# Supplementary Materials: Toward Overcoming the Challenges in the Comparison of Different Pd Nanocatalysts: Case Study of the Ethanol Oxidation Reaction

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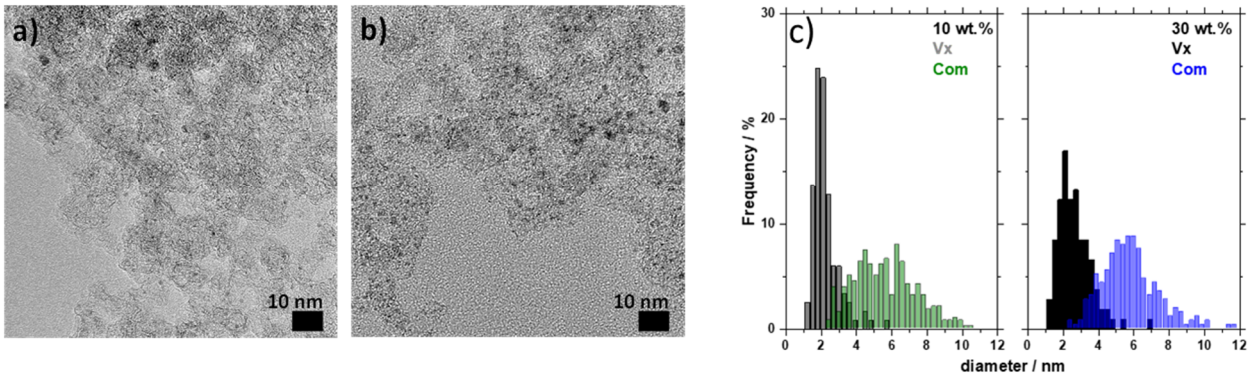


**Figure S1.** (a,b) TEM micrographs from Figure 1a,b reported for clarity for Pd/Vx (a) 10 wt.% and (b) 30 wt.%. (c) Size distribution obtained from TEM analysis of different Pd NPs on carbon support with different loading as indicated. 'Vx' stands for Vulcan and refers to the home-made material and 'Com' to the commercially available materials.

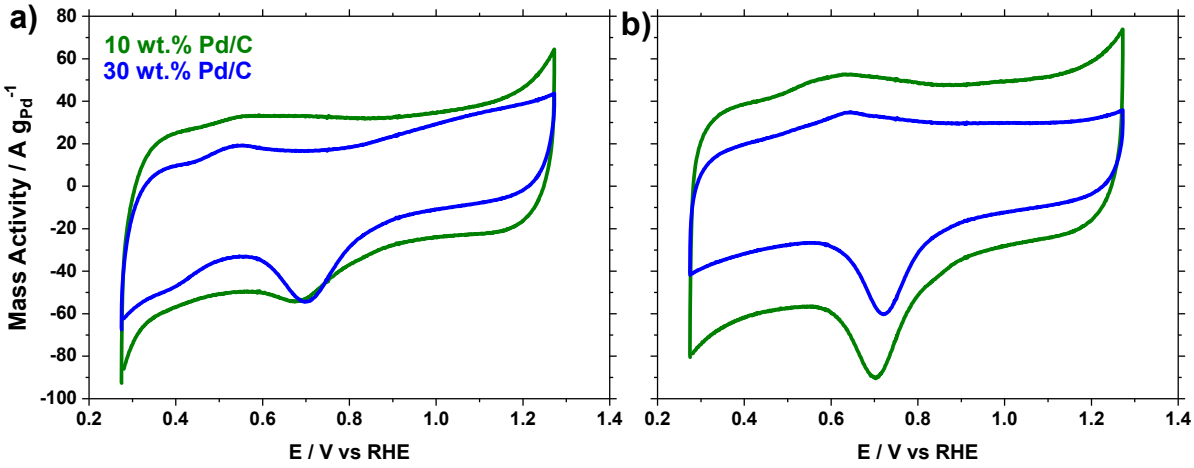


**Figure S2.** Cyclic voltamnograms of the Pd/C with different loading as indicated for ECSA determination in 1 M KOH. The scan rate during CV measurements was 50 mV.s$^{-1}$. Argon was purged in electrolyte during all measurements performed in 1 M KOH without rotation of the electrode.

The ECSA was estimated by converting the charge related to the reduction peak around 0.7 V *vs.* RHE. The capacitance can be related to the 'distance' between the featureless part of the cyclic voltammograms (e.g. at 1.0 V *vs.* RHE).

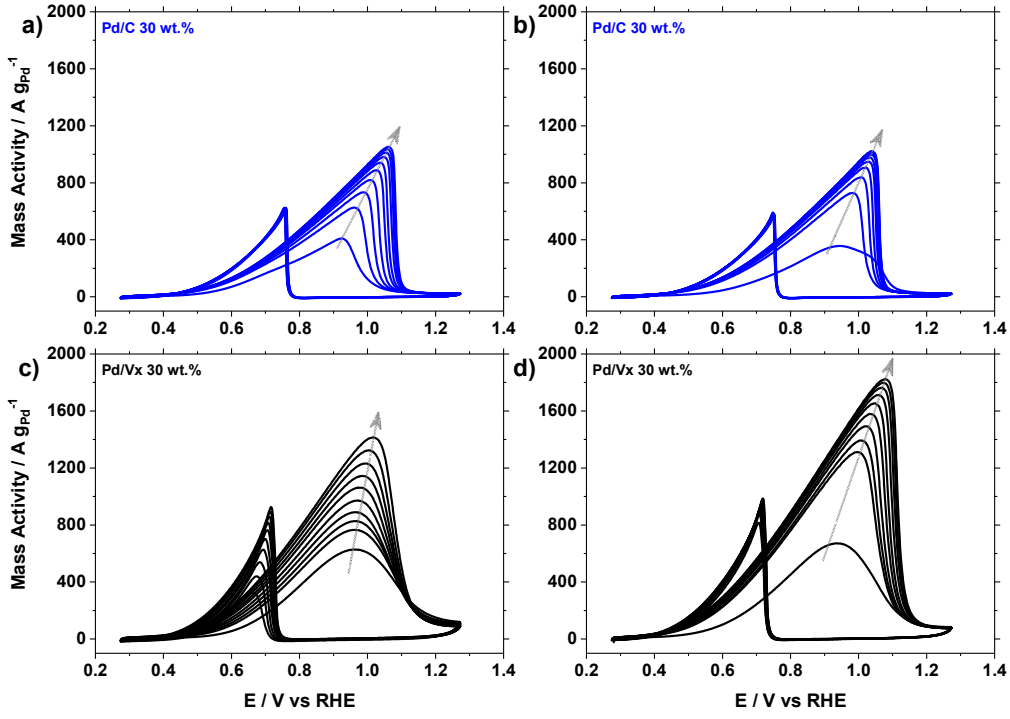


**Figure S3.** Example of 1st to 10th cyclic voltammograms of (a,b) commercial 30 wt.% Pd/C (a) before and (b) after CA, (c,d) home-made 30 wt.% Pd/Vx (c) before and (d) after CA at 0.71 V *vs.* RHE. The scan rate during CV measurements was 50 mV.s$^{-1}$. Argon was purged in electrolyte during all measurements performed in 1 M ethanol in 1 M KOH without rotation of the electrode.

**Table S1.** Samples used for averaged electrochemical values reported.

| | **Nominal mass of Pd on the electrode in μg**<br>**μL Nafion at 1 % used for the ink preparation - 'A' indicates that 10 μL acid was used in the ink composition** | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Sample** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **11** | **12** |
| **10 wt.%** | 10 | 3.33 | 10 | 10 | 10 | 3.33 | 3.33 | 3.33 | 10 | - | - | - |
| **Pd/C** | 10 | 10 | 20 | 10-A | 20-A | 20 | 20-A | 10 | 20-A | | | |
| **30 wt.%** | 10 | 3.33 | 10 | 10 | 10 | 3.33 | 3.33 | 10 | 10 | 3.33 | - | - |
| **Pd/C** | 10 | 10 | 10 | 10-A | 20-A | 20 | 20-A | 10 | 20 | 10-A | | |
| **10 wt.%** | 10 | 3.33 | 10 | 10 | 10 | 3.33 | 3.33 | 3.33 | 3.33 | 3.33 | 3.33 | - |
| **Pd/Vx** | 10 | 10 | 10 | 10-A | 20-A | 20 | 20-A | 10 | 20 | 20 | 10 | |
| **30 wt.%** | 10 | 3.33 | 10 | 10 | 10 | 3.33 | 3.33 | 10 | 10 | 3.33 | 10 | 10 |
| **Pd/Vx** | 10 | 10 | 20 | 10-A | 20-A | 20 | 20-A | 10 | 20-A | 10-A | 10 | 10-A |

Across the literature various 'ink' composition are used and there is therefore no 'standard' way to prepare the related samples: different mass of catalysts of Pd used, different loading, different ink composition, different electrolytes [1–7].

The average electrochemical values reported in Table 1, once average to the identical ink preparation in grey in Table S1 are given in Table S2.

**Table S2.** Equivalent of Table 1 considering only the samples in grey in Table S1.

| | **Commercial** | | **Synthesized** | |
|---|---|---|---|---|
| **wt.%** | **10** | 30 | 10 | 30 |
| **MA** after 60 minutes CA / $\mathbf{A \cdot g^{-1}}$ | 30.3 ± 12.3 | 62.1 ± 23.2 | 73.1 ± 44.9 | 114.0 ± 22.6 |
| **ECSA** before EOR / $\mathbf{m^2 \cdot g^{-1}}$ | 8.1 ± 3.2 | 17.6 ± 7.7 | 36.4 ± 27.8 | 63.3 ± 26.5 |
| **ECSA** after EOR / $\mathbf{m^2 \cdot g^{-1}}$ | 20.4 ± 6.4 | 21.0 ± 7.4 | 22.8 ± 14.6 | 36.8 ± 8.8 |
| **SA** after EOR / $\mathbf{A \cdot m^{-2}}$ | 1.7 ± 0.9 | 3.0 ± 1.1 | 3.8 ± 1.9 | 3.2 ± 0.9 |

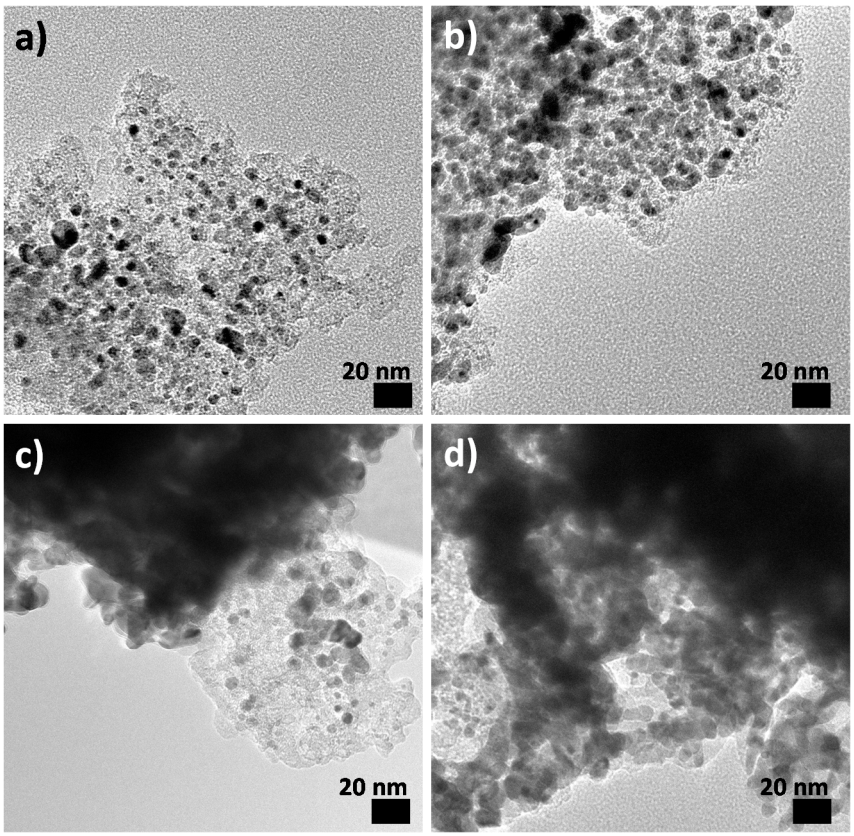


**Figure S4.** TEM micrographs of commercial Pd/C (a,b) before and (c,d) after electrochemical treatment for commercial samples with (a,c) 10 wt.% and (b,d) 30 wt.%.

Both samples before and after electrochemical treatment show large agglomeration of the Pd. This seems to be more pronounced after electrochemistry. TEM allows to screen only a finite number of spots and NPs but indicates that most of the smaller NPs well identified in Figure S4a,b disappeared after electrochemical testing.

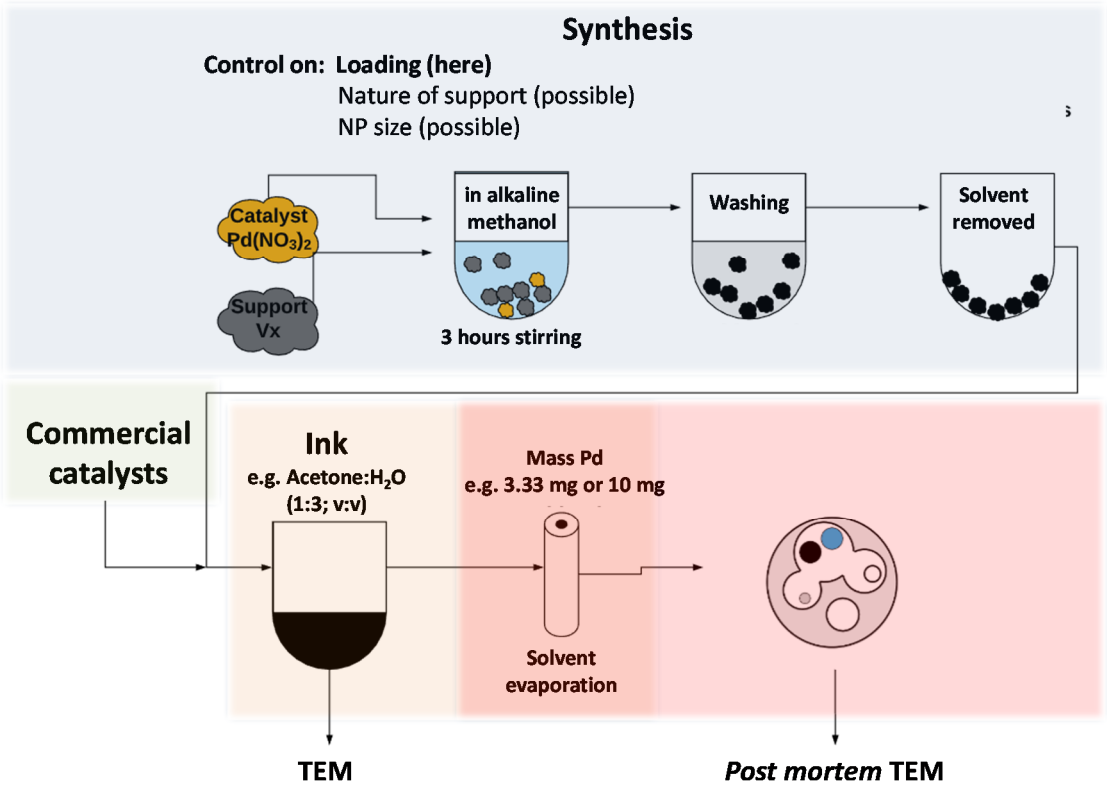


**Figure S5.** Work flow for catalyst synthesis, electrochemical evaluation and post mortem characterization.

## References

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