



Article Platinum-Containing Nanoparticles on N-Doped Carbon Supports as an Advanced Electrocatalyst for the Oxygen Reduction Reaction

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Abstract: New highly active electrocatalysts were obtained by depositing bimetallic Pt-Cu nanoparticles on the surface of an N-doped carbon support. The structural–morphological characteristics and electrochemical behavior of the catalysts were studied. Using current stress testing protocols, their resistance to degradation was assessed in comparison with that of a commercial Pt/C material. A combined approach to catalyst synthesis that consists in alloying platinum with copper and doping the support makes it possible to obtain catalysts with a uniform distribution of bimetallic nanoparticles on the carbon surface. The obtained catalysts exhibit high activity and durability.



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). **Keywords:** nanoparticles; Pt electrocatalysts; N-doped carbon support; bimetallic nanoparticles; oxygen reduction reaction; stress testing; catalyst durability; catalyst stability

1. Introduction

Low-temperature fuel cells with a proton exchange membrane (PEMFCs) are an important part of the intensively developing hydrogen power engineering [1–3]. Electrocatalysts are the key component of such electrochemical devices [3–5]. In almost all commercial PEMFCs, platinum or Pt-M nanoparticles that are anchored on micro/nanoparticles of carbon supports are used as catalysts for accelerating current-forming reactions (oxygen electroreduction, hydrogen electrooxidation) [3–6].

One of the main research areas in the field of increasing the activity and durability of cathode electrocatalysts is the synthesis and study of materials based on platinum alloys with some d-metals (Ni, Co, Cu) [7–9]. The atoms of the alloying component are capable of improving the NPs' activity due to several effects: the formation of a new metal electronic structure; a decrease in the interatomic distance in the alloy lattice, which facilitates the adsorption of oxygen molecules; an increase in the surface roughness; the formation of a thin platinum shell on the alloy particle surface; the increase in the resistance of platinum toward degradation [8–11]. One of the problems limiting the use of such materials in PEMFCs is the selective dissolution of the alloying component, resulting in membrane poisoning [12,13]. Many studies have shown that a preliminary acid treatment of bimetallic catalysts, leading to the formation of so-called "de-alloyed" nanoparticles, significantly reduces an alloy's selective dissolution intensity during the subsequent catalyst operation [13–16]. Previously, we proposed methods for preliminary electrochemical [17] and acid [18] treatments of platinum–copper catalysts and showed the high activity of the resulting de-alloyed materials. Moreover, the possibility of using de-alloyed PtCu/C catalysts in membrane-electrode assembly (MEA) of hydrogen-air fuel cells was demonstrated in [18].

It is known that during the operation of a PEMFC, its power decreases [19,20]. This fact may be due to various reasons, including a decrease in the membrane proton conductivity, gas permeability of the catalytic layer, and electrocatalyst degradation, which causes a decrease in its activity [19–21]. Recent publications have widely discussed the nature of the phenomena leading to the decrease in catalyst activity and, hence, of MEA as a whole [22,23]. It has been established that catalyst degradation is caused by various processes; each of them affects the nano-/microstructure and, as a result, the electrochemical behavior. The main catalyst degradation mechanisms are: (1) the dissolution, reprecipitation, and agglomeration of small platinum nanoparticles (less than ~3 nm) [24,25]; (2) the selective dissolution of the d-metal from bimetallic nanoparticles [23]; (3) carbon support oxidation, which causes the detachment of platinum-containing nanoparticles and the loss of their contact with the support [26,27]; (4) the poisoning of the platinum surface due to the chemisorption of some compounds that are formed during the operation of the PEMFC [28,29]. The role of each mechanism in the catalysts' degradation, depending on their composition, structure, and operating conditions, is not well understood. However, even identifying the key causes of catalysts' degradation under different conditions does not solve the problem of improving their durability or stability by itself. Obviously, the ways to increase the stability have much to do with the improvement of the hierarchical microstructure and composition control of the metal-carbon-nanostructured material.

A number of studies [30,31] have noted that the positive impact of platinum alloying with other metals not only increases ORR activity, but also increases the resistance of metal nanoparticles toward aggregation, which is also important for the cathode catalyst's durability.

The carbon support oxidation during an electrocatalyst's operation is known to be one of the most important and irreversible reasons for degradation [32]. Obviously, the composition, structure, and properties of the carbon support significantly influence the stability of the applied catalysts [33]. Recent research has shown that nitrogen doping of a carbon support makes it possible to create additional oxygen electroreduction active sites (surface fragments containing nitrogen atoms in pyrrole and pyridine). First of all, this has a positive effect on the activity of platinum-free and platinum–carbon catalysts in alkaline media [34–37]. The presence of nitrogen-containing groups on the support surface can also improve the uniformity of the platinum nanoparticles' distribution during the wet synthesis of Pt/C catalysts [38]. In a recent study, we showed that the deposition of Pt nanoparticles onto a N-doped carbon support surface allows one to obtain electrocatalysts with a uniform spatial distribution of nanoparticles and with a narrow size dispersion, increased activity, and increased stability compared to a catalyst based on an undoped support [39].

This study is based on the hypothesis that a combination of two approaches that have previously been proven to be effective would yield advanced platinum-based electrocatalysts that show both high stability and activity in the ORR. The new approach is to use a nitrogen-doped carbon support and deposit bimetallic Pt-Cu nanoparticles on its surface instead of pure platinum particles.

2. Results

The obtained PtCu/C and Pt/C materials, as well as the commercial Pt/C catalyst JM20, contained a similar platinum mass fraction—about 20 wt% (Table 1). To prevent (or to reduce the intensity of) selective dissolution of copper from PtCu nanoparticles, the bimetallic catalysts were pre-treated in nitric acid (see the experimental methods). The compositions of the metal component in the de-alloyed PtCu/KB and PtCu/KB-N catalysts obtained were $PtCu_{0.29}$ and $PtCu_{0.24}$, respectively.

Sample	Mass Fraction of Pt, %	Mass Fraction of Pt + M, %	D _{av} , nm (XRD)	D _{av} , nm (TEM)
Pt/KB-N	22.0	22.0	<1.0	2.0 ± 0.1
PtCu/KB	19.6	21.4	2.9 ± 0.1	3.6 ± 0.2
PtCu/KB-N	22.0	23.7	2.7 ± 0.1	2.9 ± 0.1
JM20	20.0	20.0	2.4 ± 0.1	2.7 ± 0.1

Table 1. Structural characteristics of the obtained catalysts and the commercial Pt/C analogue.

To confirm the nitrogen doping of the carbon support, a comparative analysis of the Raman spectroscopy for the carbon material before and after N doping was initially carried out. The Raman spectra showed that the KB and KB-N carbons had two distinct peaks at around 1346 and 1601 cm⁻¹ for KB and 1355 and 1600 cm⁻¹ for KB-N (Figure S1), which correspond to the D-band and G-band [40], respectively. Note that after carbon doping, the position of the D-band shifted to higher values and the I_{D1}/I_{G} intensity ratio decreased, which shows the effect of the doping process on the carbon support's structure [41].

The X-ray diffraction patterns of the synthesized catalysts showed the carbon support peaks and the (111) and (200) faces of the platinum-containing NPs with the fcc structure (Figure 1). For the commercial Pt/C catalyst JM20, platinum peaks were observed at the characteristic 2-theta values of 39.8 and 46.3 degrees, and the peak of the C(002) carbon was observed at 25 degrees. For the Pt/KB-N and PtCu/KB-N materials that were synthesized on the N-doped carbon support, the C(002) maxima were shifted towards larger 2-theta angles compared to JM20 and PtCu/KB, which may have been caused by the influence of nitrogen atoms [38]. The XRD pattern of the Pt/KB-N sample showed a shift in the Pt(111) maxima toward smaller 2-theta angles compared to those of the Pt/C catalyst JM20. This could also be associated with the influence of nitrogen atoms [38]. Apparently, the interaction of Pt NPs with nitrogen heteroatoms led to the distortion of the platinum crystal lattice and to an increase in the interatomic distance. The broadening of Pt reflections in all XRD patterns was associated with the small size of the NPs. In this case, the (111) and (200) peaks for Pt/KB-N merged into a single asymmetric peak. The Pt/KB-N sample was characterized by the smallest average size of platinum crystallites in comparison with the other catalysts studied—about 1 nm (Table 1).



Figure 1. XRD patterns of the obtained and commercial Pt/C catalysts.

There was a shift in the maxima of the (111) and (200) peaks towards larger 2-theta angles for the PtCu/KB and PtCu/KB-N samples (Table 1, Figure 1). This was caused by the doping of the Pt NPs with copper atoms and, as a result, a decrease in the interatomic distance in the crystal lattice.

The TEM of the platinum-containing materials showed that the nanosized particles distributed over the carbon support had a spherical shape (Figure 2). The bimetallic samples were characterized by the presence of a small number of agglomerates (Figure 2e,i). Observations of the micrographs of the platinum and platinum–copper catalysts based on the N-doped carbon support showed a uniform spatial distribution of NPs over the carbon surface. Moreover, the NPs' size distribution histograms for the Pt/KB-N and PtCu/KB-N materials showed a narrower dispersion in comparison with those for PtCu/KB and the commercial Pt/C analogue (Figure 2d,h,l,p). The nitrogen atoms intercalated into the carbon support are likely promote the formation of many active sites on which NPs are formed or deposited. The authors of [42] noted that the mesopore edges of N-doped carbon could be such active centers.

The average NP size determined from the TEM results did not coincide with the average crystallite size (XRD). This was due to the different principles of calculation, the small size of the NPs, and the fact that one particle could consist of several crystallites (Table 1) [43]. The average NP size in the Pt/KB-N catalyst was the smallest of the materials studied, amounting to about 2 nm (Table 1). The presence of overlapped nanoparticles and larger particles (up to 6.5 nm) was typical for the PtCu/KB sample (Figure 2h).

Figure 3 shows the results of surface elemental mapping for the bimetallic de-alloyed PtCu/KB and PtCu/KB-N materials, which confirmed the coincidence of the copper and platinum atoms' location in the samples (Figure 3b,c,f,g). This means that the NPs formed in both samples were indeed two-component ones. EDX line scanning of the PtCu NP composition also confirmed the presence of two components in the nanoparticles (Figure 3a,d,h,i).

In addition, the oxidation kinetics for the initial and N-doped supports were compared by using the TGA method (Figure S2). High-temperature oxidation thermograms of the PtCu/C materials and the commercial Pt/C sample JM20 had a form that is typical for platinum–carbon catalysts, and they did not have serious differences in the oxidation kinetics (Figure S2) [44]. There was an additional peak in the DSC curve of the PtCu/KB sample in the high-temperature region. This peak could have been caused by the significant proportion of carbon particles that were unevenly coated with metal NPs, including agglomerates [44].

An important parameter for the evaluation of electrocatalysts' morphological characteristics is ESA. For materials with a close Pt-loading, the ESA value is higher when the NPs' size is smaller and their surface distribution is more uniform [21]. Based on the results of cyclic voltammetry (Figure S3), the ESA values of the platinum-based materials were calculated (Figure 4). The Pt/C-N catalyst containing the smallest platinum NPs ($D_{av} \approx 2 \text{ nm}$) had the highest ESA. The Pt/C-N sample had the lowest ESA value (Figure 5). The reduced ESA of this sample was because it had the largest average NP size ($D_{av} \approx 2.9 \text{ nm}$) (Table 1) and due to the presence of agglomerates consisting of several particles (Figure 2i,j).



Figure 2. TEM of the samples: Pt/KB-N (**a**–**c**), PtCu/KB (**e**–**g**), PtCu/KB-N (**i**–**k**), JM20 (**m**–**o**), and NP size distribution histograms for the corresponding materials (**d**,**h**,**l**,**p**).

A study of the oxygen electroreduction kinetics using a rotating disc electrode (see the experimental methods) confirmed the four-electron reaction mechanism for all of the catalysts studied. Both before stress testing and after it, the bimetallic catalysts' specific activity crucially exceeded that of the studied Pt/C catalysts (Figure 4). The differences in the initial catalysts' mass activity were not major; the behavior of the catalysts after stress testing is described below. As noted earlier, the high specific activity of the Pt-Cu catalysts was due to the promoting effect of copper on the ORR activity of platinum.



Figure 3. STEM images of bimetallic catalysts (**a**,**e**,**h**). The green arrow shows the direction of the EDX line scanning of the NPs (**a**,**h**). Elemental mapping of PtCu/KB (**b**,**c**) and PtCu/KB-N (**f**,**g**). EDS line scan of NPs for the PtCu/KB (**d**) and PtCu/KB-N (**i**) samples.



Figure 4. CVs of samples activated in the potential range of 0.04–1.00 (**a**). Linear voltammograms of oxygen electroreduction on the studied catalysts at a disk rotation speed of 1600 rpm (**b**). The 1 j⁻¹ dependence of $\omega^{-1/2}$ at a potential of 0.90 V (**c**); 0.1 M HClO₄.

For the stress testing, we used a new protocol that was proposed and detailed by Nagai et al. [45]. In this case, stress testing was carried out in an oxygen atmosphere, which better corresponded to catalyst operation in PEMFCs in real life. After 10,000 stress-test cycles, the ESA values decreased for all materials (Figure S4). There was a shift in $E_{1/2}$ towards lower potentials on the studied samples' ORR voltammograms, which were measured after the stress test. The calculated values of the specific and mass activities of the catalysts in the ORR were decreased (Figure S5). The greatest decrease in the values of ESA, $E_{1/2}$, and mass activity and, consequently, the lowest stability, were demonstrated by the commercial Pt/C sample JM20 (Figure S4d and Figure 5).



Figure 5. ESA values (**a**), mass activity (**b**), and specific activity (**c**) of the catalysts before and after the stress test.

The effects of stress testing on the rest of the catalysts' behavior require further analysis and discussion. The ESA value decreased the least for the Pt/C-N sample (Figure S4). This could be due to the interaction of platinum NPs with nitrogen-containing sites on the support surface, which hampered the NPs' movement over the surface and their subsequent agglomeration or detachment. At the same time, this material was characterized by a substantial decrease in specific activity and, as a result, mass activity after the stress test (Figure 5b,c). The surface of the platinum NPs appeared to be restructuring during the stress test. This led to a decrease in the proportion of the most active ORR centers [46].

The decrease in the bimetallic catalysts' ESA was accompanied by a moderate decrease in their specific activity, which was least pronounced for the catalyst based on the N-doped support (Figure 5a). In addition, the PtCu/KB-N catalyst not only demonstrated the highest relative stability of mass and specific activities in the ORR, but also had the high residual values of these parameters after the stress test (Figure 5b,c and Figure S6).

Thus, the nitrogen doping of the carbon support positively affected the stability of both platinum and platinum–copper nanoparticles. However, the small-sized platinum nanoparticles showed a vital decrease in specific activity during the stress test. At the same time, the specific activity of the larger bimetallic particles decreased much less.

It was interesting to follow the changes in the bimetallic catalysts' compositions at different stages of their evolution. For this purpose, the previous analysis of the bimetallic catalysts' compositions in the "as-prepared" state was supplemented with the determination of their composition after the electrochemical activation stage, as well as after stress testing. It turned out that the PtCu/KB-N material had the highest stability: its composition did not change after the stress test (Figure 6).



Figure 6. Compositions of the metal component in the bimetallic catalysts in the "as-prepared" state, after the electrochemical activation, and after the stress test.

When comparing images of the samples based on an N-doped support after the stress test, it can be seen that the fraction of NP agglomerates with a size of 7–10 nm increased in these catalysts (Figure 7a,d). This was a consequence of the coalescence of aggregated (closely located) Pt or PtCu crystallites after the stress test. The change in the histogram form of the NPs' size distribution for the Pt/C-N catalyst reflects a decrease in the fraction of 1–2.5 nm NPs and an increase in the fraction of NPs larger than 3–6 nm (Figure 7c). For the PtCu/C-N sample, the form of the analogous histogram changed insignificantly (Figure 7f). Note that an increased fraction of nanoparticles with sizes of 1.5–2.0 nm and 4.5–7 nm was observed for this sample after the stress test.



Figure 7. TEM of the Pt/KB-N (**a**,**b**) and PtCu/KB (**d**,**e**) samples after the stress test. Size distribution histograms of the corresponding materials before and after the stress test (**c**,**f**).

The elemental mapping of the PtCu/KB-N catalyst's surface after the stress test, as well as the EDX line scanning of the individual NP composition, confirmed: (i) the retention of copper atoms in the catalyst and (ii) the uniform localization of Cu and Pt atoms in the NPs (Figure 8).



Figure 8. STEM images (**a**,**d**) and elemental mapping (**b**,**c**) of the PtCu/KB-N material after the stress test. The green arrow shows the direction of EDX line scanning (**d**). Composition of NPs according to the EDX line scan (**e**).

3. Materials and Methods

3.1. Synthesis of the Modified Support

To modify the KetjenBlack EC-600JD carbon support, acetonitrile was used as a nitrogen source. A support portion was loaded into a U-shaped quartz reactor. Argon saturated with acetonitrile vapor at room temperature was passed through a reactor with a carbon support at a temperature of 890 °C with a flow rate of 0.4 cm³ s⁻¹ for 4 h. To produce a sufficient amount of the modified support, the procedure was repeated several times. The nitrogen on the support surface was previously demonstrated to be mainly present in the form of pyridine and pyrrole [34,39].

3.2. Synthesis of Catalysts

The platinum–carbon material was obtained through chemical reduction by following the methodology detailed in [39]. A nitrogen-doped carbon support was used as a substrate, and an aqueous solution of formaldehyde was used as a reducing agent. The resulting platinum–carbon electrocatalyst was labeled Pt/C-N.

The synthesis of platinum–copper catalysts was carried out in parallel on the Ketjen-Black EC-600JD and N-doped KetjenBlack EC-600JD carbon supports. For this purpose, weighed portions of supports were dispersed in 30 mL of ethylene glycol ($C_2H_4(OH)_2$). Then, the calculated amounts of platinum ($H_2PtCl_6\cdot 6H_2O$) and copper (CuSO₄·5H₂O) precursors of 6.74 mg (Pt) mL⁻¹ and 5.1 mg (Cu) mL⁻¹, respectively, were then added to each suspension. The suspension's pH was further increased to 10 with an aqueous solution of 0.5 M NaOH, and a reducing agent of -0.5 M sodium borohydride solution, taken in a fourfold excess, was added. The mixture was kept for an hour at room temperature with constant stirring on a magnetic stirrer. The products were then filtered and repeatedly washed with portions of isopropyl alcohol and bi-distilled water. The resulting catalysts were dried in the desiccator over P_2O_5 for 24 h. In this way, materials with compositions of PtCu_{0.73} and PtCu_{0.71} were obtained on undoped and doped carbon supports, respectively.

Further, the obtained samples were treated in acid; the materials were kept in a 1 M HNO₃ solution for three hours with stirring at room temperature to obtain a "de-alloyed" structure and to remove copper and copper oxide from the catalysts' surface. The resulting materials obtained based on the original and N-doped carbon supports are labeled as PtCu/KB and PtCu/KB-N, respectively.

3.3. Attestation of Catalysts' Structural and Morphological Characteristics

The mass fractions of the metals in the electrocatalysts were determined through gravimetry of the mass of the residue that did not burn when heated to 800 °C, taking into account the oxidation of Cu to CuO for the bimetallic catalyst.

The Pt:Cu ratio in the bimetallic samples was determined through X-ray fluorescence analysis (XRF) on an RFS-001 spectrometer with total external reflection of X-ray radiation (Scientific Research Institute of Physics, Southern Federal University). The sample exposure time was 300 s.

X-ray diffraction patterns were recorded on an ARL X'TRA powder diffractometer, as detailed in [47]. For the most intense reflection (111), the average crystallite size of the metallic phase was determined using the Scherrer equation [47]. Note that the half-width of the <111> peak for supported PtCu materials can be superposition of the reflections of two phases based on copper and platinum, forming a "solid solution". Therefore, the crystallite sizes calculated from it should be treated with caution. The accuracy of the determination of the average crystallite diameter ($D_{av,cr}$) was $\pm 5\%$.

The size of the platinum NPs and the features of their spatial and size distributions were studied through transmission electron microscopy (TEM) using JEM-2100 (JEOL, Tokyo, Japan) and FEI Tecnai G2 F20c; (FEI, Hillsboro, OR, USA) microscopes. For the measurements, 0.5 mg of the catalyst was placed in 1 mL of isopropanol and dispersed with ultrasound. A drop of the resulting suspension was applied to a copper grid coated with an amorphous carbon layer, which was dried in air at room temperature for 20 min.

The histograms of the NP size distribution in the catalysts were plotted from the results of the determination of the sizes of at least 400 particles that were randomly selected from TEM images in different parts of the samples. The accuracy of the determination of the average NP size ($D_{av,NP}$) was $\pm 5\%$.

Thermal analysis of obtained materials was performed using a combined TGA and DSC/DTA analyzer (NETZSCH STA 449 C) in an atmosphere consisting of 80% N₂ and 20% O₂ in the temperature range from 25 to 800 °C at a heating rate of 10 °C/min and a gas flow rate of 20 mL min⁻¹ using corundum crucibles. The weight of samples used for oxidation was 2–4 mg.

The Raman spectra were detected by using a Renishaw in Via Reflex Raman spectrometer with a spectral resolution better than 1 cm⁻¹.

3.4. Attestation of the Electrochemical Characteristics of the Catalysts

Electrochemical measurements were carried out in a three-electrode cell on a VersaSTAT3 potentiostat using a rotating disk electrode (RDE) (Pine Research Instruments, Durham, NC, USA). A saturated silver chloride electrode was used as a reference electrode. Potentials were given relative to a reversible hydrogen electrode (RHE).

To prepare a catalyst suspension (catalytic ink), the sample mass was calculated in such a way that, upon subsequent deposition of the catalyst on the electrode, the mass of platinum was 20 μ g (Pt) cm⁻². A 1% aqueous emulsion of Nafion[®] polymer, deionized water, and isopropyl alcohol was then added to the catalytic ink.

Initially, the activation stage was carried out in a three-electrode cell filled with a 0.1 M $HClO_4$ solution saturated with Ar at atmospheric pressure and 25 °C. For this, 100 cyclic voltammograms were recorded in the range from 0.04 to 1.0 V at a rate of 200 mV s⁻¹.

To measure the value of the electrochemically active surface area (ESA) on a stationary electrode, 2 cyclic voltammograms were recorded with a potential sweep rate of 20 mV s⁻¹ in the potential range of 0.04–1.0 V. The ESA of the samples was calculated using the second cyclic voltammogram over the hydrogen adsorption/desorption region, as described in [48]. The accuracy of ESA determination was $\pm 10\%$.

The study of the oxygen electroreduction reaction kinetics was carried out in an electrolyte saturated with oxygen by recording linear voltammograms in the potential range of 0.02–1.1 V; the potential sweep rate was 20 mV s⁻¹, and the disk electrode rotation speeds were 400, 900, 1600, and 2500 rpm [49]. The activity of the catalysts in the ORR (I_k is the kinetic current) was determined from normalized voltammograms considering the contribution of mass transfer at a potential of 0.90 V (RHE) [49,50]. For this, a graph was plotted in the Koutetsky–Levich coordinates—1/j— $1/\omega^{0.5}$, where j is the kinetic current density (referring to the geometric area of the RDE) and ω is the electrode rotation speed. Given the area of the RDE, the value of the I_k activity was calculated. The mass activity (I_{mass}) was calculated by dividing the kinetic current by the mass of platinum loaded onto the electrode. The number of electrons participating in the ORR was determined by the tangent of the straight-line angle in the coordinates 1 j⁻¹—1 $\omega^{-0.5}$.

Stress testing then was conducted in start/stop mode. For this purpose, 10,000 cycles were recorded in an atmosphere of oxygen on a stationary electrode in the range of 0.4–1.0 V with a hold of 3 s at extreme potentials, as described in detail in [45]. The ESA was measured before and after the stress test. The resistance to material degradation was evaluated with the change in ORR activity according to the formula: Stability = $(I^{10,000}_{mass}/I^0_{mass}) \times 100\%$, where I^0_{mass} is the initial value of the catalyst's mass activity in the ORR; $I^{10,000}_{mass}$ is the value of the catalyst's mass activity in the ORR after 10,000 testing cycles. The degradation degree (DD) was calculated with the formula: DD = 100 – Stability, %.

The commercial Pt/C catalyst JM20 (HiSPEC3000, Johnson Matthey) was studied as a conventional catalyst.

4. Conclusions

In summary, a highly efficient, stable electrocatalyst for the ORR was obtained through wet synthesis that included the chemical deposition of small (2–4 nm) Pt-Cu alloy NPs on an N-doped carbon support surface. The reason for the increased ORR activity of the bimetallic PtCu/C and PtCu/C-N catalysts is the influence of copper on Pt in the NPs. The observed effect of the increase in the spatial uniformity of the NPs for the Pt/C-N and PtCu/C-N samples is associated with the use of an N-doped carbon support. In our opinion, this is a result of the combination of an optimal structure (porosity and the pattern of the NPs' arrangement in pores) and the positive effect of nitrogen atoms, which are intercalated into the carbon, on the strength of the adhesion of Pt and Pt-Cu NPs to the support.

The combined approach to the synthesis of electrocatalysts that consisting in the combination of an N-doped carbon support and bimetallic nanoparticles had a positive effect on the stability of the synthesized PtCu/KB-N material. The residual specific activity of the PtCu/C-N catalyst is 1.2 times higher than that of PtCu/C and 3–5 times higher than that of Pt/C analogues. The increased morphological stability of this sample during long-term stress testing is due to the high spatial uniformity of the distribution of bimetallic NPs and their better anchoring. The acid treatment of the Pt-Cu material made it possible to obtain a de-alloyed catalyst characterized by a stable composition during the long-term electrochemical measurements. These catalysts obtained through this combined approach are of undoubted interest for use in MEAs of hydrogen–air fuel cells.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/catal12040414/s1, Figure S1: Raman spectra of undoped and N-doped carbons materials; Figure S2: (a,c) TGA and (b,d) DSC curves of carbon support (a,b) and catalysts (c,d) oxidation; Figure S3:CVs at the stage of catalysts electrochemical activation: Pt/KB-N(a), PtCu/KB-N(b), PtCu/KB(c), JM20(d). The sweep rate of the potential is 100 mV s⁻¹; Figure S4: CVs: initial and after the stress test in oxygen atmosphere: Pt/KB-N(a), PtCu/KB-N(b), PtCu/KB(c), JM20(d). Electrolyte is 0.1 M HClO4. Black—initial curves; Red—end curves.; Figure S5: LSV ORR curves before and after the stress test: Pt/KB-N(a), PtCu/KB-N(b), PtCu/KB(c), JM20(d). Rotation speed of RDE is 1600 rpm. Electrolyte is 0.1 M HClO4.; Figure S6: Relative stability and degradation degree of such parameters: mass and specific activity of obtained and commercial samples. The red color indicates the calculated value of corresponding stability for each sample.

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Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

- PEMFC Proton exchange membrane fuel cells
- NPs Nanoparticles
- MEA Membrane–electrode assembly
- XRD X-ray diffraction
- TEM Transmission electron microscopy

- EDX Energy-dispersive X-ray spectroscopy
- TGA Thermogravimetric analysis
- DSC Differential scanning calorimetry
- ESA Electrometrically active surface area
- CV Cyclic voltammetry
- ORR Oxygen reduction reaction
- STEM Scanning transmission electron microscopy
- RDE Rotating disk electrode
- RHE Reversible hydrogen electrode
- XRF X-ray fluorescence analysis

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