

Supplementary Materials: Insight on Single Cell Proton Exchange Membrane Fuel Cell Performance of Pt-Cu/C Cathode

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As-prepared PtCu₃/C catalyst has a wide particle size distribution between 5-200 nm, ordered PtCu₃ Pm3m phase, Pt-rich overlayer and initially exhibits no porosity (Figure S1 a-f). However, after 200 potentiodynamic cycles referred to here as “electrochemical activation” (EA), porosity was observed in particles larger than approximately 30 nm and in those having a higher copper content (see Supplementary Materials, Figure S1 g-h and S2). By contrast, smaller particles displayed a ‘core-shell’ structure (with a Pt-rich overlayer and a PtCu₃ core), in accordance with our previous study [1].

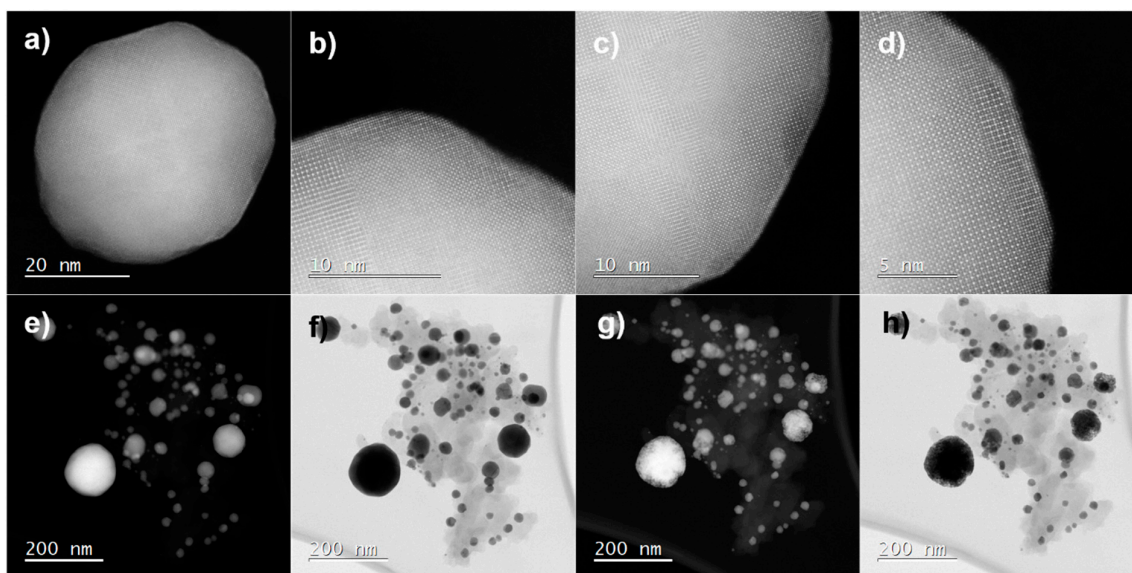


Figure S1. High-resolution STEM micrographs of different regions of PtCu₃ nanoparticle (a-d). IL-STEM analysis of PtCu₃ electrocatalyst before and after dealloying (dark field e,g and bright field; f,h).

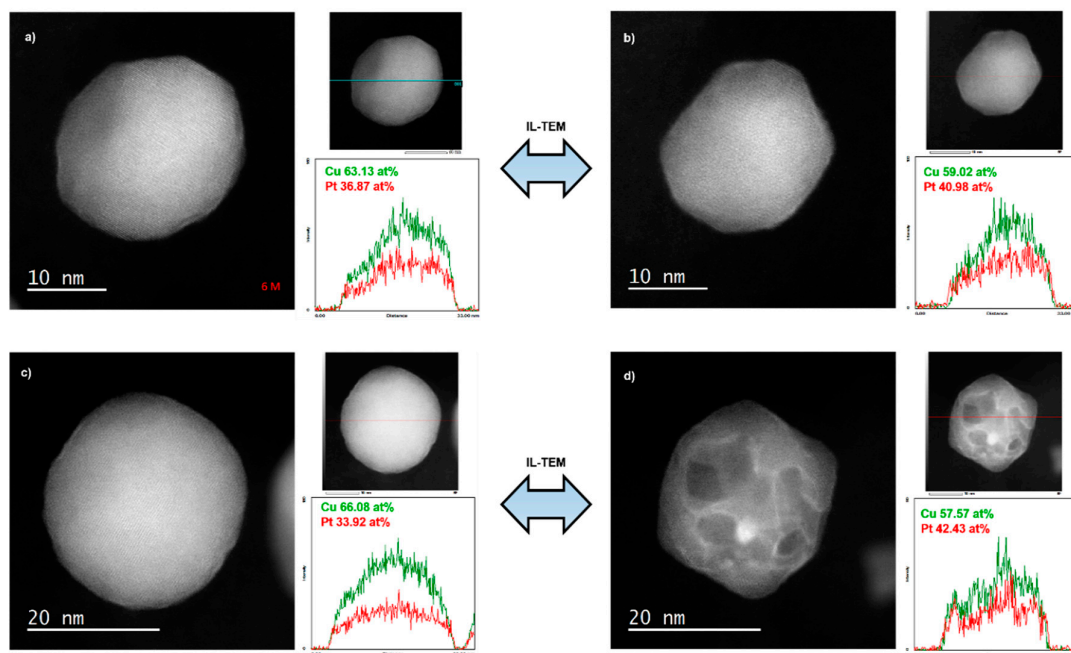


Figure S2. IL-STEM and IL-EDX line scans of PtCu₃ electrocatalyst. Formation of (a,b) core shell and (c,d) porous PtCu₃ nanoparticle.

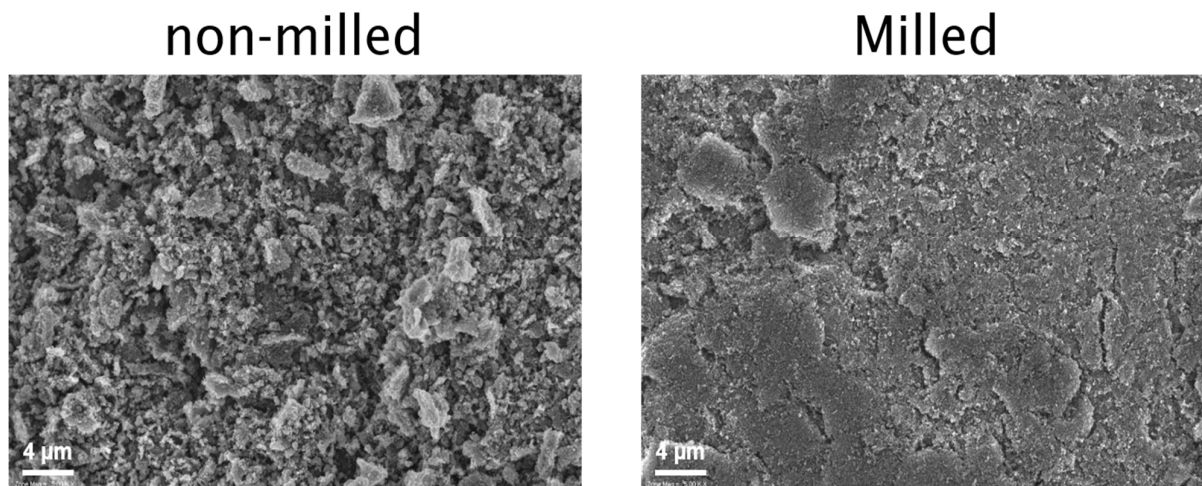


Figure S3. Comparison of milled (right) and non-milled (left) Pt-Cu/C analogues.

Table S1. Weight % of Pt and Cu as well as Pt:Cu ratio for all three PtCu₃/C analogues (based on ICP-MS digestion experiments).

Sample	Pt (wt%)	Cu (wt%)	Ratio (Pt:Cu)
PtCu ₃ /C	20.27	18.75	1.08
PtCu ₃ /CA	19.70	14.40	1.36
PtCu ₃ /CAM	21.41	16.08	1.33

Table S2. TF-RDE results for PtCu₃/C analogues (Electrochemical activation-EA: 0.05 – 1.2 V_{RHE}, 300 mV s⁻¹).

PtCu ₃ /CA	ESA _{CO} [m ² /g _{Pt}]	Specific activity [mA/cm] @0.9 V	Mass activity [mA/g _{Pt}] @0.9 V
After 200 cycles (EA)	43	3.2	1.25
PtCu ₃ /CAM	ESA _{CO} [m ² /g _{Pt}]	Specific activity [mA/cm] @0.9 V	Mass activity [mA/g _{Pt}] @0.9 V
After immersion in the electrolyte	23	0.37	0.08
After 200 cycles (EA)	32	2.70	0.85

Table S3. Values of parameters in model by Kulikovskiy [2] used to fit the experimental PtCu curves. The meaning of parameters is displayed below the table.

c_h [mol cm ⁻³]	8.0e-6	2.3e-6	3.0e-6	6.0e-6
c_{ref} [mol cm ⁻³]	8.1e-6	8.1e-6	8.1e-6	8.1e-6
V_{oc} [V]	0.993	1.026	0.993	1.026
R_{ohm} [Ω cm ²]	0.15	0.37	0.11	0.14
i^* [A cm ⁻³]	5.1	11	19	5.2
σ_t [Ω cm ⁻¹]	0.070	0.070	0.070	0.070
l_t [cm]	0.001	0.001	0.001	0.001
l_b [cm]	0.025	0.025	0.025	0.025
b [V]	0.030	0.030	0.030	0.030
D_b [cm ² s ⁻¹]	0.029	0.029	0.029	0.029
D [cm ² s ⁻¹]	1.5e-4	4.5e-4	2.9e-4	2.5e-4
c_h^* [mol cm ⁻³]	1.3e-5	1.3e-5	1.3e-5	1.3e-5

c_h : Oxygen concentration in the channel

c_{ref} : Reference oxygen molar concentration

V_{oc} : Cell open-circuit potential

R_{ohm} : Cell ohmic resistivity

i^* : Volumetric exchange current density

σ_t : CCL ionic conductivity

l_t : Catalyst layer thickness

l_b : GDL thickness

b : Tafel slope

D_b : Oxygen diffusion coefficient in the GDL

D : Oxygen diffusion coefficient in the CCL

c_h^* : Oxygen concentration at the channel inlet

In the case of impedance spectra no fitting was carried out. Instead of that, the parameter values obtained from the fit of polarisation curves were directly inserted into the impedance model and the corresponding impedance spectra for each of the sample simulated. Any correspondence with measured spectra thus means that both models describe the measurements quite well and consistently. Indeed, as seen from the examples of fit (Figure 5), there is quite a good match between the measured spectra and the model prediction at high frequencies. At lower frequencies, however, there is some significant deviation –seen as another possible semicircle. That semicircle is not predicted with the Kulikovsky's model under the present conditions. Thus its origin is difficult to discuss in more detail. One origin, however, could be some instability (drift) of polarisation curve at the conditions where the impedance was collected (see Figure 5b). Another aspect that is not covered by the model is (severe) inhomogeneity of sample in terms of agglomeration and other morphological non-uniformities. Despite this deviation, however, we find it rather surprising that the model gives rather good quantitative match (in terms of high frequency intercept and high frequency arc) with the actual measurements.

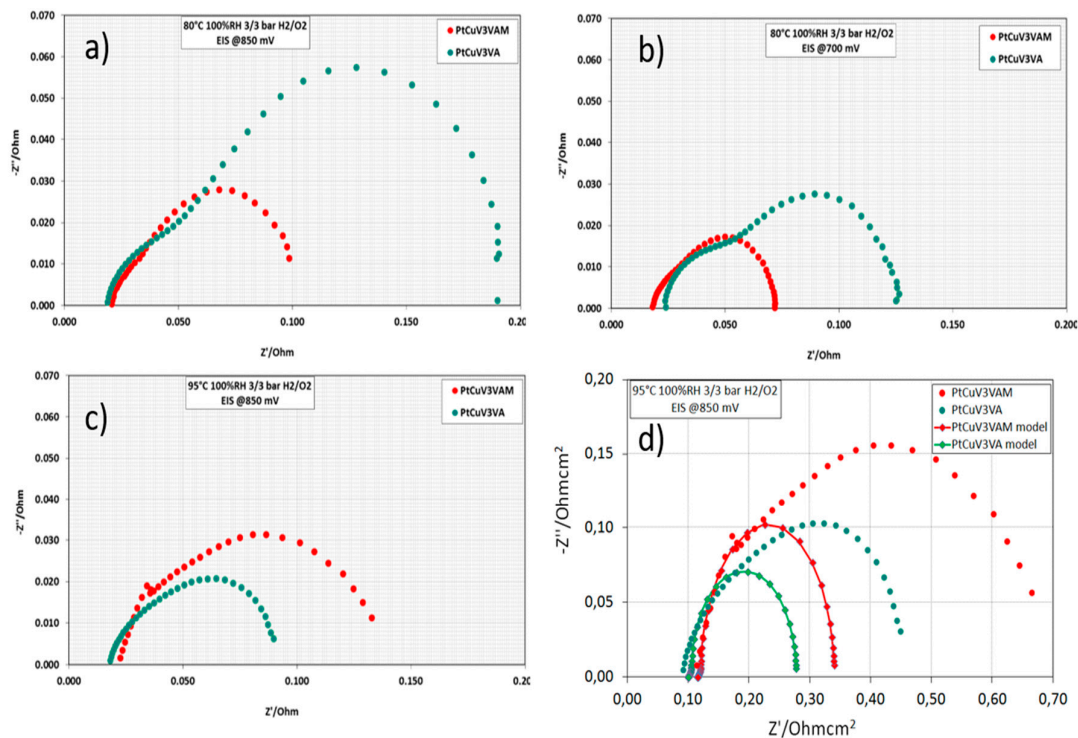


Figure S4. Impedance spectra for both alloys obtained at 80 °C (a,b) and at 95 °C (c). The spectra were measured under polarisation conditions (@850 mV) with exception of graph b (@700 mV). **d**) Comparison of measured and simulated impedance spectra of un-milled (green) and milled (red) PtCu₃/C catalyst at 95 °C and 850 mV. Circles: measured EIS spectra (units: Ohm); diamonds: EIS spectra simulated with parameters obtained from polarization curves fitted with model [2]. **b**) Zoom-in into polarisation curve at conditions where impedance spectra were collected. The horizontal movement of measured points indicates some drift of the system which might be one of the reasons for deviation between the measurements and model predictions.

References

- [1] N. Hodnik, C. Jeyabharathi, J.C. Meier, A. Kostka, K.L. Phani, A. Rečnik, M. Bele, S. Hočevar, M. Gaberšček, K.J.J. Mayrhofer, Effect of ordering of PtCu₃ nanoparticle structure on the activity and stability for the oxygen reduction reaction., *Phys. Chem. Chem. Phys.* 16 (2014) 13610–5. doi:10.1039/c4cp00585f.
- [2] A.A. Kulikovskiy, A Physically–Based Analytical Polarization Curve of a PEM Fuel Cell, *J. Electrochem. Soc.* 161 (2013) F263–F270. doi:10.1149/2.028403jes.