



Supporting Information

for

Stability and activity of platinum nanoparticles in the oxygen electroreduction reaction: is size or uniformity of primary importance?

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Beilstein J. Nanotechnol. **2021**, *12*, 593–606. [doi:10.3762/bjnano.12.49](https://doi.org/10.3762/bjnano.12.49)

Experimental and theoretical methods used to obtain catalyst parameters

X-ray study

The average platinum crystallite size D_{Av} was calculated using the Scherrer equation [1].

$$D_{Av} = K\lambda / (\text{FWHM} \cos \theta), \quad (\text{S1})$$

where λ is the wavelength of the monochromatic radiation (in Å), FWHM is the reflex half 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), and θ is the angle of incidence of the X-ray beam (in radians).

An example of processing the X-ray diffraction pattern of a Pt/C catalyst using the SciDavis program, which makes it possible to refine the calculation of the D_{Av} , is shown in Figure S1.

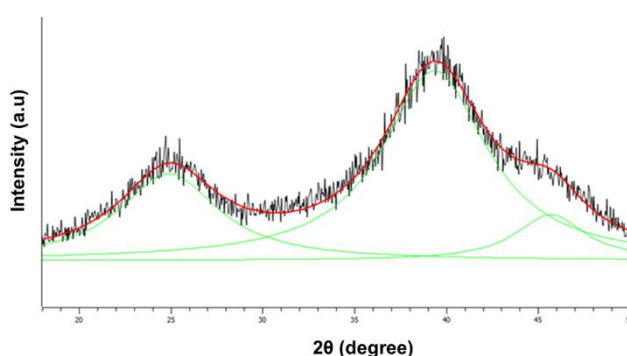


Figure S1: An example of X-ray diffractogram fitting using the SciDavis software.

Determination of the electrochemically active surface area of the catalysts by cyclic voltammetry

The electrochemically active surface area (ESA) was calculated from the charge amount consumed for desorption Q_d and adsorption Q_{ad} of hydrogen using the formula:

$$\text{ESA} = ((Q_d + Q_{ad}) \cdot 0.5) / (210 \cdot m(\text{Pt}) \cdot 1000), \quad (2)$$

where ESA is the area of electrochemically active platinum surface ($\text{m}^2 \cdot \text{g}^{-1}(\text{Pt})$), Q_d and Q_{ad} (i.e., the charge amount consumed for electrochemical desorption and adsorption of atomic hydrogen, respectively, (μC) (Figure S2)), 210 is the charge required for the formation/oxidation of an atomic hydrogen monolayer per 1 cm^2 of platinum surface ($\mu\text{C cm}^{-2}$), $m(\text{Pt})$ is the platinum weight on the electrode (g).

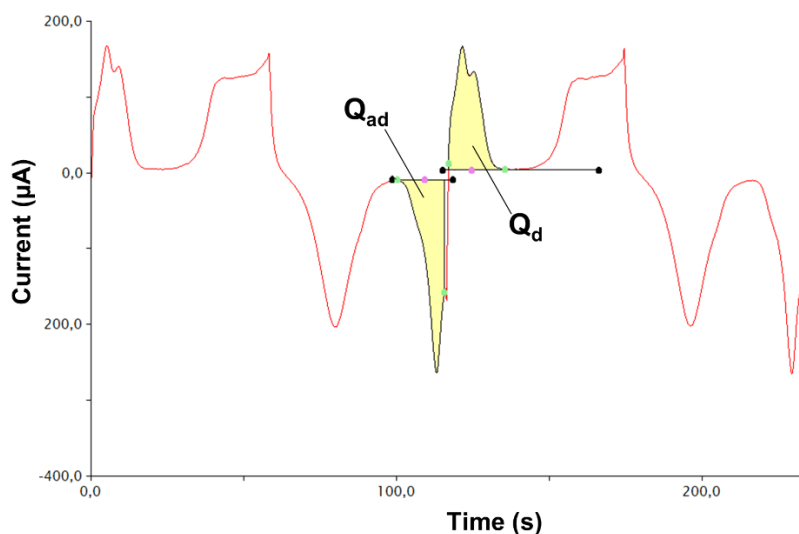


Figure S2: Current as a function of time during CV recording. The areas on the graph are highlighted for the calculation of the charge amount: Q_{ad} - the amount of electricity spent on atomic hydrogen adsorption; Q_d is the amount of electricity consumed for atomic hydrogen desorption.

The charge amount was determined from the cyclic voltammogram (CV) as the area under the line of the current–time dependence in the potential range of 0.04–0.40 V minus the contribution of the double-layer region.

Determination of the catalytic activity in the ORR

To take into account the contribution of the ohmic potential drop and processes not associated with ORR, the voltammograms obtained when the potential was swept towards more positive values (Figure S3) were normalized according to generally accepted techniques, as presented below in more detail. For this, the potential of the electrode under study was refined using the formula:

$$E = E_{\text{set}} - I \cdot R, \quad (3)$$

where E_{set} is the set value of the potential, $I \cdot R$ is the ohmic potential drop equals to the product of the current (I) and the resistance (R) of the solution layer between the reference and work electrodes, which was 23Ω [2].

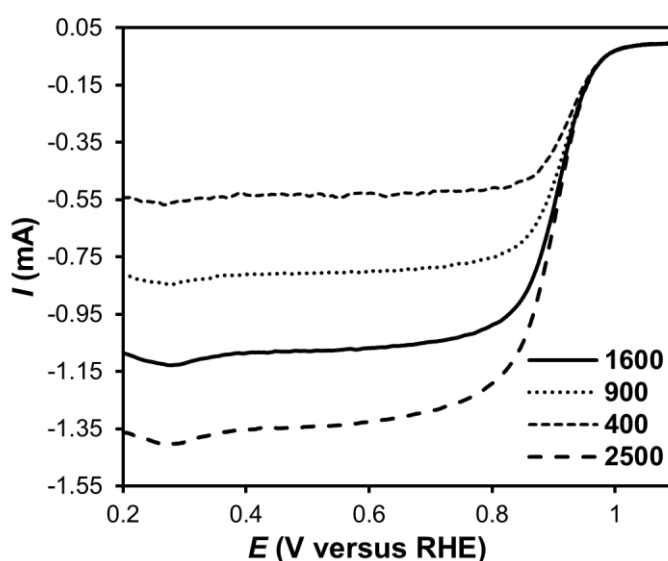


Figure S3: Potentiodynamic polarization curves of ORR at different speed values of the disk rotation. 0.1 M HClO_4 . O_2 atmosphere. Potential speed rate is $20 \text{ mV} \cdot \text{s}^{-1}$.

The contribution of the processes occurring at the electrode in the deoxygenated solution (Ar atmosphere) was taken into account by subtracting from the voltammogram a similar curve recorded at the same electrode during measurements in an Ar: $I(\text{O}_2) - I(\text{Ar})$ atmosphere. The ORR activity of the catalysts (kinetic current) was determined from normalized

voltammograms taking into account the contribution of mass transfer under the conditions of RDE [3].

The kinetic current was calculated using the Koutetskiy–Levich equation:

$$1/j = 1/j_k + 1/j_d, \quad (4)$$

where j is the experimentally measured current, j_d is the diffusion current, and j_k is the kinetic current. The kinetic currents were calculated for a potential of 0.90 V (RHE). Dividing the kinetic current by the mass of platinum loaded onto the electrode and the ESA, we obtained such activity parameters as mass (I_{mass}) and specific (I_{sp}) currents, respectively. The number of electrons involved in ORR was determined by the angle of the line in coordinates $1/j - 1/\omega^{0.5}$.

Evaluation of the degradation degree of the electrocatalysts in the process of multiple cycling

The stability was assessed by the ratio of platinum ESA values after (ESA_j) and before (ESA_0) the stress test using the formula:

$$\text{Stability} = (\text{ESA}_j / \text{ESA}_0) \cdot 100\%, \quad (5)$$

where j is the number of potential sweep cycles carried out before a particular measurement of ESA.

The degree of degradation (DD) was calculated using the formula:

$$\text{DD} = (1 - \text{ESA}_j / \text{ESA}_0) \cdot 100\%. \quad (6)$$

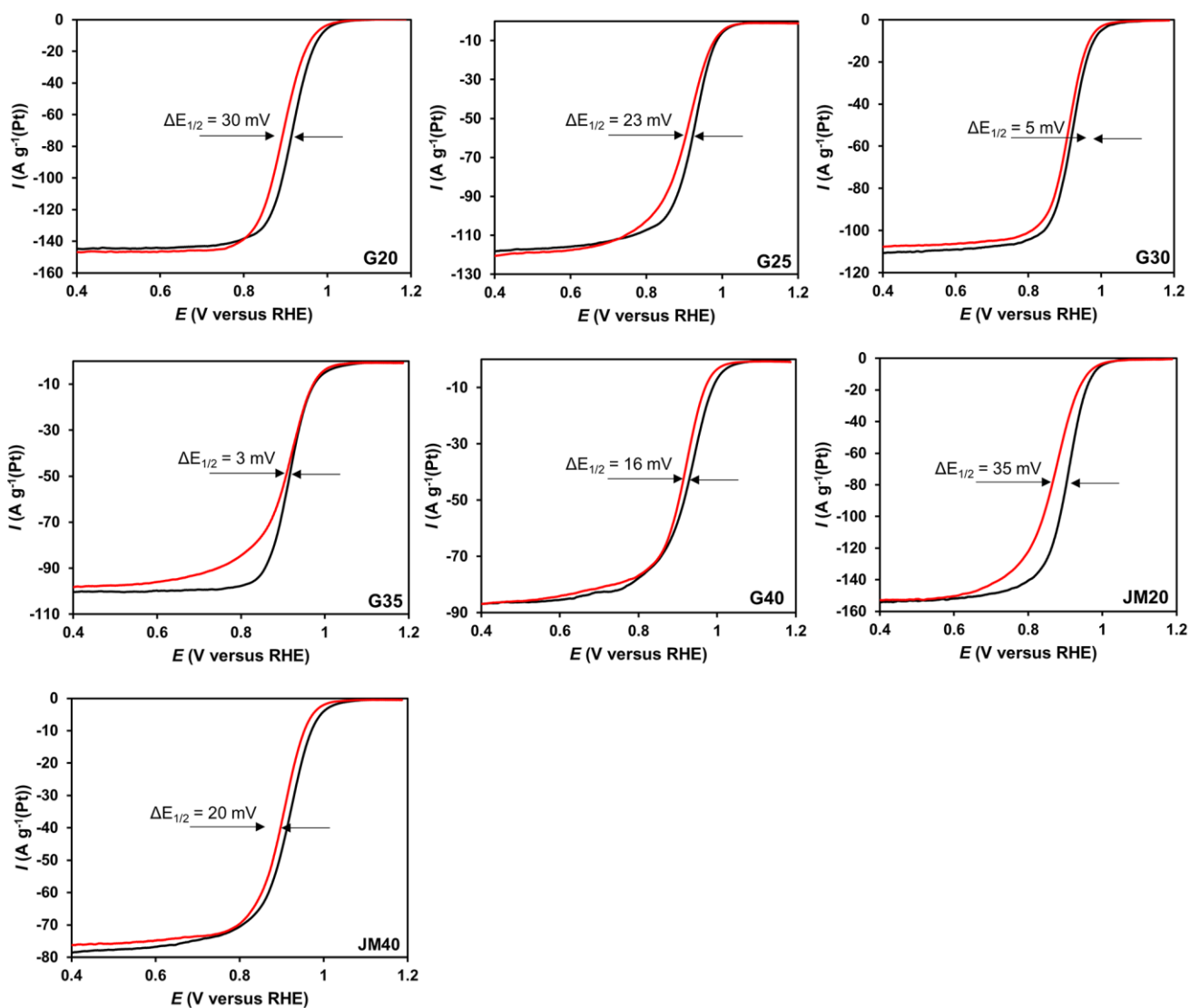


Figure S4: Potentiodynamic polarization curves of ORR before the start (black) and after completion (red) of stress testing. The rotation speed of the RDE is 1600 rpm. 0.1 M HClO₄. O₂ atmosphere. The potential sweep rate is 20 mV·s⁻¹.

References:

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