

Supplementary Materials

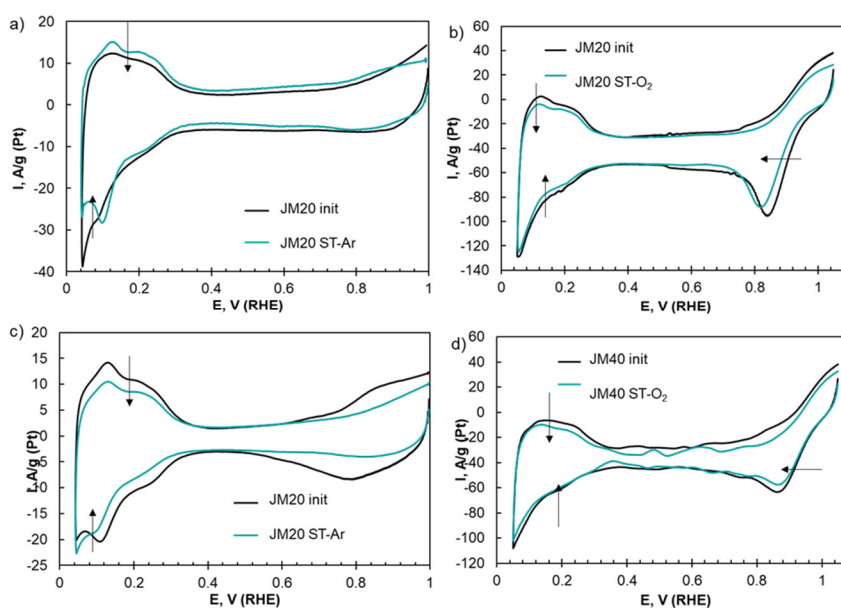


Figure S1. The cyclic voltammograms for the electrocatalyst before and after the stress testing: (a) JM20 in an Ar atmosphere, the electrolyte is 0.1 M HClO₄, the potential sweep rate is 20 mV/s; (b) JM20 in an O₂ atmosphere, the electrolyte is 0.1 M HClO₄, the potential sweep rate is 50 mV/s at the rotation speed of 50 rpm; (c) JM40 in an Ar atmosphere, the electrolyte is 0.1 M HClO₄, the potential sweep rate is 20 mV/s; (d) JM40 in an O₂ atmosphere, the electrolyte is 0.1 M HClO₄, the potential sweep rate is 50 mV/s at the rotation speed of 50 rpm.

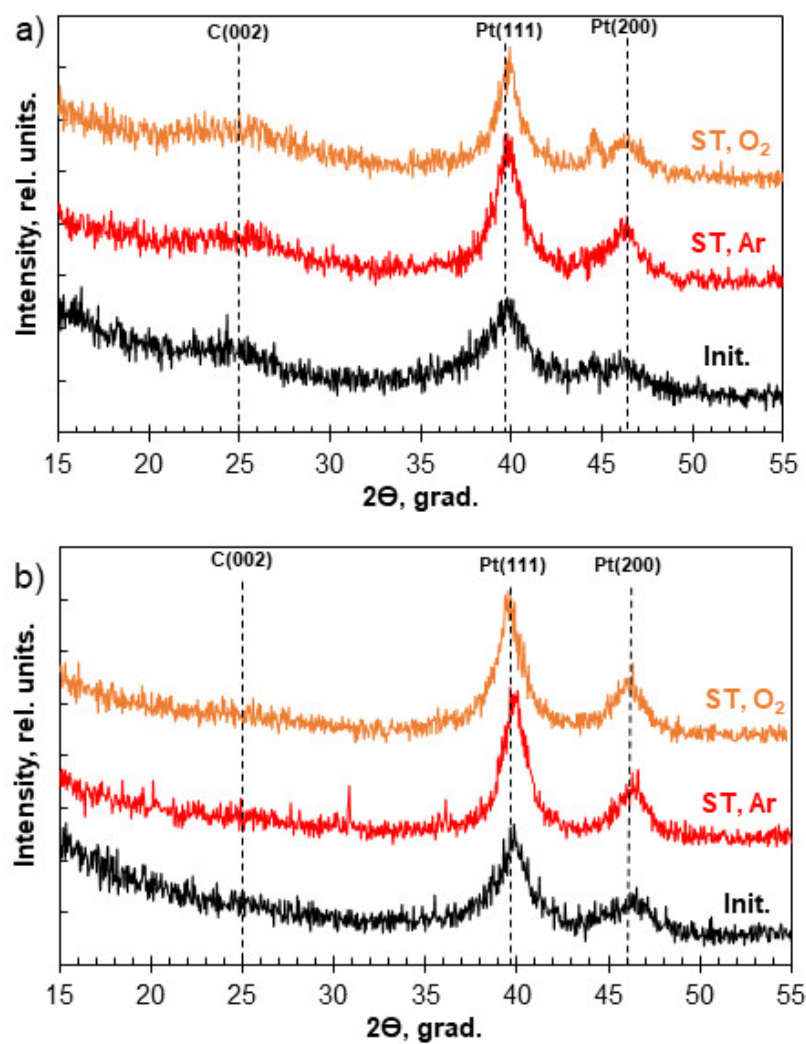


Figure S2. The X-ray diffraction patterns for (a) JM20 and (b) JM40 before and after the ADT in the electrolyte saturated with Ar or O₂.

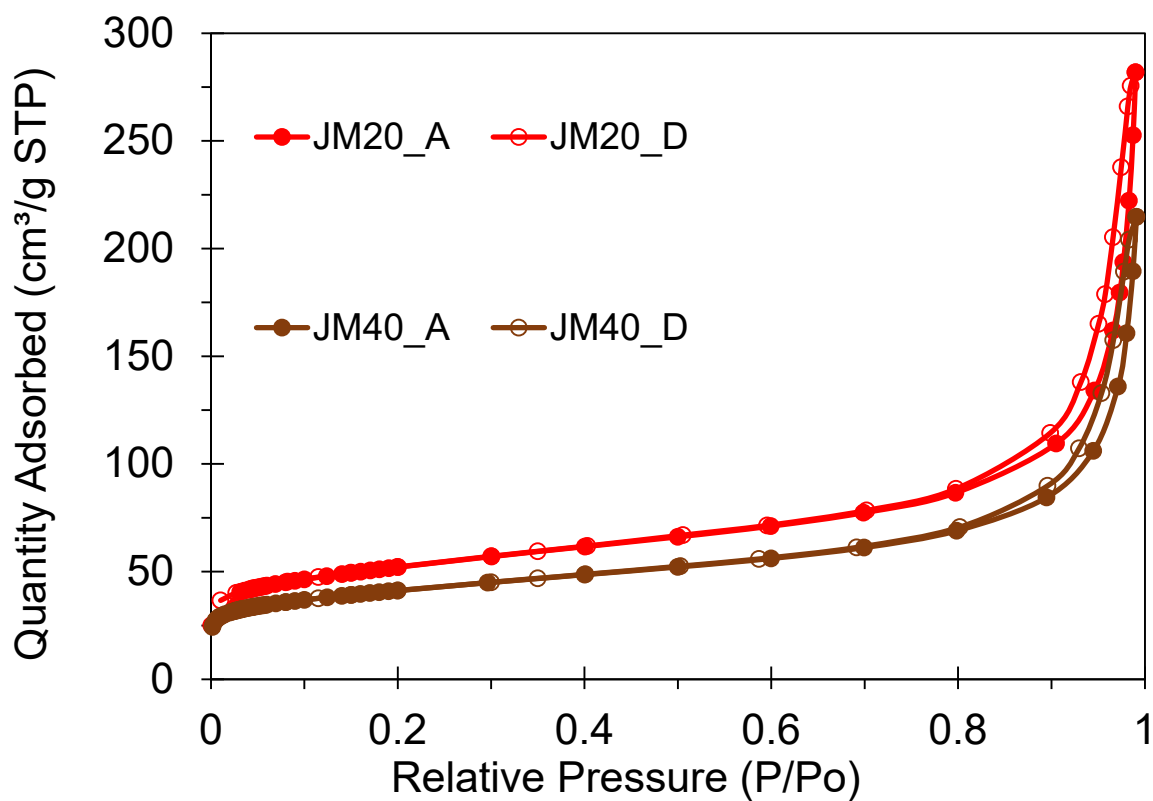


Figure S3. Nitrogen adsorption/desorption curves for the commercial Pt/C materials JM20 and JM40.

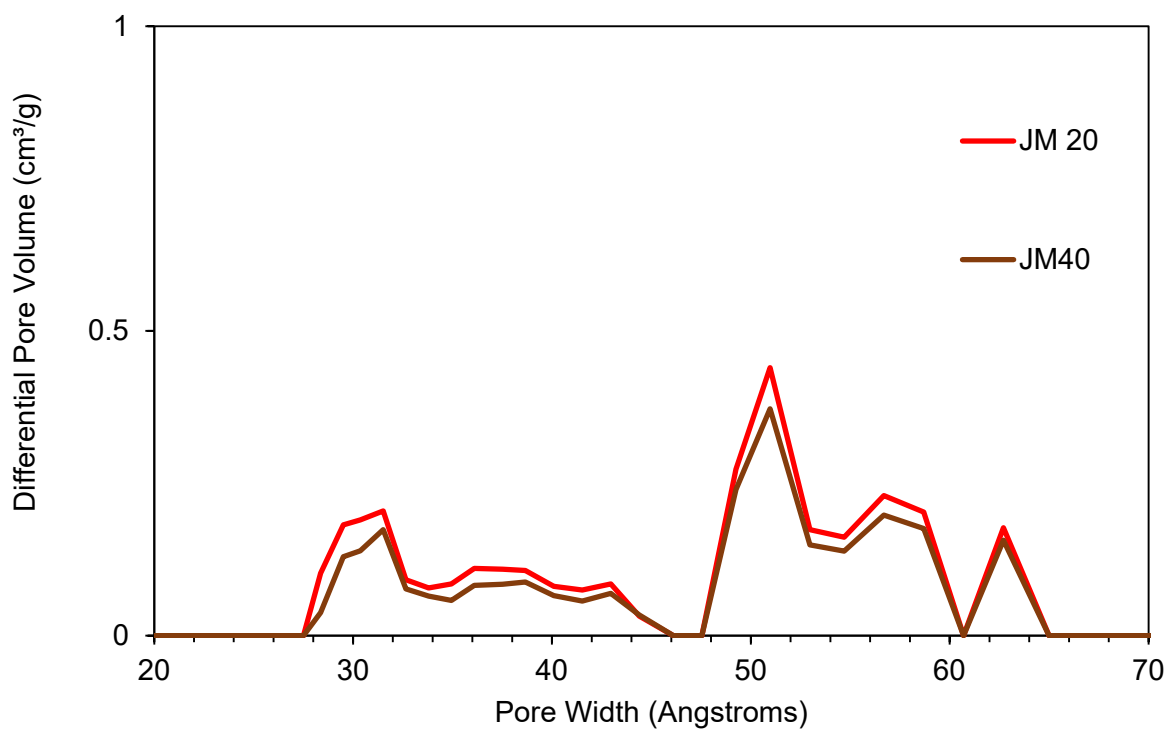


Figure S4. The pore size distribution for the commercial Pt/C materials JM20 and JM40.

Study of the catalytic structure

BET analysis was performed using a Micromeritics ASAP 2020 Physisorption BET instrument.

1.1 X-ray examination

The X-ray diffraction patterns for the samples studied were recorded in the range of angles of $20 \leq 2\theta \leq 55$ degrees by step-by-step scanning with the detector movement step of 0.02 degrees [1].

The X-ray diffraction patterns were processed using the SciDavis software to extract the peak parameters correctly, this being of particular importance when peaks overlapped over one another in the case of small particle sizes [1]. The average crystallite size (D_{Av}) was calculated by the Scherrer formula, as described below:

$$D_{Av} = K\lambda / (FWHM \cos\theta),$$

where λ is the wavelength of the monochromatic radiation (in Å),

FWHM is the reflex full width at half maximum (in radians),

$K = 0.89$ is the Scherrer's constant,

D_{Av} is the average thickness of the "stack" of reflecting planes in the coherent scattering region (in Å),

θ is the angle of incidence of the X-ray beam (in radians). The error margin was $\pm 8\%$.

1.2 Transmission electron microscopy

To prepare the sample for measurements, 0.5 mg of the catalyst were placed in 1 ml of isopropanol and dispersed with ultrasound for 10 min. A drop of the resulting suspension was applied to the standard copper grid covered with a 5–6 nm thick layer of amorphous carbon. The sample was then dried in air at room temperature for 60 min.

1.3 Preparation of catalytic inks for electrochemical measurements

When obtaining the suspension of the Pt/C catalysts (catalytic inks), the sample weight was calculated in order that with 8 μ l of the catalytic suspension being successively applied to the electrode, the platinum weight should be 20 μ g_{Pt}cm⁻². 100 μ l of the Nafion® polymer 1 % aqueous emulsion and 100 μ l of deionized water were then added with introduction of 1800 μ l of isopropyl alcohol (extra-pure grade). The suspension was dispersed with ultrasound for 25 min at 5–15 °C with alternate stirring every 5 min. Before applying the suspension, the glass–carbon end face of the RDE had been polished and then rinsed with isopropyl alcohol. An 8 μ l aliquot of the inks was sampled with a pipette tip with constant stirring and applied to the end face of the polished and degreased glass–carbon electrode with the area of 0.196 cm². The electrode was then dried in air for 15 min with the rotation speed of 700 rpm. In this way, the catalytic layer was formed on the RDE.

1.4 ESA calculation

Based on the half-sum of the charge amounts consumed for the electrochemical adsorption (Q_{ad}) and desorption (Q_d) of atomic hydrogen during the registration of CVs [1], the ESA was calculated according to the formula:

$$ESA = QH / [R \times L],$$

where ESA is the area of the electrochemically active platinum surface, cm²/g(Pt),

$Q_H = (Q_{ad} + Q_d)/2$ is the charge amount consumed for the electrochemical adsorption and desorption of hydrogen,

R is the charge amount consumed for the adsorption/desorption of an atomic hydrogen monolayer, $210 \mu\text{C}/\text{cm}^2(\text{Pt})$,

L is the platinum weight on the electrode, g.

The error margin for the ESA calculation was $\pm 10\%$

1.5 ORR measurement

To determine the ORR activity of the catalysts, a series of LSVs were measured in the potential range from 0.02 to 1.1 V at the potential sweep rate of 20 mV/s. The electrolyte was pre-oxygenated for 60 min with the RDE rotation speed of 700 rpm. To account for the contribution of the ohmic voltage drop, the potential of the electrode studied was refined by the formula: $E = E_{\text{set}} - I \cdot R$, where E_{set} is the set value of the potential, $I \cdot R$ is the ohmic potential drop equal to the product of the current strength by the resistance of the solution layer between the reference electrode and the electrode studied, which was 23 ohms. The contribution of the processes proceeding on the electrode in a deoxygenated solution (an Ar atmosphere) was taken into account by subtracting the equivalent curve, recorded on the same electrode during the measurements in an Ar atmosphere: $I(\text{O}_2) - I(\text{Ar})$, from the voltammogram, as described in [2]. The LSVs were recorded at the RDE rotation speeds of 400; 900; 1,600; and 2,500 rpm. The ORR activity of the catalysts (the kinetic current) was determined by the normalized voltammograms, taking into account the contribution of mass transfer under conditions of using the RDE [3,4]. The kinetic current at the potential of 0.90 V (RHE) was calculated using the Koutetsky–Levich equation: $1/j = 1/j_k + 1/j_d$, where j is the experimentally measured current, j_d is the diffusion current, and j_k is the kinetic current.

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Table S1. Publication data on activity and stability of commercial Pt/C electrocatalyst.

Sample	Stress test condition	ESA, m ² /g(Pt)		I, A/g(Pt)		Stability, %	Ref.
		Initial	After ST	Initial	After ST		
JM20	10,000 cycles 0.4 and 1.0 V, 3s, (PP), 0.1M HClO ₄ , Ar	84	56	254	152	67	This work
JM20	10,000 cycles 0.4 and 1.0 V, 3s (PP), 0.1 M HClO ₄ , O ₂	84	48	254	108	57	This work
JM20	18,000 cycles 0.6-1.0 V 0.1M HClO ₄ , O ₂	81	70	299	-	87	5
JM20	10,000 cycles 0.6 – 1.4 V 0.5M H ₂ SO ₄ , N ₂	47	10	-	-	22	6
JM20	10,000 cycles 0.60 - 1.05 V air-contained 0.1M HClO ₄	79	52	210	110	66	7
JM20	10,000 cycles 0.6 – 1.2 V 0.1M HClO ₄ , N ₂	60	12	72	-	20	8
JM20	5000 cycles 0.6 – 1.2 V 0.1M HClO ₄ , N ₂ ,	56	34	74	20	61	9
JM40	10,000 cycles 0.4 and 1.0 V, 3s (PP), 0.1M HClO ₄ , Ar	56	43	159	108	77	This work
JM40	10,000 cycles 0.4 and 1.0 V, 3s (PP), 0.1M HClO ₄ , O ₂	56	46	159	135	82	This work
JM40	30,000 cycles 0.6-1 V 0.1M HClO ₄ ,	54.8	38	230	-	70	10
JM40	5000 cycles 0.6 – 1.24 V 0.5M H ₂ SO ₄ , N ₂ ,	46	8	-	-	17	11
JM40	6000 cycles 0.6 – 1.0 V	51	34	-	-	67	11

	0.5M H ₂ SO ₄ , N ₂						
JM40	10,000 cycles 0.6 – 1.0 V 0.1M HClO ₄ , N ₂	40	-	76.4	-	-	12

*(PP) - rectangular pulses in the potential

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