Electronic Supplementary Material

Kinetics of platinum nanoparticles nucleation in polyol synthesis over a wide pH range and properties of Pt/C catalysts

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2. EXPERIMENTAL METHODS

2.1. Chemicals and Materials

The following chemicals and materials were used in the experimental work: carbon support Vulcan XC72 (Cabot Corporation, USA), ethylene glycol (top grade, not less than 99.8%, Rehacor, LLC, Russia), $H_2PtCl_6 \cdot 6H_2O$ (TU 2612-034-00205067-2003, mass fraction of Pt 37.6%, Aurat, Russia), sulfuric acid (JSC Vekton, Russia), sodium hydroxide (Rehacor, LLC, Russia), distilled H_2O (conductivity <5 μS/cm, GOST 58144–2018), perchloric acid $HClO_4$ (extra pure, Sigma-Aldrich), Ar (99.9%, Globus, Russia), 10% aqueous Nafion® solution D1020, O_2 (from electrolyzer).

2.2. Methods and conditions for preparation of the Pt/C materials

The synthesis of colloidal platinum NPs and Pt/C materials was carried out by the polyol method using ethylene glycol as the reducing agent. For this purpose, ethylene glycol with a volume of 107 mL was mixed with 4.4 mL of an aqueous NaOH solution of different concentrations in a chemical reactor with a volume of 250 mL, based on the molar ratios of the alkali to the platinum precursor (S) equal 0, 2, 5, 6.4, 8, 10, and 15. The resulting reaction mixture was heated to 90 °C with constant stirring. After reaching the set temperature, the reaction mixture was purged with Ar for 30 min. Then, without stopping heating and purging with argon, 20 mL of an aqueous 0.035 M solution of H_2PtCl_6 were introduced into the reactor with stirring. After the reaction was completed, the heating was ceased and the mixture was cooled naturally for 1 h with stirring. The Vulcan XC72 carbon support was then added to the colloidal solution of platinum NPs in the amount necessary to obtain the Pt/C material with a platinum mass fraction of 42% wt. The resulting suspension was stirred for 12 h, with 10 mL of a 2 M aqueous sulfuric acid solution being added to more effectively precipitate the platinum NPs onto the support. After 1 h, the product was filtered with a Büchner funnel using ashless filters, and the precipitate was repeatedly rinsed with bidistilled water and isopropanol. The resulting Pt/C material was dried in a drying cabinet at 60 °C and then in a desiccator over P_2O_5 for 24 h.

The Pt/C materials in the carbon suspension were synthesized as described above, but the carbon support was introduced into the reaction medium before the synthesis. For this purpose, the suspension of the Vulcan XC72 carbon support was dispersed in ethylene glycol and mixed with an aqueous alkali solution of the corresponding concentration. The subsequent synthesis, filtration, and drying of the material were performed in the same way as described above.

The resulting materials are hereinafter referred to as S0, S2, S5, S6.4, S8, S10, and S15 in accordance with a molar ratio ($S=[OH^-]/[Pt(IV)]$) used during the corresponding synthesis.

Figure S1 shows a diagram of the synthesis carried out using the above-described method.

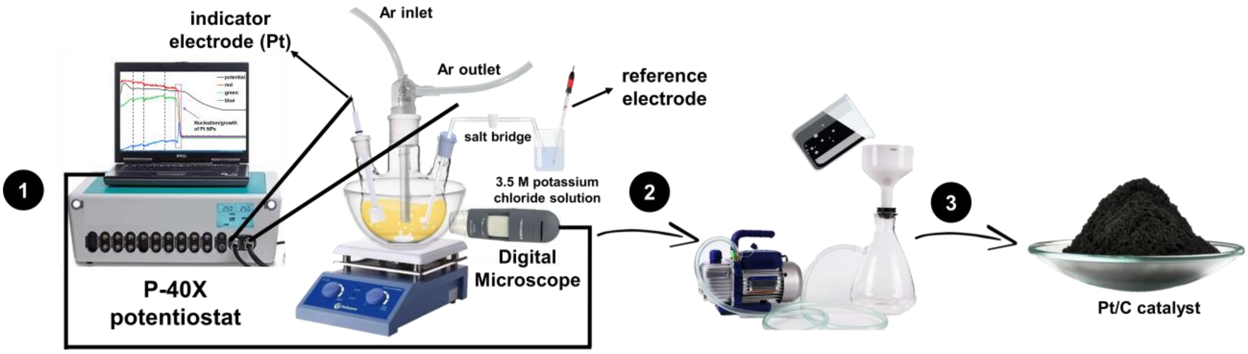

Figure S1. Schematic diagram of the setup for performing synthesis with in situ recording of changes in reaction medium color and indicator electrode potential.
(1) Setup including a chemical reactor and measuring equipment. The chemical reactor is equipped with an indicator platinum electrode, an electrochemical bridge, one leg of which is placed in the reactor, and the other, together with the silver chloride reference electrode, is immersed in a 3.5 M potassium chloride solution. The electrodes are connected to a potentiostat. A Digital USB Microscope Camera connected to a computer is placed on the side of the reactor, designed to record the color of the reaction medium. First, a solution containing ethylene glycol, water and NaOH is heated in the reactor. The solution is purged with Ar. Upon reaching the required temperature and after 30 minutes of purging with Ar, a solution of H2PtCl6 is added to the reactor. 10-15 minutes before the start of adding the H2PtCl6 solution to the reactor, we began to record the potential of the indicator electrode and the intensity of the three components of the solution color. (2) After the reaction medium has completely blackened due to the formation of platinum nanoparticles and the system potential has subsequently stabilized, the heating is turned off and the Vulcan XC72 carbon carrier is added.
(3) Upon completion of the synthesis, the Pt/C catalyst is separated, washed and dried.

2.3. Methods for studying the kinetics of transformation of Pt(IV) into Pt(0)$_x$

2.3.1. Control over changes in the coloring components of the reaction medium

During the Pt(IV) reduction, which led to the formation of a colloidal solution of platinum NPs in an aqueous ethylene glycol mixture, the coloring of the reaction medium changed from light yellow to black. The change in the coloring is due to the reduction of Pt(IV) ions (light yellow) to

$Pt(0)_X$ NPs (black). The Celestron Handheld Digital USB Microscope Deluxe digital microscope was used to register a color of the solution during synthesis. To quantify the solution coloring intensity, we used a software developed by us that converts the coloring of the solution into three components of the additive RGB color model [1], in which each shade of the continuously recorded image was determined by the contributions of three primary colors: red, green, and blue. This made it possible to graphically interpret the processes proceeding in the reaction medium, displaying a change in the quantitative content of each component over time.

2.3.2. Spectrophotometry (UV–Vis spectroscopy)

Spectral studies were performed using the equipment provided by the Shared Use Center "Molecular Spectroscopy" of the Southern Federal University. The electronic absorption spectra were recorded using the Cary 50 spectrophotometer (Varian, USA) in the wavelength range from 220 to 800 nm.

To perform the spectrophotometric studies of changes in the optical density during the formation of platinum NPs, we conducted sampling of the reaction medium at different stages of the synthesis. The volume of each sample was 100 µL. Since in situ spectrophotometric studies cannot be carried out in concentrated solutions, the freshly collected samples of 20 µL in volume were diluted in 1,980 µL of deionized water. At the same time, the molar ratios of various forms of platinum contained in the reaction medium did not change, with their concentrations decreasing 100-fold. When measuring the optical density, the volume of the solutions in the cuvettes was 2 mL, and the optical path length was 1 cm. Cuvettes filled with a reaction mixture not containing H_2PtCl_6 and 99-fold diluted with water were used as the reference samples.

The sampling was carried out in the course of polyol synthesis in the solution with a molar ratio of the alkali to the platinum precursor of S = 8. The numbers of the samples, the corresponding sampling time counted from the moment the platinum precursor was added to the reaction medium, and the potential of the indicator electrode at the time of sampling are shown in Table S1. Sample No. 0 corresponds to the moment when the platinum precursor was added to the reaction medium.

Table S1. Numbers of the samples, corresponding sampling time counted from the moment of introducing the platinum precursor, and indicator electrode potential values corresponding to each sample.

Sample No.	Sampling time, s	E, mV
0	0	-663
1	75	-418
2	180	-405
3	305	-385
4	360	-373

5	390	-361
6	420	-346
7	450	-321
8	480	-280
9	510	-232
10	540	-198
11	570	-181
12	600	-181
13	620	-204
14	660	-212
15	730	-207

2.3.3. Control over changes in the potential of the indicator electrode

In the course of synthesis, we measured a potential of the platinum indicator electrode immersed in the reaction medium. For this purpose, the reactor was equipped with a salt bridge, one tube of which was lowered into the reaction mixture and filled with the reaction mixture (before adding a solution of chloroplatinic acid). The second tube was filled with a 3.5 M potassium chloride solution and lowered into a beaker with a solution of the same composition in which the silver chloride electrode (reference electrode) was located. The electrodes were connected to the P-40X potentiostat (Elins LTD, Russia), which was used to record the electrodes potential difference that was identical to the redox potential of the medium. The values of the potentials on the chronopotentiometric curves measured during synthesis are given in the work relative to the standard hydrogen electrode (SHE).

2.4. Methods of studying the Pt/C materials

2.4.1. Determination of platinum content in the Pt/C materials

The sample suspension of 0.0200 g was placed in the weighed porcelain crucible and calcined at 800 °C for 1 h in a muffle furnace. After cooling, the mass of the crucible with the unburned residue (platinum) was recorded and the platinum mass fraction was thus calculated:

$$\omega(\mathrm{Pt}) = (m_{(c+res)} - m_{(c)})/m_{(sample)} \qquad (1),$$

where $\omega(\mathrm{Pt})$ is the mass fraction of Pt in the sample,

$m_{(c)}$ is the crucible’s mass,

$m_{(c+res)}$ is the crucible’s mass with the residue after calcination, and

$m_{(sample)}$ is the sample weighed amount.

The error of the method was ±1%.

2.4.2. X-ray powder diffraction analysis

The X-ray diffraction patterns were recorded at room temperature using the ARL X`TRA powder diffractometer (Thermo Scientific, Switzerland) with the Bragg-Brentano geometry (θ-θ) and the filtered CuKα radiation ($\lambda = 0.154056$ nm). The materials X-ray diffraction patterns were recorded in the 2θ angle range of 15–55°. The fitting of the X-ray diffraction patterns with the SciDAVis software was performed using the Lorentz function. The results of the approximation and the separation of contributions from different reflections were used in further calculations. The average crystallite size of the metal phase D(Cr) was determined by the Scherrer equation for a more intense peak (111) [2,3]:

$$D(Cr) = K \cdot \lambda / (FWHM \cdot \cos\theta) \qquad (2),$$

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

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

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

D(Cr) is the average thickness of a "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). The error margin was ±8%.

2.4.3. Transmission electron microscopy

The size of Pt NPs (DNP) as well as the features of their size and spatial distributions were studied by transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), and secondary electron imaging microscopy (SEI), using the JEOL JEM-F200 microscope with an accelerating voltage of 200 kV, the cold field emission gun with a current of 12–15 µA, the double-tilt Be specimen holder JEOL EM-01361RSTHB, and the CMOS AMT camera. 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. Next, the sample was dried in air at room temperature for 60 min. The histograms of the Pt NPs size distribution in the catalysts were plotted, considering the results of size determination for at least 400 particles randomly selected in the TEM micrographs at different sections of the sample. The error margin was ±0.2 nm.

2.5. Electrochemical research methods

The rotating disk electrode (RDE) method was used to study the electrochemical behavior of the Pt/C materials obtained. For this purpose, a catalytic layer of the studied materials was formed on the glass–carbon end face of the electrode. A 0.0040 g catalyst suspension was mixed with 200 µL of deionized H_2O, 20 µL of a 5% aqueous Nafion solution, and 1,800 µL of extra pure isopropanol. The resulting suspension was treated with ultrasound in an ultrasonic bath for 25 min at a temperature not exceeding 20 °C. A 6 µL drop of the catalytic ink was then applied to the end face of the electrode using a pipette tip, which was dried at rotation and a temperature of 23 °C. The formed catalytic layer contained 20 μg_{Pt} cm^{-2}.

The study of the Pt/C materials electrochemical behavior was carried out in a three-electrode cell, with the catalytic layer formed at the RDE end face acting as the working electrode, a platinum wire acting as the counter electrode, and a silver chloride electrode acting as the reference electrode (0.208 V). 0.1 M $HClO_4$ was used as the electrolyte. The measurements were performed using the VersaSTAT3 potentiostat (Ametek, USA). The potentials in the section of the paper concerned with the catalysts electrochemical behavior are given relative to the reversible hydrogen electrode (RHE).

2.5.1. Activation of the Pt/C surface and determination of the electrochemically active surface area

The activation of the electrode surface formed from the studied Pt/C materials was performed by applying 100 current–voltage cycles of the potential sweep in the range of 0.04–1.0 V (RHE) at a scanning rate of 200 mV/s in 0.1 M perchloric acid saturated with Ar. Two cyclic voltammograms (CVs) were then recorded in the potential range of 0.04–1.0 V (RHE) at a scanning rate of 20 mV/s. According to the second CV, the electrochemically active surface area (ESA) was calculated by the charge amount consumed for the adsorption and desorption of a hydrogen monolayer, as described in [4]:

$$\mathrm{ESA} = \frac{0.5*(Q_{ad} + Q_d)}{210*m(Pt)*1000} \qquad (3),$$

where ESA is the electrochemically active surface area of platinum ($m^2\ g_{Pt}^{-1}$), Q_{ad} and Q_d are the charge amounts consumed for the electrochemical adsorption and desorption of atomic hydrogen, respectively (μC), 210 is the charge required for the formation/oxidation of an atomic hydrogen monolayer per 1 cm^2 of the platinum surface ($\mu C\ cm^{-2}$), and m(Pt) is the platinum weight at the electrode (g). The error margin was ±10%.

2.5.2. Determination of the catalysts activity in the oxygen electroreduction reaction

To determine the catalytic activity in the oxygen electroreduction reaction (ORR), the electrolyte (0.1 M $HClO_4$) was saturated with oxygen for 1 h at atmospheric pressure. Then, following the electrode activation, a series of linear sweep voltammograms (LSVs) were recorded at RDE rotation speeds of 400, 900, 1,600, and 2,500 rpm in the potential range of 0.1–1.1 V (RHE) at a scanning rate of 20 mV/s. The ORR kinetic parameters were calculated for a potential of 0.90 V (RHE) by plotting and interpreting the linear dependence in the Koutetsky–Levich coordinates [5]. The ORR activity of the catalysts was determined by the values of the kinetic current divided by the mass of platinum at the electrode (mass activity – I_{mass}) or by the surface area of platinum (specific activity – I_{sp}). The error of the method was ±10%.

The potential of the electrode studied was refined by the formula:

$$E = E_{set} - IR \qquad (4),$$

where E_{set} is the set value of the potential and IR is the ohmic potential drop equal to the product of the current (I) by the resistance (R) of the solution layer between the reference and working electrodes, which was 23 Ω.

The contribution of the processes occurring at the electrode in a deoxygenated solution (Ar atmosphere) was taken into account by subtracting from the voltammogram an equivalent curve recorded at the same electrode during the measurements in Ar: $I(O_2) - I(Ar)$. The ORR activity of the catalysts (kinetic current) was determined from the normalized voltammograms, with the contribution of mass transfer under the RDE conditions being taken into account.

The kinetic current was calculated using the K–L equation:

$1/J = 1/J_k + 1/J_d$ (5),

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). The number of electrons involved in the ORR was determined by the angle of the line in the $1/J - 1/\omega^{0.5}$ coordinates. The systematic error of the activity measurement was 10%.

As an assessment of the electrocatalysts degradation resistance, the AST protocol was used, which consisted in the overlap of the potential pulses of 0.4 ; 1.0 V for 3 s during 10,000 cycles in an electrolyte saturated with O_2 at 23 °C [6]. The duration of one measurement was ~17 h. After the AST, the electrolyte was replaced, followed by the repeated activation stage, after which the residual ESA and ORR activity values were measured [7,8].

The degradation resistance was assessed by changing the ESA of platinum before ($ESA_{initial}$) and after ($ESA_{after\ AST}$) the stress testing. The degradation degree was calculated according to the formula: $(DD_{ESA}) = ((ESA_{initial} - ESA_{after\ AST}) / ESA_{initial}) * 100\%$ (6).

The DD_{Imass} value was calculated similarly by changes in the ORR mass activity.

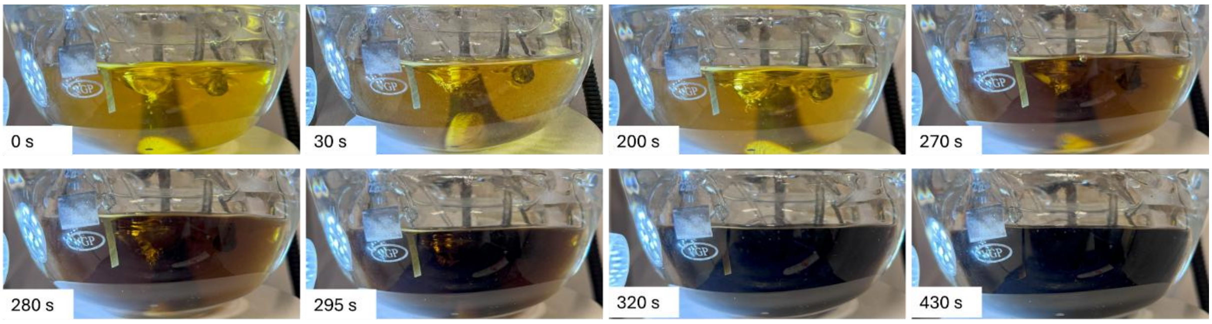

Figure S2. Change in the reaction medium coloring during the synthesis of platinum NPs

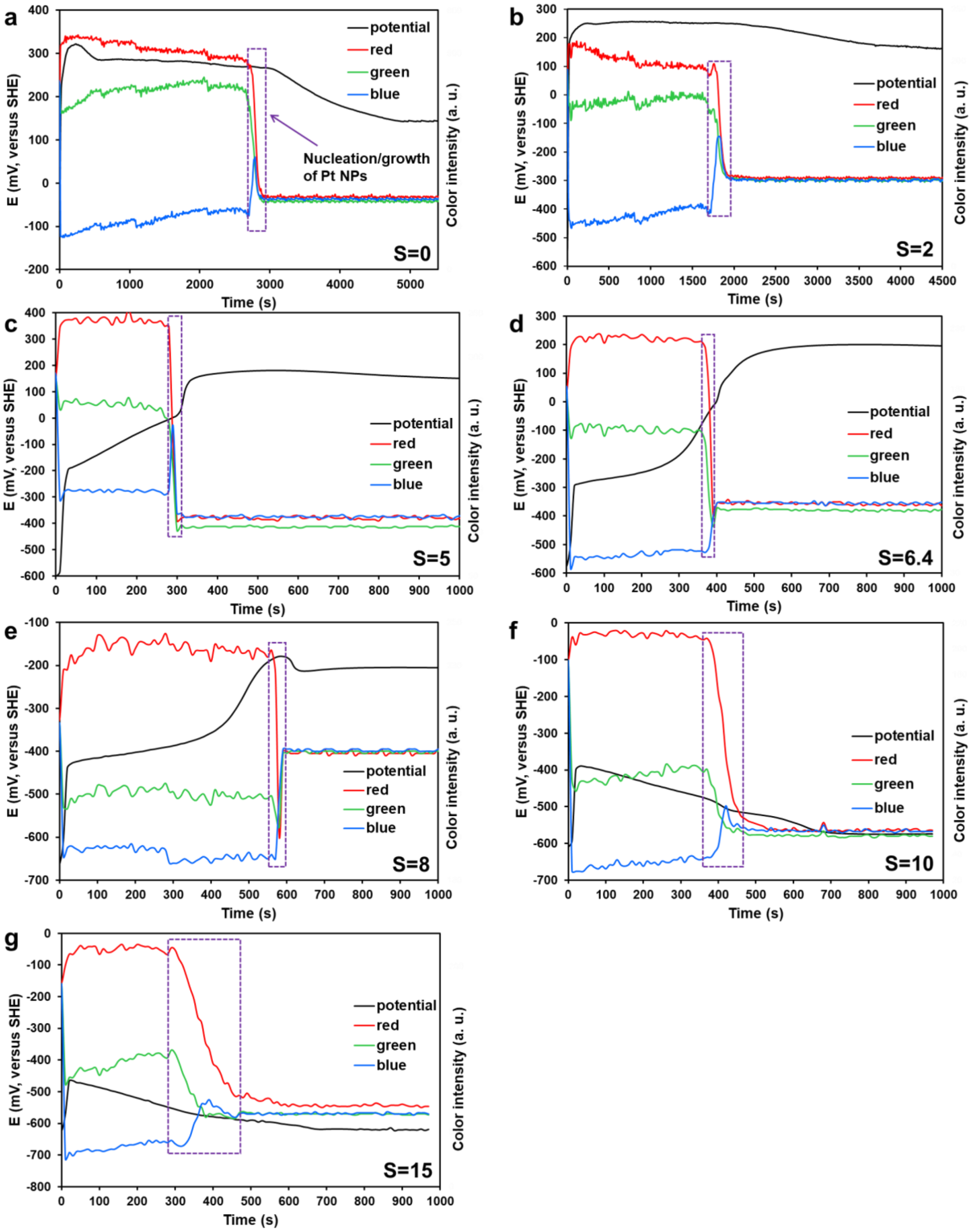

Figure S3. Changes in the coloring three components (colored lines) and the redox potential (black line) of the reaction medium during the synthesis of platinum NPs in the solutions at S=0 (a), S=2 (b), S=5 (c), S=6.4 (d), S=8 (e), S=10 (f), and S=15 (g).

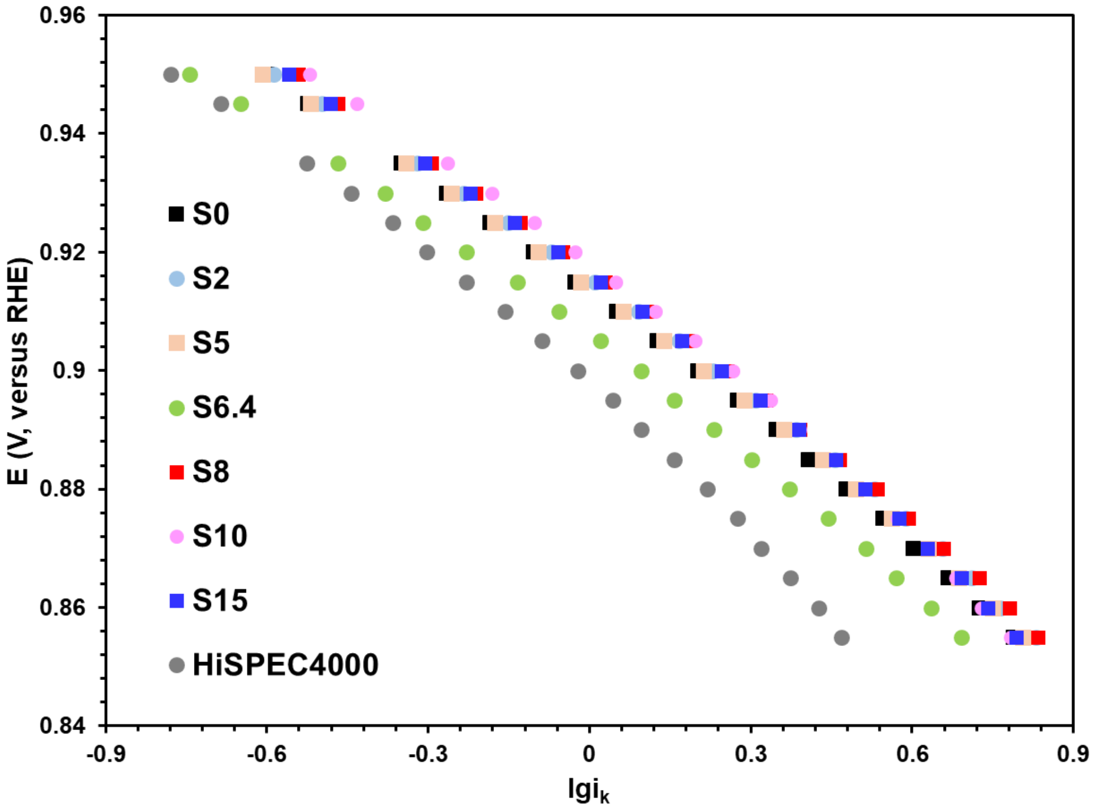

Figure S4. Tafel dependence of the potential on the kinetic current Braggian logarithm from the ORR curve at 1,600 rpm.

References

[1] Hirsch Robert. Exploring colour photography: A complete guide. Laurence King Publishing 2005:352.

[2] Langford JI, Wilson AJC. Scherrer after sixty years: A survey and some new results in the determination of crystallite size. J Appl Crystallogr 1978;11:102–13. https://doi.org/10.1107/S0021889878012844.

[3] Vega L, Garcia-Cardona J, Viñes F, Cabot PL, Neyman KM. Nanostructuring determines poisoning: tailoring CO adsorption on PtCu bimetallic nanoparticles. Mater Adv 2022;3:4159–69. https://doi.org/10.1039/D2MA00196A.

[4] Sharma R, Gyergyek S, Andersen SM. Critical thinking on baseline corrections for electrochemical surface area (ECSA) determination of Pt/C through H-adsorption/H-desorption regions of a cyclic voltammogram. Appl Catal B 2022;311. https://doi.org/10.1016/J.APCATB.2022.121351.

[5] Shinozaki K, Zack JW, Richards RM, Pivovar BS, Kocha SS. Oxygen reduction reaction measurements on platinum electrocatalysts utilizing rotating disk electrode technique. J Electrochem Soc 2015;162:F1144–58. https://doi.org/10.1149/2.1071509jes.

[6] Nagai T, Jahn C, Jia H. Improved Accelerated Stress Tests for ORR Catalysts Using a Rotating Disk Electrode. J Electrochem Soc 2019;166:F3111–5. https://doi.org/10.1149/2.0161907JES.

[7] Paperzh K, Alekseenko A, Pankov I, Guterman V. Accelerated stress tests for Pt/C electrocatalysts: An approach to understanding the degradation mechanisms. Journal of

Electroanalytical Chemistry 2024;952:117972. https://doi.org/10.1016/J.JELECHEM.2023.117972.

[8] Paperzh K, Moguchikh E, Pankov I, Belenov S, Alekseenko A. Effect of AST Atmosphere on Pt/C Electrocatalyst Degradation. Inorganics (Basel) 2023;11:237. https://doi.org/10.3390/INORGANICS11060237/S1.