Supplementary Information

Oxidatively Induced Exposure of Active Surface Area during Microwave Assisted Formation of Pt_3Co Nanoparticles for Oxygen Reduction Reaction

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The current (i) is related to the kinetic current (i_k) and diffusion limited current (i_L) by the equation (Koutecky – Levich)

$$\frac{1}{i}=\frac{1}{i_k}+\frac{1}{i_L}=\frac{1}{i_k}+\frac{1}{0.62nFACD^{2/3}\nu^{-1/6}\omega^{1/2}}, \tag{S1}$$

where F is Faraday constant; C is the O_2 concentration in saturated 0.1 M $HClO_4$ (*1.26×10^{-6} mol cm^{-3}*); ν is the electrolytes kinematic viscosity (*0.00893 cm^2 s^{-1}*); ω is the angular rotational frequency; D is the O_2 diffusion coefficient in the electrolyte (*1.93×10^{-5} cm^2 s^{-1}*); A is the surface area and n is the electron transfer number. j_k was used to calculate both specific and mass activities. The mass activities were then acquired by j_k normalized by the determined total Pt-mass on the electrode (Loading from TGA result while assuming 3:1 Pt:Co atomic ratio) and, after electrochemical active surface area had been obtained through CO-stripping, specific activities was obtained by j_k normalized by the measured electrochemical platinum surface area on the electrode.

H_2/O_2 PEM fuel cell tests were performed on Pt/C and Pt_3Co/C. The electrodes were prepared by spraying an ink formulated with 4 mg ml^{-1} catalyst powder in 90 % 2-propanol in $(H_2O)_{DI}$ and 33 wt.% Nafion® (DE 520, Ion Power) by 30 min sonication. The spraycoating was performed with a Badger® Krome Renegade airbrush connected to an N_2 pressure of 3 bar by carefully spraying in a serpentine motion on the substrate (Sigracet GDL 24 BC). The electrodes were set to dry overnight on a hotplate at 60 °C. Membrane electrode assemblies (MEAs), were produced by sandwiching two electrodes (each with metal loading of about 0.2 mg cm^{-2}) with a Nafion® NR211 membrane by hotpressing at 120 kg cm^{-2} for 3 min at 130 °C with a hot-pressing apparatus (Stahls Hotronix® 6″x6″ heat press). All membranes were pre-treated before use at 80 °C in $(H_2O)_{DI}$, 3 % H_2O_2, $(H_2O)_{DI}$, 0.5 M H_2SO_4 and finally $(H_2O)_{DI}$ respectively and stored in $(H_2O)_{DI}$ until use.

MEAs were loaded into 5 cm2 cell fixture (Baltic FuelCells GmbH) connected to a Scribner 850e fuel cell test station operating at 60 °C. O_2 and H_2 were both humidified to 95% RH (and supplied at a rate of 100 ml min^{-1}). Conditioning took place by keeping the potential constant at 0.55 V until reaching stable performance. Note: Pt/C required appr. 12 h while Pt_3Co/C required a total of appr. 50 h conditioning before stable performance could be reached. Polarization curves were then recorded with increments of 200 mA and 5 min stabilization per data point.

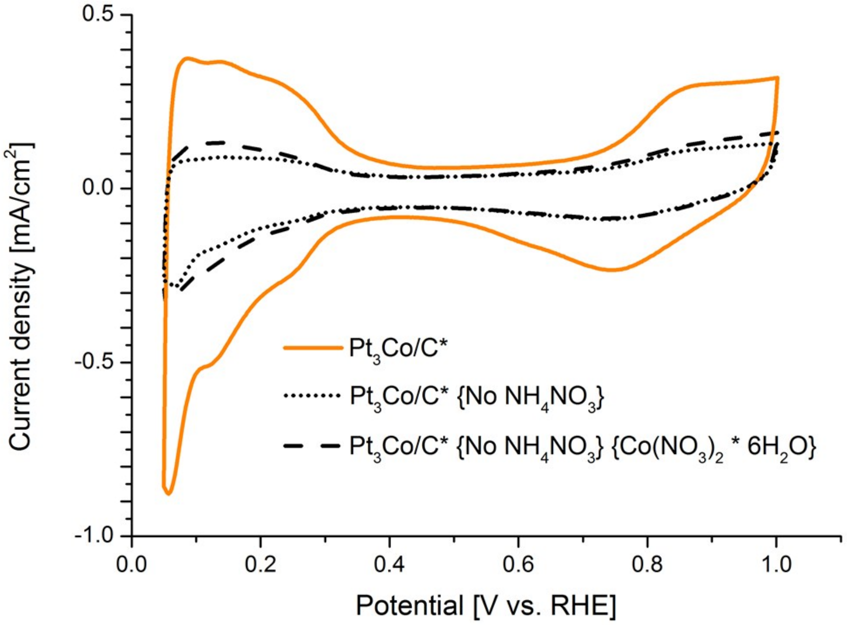

Fig. S1. *ECSA measurements by H_{UPD} in Ar saturated 0.1 M $HClO_4$ comparing Pt_3Co/C* with and without added NH_4NO_3 during synthesis. The significant difference in ECSA demonstrates the necessity of an oxidative source while forming NPs with organic precursors in this fashion. As a proof of concept, the dashed line in addition show a sample where the Co-acetate was replaced with $Co(NO_3)_2$ * $6H_2O$ also with omitted NH_4NO_3 showing that the nitrate decomposition of this Co precursor was not enough to overcome the ECSA of Pt3Co/C*. Note: both reference samples here had to be stopped after ca. 2 min due to excessive heat build-up.*

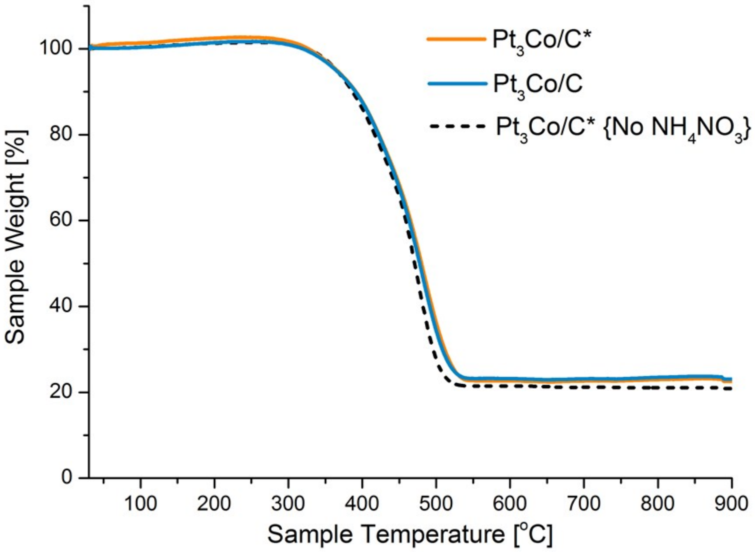

Fig. S2. *Thermogravimetric measurements of the synthesized Pt$_3$Co/C* (22.5 wt.%) and Pt$_3$Co/C (23.0 wt.%) samples as well as Pt$_3$Co/C* where the addition of ammonium nitrate was omitted in the synthesis (21.0 wt.%).*

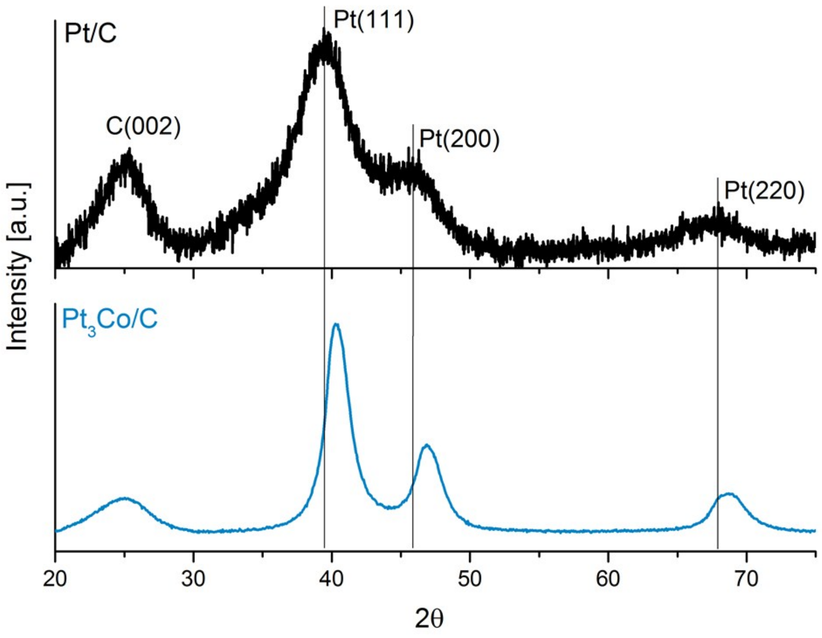

Fig. S3. *X-ray diffraction pattern of Pt/C compared to Pt$_3$Co/C. The upshift on Pt fcc reflections support Co incorporation.*

Table S1. *Measured kinetic currents (in mA) recorded from LSV curves before and after the accelerated degradation procedure.*

	Pt/C	Pt_3Co/C*	Pt_3Co/C
Initial i_k *[mA]*	0.8498	1.0444	1.4711
i_k post 6k cycles *[mA]*	0.6978	0.8477	1.1474

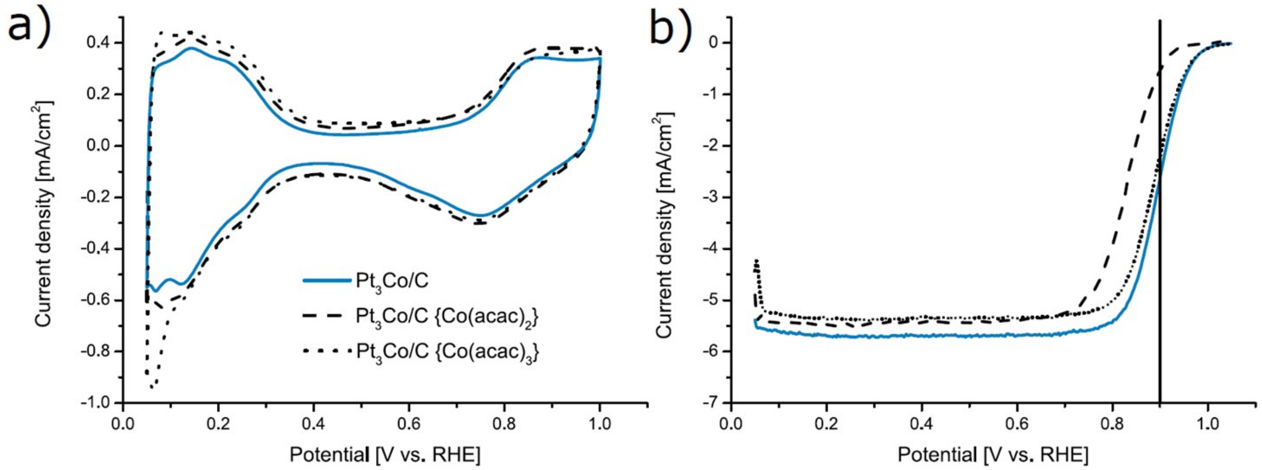

Fig. S4. *LSV characteristics (a) and H_{UPD} curve (b) of Pt_3Co/C as compared to the same synthesis procedure, but with Co(II) and Co(III) metal acetylacetonates. Despite also having satisfactory revealed ECSA, these organic precursors resulted in worse activity than for Pt_3Co/C, thus strengthening the confidence in that the correct Co precursor was selected in our study. Note: The selections of Co precursors were limited since similar reaction conditions to Pt_3Co/C* could not be reached, presumably due to a modification of their dielectric properties, making viable comparisons problematic. Both commercially available Co acetylacetonate salts however were visibly similar and a full 5 min initial reaction could be achieved.*

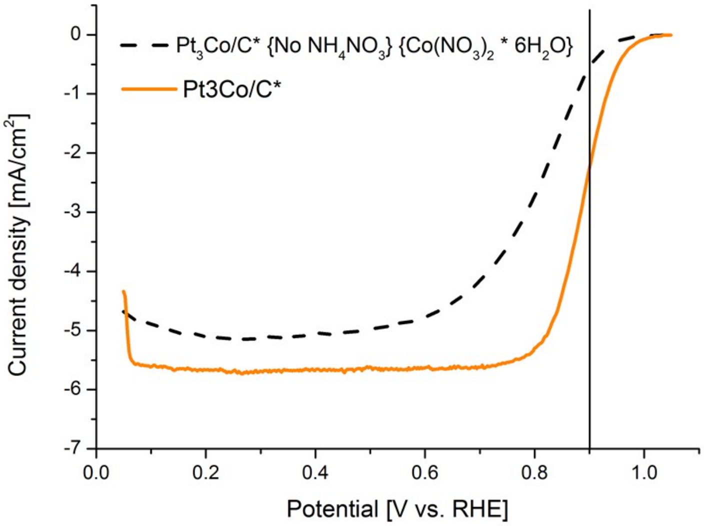

Fig. S5. *LSV curve of* $Pt_3Co/C*$ *compared to* $Pt_3Co/C*$ *produced with a Co-nitrate precursor and omitted* NH_4NO_3 *with a 2 min synthesis, very similar to our previous study with successful synthesis of* Pt_3Y/C *shown in ref.*[1]*. Our results show that this approach is not feasible for* Pt_3Co*. ECSA cv-curve of this catalyst can be found in fig. S1.*

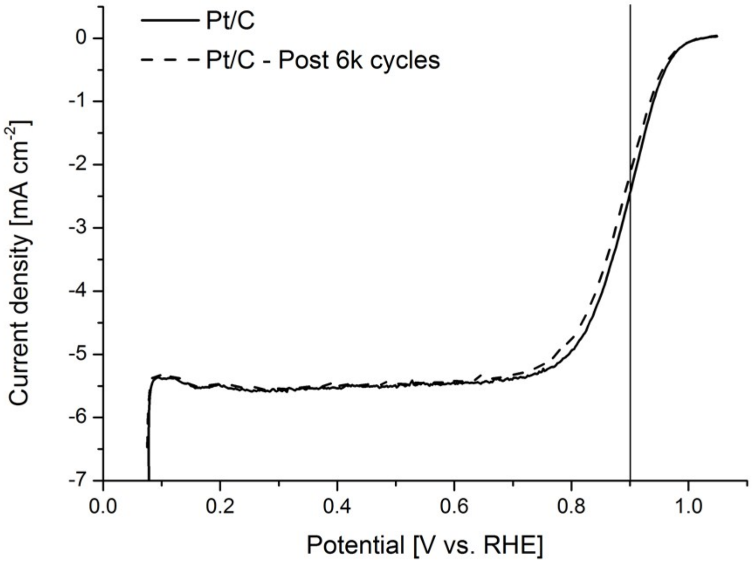

Fig. S6. *LSV characteristics of Pt/C with the LSV profile post 6000 cycles between 0.6 and 1.0 V vs. RHE in* O_2 *saturated* $HClO_4$*. The accelerated degradation test resulted in an 18 % loss of* j_k*.*

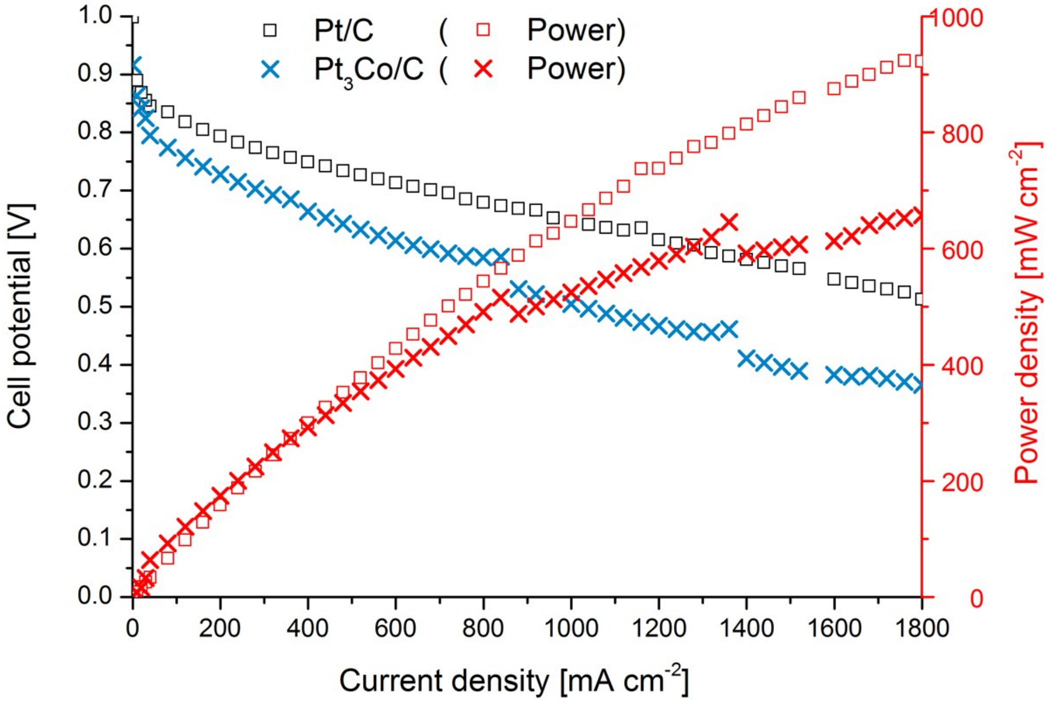

Fig. S7. *H_2/O_2 PEM fuel cell performance evaluation of Pt/C and Pt_3Co/C. Polarization curves were recorded after conditioning at 0.55 V until reaching stable performance. Tests performed with lower nafion content (~20 %) with Pt_3Co/C resulted in delamination of the catalyst layer from the membrane and are therefore not comparable.*

References

(1) Sandström, R.; Gracia-Espino, E.; Hu, G.; Shchukarev, A.; Ma, J.; Wågberg, T. Yttria Stabilized and Surface Activated Platinum (Ptxyoy) Nanoparticles through Rapid Microwave Assisted Synthesis for Oxygen Reduction Reaction. *Nano Energy* **2018,** *46*, 141-149.