

Supporting Information

Climbing the Oxygen Reduction Reaction Volcano Plot with Laser Ablation Synthesis of Pt_xY Nanoalloys.

Riccardo Brandiele, Andrea Guadagnini, Leonardo Girardi, Goran Dražić, Maria Chiara Dalconi, Gian Andrea Rizzi, Vincenzo Amendola, and Christian Durante.*

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S1 EXPERIMENTAL SECTION

Mesoporous Carbon (MC) (Sigma Aldrich, 200 nm particle size, >99.95%), Nafion (Sigma Aldrich, 5 wt% in EtOH), HClO₄ (Fluka, Traceselect® 67-72%), H₂SO₄ (Fluka, Trace-select® >95%), HCl (Sigma Aldrich - ACS grade), NOCHROMIX, (Sigma Aldrich-Glass- Cleaning Reagent), Pt/C TKK Tanaka standard (Pt 50%_w), ethanol (HPLC grade, Sigma Aldrich) were used as received without further purification. Alpha Gaz O₂ and Ar were supplied by Air Liquid at the highest available purity. Platinum target (99.9%) and Platinum/Yttrium target (Pt:Y 3:1 AT% ratio, 99.9%), thickness: 1.0mm nominal, size: 10mm x 15mm nominal were purchased from Goodfellow.

S1.1 Synthesis

Pt_xY and Pt NPs were synthesized by laser ablation in solution (LASiS), focusing a Q-switched Nd- YAG laser (1064 nm, 6 ns, 50 Hz, 70 mJ/pulse) with a 10 cm focal lens up to a fluence of 9 J cm⁻² on a Pt₃Y commercial standard target dipped in ethanol solution saturated with Argon. The final Pt NPs concentration was reached by evaporating the solvent in a rotating evaporator until a final concentration of 0.2 mg mL⁻¹. The NPs were washed in 1 M H₂SO₄ at room temperature for removing as much as possible the yttrium oxide shell, but avoiding agglomeration. In brief, the Pt_xY-E NPs and the solvent were separated by vacuum filtration on a nylon nanometric filter (GVS, nylon 0.2 mm, 47 mm membrane diameter). After the separation, the NPs were washed in a Büchner with 100 mL of a 1 M H₂SO₄ solution at room temperature (25 °C). The resulting nanoparticles were thoroughly rinsed with 400 mL of ultra-pure water and 100 mL of ethanol. The resulting NPs were then dispersed in ethanol and supported on a commercial high surface area carbon black. Pt NPs were also synthesized following the same protocol and used as reference material for evaluating the catalytic activity in the oxygen reduction reaction. The NPs deposition process on the commercial carbon support consists in mixing 2 mL of Pt_xY-E or Pt NPs dispersed in ethanol, 0.2 mL of milliQ water, 5 mL of a Nafion solution (5 wt% in EtOH) and commercial carbon as carbon support (1.9-2.5 mg depending on the NPs concentration in ethanol solution). The resulting dispersion was bath sonicated for 2 hours at room temperature for a proper dispersion of metal and metal alloyed NPs over the carbon support and inside the accessible pores. This procedure produces an ink that can be directly employed in the electrochemical characterization.

S1.2 Characterization

The Pt and Pt₃Y solutions were analyzed by UV-Vis Spectroscopy, using a 10 mm quartz cell and a JASCO V770 UV-vis-NIR spectrophotometer.

The platinum-yttrium weight ratio was evaluated using ICP-MS by means of an Agilent Technologies 7700x ICP-MS (Agilent Technologies International Japan, Ltd., Tokyo, Japan). A Microwave Digestion System (CEM EXPLORER SP-D PLUS) was used for the acid digestion. In brief, ca.2 mL of Pt_xY-E solution was thermal treated to remove the solvent, afterwards the material was transferred in glass reactor and the metallic sample was treated with 1 g of HNO₃ and 2 g of HCl. The calibration standards were a multi-element calibration standard-3 (Ultra-scientific multistandard ICP-MS IMS-103) 100 mL: 10 mg L⁻¹ of Sb, Au, Pt, Rh, Hf, Ru, Ir, Te, Pd and Sn in a 10% HCl/1% HNO₃ matrix And an internal standard mix (Agilent), 100 mL: 10 mgmL⁻¹ of Bi, Ge, In, Sc, Tb, Y and Li in 5% HNO₃.

Transmission Electron Microscopy (TEM) was performed with a FEI Tecnai G2 12 operating at 100 kV and equipped with a TVIPS CCD camera. Pt and Pt_xY NPs were drop casted on copper grids coated with amorphous carbon films. Detailed microstructural investigation was performed using Cs probe corrected Scanning transmission electron microscope (Jeol ARM 200 CF) with attached Jeol Centurio EDXS system with 100 mm² SDD detector and Gatan Quantum ER Dual EELS system. To avoid electron beam induced damage, 80 kV accelerating voltage was used. Samples in powder form were transferred to lacey carbon coated copper TEM grids.

XRD measurements were acquired by using a Panalytical X'Pert Pro diffractometer equipped with a Co anode X-ray tube (40 kV, 40 mA), Bragg–Brentano optical module, and X'Celerator. Diffraction patterns were collected in the 2θ = 5°-50° range, with 2θ = 0.0338

virtual step size, counting an equivalent time of 100 s per step. The average dimensions of ordered crystalline domains (crystallite sizes) were estimated by line-profile analysis by using the W-H plot method as implemented in High Score Plus v. 3.0.

XPS measurements were performed in an ultra-high vacuum chamber (base pressure $<5 \times 10^{-9}$ mbar), equipped with a double anode X-ray source (omicron DAR-400), a hemispherical electron analyzer (omicron EIS-125) at room temperature, using non-monochromatized Mg Ka radiation ($h\nu = 1253.6$ eV), and a pass energy of 50 eV and 20 eV for the survey and the single spectral windows, respectively. The calibration of the binding energy scale was performed by using Au 4f as the reference (B.E. Au 4f = 84.0 eV). The Pt_xY target was cleaned by 9 sputtering cycles before acquiring the measurements.

Cyclic Voltammetry (CV) and Linear Sweep Voltammetry (LSV) was performed in 0.1 M HClO₄ solution using a standard three electrode system. A glassy carbon (GC) rotating disk electrode (RDE) (5 mm of diameter, geometric surface area 0.196 cm²) as working electrode, a commercial platinum ring (AMEL instrument for Electrochemistry) and a homemade Reversible Hydrogen Electrode (RHE) as reference electrode. The working electrode tip was firstly cleaned using diamond pastes with different grid (3 mm, 1 mm and 0.25 mm) and sonicated in Milli-Q water for 5 min at a temperature lower than 30 °C. The RHE was prepared before each electrode characterization. The Electrochemical characterization was performed using a Bio-Logic SAS SP-300 galvanostat/potenziostat.

S1.3 Electrochemical Characterization

Electrodes were prepared by drop casting 20 μL or the suitable volume of catalyst ink necessary to reach a platinum loading of 15 μg cm⁻² on the GC electrode surface. The ink was formulated considering a final total metal loading of 30 % with respect to carbon. The ink used for the drop-casting was formulated by mixing 2mL of Pt_xY-E NPs, 0.2 mL of milliQ water, 5 mL of a Nafion solution (5 wt% in EtOH) and MC as carbon support. The ink was sonicated for 2h at room temperature before the deposition. The catalyst was electro-activated by a series of voltammetric cycles at a scan rate of 50 mV s⁻¹. Several potential windows were tested, and it was found that the highest activation is reached when the potential of the working electrode is swept between 0.0 - 1.3 V vs RHE.

S1.4 Determination of the Electrochemical parameters

The figure underneath shows the characteristic voltammetric profiles for the commercial Pt/C Tanaka standard (Pt 50%_w) obtained in Ar purged 0.1 M HClO₄ after the electrochemical activation procedure. The voltammogram is characterized by three different voltammetric features; the left side (between 0.35 V vs RHE and 0 V vs RHE) corresponds to the H₂ adsorption/desorption (H_{upd}) region and H₂ evolution, the middle zone to the double layer charging current and the right side to the oxide-hydroxide formation and reduction.

The kinetic parameters ($E_{1/2}$, j_{lim} and j_k) were evaluated with linear sweep voltammetry (LSV) at rotating disk electrode (RDE) at a rotation rate 1600 rpm and a scan rate of 20 mV s⁻¹ in the potential range 0.05 V – 1.1 V vs. RHE. The electrochemical platinum surface area (EPSA) was determined by the coulometry of the hydrogen under-potential deposition (H_{upd}), using a conversion parameter of 210 mC cm⁻².

$$EPSA = \frac{H_2 \text{ Desorption Area [mA V]}}{\text{Scan Rate [mV s}^{-1}\text{]}} * \frac{1}{210 [\text{mC cm}^{-2}]} \quad \text{eq. S1}$$

The ECSA (Electrochemical Surface Area) was calculated by the normalization of EPSA with respect to the platinum loading.

$$ECSA = \frac{EPSA [\text{cm}^2]}{m_{Pt} El [\text{mg}]} \quad \text{eq. S2}$$

Figure below shows also the linear sweep voltammetry at 20 mV s⁻¹ of Pt/C with a rotation rate of 1600 rpm, recorded in O₂ saturated HClO₄ 0.1 M solution. The voltammetry can be divided in three different regions, between 1.05 V vs RHE and 0.85 V vs RHE, is present the kinetic region, the right zone between 0.05 V vs RHE and 0.55 V vs RHE correspond to the diffusion region, while the middle zone corresponds to the mixed kinetic diffusion region. $|j_{lim}|$ is the absolute value of limited current.

The limiting current was determined graphically in the diffusion limited region (0.25 V vs RHE and 0.75 V vs. RHE) after the subtraction of the background current recorded in Ar saturated electrolyte under otherwise the same experimental conditions, i.e., scan

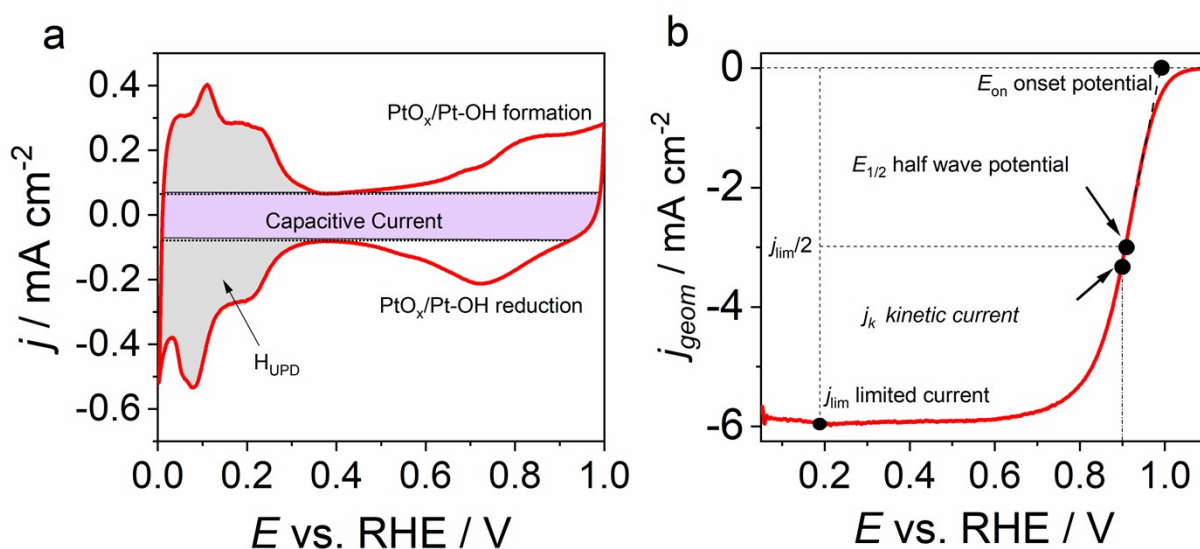
rate, angular velocity, potential window, and after normalization with respect to the geometrical surface area (0.196 cm²). $E_{1/2}$ is the half wave potential and is calculated at the half of the limiting current. The kinetic current was calculated in according to the eq. S3, in other words the kinetic current is the instant current corrected for the mass transfer contribution.

$$i_k = \frac{i \cdot i_{lim}}{i_{lim} - i} \quad \text{eq. S3}$$

Where i is the instant current expressed by the Koutecky-Levich (K-L) equation

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_{lim}} = \frac{1}{nFkC_{O_2}} + \frac{1}{0.62nF(D_{O_2})^{2/3}v^{-1/6}C_{O_2}\omega^{1/2}} \quad \text{eq. S4}$$

and i_{lim} is the diffusion limiting current determined when the current reach a constant plateau. C_{O_2} ($1.38 \cdot 10^{-6}$ mol cm⁻³) and D_{O_2} ($1.67 \cdot 10^{-5}$ cm² s⁻¹) are the concentration and diffusion coefficient of dioxygen in 0.1M HClO₄, v (~ 0.01 cm² s⁻¹) is the kinematic viscosity and ω (s⁻¹) the angular velocity of the RDE.^[1,2]



a) Cyclic voltammetry of Ar saturated 0.1 M HClO₄ solution recorded at a scan rate of 50 mV s⁻¹ on commercial Pt/C b) RDE linear sweep voltammetry of O₂ recorded on commercial Pt/C in O₂-saturated 0.1 M H₂SO₄ solution at a scan rate of 20 mVs⁻¹ and rotation rate of 1600 rpm.

The Mass Activity (MA) and the Specific Activity (SA) were determined at a potential of 0.9 V vs. RHE, where the influence of mass transport is zero. The kinetic current density at 0.9 V vs. RHE can be referred to the EPSA (Specific Activity, SA) and to the platinum loading (Mass Activity).

$$SA [mA cm^{-2}] = \frac{i_k}{EPSA} \quad \text{eq. S5}$$

$$MA [A g^{-1}] = \frac{i_k}{m_{Pt}} \quad \text{eq. S6}$$

Where m_{Pt} is the platinum loading and EPSA is the electrochemically active surface areas determined by coulometry of the hydrogen adsorption/desorption region using a charge of 210 mC cm⁻².^[3] Tafel analysis was performed by plotting $\log i_k$ versus potential in the kinetically controlled region (0.8 - 1.05 V vs. RHE) from which the Tafel slope and the kinetic current at the specific potential of 0.9 V vs. RHE can be obtained for the comparison of different catalysts. At least nine independent measurements were made for each catalyst: data are reported as mean values and the uncertainty is reported as the standard deviation.

S1.5 Stability test procedures

For the electrochemical measurements carried out in 0.5 M KOH a Hg/HgO reference electrode (AMEL instruments for Electrochemistry) was employed. Calibration of this reference electrode was performed in a standard three-electrode system with polished Pt wires as working and counter electrodes, and the Hg/HgO electrode as the reference electrode. The supporting electrolyte was 0.5 KOH and it was first purged with Ar and then saturated with high purity H₂. Linear sweep voltammetry was performed at a scan rate of 0.5 mV s⁻¹ from 0.9 V to 1 V vs. MMO, and the thermodynamic potential for the hydrogen electrode reactions was identified as the value when the current crossed zero. In 0.5M KOH, the zero current point was at -0.947 V vs Hg/HgO.

S1.6 Stability test procedures

Catalyst durability was tested in accelerated stability tests by cycling the potentials in the range of 0.6–1.05 V (vs. RHE) in O₂ saturated 0.1 M HClO₄ solution with a scan rate 0.5 V s⁻¹; ORR polarization curve at 1600 rpm and 20 mV s⁻¹ and the CV at 50 and 20 mV s⁻¹ were recorded after each 1000 voltammetric cycles and results were compared to the Pt/C TKK standard under the same conditions.

S2 Supporting Figures

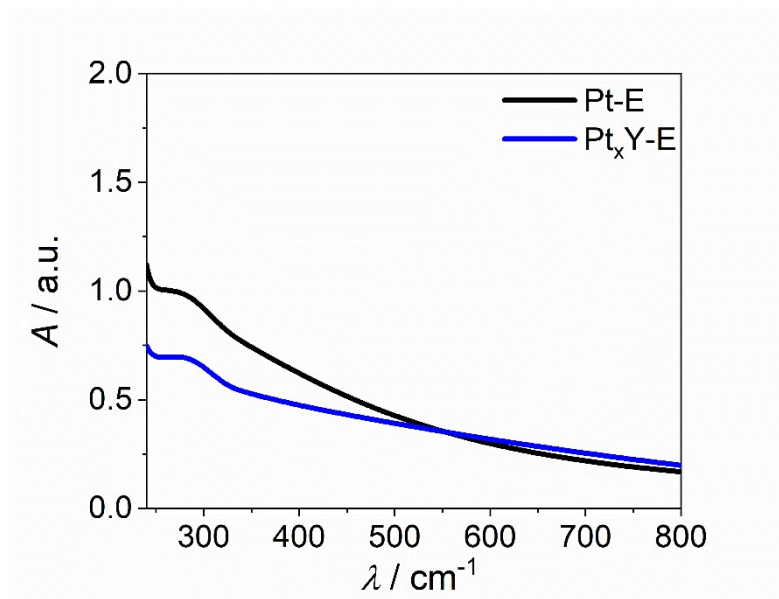


Figure S1: UV-Vis absorption spectra for Pt-E (black line) and Pt_xY-E (blue line). NPs concentration $\sim 30 \text{ g L}^{-1}$. The absorption spectra for each catalyst were recorded in a quartz cuvette with 1 cm optical path and using ethanol as solvent.

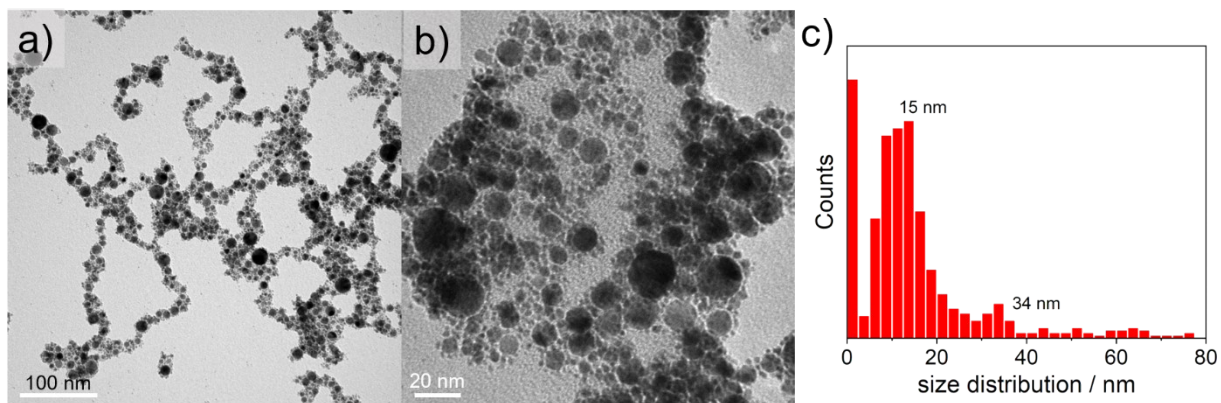


Figure S2: (a,b) TEM images for Pt-E NPs at different magnification and (c) dimensional distribution

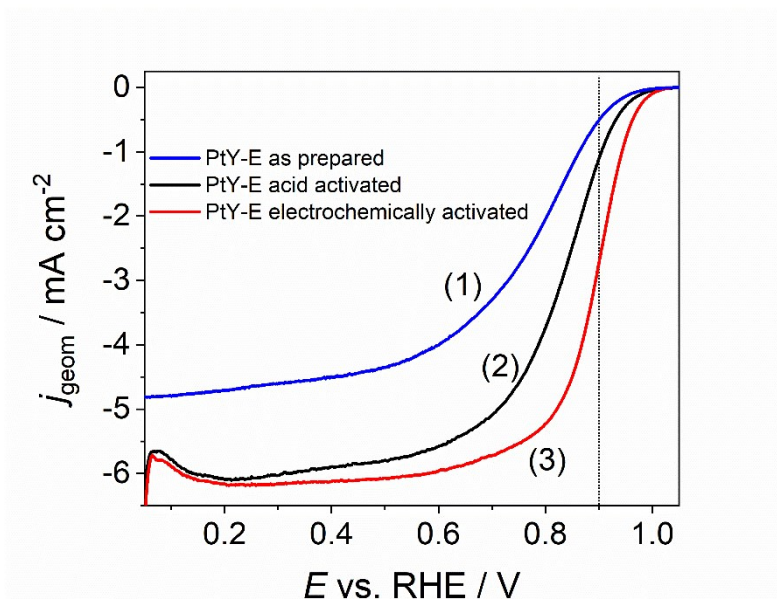


Figure S3. Effect of acid and electrochemical activation on Pt_xY-E/C. LSVs recorded at a scan rate of 20 mV s⁻¹ in O₂-saturated 0.1 M HClO₄ at 25 °C, rotation rate 1600 rpm.

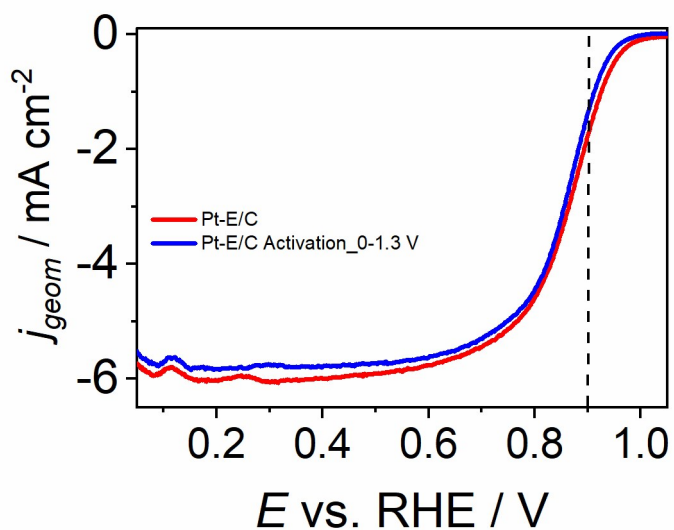


Figure S4. Effect of electrochemical activation on Pt-E/C. LSVs recorded at a scan rate of 20 mV s⁻¹ in O₂-saturated 0.1 M HClO₄ at 25 °C, rotation rate 1600 rpm.

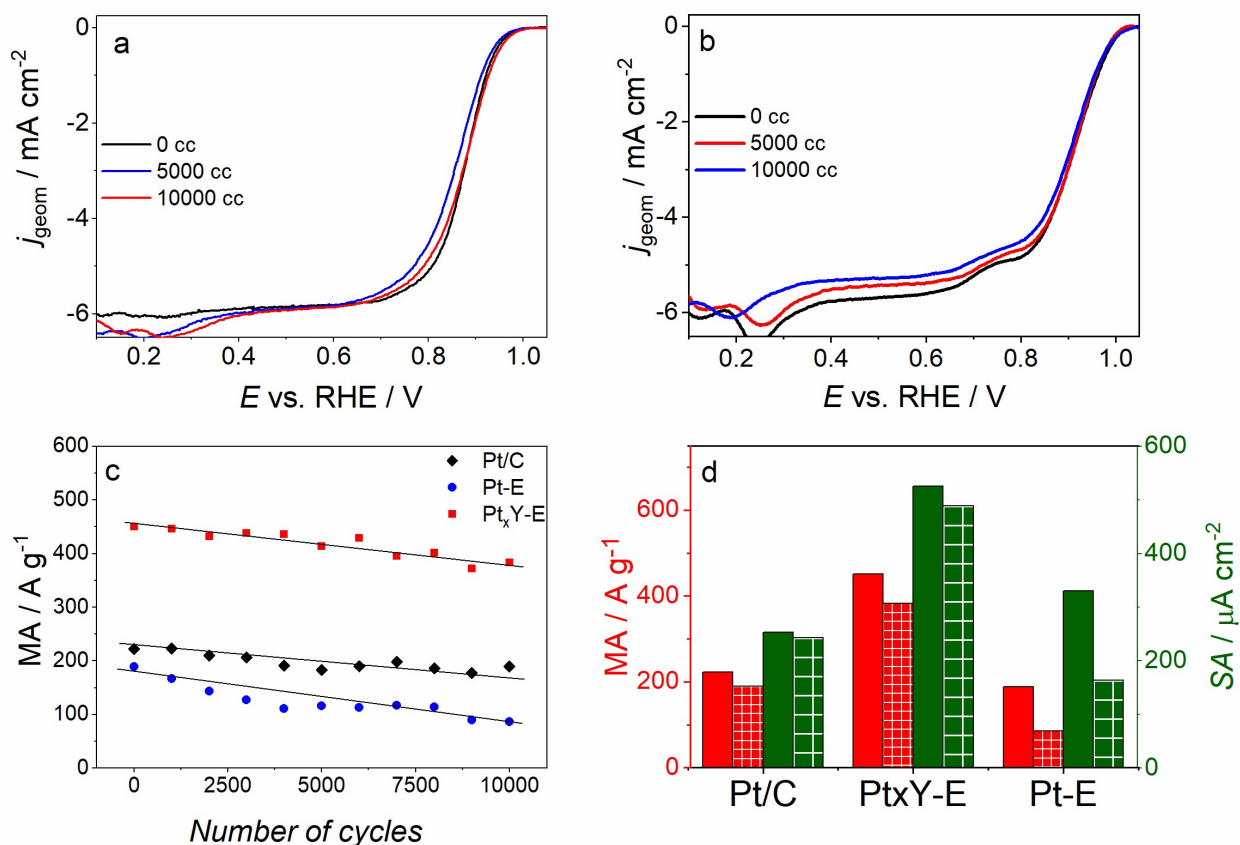


Figure S5. LSV recorded before and after accelerated stability test in 0.1 HClO₄ ($\omega = 1600$ rpm, $v = 20$ mV/s) first steady cycle (black line) and after 10000 cycles (blu line), for a) Pt-E and b) Pt_xY-E; c) variation of the mass activity during the stress test for Pt/C Tanaka standard, Pt-E and Pt_xY-E; d) mass activity and specific activity before and after the stability test for the investigated catalysts

S3 Supporting Tables

Table S1: Metal Loading of the Pt catalysts, the platinum and yttrium concentration and the final metallic content determined by ICP-MS

	Pt	Y	Pt/Y	Concentration
	% _w	% _w	molar ratio	mg mL ⁻¹
Pt-E	100	-	-	0.57
PtY-E	87.2	12.8	3.1	0.26

Table S2. Unit cell parameters obtained by Le Bail fitting.

Pt _x Y Target-	a (Å)	vol	starting vol	delta %		
Pt ₂ Y	7.5124±0.0002	423.97±0.03	434.83	-2.50		
Pt ₃ Y	4.0708±0.0001	67.457±0.005	67.369	0.13		
Pt _x Y-E	a (Å)	vol	starting vol	delta %	Lvol-FWHM (nm)	k
Pt ₂ Y	7.5198±0.0005	425.23±0.08	434.83	-2.21	13.8±0.2	0.9

Lvol-FWHM: average of the crystallite-size distribution obtained with the Scherrer method assuming isotropic sizes. Crystallite = coherently diffracting domain. K: shape constant.

Table S3 Electrochemical data obtained from liner sweep voltammetry at RDE in O₂-saturated 0.5 M KOH.

	j_L	$E_{1/2}$	i_k	MA	EPSA	ECSA	SA
	mA cm ⁻²	V vs.RHE	mA	A g ⁻¹	cm ²	m ² g ⁻¹	mA cm ⁻²
Pt/C	4.81 ± 0.5	0.880 ± 0.007	0.51 ± 0.01	174 ± 12	2.17 ± 0.08	73.8 ± 2.7	0.236 ± 0.014
Pt _x Y-E	5.09 ± 0.06	0.938 ± 0.006	1.93 ± 0.17	656 ± 58	2.53 ± 0.09	86.1 ± 3.1	0.762 ± 0.095
Pt-E	4.33 ± 0.07	0.901 ± 0.008	0.70 ± 0.11	237 ± 37	1.42 ± 0.011	48.3 ± 3.7	0.491 ± 0.114

S4 Bibliography:

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