

Supplementary materials

Electrochemical activation and its prolonged effect on the stability of bimetallic electrocatalysts for PEMFC.

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1. Materials and Methods

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, Switzerland) with a Bragg-Brentano geometry (θ - θ) using filtered CuK α radiation ($\lambda = 0.154056$ 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 (D_{av}) was determined by the Scherrer equation for a more intense peak $\langle 111 \rangle$. 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 $\langle 111 \rangle$ 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 D_{av} was $\pm 5\%$.

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.

1.2 Electrochemical methods

The electrochemical behavior of metal-carbon materials was studied by voltammetry using potentiostat-galvanostat VersaSTAT 3 (Ametek, USA). The measurements were carried out in the standard three-electrode cell in the 0.1 M HClO₄ solution at the temperature of 25°C. The saturated silver chloride electrode was used as a reference electrode. The platinum wire was used as a counter electrode. The potential values in the work are given relative to the reversible hydrogen electrode (RHE).

To obtain the suspension of metal-carbon catalysts (the catalytic “inks”), 1.8 ml of isopropanol, 100 µl of the Nafion 1% solution, and 100 µl of deionized water were added to the 6-mg sample. The resulting suspension was carefully dispersed and stirred. Next, 8 µl of the catalytic inks was applied to the end of the rotating disk electrode, with the exact weight of the drop being recorded. Thus, the loading of platinum on the electrode is 23.3 µg/cm² and 25.0 µg/cm² for material S1 and S2, respectively. The working electrode was dried in air for 5 minutes at the rotation of 700 rpm.

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 or from 0.04 to 1.2 V at the rate of 200 mV/s. Depending on the activation protocol used, the samples are called SX_{1.0} and SX_{1.2} respectively. 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 Q_{ad} and desorption Q_d of hydrogen was estimated:

$$ESA = \frac{0.5(Q_{ad} + Q_d)}{210 \cdot m(Pt) \cdot 1000} \quad (1),$$

where ESA is the area of electrochemically active platinum surface (m² g⁻¹ (Pt)), Q_{ad} and Q_d (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 ($\mu\text{C cm}^{-2}$), $m(\text{Pt})$ 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:

$$E = E_{\text{set}} - IR \quad (2),$$

where E_{set} 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 23Ω .

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: $I(\text{O}_2) - I(\text{Ar})$ 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:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} \quad (3),$$

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 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 $1/j - 1/\omega^{0.5}$. The systematic error of the activity measurement was 10%.

Stability study

Accelerated degradation tests were carried out by cycling the catalyst for 5000 cycles in the potential range of 0.6–1.0 V. After 500, 2500 and 5000 cycles, the electrochemically active surface area was measured. After 5000 cycles, LSVs were recorded and activity in the ORR was calculated as described above.

Under the durability of catalysts is meant the ratio of residual characteristics (after ADT) to the initial (before ADT). The durability of such characteristics as *ESA*, mass and specific activity of the catalysts, which were subjected to activation in the ranges of 0.04–1.0 V and 0.04–1.2 V, was evaluated.

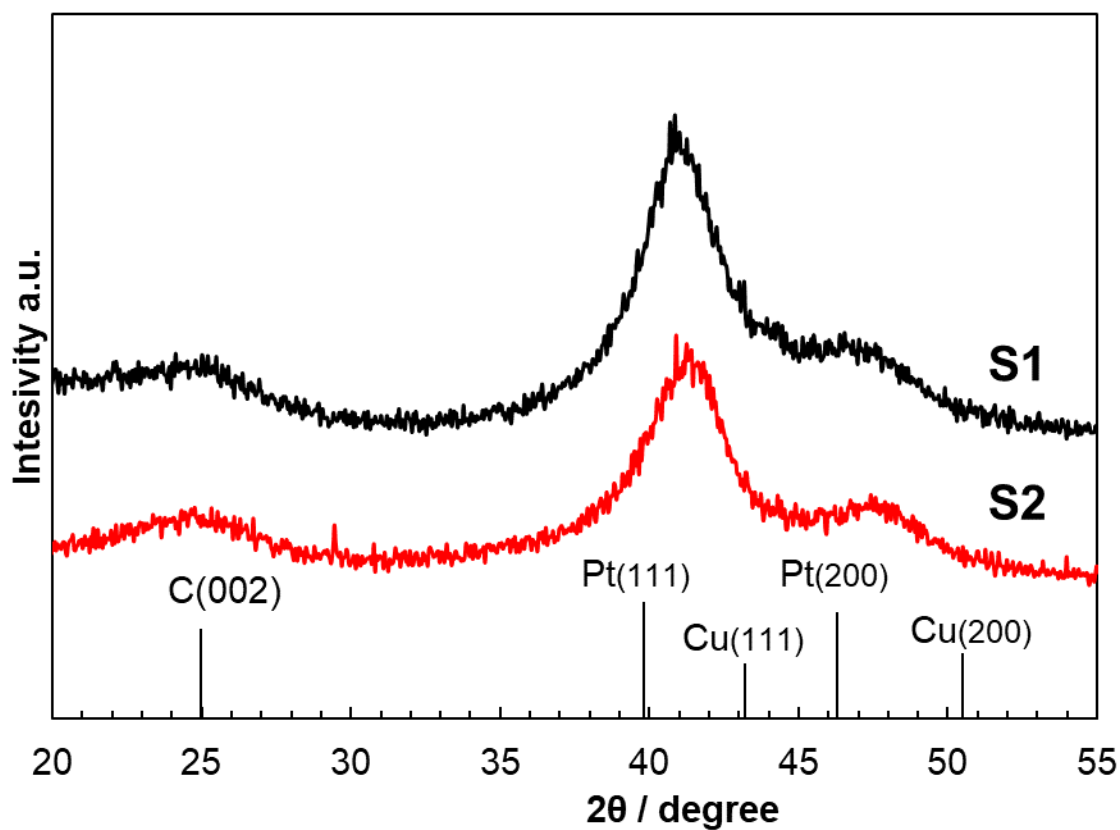


Figure S1. XRD patterns of PtCu/C catalysts.

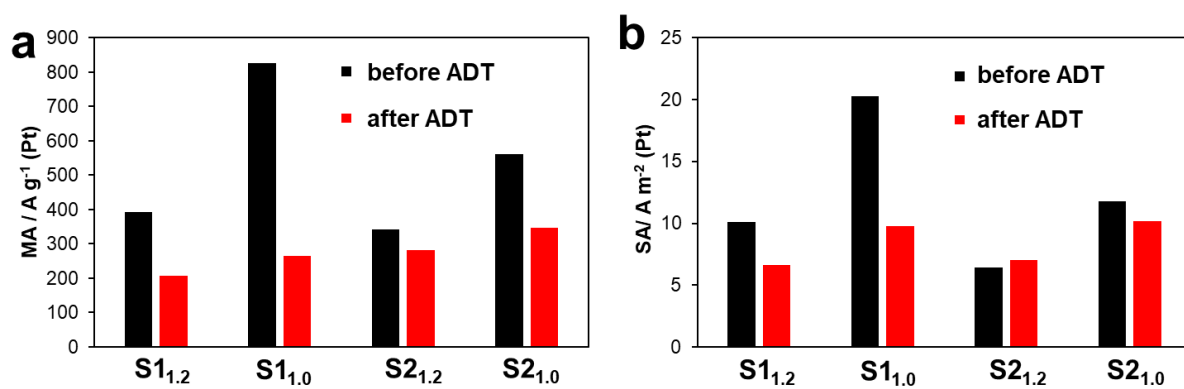


Figure S2. The mass-activity (a) and specific activity (b) of the PtCu/C catalysts before and after the ADT.