



Article 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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Abstract: PtM/C (M = Co, Ni, Cu, Ru) catalysts were prepared by wet-synthesis methods. The composition and structure of the synthesized materials were estimated by TXRF, XRD, TEM, HAADF-STEM, EDX, and TGA/DSC methods. According to the CV and LSV methods, the PtCu/C material is characterized by the highest activity in the ORR compared to the other materials studied. The PtRu/C catalysts also exhibit the highest activity in the MOR. Studying the durability of the obtained bimetallic catalysts using accelerated stress testing has allowed for the detection of the most promising materials, whose characteristics would be superior to those of the commercial Pt/C analog. This study has shown that wet-synthesis methods allow obtaining bimetallic catalysts characterized by higher activity and enhanced durability. This research also indicates that special attention should be given to the possibility of scaling these synthesis techniques, which makes the aforementioned catalysts promising for commercial applications.

Keywords: electrocatalysts; ORR; PEMFCs; Pt-based; nanoparticles; PtM nanoparticles; MOR activity; durability

1. Introduction

Proton-exchange membrane fuel cells (PEMFCs) play an increasingly important role in the development of green energy [1]. In commercial applications, Pt/C electrocatalysts are gradually being replaced by catalysts based on bimetallic nanoparticles (NPs) [2]. It is assumed that the Pt/C catalysts' activity can be significantly increased if it is possible to control both the shape and the size of the NPs under the conditions of scaled synthesis [3]. Nevertheless, this issue is still to be addressed. At the same time, with regard to the PtM/Ccatalysts, it has proved to be possible to obtain materials with different compositions and structures exhibiting notably improved functional characteristics compared to those of Pt/C [4–7]. Recently published surveys present an in-depth analysis of these catalysts' composition and microstructure as well as the reasons for their high performance when using them primarily on the cathode electrode of PEMFCs and on both the cathode and anode electrodes of direct alcohol PEMFCs [8,9]. Adding a transition metal (Ni, Co, Fe, Cu, etc.) to platinum affects the structure of the NPs' crystal lattice as well as the localization of the d-band center [10-13], which is conducive to an increase in the specific catalytic activity in the oxygen reduction reaction (ORR) and in the reactions of the oxidation of organic compounds. Moreover, the alloying decreases the content of the precious metal in the catalyst.

At the same time, the literature still provides contradictory data on the effect of the alloying of platinum on the catalysts' durability [14,15]. Some of the authors point out



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Copyright: © 2023 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/). an increase in the durability of the PtM/C catalysts compared to Pt/C, whereas a series of references, on the contrary, report on its decrease [16–18]. The issue is that both the nature of the alloying component and the bimetallic catalysts' composition and microstructure affect their durability. The search for optimal compositions and microstructures is still ongoing, which in turn causes the development of different methods to obtain PtM/C catalysts [1,8,19,20]. When obtaining high-performance ORR catalysts, Ni [21–25], Co [26–30], and Cu [31–37] are the most commonly used alloying components for platinum among other metals [38,39]. The use of ruthenium as the alloying component for platinum is connected to another type of influence that is different from that for nickel, cobalt, and copper. The PtRu/C catalysts exhibit a higher tolerance to CO [40] and intermediate products of the organic compounds' oxidation due to the implementation of the bifunctional catalysis mechanism [41]. Therefore, they are mainly used on the anode of PEMFCs and direct methanol fuel cells (DMFCs).

The conditions of the Pt-based catalysts' synthesis and pretreatment have a significant effect on the composition, the average size, and the shape of NPs as well as the uniformity of their distribution over the support surface and, thus, the activity and the durability of the obtained electrocatalysts [1,42]. It is noteworthy that the most commonly used methods to control the microstructure of the bimetallic catalysts are connected to the use of organic stabilizing agents that subsequently need removing by means of additional complex manipulations, which generally have a negative effect on this microstructure [1]. Obtaining the catalysts using up–down methods, including, for example, magnetron sputtering, is complicated by the need to use sophisticated equipment, which makes it difficult to scale these synthesis techniques up. In this regard, the ways for the efficient control of the wet synthesis of bimetallic catalysts, the complexity of scaling the technology, when moving from the laboratory to factory production levels, should be mentioned [1].

Despite a variety of studies, there is still no undoubted answer regarding an optimal alloying component due to the fact that its cumulative effect is determined by a range of the aforementioned factors. It is not surprising that the results obtained by various authors often contradict each other. A systematic comparison of a series of PtM/C materials containing different alloying components and characterized by close compositions and microstructural characteristics is still assumed to be relevant.

Facile methods to obtain PtM/C (M = Co, Ni, Cu, Ru) catalysts, which could be considered as high-performance in terms of both the increased ORR activity or activity in the methanol oxidation reaction (MOR) and the enhanced durability compared to the Pt/C materials, are described in this work. It should also be noted that the methods used in this research are promising for commercial applications.

2. Results and Discussion

2.1. The Morphology of the Obtained Catalysts

According to the results of the X-ray powder diffraction (XRD) analysis (Figure 1), the obtained PtM/C (M = Ni, Cu, Co, Ru) catalysts contain the carbon phase and the metal phase of platinum with the face-centered cubic structure (Fm-3m). The reflections corresponding to the metal phase are notably widened, which testifies to the formation of nanodispersed materials. The average crystallite size of the metals for the PtNi/C, PtCo/C, and PtCu/C catalysts calculated using a width at half-maximum of the 111 reflection has proved to be 2.3 to 2.6 nm (Table 1). The reflections corresponding to the platinum phase for these catalysts are greatly shifted to the high-angle region of 2θ , which indicates the decrease in the crystal lattice parameter of the metals (Table 1) relative to the platinum phase. This decrease is due to the penetration of the alloying component into the composition of the Pt-based solid solution [32,43]. Using Vegard's law, it is possible to estimate the composition of the solid solution constituting the bimetallic NPs using the value of the crystal lattice parameter [44]. The PtNi/C and PtCu/C materials have been established to

demonstrate a greater degree of the alloying of platinum (the greater change in the crystal lattice parameter) than the PtCo/C catalyst (Table 1).



Figure 1. The X-ray diffraction patterns of the obtained PtM/C catalysts: 1—PtRu/C; 2—PtCo/C; 3—PtCu/C; 4—PtNi/C.

| Table 1. The composition | and the structural | l characteristics of the | obtained PtM/C | dectrocatalysts |
|--------------------------|--------------------|--------------------------|----------------|-----------------|
| | | | | |

| Sample | ω (Pt + M), wt.% | ω (Pt), wt.% | D _{av} , nm (XRD) | Crystal Lattice Parameter, Å | Composition (XRD) | Composition (XRF) |
|--------|------------------|--------------|----------------------------|---------------------------------|----------------------|----------------------|
| PtCu/C | 30.2 | 22.8 | 2.3 | 3.857 | PtCu _{0.3} | PtCu _{1.0} |
| PtNi/C | 23.7 | 20.1 | 2.6 | 3.848 | PtNi _{0.3} | PtNi _{0.6} |
| PtCo/C | 16.6 | 14.0 | 2.4 | 3.893 | PtCo _{0.1} | PtCo _{0.6} |
| PtRu/C | 27.2 | 19.2 | <1.0 | - | _ | PtRu _{0.8} |

The X-ray diffraction pattern of the PtRu/C material demonstrates a notably wide reflection in the 2θ angle range of $30-50^{\circ}$, which may be caused by a considerably small crystallite size (less than 1 nm). On the other hand, when obtaining the PtRu/C material, the formation of the finely dispersed RuO phase is also possible; the reflections of this phase overlap with the reflections of the platinum phase or the PtRu solid solution. Therefore, due to the features of the X-ray diffraction pattern for the PtRu/C material, the average size of particles as well as the crystal lattice parameter of the metal phase cannot be calculated.

The results of transmission electron microscopy (TEM) (Figure 2) have proved the presence of metal NPs of a different size deposited on the carbon support surface for all four PtM/C catalysts obtained. The average size of NPs and their size and spatial distributions depend on the nature of the alloying component. For example, the PtCu/C and PtNi/C materials are characterized by the largest metal particles with average sizes of 4.0 and 4.8 nm, respectively. At the same time, the PtCu/C material exhibits the nonuniformity of the NPs' distribution over the carbon support surface (Figure 2a) as well as the NPs' significant agglomeration. The distribution of NPs over the support surface in the PtNi/C material is more uniform than that in the PtCu/C sample (Figure 2a,d). The average size of NPs is smaller and the NPs' spatial distribution is more uniform in the PtCo/C catalyst (Figure 2) than in the PtCu/C and PtNi/C materials. It is noteworthy that the

PtRu/C catalyst is characterized by the smallest size of particles (1.9 nm) that are uniformly distributed over the carbon support surface (Figure 2j) coupled with the narrow size dispersion (Figure 2l).



Figure 2. The TEM micrographs of the PtM/C samples: PtCu/C (**a**,**b**), PtNi/C (**d**,**e**), PtCo/C (**g**,**h**), PtRu/C (**j**,**k**); the histograms of the NPs' size distribution (**c**,**f**,**i**,**l**) in the corresponding materials.

The elemental mapping of individual sections of the PtM/C catalysts has proved the presence of the bimetallic NPs containing platinum and the corresponding alloying component on the carbon support surface (Figure 3). At the same time, all the materials studied are characterized by the almost complete absence of the monocomponent Pt or M NPs (Figure 3).



Figure 3. The EDX mapping of the PtM/C sample: the STEM micrographs of a surface section (**a**,**d**,**g**,**j**); the distribution maps of copper (**b**), nickel (**e**), cobalt (**h**), ruthenium (**k**), and platinum (**c**,**f**,**i**,**l**).

The study of the PtM/C materials using thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) allows both calculating the total content of the metal phase and determining the characteristic temperatures of the beginning of the carbon material's oxidation and its maximum rate as well as examining the features of this process depending on the composition and the microstructure of the deposited metal NPs [45–50].

The measured TGA and DSC curves of the Pt/C and PtM/C catalysts' oxidation have the appearance typical for this material type [45,46,49] (Figure 4a). They demonstrate several more or less pronounced regions: the extended low-temperature region, within which the sample weight slightly decreases (Figure 4a, region 1); the region of the rapid weight loss of the carbon support (Figure 4a, region 2); and, finally, the region of the high-temperature oxidation corresponding to the combustion of previously unoxidized residual carbon (Figure 4a, region 3). During the heating process, the sample weight loss caused by the oxidation of the carbon support is accompanied by the corresponding thermal effects, which are reflected in the form of maxima on the DSC curve (Figure 4b). The combustion maximum for the conventional Pt/C material (Figure 4b) is localized in the lower temperature region (the intense combustion range of 390–430 °C) compared to the PtM/C materials. It is evident that the nature and the concentration of the alloying metal in the catalysts have a significant effect on the kinetics of their oxidation. For example, the combustion maximum for the PtRu/C catalysts (Figure 4b) is localized in the lower temperature region (446 °C) of the DSC curves compared to the PtCu/C material (469 °C) and, especially, the PtCo/C (513 °C) and PtNi/C (581 °C) samples. Notably, the width of the intense oxidation range for various materials depends on the nature of the alloying component. The PtCo/C and PtNi/C materials, as well as the Pt/C catalyst, are characterized by carbon oxidation in a wider temperature range compared to that of the PtCu/C and, especially, PtRu/C samples, with the oxidation proceeding in the much narrower temperature range. In the case of the PtRu/C catalyst, this may also be connected to the most uniform spatial distribution of metal NPs (Figure 2i,k,l) [49].



Figure 4. The TGA (a) and DSC (b) curves of the obtained PtM/C catalysts.

2.2. The Electrochemical Behavior of the Catalysts

A thin layer of the catalysts was applied to the studied electrode using the catalytic "inks" (see Section 3). It is worth noting that the composition of the catalytic inks for the PtCo/C sample was optimized to obtain a more stable and more evenly applied suspension (Figure S1).

During the activation, the development of the electrode surface occurs. By the hundredth cycle, the hydrogen region (E = 0.04-0.3 V) of the cyclic voltammograms (CVs) for the Pt/C, PtCo/C, and PtNi/C samples exhibits characteristic peaks of the platinum planes [51] (Figure S2). It should be noted that the CVs for all the bimetallic catalysts demonstrate no peaks of the alloying components' dissolution from both the individual phase and the Pt–M alloy [52]. It is known that when the electrode is exposed to the acidic electrolyte, the amorphized oxides of the alloying components can be dissolved from the surface of the electrode due to their chemical interaction with the acid contained in the electrolyte. Moreover, during the cycling, all the PtM/C catalysts are characterized by the selective dissolution of M leading to the formation of the de-alloyed bimetallic NPs, with their surface enriched with platinum atoms [53]. As a result, the content of the alloying

component decreases in all the studied bimetallic materials after the electrochemical activation. The composition of the de-alloyed catalysts corresponds to the following formula: $PtM_{0.1}$ – $PtM_{0.2}$ (Table S1).

The CVs of the standardized catalysts have the appearance typical for the Pt/C and PtM/C materials (Figure 5). An essential parameter for estimating the structural and morphological characteristics of Pt-based catalysts is the electrochemically active surface area (ESA) [54]. Based on the results of the cyclic voltammetry, the ESA values have been calculated using the adsorption/desorption of hydrogen for the Pt-based materials (PtCu/C, PtCo/C, and PtNi/C) and CO stripping voltammetry for all the catalysts (Table S1). Interestingly, a series of publications point out that the ESA values determined using the adsorption/desorption of hydrogen may be understated for the bimetallic catalysts. Therefore, it is recommended that the additional method of assessing the value, i.e., CO stripping voltammetry, should be used [55].



Figure 5. The CVs of the PtM/C and Pt/C electrodes after the activation stage (**a**); the CO stripping of the PtM/C and Pt/C samples, the electrolyte is the 0.1 M HClO₄ solution saturated with Ar at atmospheric pressure (**b**); the ESA values determined by the adsorption/desorption of hydrogen (black bars) and CO stripping (blue bars) (**c**).

The PtRu/C material is characterized by the highest ESA_{CO} value due to the small average size of NPs (1.9 nm), their uniform spatial distribution, and the absence of aggregates (Table S1). The lower ESA of the PtCu/C and PtNi/C samples is caused by the biggest average size of NPs in these materials (about 4.0 and 4.8 nm, respectively) (Figure 2c,f) and the presence of agglomerates consisting of several NPs (Figure 2a,d).

It should be noted that the localization of the CO oxidation maximum in the CVs depends on the composition of the catalyst studied. For example, in the case of the Pt/C material, the oxidation begins and proceeds at more positive potentials (a maximum of about 0.8 V) compared to the bimetallic catalysts. Moreover, some bimetallic materials (e.g., PtCo/C) are characterized by the presence of several CO oxidation maxima (Figure 5b). The presence of several maxima of the CO oxidation current may be connected to the nonuniformity of the NPs' distribution in their size, composition, and shape [54,56–59]. The PtRu/C catalyst is characterized by the lowest potentials of the beginning and the maximum of the CO oxidation, which, as noted above, is connected to the bifunctional mechanism of the oxidation (Figure 5b).

The study of the kinetics of the oxygen electroreduction in different catalysts by utilizing the rotating disk electrode (RDE) technique (see the Supplementary Materials) has proved the four-electron mechanism of the reaction. The value of the kinetic current (I_k) grows in the order PtRu/C < PtCo/C \leq Pt/C < PtNi/C << PtCu/C (Table S1). The high ORR activity of the platinum–copper, platinum–nickel, and platinum–cobalt catalysts is connected to the promoting effect of the alloying components (Figure 6a) [10,12,13,60]. It is known that atoms of the alloying component may increase the activity of platinum due to a number of factors, including the formation of a new electronic structure of the metal, the decrease in the interatomic spacing in the metal lattice facilitating the adsorption of oxygen molecules, and the increase in the tolerance of platinum to the oxidation (Table 1). The PtCu/C catalyst is characterized by the highest ORR activity compared to the other

materials synthesized. Its value is twice as high as the mass activity of the PtNi/C and PtCo/C samples and 3 times higher than the mass activity of Pt/C (Table S1, Figure 6a). It is noteworthy that nickel [21–25] and cobalt [21,26,27,29,30] are most commonly used in the literature as the most promising alloying components when comparing the ORR activities of different PtM/C catalysts, with only a few publications mentioning copper [61,62]. Therefore, the question of choosing an optimal alloying component for the most active catalyst in the ORR is still relevant, presumably depending on both the nature of the alloying component and the microstructure of the catalyst used.



Figure 6. The mass (red bars) and specific (green bars) ORR activities of the bimetallic catalysts (**a**); the relative stability of the catalysts during the AST calculated from the change in the ESA (black bars) and the mass activity in the ORR (red bars) (**b**).

After 5000 cycles of long-term stress testing, the ESA values decrease for all the catalysts (Table 2). The linear sweep voltammograms (LSVs) of the ORR measured before and after the stress testing demonstrate the shift of $E_{1/2}$, which indicates the decrease in the catalysts' activity (Figures 6 and 7). The PtCu/C samples are characterized by the greatest shift of $E_{1/2}$ (Figure S3c). At the same time, the commercial Pt/C catalyst and the PtCo/C and PtRu/C materials exhibit the lowest $E_{1/2}$ values and mass activity values after the accelerated stress testing (AST) (Figure 7d, Table 2). In this regard, the PtRu/C catalyst demonstrates the shift of $E_{1/2}$ by 35 mV to the high-potential region, which is compliant with the increase in the ORR activity after the long-term stress testing (Figure S3b). This effect is connected to the dissolution and the redeposition of ruthenium atoms as well as the increase in the platinum surface, which is observed experimentally (Table 2). Nevertheless, the ORR activity is significantly lower for this catalyst than for the other PtM/C materials studied.

| Sample | ESA, $m^2 g^{-1}$ (Pt) H | I, mA | I, A m ⁻² (Pt) | E _{1/2} , V | Number, ē |
|--------|--------------------------|-------|---------------------------|----------------------|-----------|
| PtCu/C | 22 | 1.7 | 15.8 | 0.92 | 4.0 |
| PtNi/C | 21 | 1.6 | 17.4 | 0.92 | 3.7 |
| PtCo/C | 32 | 0.3 | 3.4 | 0.87 | 4.7 |
| PtRu/C | 104 (by CO) | 0.3 | 0.6 | 0.87 | 3.4 |
| Pt/C | 66 | 0.9 | 2.8 | 0.90 | 3.8 |

Table 2. The electrochemical characteristics of the bimetallic catalysts after the AST.

The results obtained for the PtRu/C catalyst correlate well with the literature data. According to the latter, this material is not considered as promising for the ORR [63]. At the same time, due to the fact that the Ru-based catalysts are known to exhibit higher activity in the oxidation reaction of alcohols, they can be successfully used in DMFCs [41,64–66].



Therefore, the behavior of all the obtained bimetallic catalysts in the MOR has been given further examination.

Figure 7. The potentiodynamic polarization curves of the ORR: initial (**a**), after the stress testing (**d**); the dependence of the $1/I_k$ on the RDE rotation speed in the Koutetsky–Levich coordinates where I_k is the current on the disk electrode with the area of 0.19625 cm²: initial (**b**), after the stress testing (**e**); the Tafel plots: initial (**c**), after the stress testing (**f**).

The methanol oxidation reaction has been a heavily researched topic for over 50 years [67,68]. The reaction of methanol dehydrogenation and oxidation to CO is currently considered as preferable and likeliest to occur. The better catalytic effect of binary alloys compared to pure platinum is believed to be caused by two factors, i.e., the ligand (electronic) effect and the bifunctional catalysis mechanism [10–13,69]. In case of the ligand effect, the presence of the second metal component changes the electronic properties of platinum, which affects the CO adsorption on the NPs' surface. In case of the bifunctional catalysis mechanism, the oxygen-containing particles are adsorbed on the surface of the second metal, facilitating the CO oxidation at lower potentials.

Figure 8 demonstrates characteristic voltammograms of methanol oxidation in the acidic medium. The catalysts' activity has been estimated using the current density calculated in relation to the ESA or the platinum mass (Table 3). The potential scanning has been conducted in the high-potential region. At the potentials of less than 0.6 V, all the studied materials demonstrate low current values (Figure 8a). The issue is that almost the entire surface of these catalysts at lower potentials is poisoned with CO, which is the main intermediate product of methanol oxidation [41,70]. The PtRu/C catalyst is characterized by the lowest potential of the beginning of the methanol oxidation (0.4 V), which correlates well with the previously obtained data on CO oxidation (Figure 5b). At higher potentials, an increase in the current values is observed, which is equivalent to the growth of the oxidation rate of adsorbed CO. The current strength reaches its maximum at E = about 0.9 V. The MOR activity of the catalysts can be assessed using the peak current density [41]. The PtCo/C, PtNi/C, and PtRu/C catalysts exhibit higher MOR activity than the PtCu/C and Pt/C materials. The PtCo/C and PtRu/C samples are characterized by the highest current density value that is more than double that for the Pt/C catalyst (Figure 8a, Table 3).

To estimate the tolerance of the catalysts to CO, a comparison of initial and final current values has been conducted in the chronoamperograms measured at the potential of 0.6 V (Figure 8b, Table 3). The platinum–ruthenium catalyst has been shown to exhibit the highest tolerance due to a lower degree of decrease in the current values (by 36%) compared to the other samples (Figure 8b, Table 3). In addition, for these materials, the deactivation rate is defined as $(j_{60s} - j_{600s})/j_{60s}$ and is presented in Table 3 [71,72], where j_{60s} and j_{600s} are the

current values after 60 and 600 s measurements, respectively. PtNi/C and PtCo/C materials are characterized by a significantly higher degree of degradation compared to other samples. In terms of the increase in the MOR activity and the tolerance to CO, the catalysts can be arranged in the following order: PtRu/C \geq PtCo/C \gg PtNi/C > PtCu/C \geq Pt/C.



Figure 8. The CVs of the PtM/C and Pt/C catalysts, the potential sweep rate is 20 mV s⁻¹, the electrolyte is 0.5 M CH₃OH + 0.1 M HClO₄ saturated with Ar at atmospheric pressure (**a**); the chronoamperograms of the methanol electrooxidation for the PtM/C and Pt/C catalysts at the potential of 0.6 V (**b**).

| Sample | CV | | Chronoamperometry at E = 0.6 V | | | |
|--------|---|------------------------|--------------------------------|--------------------------|-------------------|--|
| | I _{max} , A g ⁻¹ (Pt) | E _{onset} , V | $I_{initial}$, $A m^{-2}$ | I_{final} , $A m^{-2}$ | Deactivation Rate | |
| PtCu/C | 417 | 0.5 | 0.4 | 0.18 | 0.22 | |
| PtNi/C | 587 | 0.5 | 0.5 | 0.16 | 0.40 | |
| PtCo/C | 759 | 0.5 | 0.7 | 0.35 | 0.34 | |
| PtRu/C | 870 | 0.4 | 0.7 | 0.45 | 0.23 | |
| Pt/C | 350 | 0.5 | 0.7 | 0.26 | 0.20 | |

Table 3. The parameters characterizing the catalysts' behavior in the MOR.

3. Materials and Methods

3.1. Chemicals and Materials

The carbon support Vulcan XC-72 (Cabot Corporation, Boston, MA, USA), ethylene glycol (a top grade, not less than 99.8%, Rehacor LLC, Taganrog, Russia), $H_2PtCl_6\cdot 6H_2O$ (TU 2612-034-00205067-2003, Pt mass fraction of 37.6%, Aurat, Moscow, Russia), CuSO₄·5H₂O (an analytical grade, JSC Vekton, Russia), Ni(NO₃)₂·7H₂O (an analytical grade, JSC Vekton, Russia), Ni(NO₃)₂·7H₂O (an analytical grade, JSC Vekton, Russia), Ni(NO₃)₂·7H₂O (an analytical grade, JSC Vekton, Russia), CoSO₄·7H₂O, RuCl₃ (TU 2625-050-00205067-2004, Ru mass fraction of 47.34%, Aurat, Russia), sodium hydroxide (Rehacor LLC), ethanol (98.0%, JSC Vekton, St. Petersburg, Russia), argon (Ar, 99.9%, Globus, Moscow, Russia), isopropanol (99.8%, Ekos-1, Moscow, Russia), and sulfuric acid (JSC Vekton, Russia) were used in the experiment.

3.2. The Preparation of the PtCu/C Catalyst

A weighed amount (0.15 g) of the carbon support was dispersed in 30 mL of EG and thoroughly mixed. A weighed amount of the $H_2PtCl_6 \cdot 6H_2O$ and $CuSO_4 \cdot 5H_2O$ solutions was added to the resulting suspension. The reduction was carried out with an excess of 0.5 M NaBH₄, adjusting the pH to 10 with sodium hydroxide. The system was kept at room temperature with constant stirring for 1 h. The resulting catalyst was separated by filtration and repeatedly rinsed with isopropanol and bidistilled water. The material was desiccator-dried over P_2O_5 for 24 h.

3.3. The Preparation of the PtNi/C Catalyst

A weighed amount (0.15 g) of the carbon support was dispersed in 30 mL of EG and thoroughly mixed. A weighed amount of the $H_2PtCl_6 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 7H_2O$ solutions

was added to the resulting suspension. The reduction was carried out with an excess of 0.5 M NaBH_4 until the pH was equal to 5 (the level created by metal precursors). The system was kept at room temperature with constant stirring for 1 h. The resulting catalyst was separated by filtration and repeatedly rinsed with isopropanol and bidistilled water. The material was desiccator-dried over P_2O_5 for 24 h.

3.4. The Preparation of the PtCo/C Catalyst

The synthesis of the composite CoO_x/C materials was carried out by the electrochemical deposition of cobalt on particles of the carbon support from the electrolyte with the following composition: $CoSO_4 \cdot 7H_2O$ -500 g/L, NaCl-15, and H_3BO_3 -45, in a specially designed cell, as described in detail in [28]. When passing the current through the cell, the metal was deposited on the surface of carbon particles in the suspension, with the working surface being constantly modified due to the diffusion and mixing processes and the evolution of gaseous hydrogen [28]. This technique made it possible to obtain a support with an oxide mass fraction of 8%. For the subsequent deposition of platinum, the method of liquid-phase borohydride synthesis at room temperature was used. The calculated loading of platinum in the PtCoO_x/C material was 17%. The carbon support was placed in the mixture of EG (60 mL) and bidistilled water (60 mL). The aqueous solution of H₂PtCl₆·6H₂O was then added in the required amount, adjusting the pH to 7 with NaOH crystals. Next, the suspension was homogenized and stirred for 5 min. A 3-fold excess of NaBH₄ in the form of the 0.15 M aqueous solution was uniformly added dropwise in 1 min. After adding the reducing agent, the suspension was allowed to stand with stirring for 30 min.

3.5. The Preparation of the PtRu/C Catalyst

A weighed amount (0.2 g) of Vulcan XC-72 was dispersed in 40 mL of EG. Next, 0.2327 g of $H_2PtCl_6 \cdot 6H_2O$ and 0.0934 g of RuCl₃ were added with constant stirring. After 20 min of stirring, 0.1081 g of NaOH was added until the pH was equal to 11. After 20 min of constant stirring, the reaction mixture was heated to 160 °C over 15 min and kept at this temperature for 3 h. The heating was then ceased, and the mixture was naturally cooled to room temperature. The product was then filtered with repeated rinsing with isopropanol and bidistilled water. The material was desiccator-dried over P_2O_5 for 24 h.

3.6. The Study of the Catalysts' Structure

The structure of the catalysts was studied by gravimetry, XRD, TXRF, TEM, HAADF-STEM, EDX, TGA, and DSC/DTA methods. A detailed description of these procedures is presented in the Supplementary Materials.

3.7. The Electrochemical Study of the Catalysts

The electrochemical behavior of the metal–carbon materials was studied by voltammetry using a VersaSTAT 3 potentiostat–galvanostat (Ametek, Berwyn, PA, USA). The measurements were carried out in a standard three-electrode cell in a 0.1 M HClO₄ solution at the temperature of 25 °C. A saturated silver chloride electrode was used as a reference electrode. A 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 μ L of Nafion 1% solution, and 100 μ L of deionized water were added to a 6 mg sample. The resulting suspension was carefully dispersed and stirred. Next, 8 μ L of the catalytic inks was applied to the end of the rotating disk electrode, with the exact weight of the drop being recorded. The working electrode was dried in air for 5 min at a rotation speed of 700 rpm.

To study the electrocatalysts, cyclic voltammetry and linear sweep voltammetry methods were used in the standard three-electrode cell. The ESA was determined by the charge amount consumed for the adsorption/desorption of hydrogen [73] and CO stripping [74]. The data were extracted from the CV. The activity in the ORR was studied by the linear sweep voltammetry method on the RDE at different rotation speeds. The current values were established according to the dependence in the Koutetsky–Levich coordinates [42].

Accelerated durability testing (ADT) was conducted by cycling the catalyst for 5000 cycles in the potential range from 0.6 to 1.0 V [75].

The preparation procedure for the catalytic inks and a detailed description of the electrochemical experiment are presented in the Supplementary Materials.

The commercial Pt/C HiSPEC 3000 electrocatalyst (Johnson Matthey, Johnson Matthey PLC, London, Great Britain) with a platinum loading of 20% was chosen for a comparative study.

4. Conclusions

Nanostructured PtM/C (M = Co, Ni, Cu, Ru) catalysts with a platinum mass fraction of about 20% and an average size of metal crystallites of about 2.5 nm (except for the PtRu/C material with a crystallite size of less than 1 nm) have been obtained by wet-synthesis methods. The PtCu/C material is characterized by the highest activity in the ORR, whereas the PtCo/C and PtRu/C catalysts exhibit the highest MOR activity. The study of the durability of the obtained bimetallic catalysts using the accelerated stress testing method has allowed detecting differences in the rate of the decrease in the ESA and the ORR activity. The residual (measured after the AST) characteristics of the PtCu/C and PtNi/C catalysts have proved to be close, significantly exceeding, at the same time, those of the commercial Pt/C analog. The study carried out has shown that wet-synthesis methods allow obtaining bimetallic catalysts with improved functional characteristics. Moreover, the possibility of scaling these techniques makes them attractive for commercial applications. At the same time, the catalysts' ORR and MOR activities as well as their durability are determined by a combination of factors connected to both the nature of the alloying component and the morphology/microstructure of the catalysts, with the latter in turn (or under similar conditions of the synthesis) depending on the nature of the alloying component.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/catal13020243/s1. 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. 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. Table S1. Composition, ESA and parameters characterizing the electrochemical behavior of PtM/C and Pt/C catalysts.

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