Supporting information

Operando SAXS Study of a Pt/C Fuel Cell Catalysts with an X-ray Laboratory Source

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Accelerated stress test

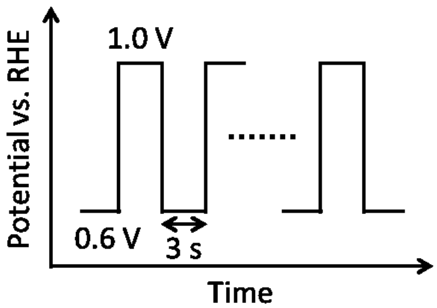

Figure S1. Sketch of the AST protocol applied in the *operando* cell.

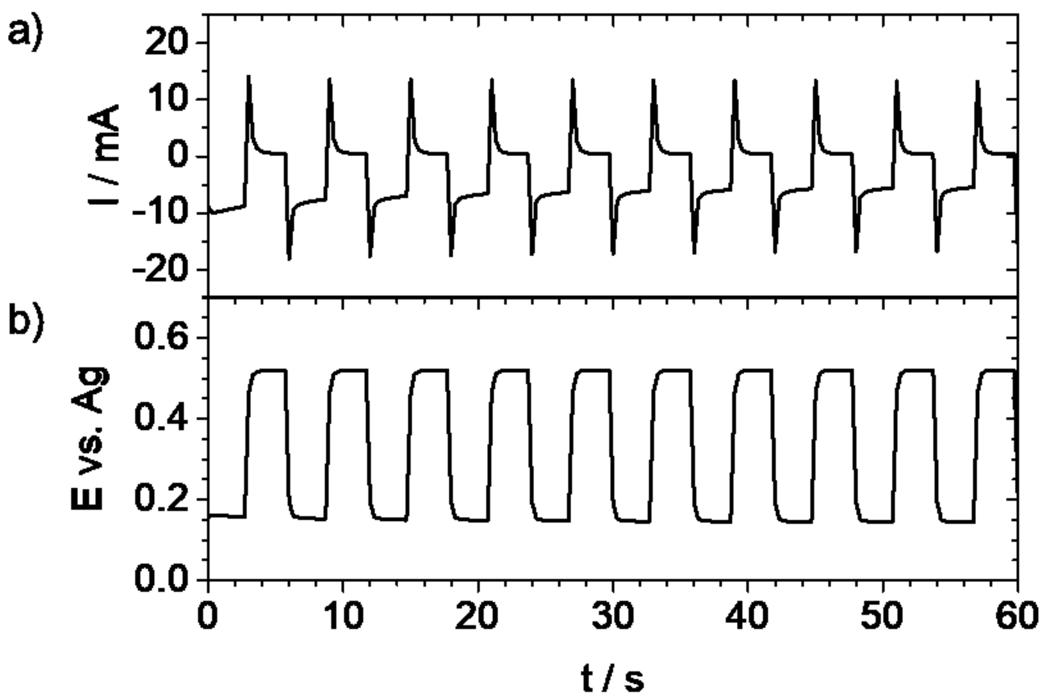

Figure S2. Examples of the a) applied (corrected) potential E vs. the Ag reference electrode and b) the measured current I during the AST at room temperature under air.

SAXS data

The average volume of nanoparticle from population 1 and from population 2, $<V>_1$ and $<V>_2$ respectively, lead to define volume fraction of population 1, Φ_{V1}, and volume fraction of population 2, Φ_{V2}, as:

$$\Phi_{V1} = \frac{N_1<V>_1}{N_1<V>_1+N_2<V>_2} = 1 - \Phi_{V2}$$

$$\frac{\Phi_{V1}}{\Phi_{V2}} = \frac{N_1 < V >_1}{N_2 < V >_2}$$

$$\frac{N_1}{N_2} = \frac{\Phi_{V1} < V >_2}{\Phi_{V2} < V >_1}$$

where N_1 and N_2 are the number of nanoparticles in the population 1 or 2 respectively.

From the SAXS data acquisition we have the relationship between the retrieved coefficient C_1 and C_2 given by $C_i = k.\ \Phi_{vi}.\ <V>_i$ where i=1 or 2 and k is a constant.

$$k = \frac{C_1}{\Phi_{V1} < V >_1} = \frac{C_2}{\Phi_{V2} < V >_2} = \frac{C_2}{(1 - \Phi_{V1}) < V >_2}$$

$$\frac{\Phi_{V1}}{1 - \Phi_{V1}} = \frac{C_1 < V >_2}{C_2 < V >_1}$$

$$\Phi_{V1} = \frac{1}{1 + \frac{C_2 < V >_1}{C_1 < V >_2}}$$

In order to weight the probability density function by the area or surface fractions we consider $<A>_1$ and $<A>_2$ as the average area of the nanoparticles from population 1 and 2, respectively:

$$\Phi_{A1} = \frac{N_1<A>_1}{N_1<A>_1+N_2<A>_2} = 1 - \Phi_{A2} = \frac{1}{1+\frac{N_2<A>_2}{N_1<A>_1}}$$

$$\Phi_{A1} = \frac{1}{1 + \frac{\Phi_{V2} < V >_1 < A >_2}{\Phi_{V1} < V >_2 < A >_1}}$$

$$\Phi_{A1} = \frac{1}{1 + \frac{C_2 (< V >_1)^2 < A >_2}{C_1 (< V >_2)^2 < A >_1}}$$

Table S1: Fitting parameters for SAXS data.

		Power law		1st population			2nd population			Diameters and deviation / nm [A.B]					
	Sample	A x 10^6	n	R_1 (Å)	σ_1	C_1	R_2 (Å)	σ_2	C_2	**d_1**	**σ_1**	**d_2**	**σ_2**	**d**	**σ**
Without electrolyte	Pristine	22	4	9.5	0.20	0.0050	25.5	0.28	0.047	1.9	0.4	5.3	1.5	2.9	0.5
With electrolyte and background recorded before EC	Before EC	-	-	7.5	0.20	0.0035	22.5	0.30	0.016	1.5	0.3	4.7	1.4	1.9	0.
	150 steps	-	-	7.5	0.20	0.0045	23.5	0.27	0.018	1.5	0.3	4.9	1.3	1.8	0.3
	300 steps	-	-	7.5	0.20	0.0044	23.5	0.22	0.017	1.5	0.3	4.8	1.1	1.9	0.3
	450 steps	-	-	7.5	0.25	0.0042	23.5	0.23	0.017	1.5	0.4	4.8	1.1	2.0	0.4
	600 steps	250	2	7.5	0.40	0.0047	24	0.23	0.019	1.6	0.7	4.9	1.1	2.3	0.6
	900 steps	250	2	7.5	0.40	0.0049	25	0.22	0.019	1.6	0.7	5.1	1.1	2.3	0.6
With electrolyte and background recorded after EC	Before EC	7	4	9.5	0.25	0.0016	24	0.27	0.016	2.0	0.5	5.0	1.4	3.1	0.6
	150 steps	4	4	10.5	0.23	0.0016	24	0.27	0.016	2.2	0.5	5.0	1.4	3.3	0.6
	300 steps	3	4	11.5	0.23	0.0016	24	0.27	0.016	2.4	0.6	5.0	1.4	3.6	0.7
	450 steps	3	4	12.5	0.23	0.0017	24.5	0.25	0.016	2.6	0.6	5.1	1.3	3.9	0.7
	600 steps	2	4	12.5	0.23	0.0015	24.5	0.23	0.016	2.6	0.6	5.0	1.2	4.0	0.7
	900 steps	2	4	12.5	0.23	0.0013	24.5	0.22	0.017	2.6	0.6	5.0	1.1	4.1	0.7

(A) evaluated as **d** $= 0.2\, e^{(ln(R)+\frac{\sigma^2}{2})}$ for a one size population, evaluated as **d**$= 0.2\, \varphi_{A1}. e^{\left(\ln(R_1)+\frac{\sigma_1{}^2}{2}\right)} + 0.2\, \varphi_{A2}. e^{\left(\ln(R_2)+\frac{\sigma_2{}^2}{2}\right)}$ for a 2 sizes population

(B) evaluated as **σ**= $0.2\sqrt{(e^{\sigma^2}-1)e^{(2\ln(R)+\sigma^2)}}$ for a one size population,

evaluated as **σ**= $0.2\sqrt{\varphi_{A1}{}^2.[(e^{\sigma_1{}^2}-1)e^{(2\ln(R_1)+\sigma_1{}^2)}]+\ \varphi_{A2}{}^2.[(e^{\sigma_2{}^2}-1)e^{(2\ln(R_2)+\sigma_2{}^2)}]}$for a two sizes populations

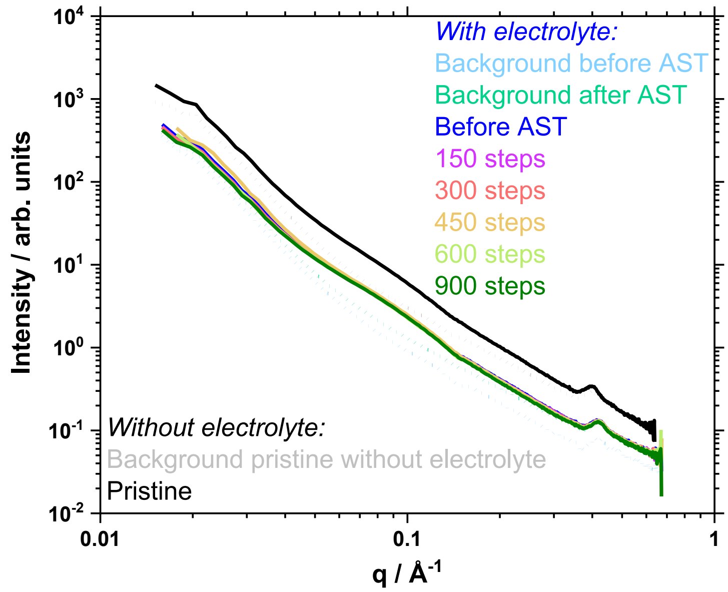

Figure S3. Overview of signal intensity for the SAXS measurements. Backgrounds are in dotted line, samples measured for different electrochemical treatment are reported as indicated.

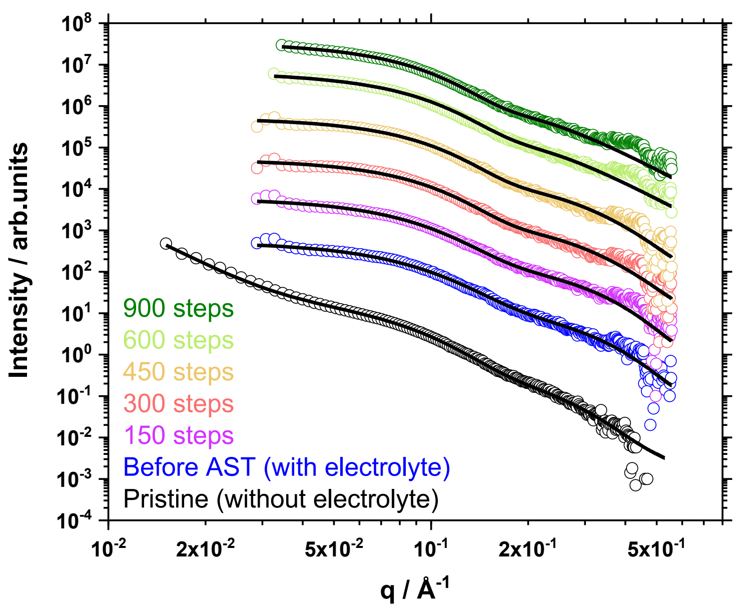

Figure S4. Overview of signal intensity for the SAXS measurements and fits after background subtraction for a background measured before electrochemical testing. The fit for the sample measured without electrolyte is also displayed.

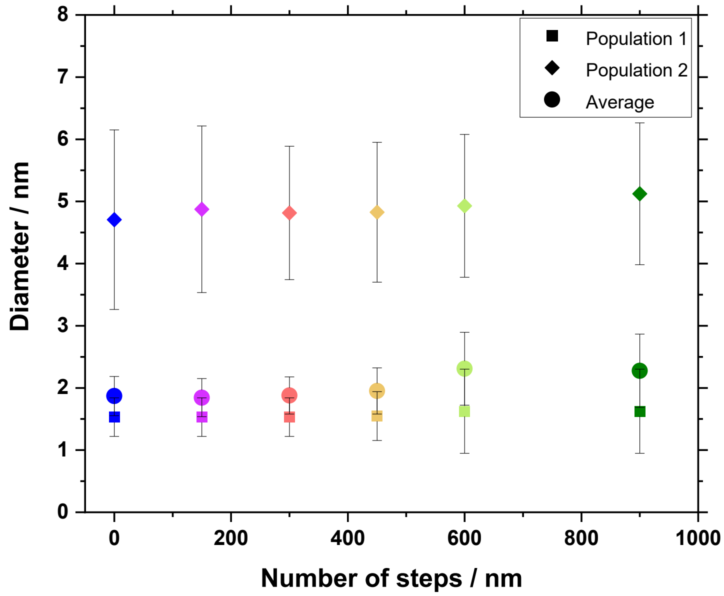

Figure S5. Diameter of the nanoparticles retrieved from SAXS data analysis using as background a background measured before electrochemical test, as a function of the number of steps for electrochemical testing and using a model taking into account two size populations.

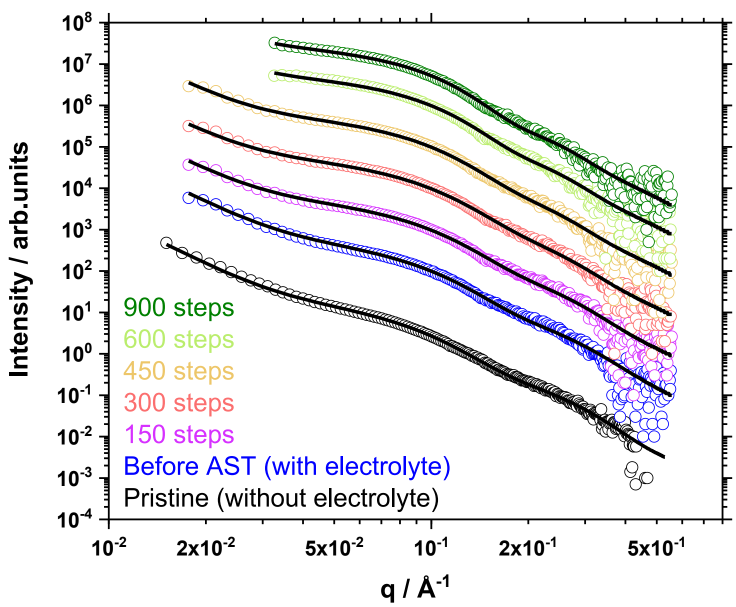

Figure S6. Overview of signal intensity for the SAXS measurements and fits after background subtraction for a background measured after electrochemical testing. The fit for the sample measured without electrolyte is also displayed.

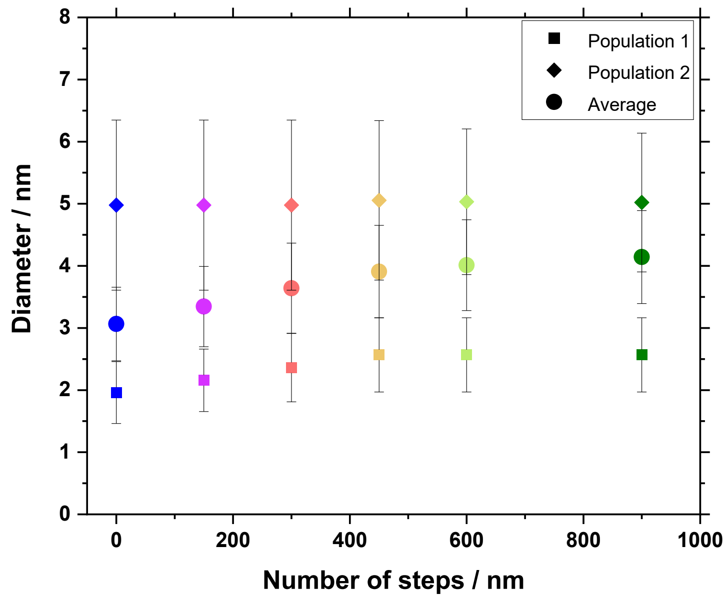

Figure S7. Diameter of the nanoparticles retrieved from SAXS data analysis using as background a background measured after electrochemical test, as a function of the number of steps for electrochemical testing and using a model taking into account two size populations.