**Supporting information**

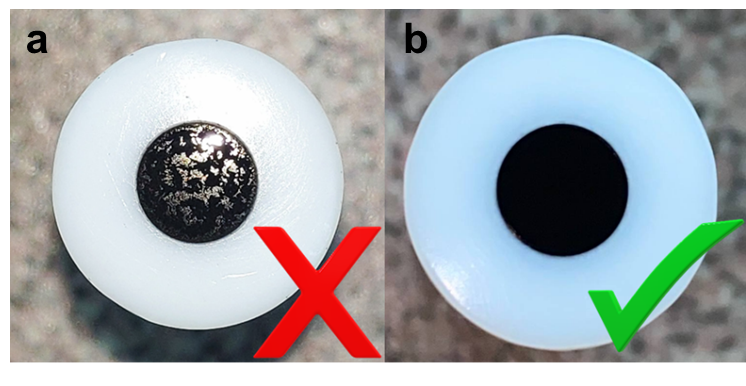
The PtM/C (M = Co, Ni, Cu, Ru) electrocatalysts: their synthesis, structure, activity in the oxygen reduction and methanol oxidation reactions, and durability

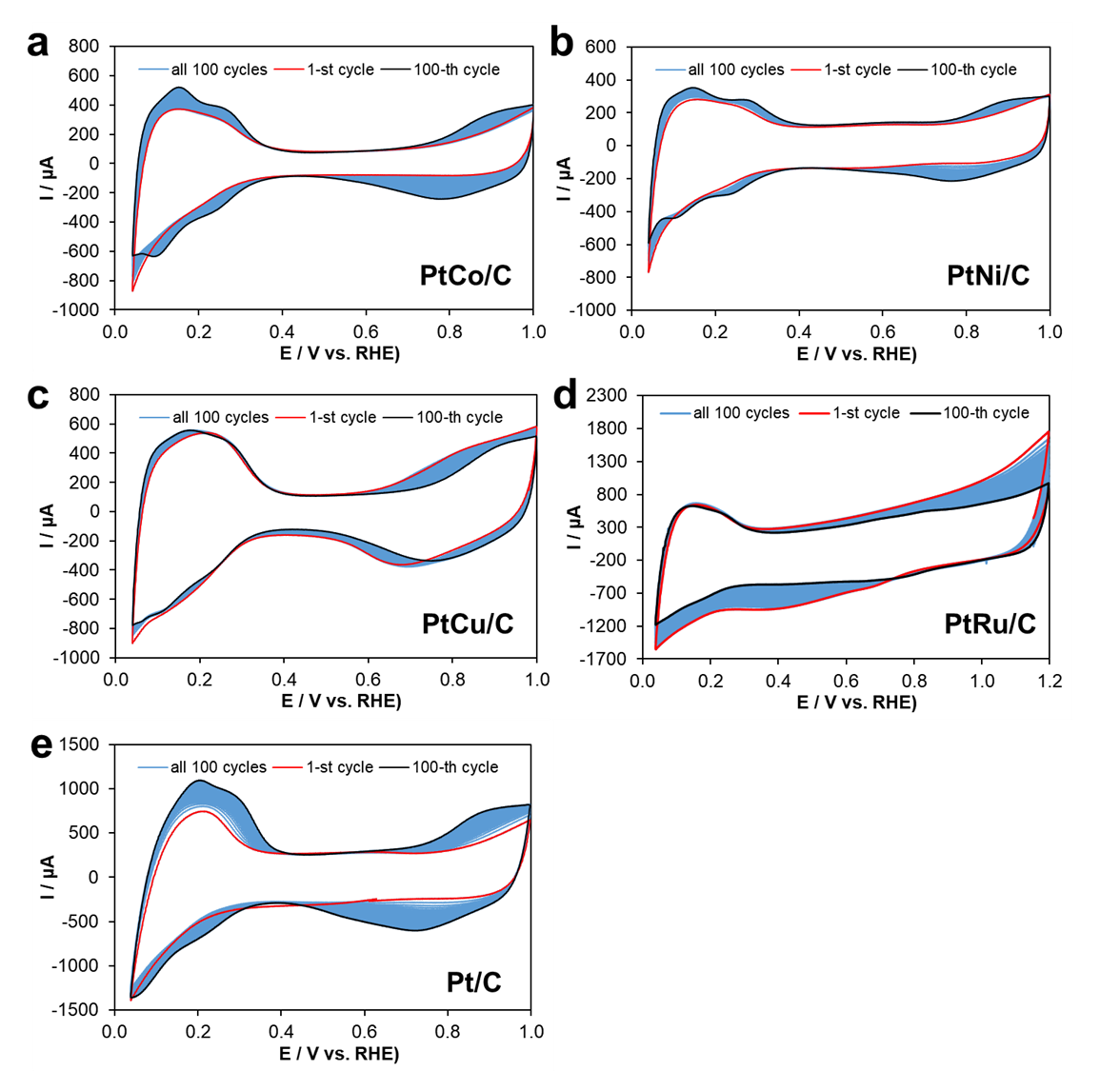
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**Figure S1.** The image of the catalytic ink layer applied to the end face of the RDE: the uneven application of the PtCo/C catalytic inks (a); the even application of the catalytic layer for the PtCo/C material with the optimized composition of the catalytic inks (b).

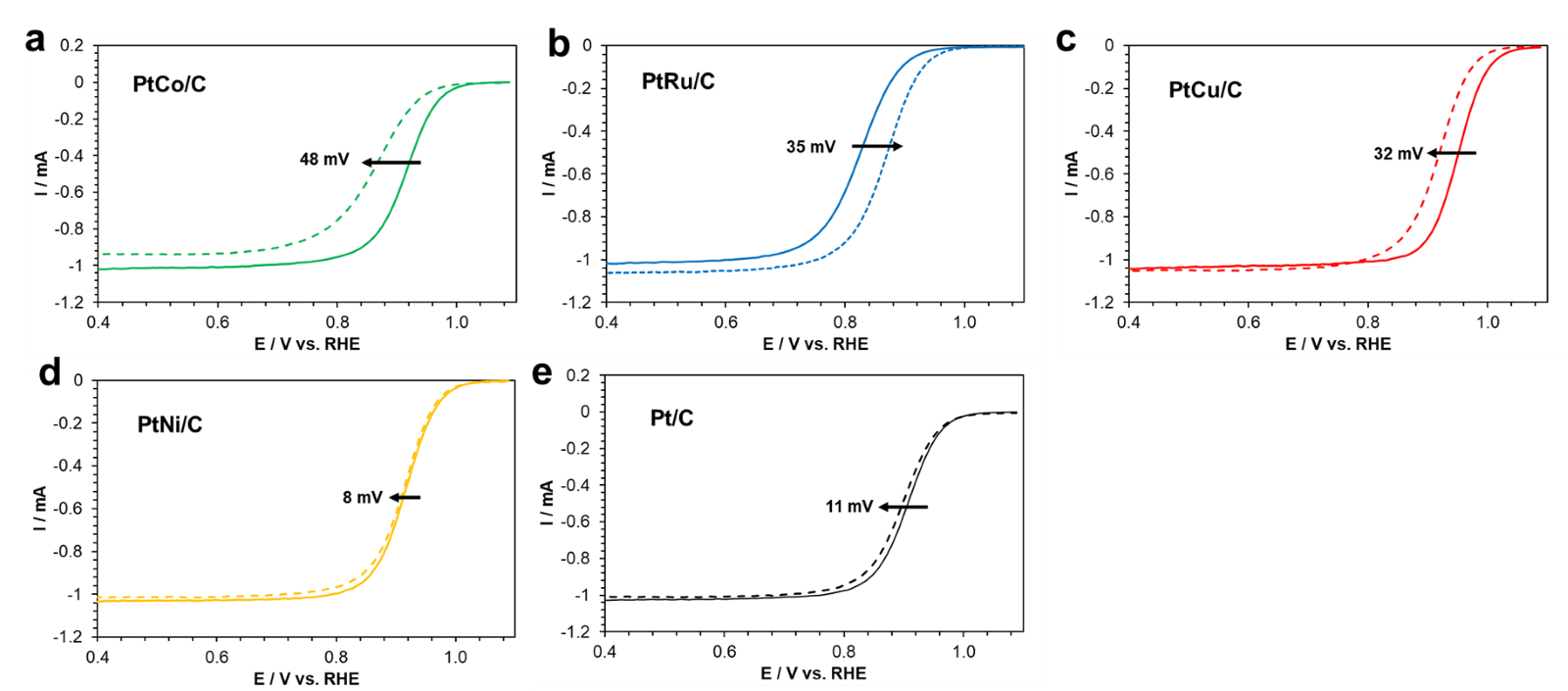


**Figure S2.** CVs at the stage of catalysts electrochemical activation. The sweep rate of the potential is 100 mV/s.

**Table S1**. Composition, ESA and parameters characterizing the electrochemical behavior of PtM/C and Pt/C catalysts.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Sample** | **Pt:M atomic ratio in catalysts by XRF** | **ESA, m2 g–1 (Pt)**  **H** | **ESA, m2 g–1 (Pt)**  **CO** | **I, A g–1 (Pt)** | **I, mA** | **I, A m–2 (Pt)** | **E1/2, V** | **Number, ē** |
| **PtCu/C** | PtCu0.2 | 41 | 38 | 827 | 5.2 | 20.4 | 0.95 | 4.1 |
| **PtNi/C** | PtNi0.1 | 32 | 38 | 438 | 1.9 | 13.6 | 0.92 | 3.6 |
| **PtCo/C** | PtCo0.2 | 45 | 51 | 413 | 1.4 | 9.2 | 0.92 | 4.0 |
| **PtRu/C** | - | - | 139 | 91\* | 0.4\* | 0.7\* | 0.84 | 3.2\* |
| **Pt/C** | - | 82 | 87 | 257 | 1.3 | 3.1 | 0.90 | 3.7 |

\* The values refer to E1/2 = 0.85 V.



**Figure S3****.** Potentiodynamic polarizing ORR curves before and after a AST. The RDE rotational speed is 1600 rpm. The electrolyte is 0.1 M HClO4 saturated with O2. The potential sweep rate is 20 mVs-1.

**1 Study of catalyst structure**

*Gravimetry analysis*

The mass fraction of metals in electrocatalysts was determined by gravimetry from the mass of the unburned residue when heated to 800 ° C, oxidation of copper to CuO being taken into account.

*X-ray fluorescence (XRF) analysis*

To determine the ratio of metals in the samples, the method of X-ray fluorescence (XRF) analysis on a spectrometer with total external reflection of X-ray radiation RFS-001 (Research Institute of Physics, Southern Federal University, (Rostov-on-Don) was used. Sample exposure time was 300 sec. Registration and processing of X-ray fluorescence spectra were carried out with the UniveRS software (Southern Federal University, Rostov-on-Don). The obtained X-ray fluorescence spectra were processed with the UniveRS software (Southern Federal University, Rostov-on-Don), the resulting accuracy being ± 0.1.

*X-ray diffraction (XRD) analysis*

X-ray diffraction patterns were recorded on the ARL X`TRA powder diffractometer (Thermo Scientific, Switzeland) with a Bragg-Brentano geometry (θ-θ) using filtered CuKα radiation (λ = 0.154056 nm) at room temperature. X-ray diffraction patterns of materials were recorded in the 2 theta angle range of 15 - 55 degrees. Fitting of X-ray diffraction patterns in the SciDAVis program was performed using the Lorentz function; the results of approximation and separation of contributions from different reflections were used in further calculations.

The average crystallite size of the metal phase (Dav) was determined by the Scherrer equation for a more intense peak <111>. Note that the particle size determined by the Scherrer formula was that of the average crystallite size (coherent scattering regions). This parameter, calculated from the FWHM of the <111> peak for PtCu/C materials should be treated with caution, since this peak might actually be a superposition of reflections of two phases based on copper and platinum. The accuracy of determining Dav was ± 5%.

*TEM and the EDX analysis*

For both the TEM and the EDX measurements, JEOL EM-01361RSTHB double-tilt beryllium specimen holder was used. For measurements, 0.5 mg of the catalyst was placed in 1 ml of isopropanol and dispersed with ultrasound. A drop of a resulting suspension was applied to a copper grid covered with a layer of amorphous carbon, which was dried in air at room temperature for 20 minutes. The TEM images were recorded at magnifications from 20000x to 800000x using 200μm and 100μm condenser apertures in the range from 500ms to 1000 ms exposure on a high-resolution CMOS AMT camera.

When the histograms of the NPs size distribution in the catalysts were constructed, the sizes of at least 300 particles, detected in the TEM images and selected at random, were taken into account.

Energy Dispersive X-Ray analysis was performed with Bruker Xflash 6T/60 Quantax 400-STEM system with 4000 channels, including an energy-dispersive Peltier-cooled XFlash detector, 0.45 mm detector thickness and -25oC working temperature.

Mapping and line-scans were performed with 200 kV primary energy at a 10 to 20 eV energy range with 16s dwell time, total measurement time from 6 to 10 minutes and an analytical throughput range from 100 to 600 kcps.

*Thermal analysis*

Thermal analysis of obtained materials was performed using a combined TGA & DSC/DTA analyzer NETZSCH STA 449 C Jupiter in an atmosphere consisting of 80 % N2 and 20% O2 in the temperature range from 40 to 800 ˚C at a heating rate of 10˚C/min and gas flow rate 20 ml min-1 using corundum crucibles. Weight of samples used for oxidation was 2-4 mg. All corundum crucibles were covered with lids which allow gas flow during measurements. This was necessary to prevent the loss of Pt/C due to the rapid exothermic reaction of carbon. Thermograms and DSC curves presented in the article show the typical results of the individual tests. In fact, the kinetics study of thermal oxidation of each material was performed several times. Results (TGA & DSC/DTA curves) are well reproduced. DSC and TGA curves for the oxidation of one of the studied Pt-based materials obtained in several experiments are shown in supplementary materials as evidence of high reproducibility.

Thermograms are represented in dimensionless units (the ordinate), where weight fraction of reacted carbon ω was defined by the formula ω = (mt - mt = 800)/(mt = 120 – mt = 800), where mt is the sample weight at a given temperature, mt = 800 is the sample weight at 800 °C, and mt = 120 is the sample weight at 120 °C. In search of a formula for calculating ω, we proceeded from the fact that at 800 °C the weight of all the samples reached a constant value due to the complete combustion of carbon. The mass of the sample at the temperature of 120 °C mt=120 corresponds to the state in which the samples no longer contain moisture.

1. **Electrochemical methods**

Before measuring the electrochemically active surface area (ESA) of the catalyst, the electrolyte was saturated with argon for 30 minutes. The electrode was then activated by setting 100 potential sweep cycles in the range from 0.04 to 1.0 V at the rate of 200 mV/s. Next, 2 cyclic voltammograms were recorded on the fixed electrode with the potential sweep rate of 20 mV/s.

*Definition of ESA*

The calculation of the ESA was carried out for the second cyclic voltammogram (CV). To do this, the amount of electricity spent on electrochemical adsorption Qad and desorption Qd of hydrogen was estimated:

(1),

where *ESA* is the area of electrochemically active platinum surface (m2 g −1 (Pt)), *Qad* and *Qd*(i.e., the charge amount consumed for 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 cm2 of the platinum surface (μC cm−2), *m(Pt)* is the platinum weight on the electrode (g). The systematic error of the ESA measurement was 10%.

The ESA of the obtained materials was also estimated by the CO stripping voltammetry. The electrochemical oxidation of CO was studied by purging the deaerated solution of 0.1 M HClO4 with the gas for 20 minutes while the working electrode was held at E = 0.1 V. The potential was then scanned in the anode direction up to 1.2 V at the sweep rate of 40 mV/s. The ESA was calculated depending on the charge amount consumed for the oxidation of the adsorbed CO, according to the formula:

(2),

where *ESA* is the area of electrochemically active platinum surface (m2 g −1 (Pt)), *QCO* (i.e., the charge amount consumed for electro-oxidation of CO (μC), *420* is the charge required for the electro-oxidation of CO monolayer per 1 cm2 of the platinum surface (μC cm−2), *m(Pt)* is the platinum weight on the electrode (g). The systematic error of the ESA measurement was 10%.

*ORR study*

The potential of the electrode under study was refined by the formula:

(3),

where *Eset* is the set value of the potential, *IR* 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 23 Ω.

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 Ar: *I*(O2) − *I*(Ar) atmosphere. The ORR activity of the catalysts (kinetic current) was determined from normalized voltammograms, with the contribution of mass transfer under the conditions of RDE being taken into account.

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

(4),

where *j* is the experimentally measured current, *jd* is the diffusion current, and *jk* is the kinetic current. The kinetic currents were calculated for the 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 (MA) and specific (SA) currents, respectively. The number of the electrons involved in the ORR was determined by the angle of the line in coordinates 1/j − 1/ω0.5.The systematic error of the activity measurement was 10%.

*MOR study*

While studying the catalysts activity in methanol oxidation reactions (MOR), methanol and perchloric acid were added to the electrochemical cell, thereby obtaining a solution of 0.1 M HClO4 + 0.5 M CH3OH. Cyclic voltammograms were recorded in the potential range of 0.04 – 1.3 V with a potential sweep rate of 20 mV/s. Chronoamperograms were measured at the potential of 0.60 V.

*Stability study*

Accelerated stress testing (AST) was performed by cyclic voltammetry. For this purpose, 5000 cycles were recorded at a potential sweep rate of 200 mV/s in an argon atmosphere on a stationary electrode in the potential range of 0.6–1.0 V. At the end of the AST, ESA and residual activity in the ORR were measured.

The resistance to degradation of materials was evaluated by changing the ESA and mass-activity (Imass) according to the formulas:

(5),

(6),

where ESA0 and are the initial values of the parameter,

ESA50000 and are the values after 5000 testing cycles.