relative intensity and the angular dependency of the signals. For this reason no AR-XPS depth profiles and Pt to La ratios are presented for  $Pt_3La$ .

	Bind	ling Energy	/ La3d 5/2	(eV)	Bine	ding Energy	/ La3d 3/2	(eV)	Relative intensity (%)				
Pt <sub>5</sub> La	La		La <sup>3+</sup>		La		La <sup>3+</sup>		La		La <sup>3+</sup>		
	f <sup>0</sup>	$f^1$	f <sup>0</sup>	$f^1$	f <sup>0</sup>	f <sup>1</sup>	f <sup>0</sup>	$\mathbf{f}^{1}$	f <sup>0</sup>	$f^1$	f <sup>0</sup>	$f^1$	
Sputtering	836.3	832.7	-	-	853.0	849.4	-	-	71	29	-	-	
Air exposed	836.3	832.7	838.4	835.0	853.0	849.3	855.2	851.7	49	14	18	19	
After EC	836.1	832.5	-	-	852.8	849.2	-	-	66	34	-	-	
Stability	836.1	832.5	-	-	852.8	849.2	-	-	66	34	-	-	

Table S2 summarizes the binding energies and the relative intensity of the fitted peaks for all the alloys of this paper.

	Binding Energy La3d 5/2 (eV)						Binding Energy La3d 3/2 (eV)						Relative intensity (%)					
Pt <sub>5</sub> Ce		Ce			Ce <sup>4+</sup>			Ce			Ce <sup>4+</sup>			Ce			Ce <sup>4+</sup>	
	f <sup>0</sup>	$\mathbf{f}^{1}$	$\mathbf{f}^2$	f <sup>0</sup>	$\mathbf{f}^1$	f <sup>2</sup>	f <sup>0</sup>	$\mathbf{f}^1$	$f^2$	f <sup>0</sup>	$\mathbf{f}^1$	$f^2$	f <sup>0</sup>	$\mathbf{f}^1$	f <sup>2</sup>	f <sup>0</sup>	$\mathbf{f}^1$	$f^2$
Sputtering	896.6	884.4	880.1	-	-	-	914.9	903.1	898.7	-	-	-	5	66	28	-	-	-
Air exposed	896.5	884.4	880.1	897.9	887.0	881.8	914.9	903.1	898.7	916.2	906.0	900.4	3	35	15	15	16	16
After EC	896.8	884.2	879.8	-	-	-	914.9	902.6	898.3	-	-	-	10	70	20	-	-	-
Stability	896.8	884.4	879.8	-	-	-	914.9	903.0	898.6	-	-	-	9	73	18	-	-	-

	Bin	ding Energy	/ La3d 5/2	(eV)	Bir	nding Energ	gy La3d 3/2	2 (eV)	Relative intensity (%)				
Pt <sub>3</sub> La	La		La <sup>3+</sup>		La		La <sup>3+</sup>		La		La <sup>3+</sup>		
	f <sup>0</sup>	$\mathbf{f}^1$	f <sup>0</sup>	$\mathbf{f}^1$	f <sup>0</sup>	$\mathbf{f}^1$	f <sup>0</sup>	$\mathbf{f}^1$	f <sup>0</sup>	$\mathbf{f}^1$	f <sup>0</sup>	$\mathbf{f}^1$	
Sputtering	836.4	832.8	-	-	853.1	849.5	-	-	69	31	-	-	
Air exposed	836.4	832.8	838.2	834.6	853.0	849.4	855.0	851.3	42	19	18	21	
After EC	836.1	832.5	-	-	852.8	849.2	-	-	66	34	-	-	
Stability	-	-	-	-	-	-	-	-	-	-	-	-	

**Table S2.** Binding energies and relative intensities of the XPS peaks for  $Pt_5La$ ,  $Pt_5Ce$  and  $Pt_3La$ . The  $f^n$  components have been divided into metallic species and oxidized species ( $La^{3+}$  and  $Ce^{4+}$ ).

Metallic peaks after electrochemical tests resemble those measured during sputter-cleaning with only minor differences: nonetheless there is a general trend towards an increase of the relative intensity of the  $f^{n+1}$  satellite in case of La and of the  $f^{n-1}$  satellite in the case of Ce. Since this a typical feature of La and Ce alloys<sup>21</sup>, such tendency is probably associated to the surface La and Ce atoms of the sputtered sample, with a lower coordination to Pt atoms. Table also shows that after stability tests, for both Pt<sub>5</sub>La and Pt<sub>5</sub>Ce, the shape, position and relative intensities were totally similar to the ones after short ORR activity test. For this reason and for brevity these spectra are not shown. No stability tests were taken on Pt<sub>3</sub>La due to the fast corrosion during ORR activity testing.

# Angle resolved depth profiles and quantification

After XPS identification of the elements present at the surface from the overview spectra, their main features were measured in detail with AR-XPS. The depth concentration profiles were obtained using the simulation tool, ARProcess (Thermo Avantage software), which uses a maximum entropy method combined with a genetic algorithm. In all cases, the simulations were based on the relative intensities between Pt 4f, O 1s and C 1s, and La 3d (or Ce 3d) at each angle, up to 65°. The most grazing angles were omitted from the analysis to reduce the influence of diffraction effects and elastic scattering. The substrate composition was assumed to be equal to the nominative composition of the alloy, which was also in good agreement with the measured composition of the sputter-cleaned alloys. The electron mean free path was approximated by the TPP-2M formula.<sup>26</sup> The adventitious C, O and Cl traces in the outmost layers of the depth profiles have been omitted for clarity.

The calculation of the Pt to La and Pt to Ce ratios was achieved by integration of the Pt 4f, La 3d and Ce 3d peaks after background removal. A Shirley-type background was chosen for this purpose. The intensities were corrected for the transmission function of the analyzer and Wagner sensitivity factors as described earlier.<sup>20</sup> However, it is known that rare earths might exhibit a rather high variability of the sensitivity factors depending on the chemical state.<sup>27</sup> With this choice a good agreement was found between the ratios measured during sputter-cleaning and the stoichiometric ones. This evidence, together with the absence of any specific composition angular dependency during the sputtering procedure, suggests that no differential sputtering occurs. All ratios were calculated as the average of two independent measurements, giving a standard deviation lower than 3 for all angles lower than 60°. At higher angles the Ce 3d and La 3d signals are rather low after electrochemical measurements and noisier, giving a higher uncertainty on the quantification. Furthermore the ratios calculated at these angles may be affected by elastic scattering effects and therefore cannot be considered as fully reliable.<sup>28</sup>

#### 6. Low Energy Ion Spectroscopy (LEIS)

In order to better quantify the Pt to Ce intensity ratios from the LEIS measurements, a Shirley-type background was subtracted from the spectra and the peaks fitted. The shape of the fitting peaks was defined as the product of a Gaussian and a Lorentzian shape. This choice provided a rather good fit of the spectra despite the slight intrinsic asymmetry of LEIS peaks. Figure S12 shows the calculated areas of the Ce and Pt peaks as a function of the total Ne<sup>+</sup> sputtering time. Their ratio is also plotted. For the first 10 minutes of measurement, the areas are not reported due to the predominance of the background related to surface contaminations. After this time, the Pt peak can be clearly observed and its area readily increases, while the Ce peak is absent or barely visible. A clear Pt enrichment is present in this time region where the Pt to Ce ratio tends to diverge. Later on also the Ce peak area increases (and the Pt to Ce ratio decreases) until both Pt and Ce signals start stabilizing at about 80-100 minutes of sputtering. At this time the Pt to Ce ratio approaches the one of the bulk, as determined from the LEIS spectra of a sputter-cleaned sample. The extremely high Pt to Ce ratio (> 10 000 after 18 minutes of sputtering) at the surface indicates the absence of Ce atoms on the surface of Pt<sub>3</sub>Ce after electrochemical testing.



**Fig. S12.** Fitted areas of Ce (red) and Pt (grey) peaks from Ne<sup>+</sup> LEIS spectra. The Pt to Ce ratio of the areas (blue) is also plotted.

# References

- 1. N. H. Krikorian, Journal of the Less Common Metals, 1971, 23, 271–279.
- 2. I. D. Weisman, L. H. Bennett, A. J. McAlister, and R. E. Watson, Phys. Rev. B, 1975, 11, 82–91.
- 3. B. Erdmann and C. Keller, *Journal of Solid State Chemistry*, 1973, 7, 40–48.
- 4. T. B. Massalski, J. L. Murray, L. H. Bennett, and H. Baker, *Binary alloy phase diagrams*, American Society for Metals, 1986.
- 5. S. Reimann and H.-J. Schaller, Journal of Alloys and Compounds, 2006, 419, 133–139.
- 6. H. Okamoto, J Phs Eqil and Diff, 2008, 29, 122–122.
- 7. A. S. Bondarenko and G. A. Ragoisha, in Progress in Chemometrics Research, Nova Publishers, 2005.
- 8. M. Escudero-Escribano, A. Verdaguer-Casadevall, P. Malacrida, U. Grønbjerg, B. P. Knudsen, A. K. Jepsen, J. Rossmeisl, I. E. L. Stephens, and I. Chorkendorff, *J. Am. Chem. Soc.*, 2012, **134**, 16476–16479.
- 9. V. Stamenković, T. J. Schmidt, P. N. Ross, and N. M. Marković, *J. Phys. Chem. B*, 2002, **106**, 11970–11979.
- 10. U. A. Paulus, A. Wokaun, G. G. Scherer, T. J. Schmidt, V. Stamenkovic, N. M. Markovic, and P. N. Ross, *Electrochimica Acta*, 2002, **47**, 3787–3798.
- 11. J. Greeley, I. E. L. Stephens, A. S. Bondarenko, T. P. Johansson, H. A. Hansen, T. F. Jaramillo, J. Rossmeisl, I. Chorkendorff, and J. K. Nørskov, *Nature Chemistry*, 2009, **1**, 552–556.
- 12. I. E. L. Stephens, A. S. Bondarenko, L. Bech, and I. Chorkendorff, ChemCatChem, 2012, 4, 341-349.
- 13. D. F. van der Vliet, C. Wang, D. Li, A. P. Paulikas, J. Greeley, R. B. Rankin, D. Strmcnik, D. Tripkovic, N. M. Markovic, and V. R. Stamenkovic, *Angewandte Chemie*, 2012, **124**, 3193–3196.
- 14. A. S. Bandarenka, A. S. Varela, M. Karamad, F. Calle-Vallejo, L. Bech, F. J. Perez-Alonso, J. Rossmeisl, I. E. L. Stephens, and I. Chorkendorff, *Angewandte Chemie International Edition*, 2012, **51**, 11845–11848.
- 15. J. Knudsen, A. U. Nilekar, R. T. Vang, J. Schnadt, E. L. Kunkes, J. A. Dumesic, M. Mavrikakis, and F. Besenbacher, J. Am. Chem. Soc., 2007, **129**, 6485–6490.
- 16. G. Jerkiewicz, Progress in Surface Science, 1998, 57, 137-186.
- 17. A. Cuesta, A. Couto, A. Rincón, M. C. Pérez, A. López-Cudero, and C. Gutiérrez, *Journal of Electroanalytical Chemistry*, 2006, **586**, 184–195.
- 18. A. A. Topalov, I. Katsounaros, M. Auinger, S. Cherevko, J. C. Meier, S. O. Klemm, and K. J. J. Mayrhofer, *Angewandte Chemie International Edition*, 2012, **51**, 12613–12615.
- 19. A. M. de Asha and R. M. Nix, Surface Science, 1995, 322, 41-50.
- 20. D. Briggs and M. P. Seah, Eds., *Practical Surface Analysis, Auger and X-ray Photoelectron Spectroscopy*, John Wiley & Sons, Volume 1., 1996.
- 21. J. C. Fuggle, Journal of the Less Common Metals, 1983, 93, 159–169.
- 22. L. Schlapbach, Solid State Communications, 1981, 38, 117–123.
- 23. J. C. Fuggle, F. U. Hillebrecht, Z. Zołnierek, R. Lässer, C. Freiburg, O. Gunnarsson, and K. Schönhammer, *Phys. Rev. B*, 1983, **27**, 7330–7341.
- 24. F. U. Hillebrecht and J. C. Fuggle, Phys. Rev. B, 1982, 25, 3550-3556.
- 25. D. D. Sarma, M. S. Hegde, and C. N. R. Rao, J. Chem. Soc., Faraday Trans. 2, 1981, 77, 1509–1520.
- 26. S. Tanuma, C. J. Powell, and D. R. Penn, Surface and Interface Analysis, 1991, 17, 911–926.
- 27. C. D. Wagner, L. E. Davis, M. V. Zeller, J. A. Taylor, R. H. Raymond, and L. H. Gale, *Surface and Interface Analysis*, 1981, **3**, 211–225.
- 28. P. J. Cumpson and M. P. Seah, Surface and Interface Analysis, 1997, 25, 430-446.